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Article

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Chemical Structures Present in Biofuel Obtained from Lignin

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Technical lignins from various sources can be converted into bio-oil with a low O/C ratio by pyrolysis in the presence of formic acid and an alcohol. By application of different analytical techniques, such as Fourier transform infrared spectroscopy (FTIR), nuclear magnetic resonance (NMR), electrospray ionization mass spectrometry (ESI−MS), and size-exclusion chromatography (SEC), it has been shown that a complete degradation of the lignin takes place irrespective of the origin. The resulting bio-oil has a low-molecular-mass distribution with a preponderance of aliphatic hydrocarbon structures. A substantial number of phenolic compounds are, however, also present, and some of these also contain carboxyl groups. The results clearly show that formic acid is a powerful supplier of atomic hydrogen. By further optimization of the pyrolysis reaction, it should be possible to further reduce the content of aromatic structures.

Introduction

The use of wood and other biomass, such as bagasse and straw, for the production of ethanol through the hydrolysis of polysaccharides and the subsequent fermentation of monomer sugars is the subject of much ongoing research.[1−3] For the development of a successful process, an efficient separation of the biomass polymers, namely, cellulose, hemicelluloses, and lignin is required. Currently, processes such as organosolv pulping,[3] steam explosion,[2] and acid hydrolysis[4] are being explored for this purpose. Irrespective of the process used, however, a large quantity of lignin will always be produced as a byproduct.[3,5] Considering the large production scale required in future ethanol biorefineries, a simultaneous pyrolytic conversion of the lignin stream into a liquid biