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Hydrogenolysis of lignin in ZnCl_2 and KCl as an inorganic molten salt medium

Abstract: Lignin can be converted into monomeric products with the aid of molten salt media. Molten zinc chloride (ZnCl_2)/potassium chloride (KCl) mixtures are suitable for this purpose. The application of an eutectic mixture with low melting points leads to similar main products as are obtained by pyrolysis. The hydrogenolysis of an organosolv lignin in molten salts of ZnCl_2 /KCl was investigated as a function of reaction temperature, residence time, and lignin concentration, and the composition of liquid products and monophenols was analyzed by gas chromatography-mass spectrometry (GC-MS). The yields can be optimized by the proper selection of the reaction temperature. A longer residence time and higher lignin concentrations lead to increased formation of solid residues and gaseous products. The liquid products mainly consist of substituted phenols derived from lignins. Polymeric products are the result of condensation reactions (i.e., the formation of new C-C linkages in the course of secondary reactions).

Keywords: eutectic mixture, GC-MS, hydrogenolysis, lignin, molten salt media, phenols, zinc chloride

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Introduction

Lignins are the most abundant natural aromatic polymers (Fengel and Wegener 1989). Lignins of wood are dissolved during pulping, and the utilization of these technical lignins as a waste material is investigated from the very

beginning of wood research. This topic has many facets, and there are still opportunities for innovative developments (Faix et al. 1995). Frequently, conventional lignin conversions are performed under reducing conditions (e.g., by means of hydrolysis without any solvents and at solid phase), but lignins can also be degraded in aqueous, aqueous/organic, and oily reaction media (Faix et al. 1995).

An interesting alternative is lignin conversion in molten salt media with low melting points (m.p.). Molten salts are liquids with low intermolecular association (Sundermeyer 1965), and the melts dissociate completely. These media have a hardly measurable vapor pressure and thermal and electrical conductivity. The heat of the reaction can be discharged quickly. Catalytically active substances remain in the melted mass during the reaction. Reaction products are not miscible with the molten media; thus, an easy separation is possible. Mixtures of various salts have a lower m.p. than their single components. A special mixture with a minimized temperature of crystallization is called eutectic (Vuori and Bredenberg 1984).

Zinc chloride (ZnCl_2) is a known catalyst in petrochemistry and coal chemistry, and this field is well investigated (Zielke et al. 1966b). Benzene, toluene, xylene, phenols, and cresols are typical degradation products (Zielke et al. 1966a). As a Lewis acid, ZnCl_2 is appropriate for hydrocracking processes and catalyzes the cleavage of polycyclic aromatic hydrocarbons, while stable monoaromatics arise (Larsen and Earnest 1979). ZnCl_2 undergoes addition on activated double bonds and cleaves these bonds by a carbenium ion mechanism (Taylor and Bell 1980). The formed catalyst complex is regenerated by protons (Derbyshire 1989).

Typically, lignins are reductively converted between 500°C and 800°C, and the reaction products are mainly monocyclic phenols, the composition of which is dependent on the lignin type. The hydrogenolysis of lignins in the presence of ZnCl_2 is not well investigated. Thus, in this study, the first results of investigation on the hydrogenolysis of lignin in ZnCl_2 as part of an inorganic molten salt will be presented. The hydrogenolysis generates phenols, solid residues, and liquid and gaseous products. The yields of the products will be presented as a function of reaction temperature, residence time, and lignin concentration.

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The composition of liquid products will be analyzed by gas chromatography-mass spectrometry (GC-MS), and the preferential formation of various compounds will be described.

Materials and methods

Spruce organosolv lignin of the type Organocell (OC), precipitated at pH 9 with technical CO₂, was purchased from the former Organocell GmbH Munich (pilot plant in Munich-Pasing, Germany). ZnCl₂ and potassium chloride (KCl) was obtained from Carl Roth (Karlsruhe, Germany).

Two different mixtures of ZnCl₂/KCl were applied for the conversion of lignin. An eutectic mixture of 45 mol% ZnCl₂ and KCl with a m.p. at 228°C (named mixture 45/55) and a corresponding mixture 68/32 (m.p. approximately 250°C) were selected (Janz 1971; Levin et al. 1975). The conversion was performed in two laboratory quartz glass units under flowing hydrogen (Figure 1). Gadget A consists of a glass tube externally heated by a tube furnace. N₂ as flushing gas and H₂ as reaction gas were fed by a three-way valve. A cooling trap with a dry ice/methanol (MeOH) mixture was placed at the end of the gadget to capture gaseous reaction products. Additional traps with toluene and ethyl acetate were placed downstream. The remaining gases were discarded and calculated as the difference to 100%. The samples were placed in a quartz glass boat in the middle of the tube. The system was flushed with N₂ and H₂ and heated up to the reaction temperature (20 K min⁻¹). The reaction time is defined as beginning from the time when the reaction temperature is reached. A comparable scaled-up gadget B (lignin amount approximately 10 g) was used to obtain the material for analytical studies. After the experimental run, the deposited reaction products were extracted and weighed after the removal of solvent. The fractionation of the extracted liquid reaction products was performed according to the fractionation scheme in Figure 2. The scheme is based on the solubility of different compounds in solutions of NaHCO₃ and NaOH. NaHCO₃ soluble compounds are labeled as acidic compounds. Weak acidic compounds, mostly phenolic, are soluble in NaOH, whereas neutral compounds are not. Fractions of phenolic and acidic compounds were acidified with 18% HCl (pH 2) and extracted with diethyl ether from the aqueous phase.

The solvent was evaporated, and all fractions were weighed. The material composition of each fraction of liquid products was estimated by GC 6890 coupled with a mass selective detector 5973A (Agilent Technologies, Karlsruhe, Germany). GC column: DB 1 column (30 m, 0.25 mm ID, 0.25 μm film thickness) with the following temperature program: isothermal phase at 100°C (5 min), heating to 300°C (15 min) at a rate of 5 K min⁻¹. The auxiliary temperature was kept at 230°C. Then, 1 μl of a sample solution was transferred by He (1 ml min⁻¹) as carrier gas and a split ratio of 20.1:1 (injector 280°C). Compound identification was achieved by ChemStation and NIST spectra library.

Results and discussion

Variation of ZnCl₂/KCl ratio

The characteristic main products can be subdivided as solid residues, extracts, condensates, and gases (Figure 3a). In the case of mixture 45/55, more than half of the lignin is converted into solid residues, and the yield of condensates is high. On the contrary, with mixture 68/32, solid residues decrease to 20% in favor of the low molecular products, and more gases are generated (20% vs. 5%). In gadget A, only small amounts of gases arise, containing mainly CO, CO₂, and H₂, but ethane, ethene, and methane are also formed in lower yields. The liberation of methane probably results from the splitting of aromatic OMe groups. At higher temperatures, ether bonds are another source of methane formation (Derbyshire 1989; Kudsy et al. 1995). ZnCl₂ supports an increasing liberation of hydrogen, compared with the experiments without melts; thus, the dehydrogenation of lignin seems to be favored (Derbyshire 1989). Figure 3b shows the composition of the liquid product in detail (i.e., the yields of phenolic, acidic, and neutral compounds), whereas the latter is dominating. There are more phenolic compounds (3–4.5%) than

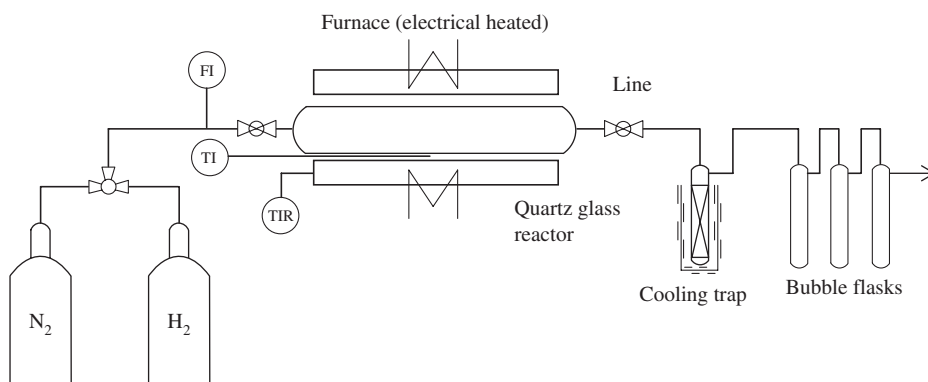


Figure 1 Scheme of the quartz glass gadget A for hydrogenolysis under flowing hydrogen.

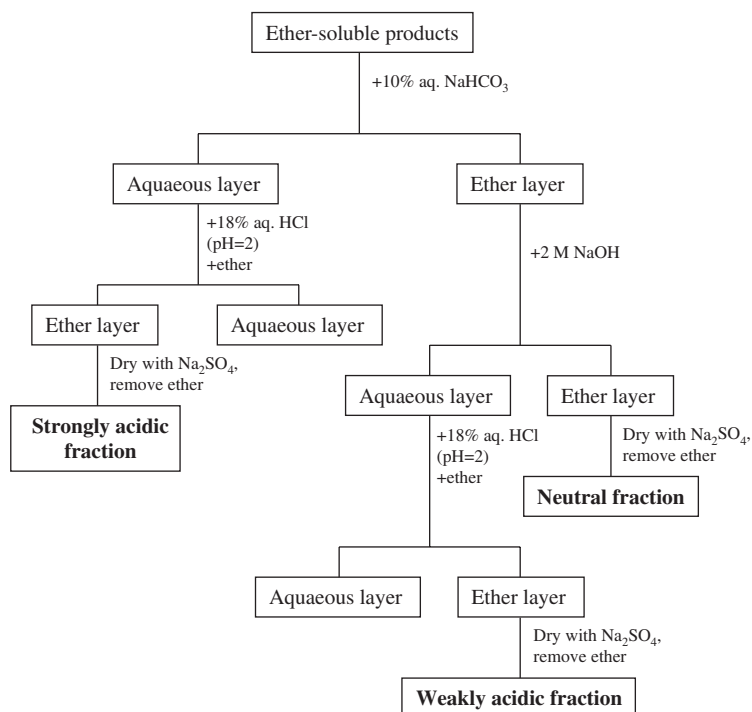


Figure 2 Alkaline liquid-liquid extraction and fractionation scheme for liquid reaction products.

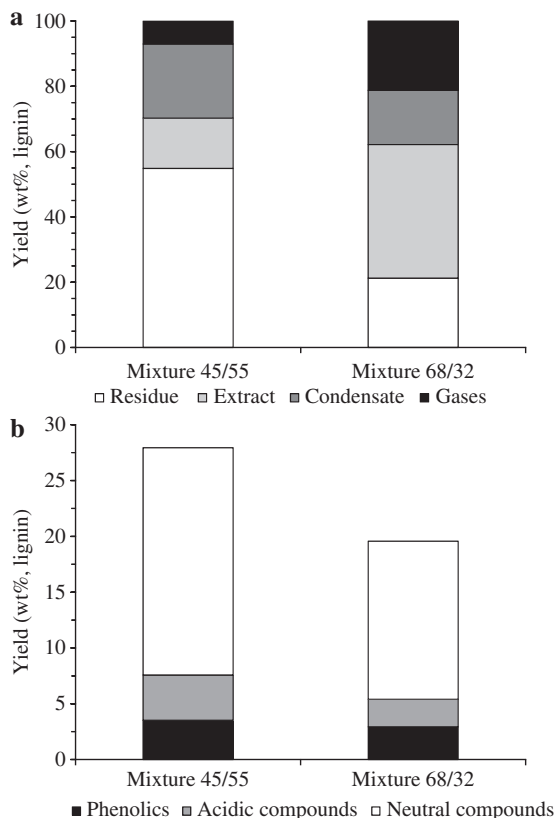


Figure 3 Yields of main products (a) and fractions of condensate (b) in the variation of mixture; gadget A, 300°C, 2 h reaction time, 20% concentration of lignin.

acidic compounds. The influence of ZnCl₂ on the ratio of the fractions is rather low. However, mixture 45/55 seems to promote the yield of neutral compounds with high molecular masses insoluble in NaOH. As pointed out above, mixture 68/32 promotes the formation of gases and condensables, which adhered to the solids as extractable products.

Temperature, reaction time, and lignin concentration

As presented in Figure 4a, the product distribution is temperature dependent. At 300°C, the solids are dominating (approximately 50% yield) followed by 27% of condensates. Increasing temperatures lead to fewer solids (approx. 30% at 450°C). The conversion efficiency is highest at 400°C, where the rapid onset of the formation of gaseous products can be observed in agreement with the results of Meier and Faix (1991).

The amount of gaseous products reaches a maximum of approximately 45% in the total mass balance with CH₄ and CO as main components, whereas the amounts of the former increases with temperature. The yields of condensates and extracts fluctuate in the range of 20% to 30% depending on the reaction temperature. The maximum of extract yields is reached at 350°C, and a

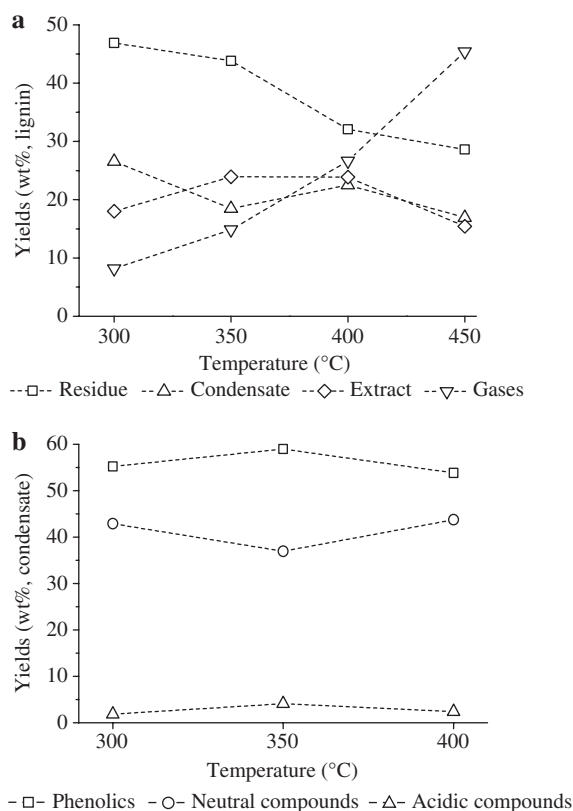


Figure 4 Yields of main products at gadget A (a) and fractions of condensate at gadget B (b) in the variation of reaction temperature; mixture 45/55 mol% (ZnCl_2/KCl), 2 h reaction time, 20% concentration of lignin.

further temperature increase does have a positive effect. At 450°C, for example, the yield of extracts is reduced to 15%. At 300°C, 25% condensates can be obtained, and this yield decreases to 15% at higher temperatures. In summary, a temperature range from 350°C to 400°C seems to be optimal for a high yield of extracts and condensates. The formation of extractable compounds from the solid is maximized only at higher temperatures.

As shown in Figure 4b, the condensates generated with gadget B are dominated by phenolic compounds (50–60%) and neutral compounds (40–50%), whereas acidic compounds arise in small yields (<5%). Increasing reaction temperature causes a slight increase of phenolic compounds at the expense of the neutral compounds. Possibly, phenolic compounds are formed from neutral compounds via secondary reactions. At 400°C, the additional formation of neutral compounds is observed, whereas the yield of phenolic compounds decrease.

The reaction time also effects the product distribution. After 1 h, the main part of the generated products is solid (Figure 5a), and the extract yields are approximately 5%. At 2 h reaction time, fewer solids and more gases arise

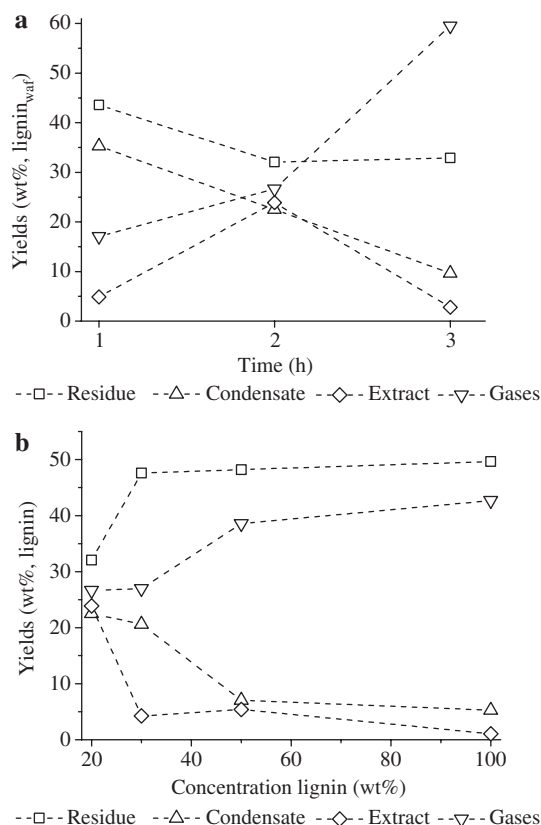


Figure 5 Yields of main products in the variation of reaction time (a) and concentration of lignin (b); gadget A, melting 45/55 mol% (ZnCl_2/KCl), 300°C reaction temperature.

and the amount of condensates decreases to 25%. Apparently, the formation of ether extractable compounds needs longer reaction times. The high yield of gases is a manifestation of secondary reactions. The lower amount of condensates corresponds to the increasing gas yields after 2 and 3 h (50%) reaction time. Consequently, the amount of liquid products decreases strongly after 3 h (condensates to 12.5% and extracts to 20%). Remarkably, the solid yields do not change significantly at longer reaction times than 2 h.

Longer reaction time leads to a direct cleavage of low molecular weight products into gases via secondary reactions (Mills 1976; Koenen 1978; Sada et al. 1992; Kudsy and Kumazawa 1999). Thermal cleavage is favored by a longer residence time of the samples within the reactor, in the course of which recondensation reactions occur. As a result, the amount of monophenols is decreasing (Wienhaus 1975; Meier et al. 1993).

With 20% lignin concentration, 30% of the lignin remains in the melt as residue (Figure 5b). With increasing lignin concentrations (up to 50%), the yields of solid residue increase up to 50% (based on lignin). A

hydropyrolytic conversion without catalysts generates the same amounts of solid residues. More gases are formed with increasing lignin concentration (20% at 20% concentration, 27% at 40% concentration, and 50% at 100% concentration). The yields of the liquid products decrease in the same measure (23% at 20% concentration and 7% at 50% concentration). With 100% of lignin concentration, no extracts are formed. Accordingly, the formation of gaseous products is favored at higher lignin concentrations, and the formation of liquid products is suppressed. At higher lignin/catalyst ratios, the influence of the catalyst decreases because of the less probability of contacts between ZnCl_2 and lignin. Thus, the noncatalyzed thermal cracking mechanism becomes prevalent. The high viscosity of the mixture supports this effect. The highest yields of liquid products are obtained at lignin concentrations between 20% and 25% as also observed by Kudsy and Kumazawa (1999).

Analysis of the liquid products

The GC chromatograms are presented in Figure 6 (results from gadget B). Only aromatic compounds are detected, mostly as monoaromatics (as substituted phenols) and more rarely polyaromatics. Only a few major compounds belong to the acidic substances extractable by means of a weakly alkaline solution. Vanillin and acetyl guaiacol belong to this group. The phenolic compounds

are extractable with a strong alkaline solution. The dominance of guaiacol and its derivatives is due to the investigated softwood lignin, as it is composed of 95% guaiacyl propanes (Fengel and Wegener 1989). The liberation of propyl guaiacol is achieved by the cleavage of β -O-4 bonds and splitting off of the alkyl side chains. Methylated phenols are released by a rearrangement of the guaiacyl units, whereas the methoxy groups are eliminated and the methyl groups are formed at intermediary states by an intramolecular group transfer mechanism (Vuori 1986) (Figure 7). The further cleavage of the alkyl side chain between the C1 of the ring and $\text{C}\alpha$ of the side chain leads to cresols (Berns 1994). Rearrangement reactions may also give rise to dimethylphenols based on a similar mechanism. The splitting of the $\text{C}\gamma$ atoms ends up in ethyl guaiacol and MeOH and/or methane. Figure 8 shows, as an example, the cleavage of C-C bonds of diphenyl ethane promoted by ZnCl_2 . The detected naphthalene and naphthalenols result from condensation reactions of aromatic fragments. Acidic catalysts, particularly ZnCl_2 , do not support hydrogenation reactions. Thus, conversion reactions are accompanied by the polymerization of the aromatic fragments and form oligomeric or polymeric compounds (Taylor and Bell 1980). Additionally, ZnCl_2 does not activate hydrogen at approximately 400°C. The protons are formed by several mechanisms through the interaction of ZnCl_2 with the substrate or through the formation of secondary or tertiary carbenium ions, which are able to abstract hydrogen (Larsen and Earnest 1979).

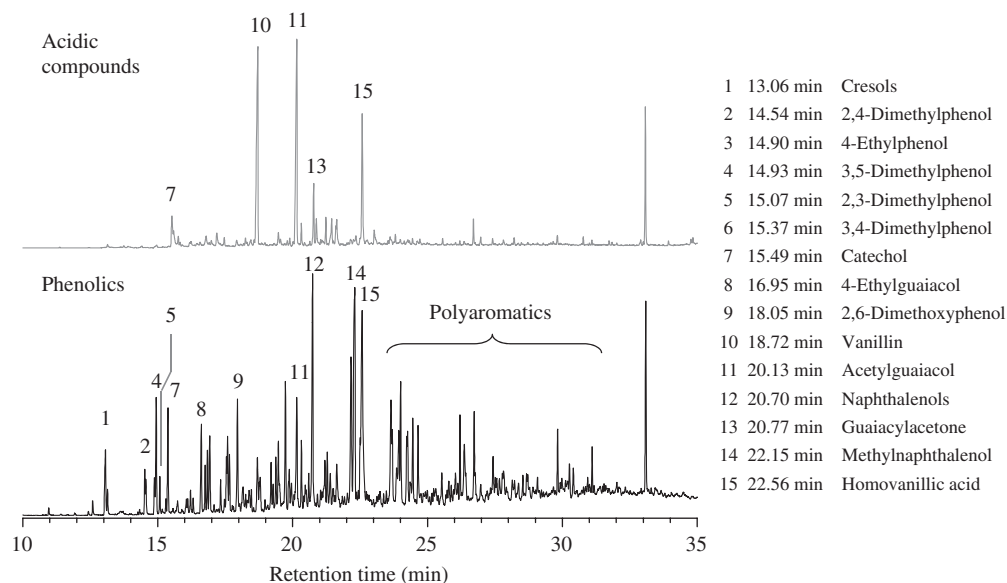


Figure 6 GC-MS chromatograms (excerpts) of liquid products from cooling trap gadget B, mixture 45/55 mol% (ZnCl_2/KCl), 300°C reaction temperature, 2 h reaction time, 20% concentration of lignin.

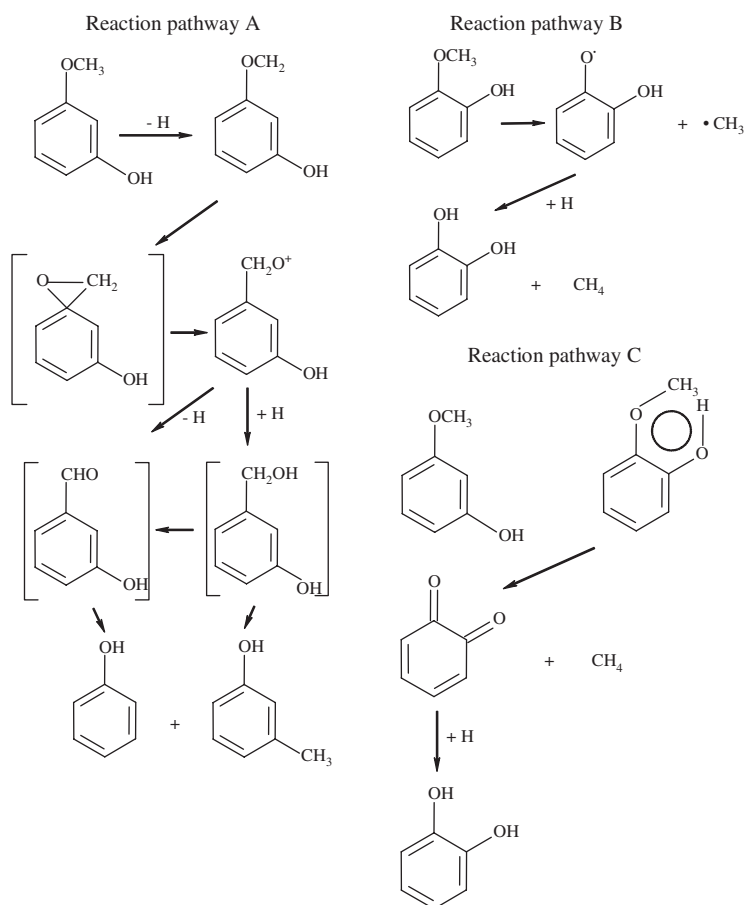


Figure 7 Reaction pathways of demethoxylation of guaiacol (Vuori 1986): (A) cresol formation by intramolecular rearrangement, (B) formation of catechol by demethylation and radical mechanism, and (C) formation of catechol via (1,5) group transfer mechanism.

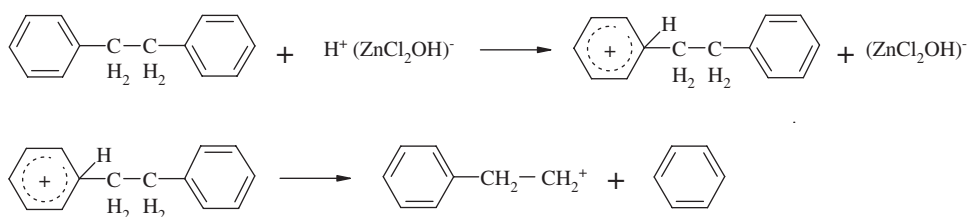


Figure 8 ZnCl_2 -promoted cleavage of C-C bonds in an example of diphenylethane (Derbyshire 1989).

Conclusions

Hydrogenolysis in zinc-containing inorganic molten salt media is a suitable method for converting lignin into monomeric compounds, a process that can be controlled by parameters such as the concentrations of zinc and lignin, reaction temperature, and reaction time. The increase of reaction temperature and time and higher concentration of lignin leads to the lowering of solid residues with a simultaneous increase of gases yields. The yields of condensates and extracts are optimal at moderate reaction

conditions, whereas their yields are minimized in favor of the gaseous products at harsh reaction conditions. As revealed by GC-MS measurements, the composition of the phenolic and weak acidic compounds is complex. All identified compounds are aromatic and dominated by substituted monophenols containing acid and aldehyde functionalities. Naphthols and other polyaromatics are generated by secondary condensation reactions. Mostly, guaiacyl structures are liberated to some extent by the intramolecular arrangement to methyl and dimethyl phenols.

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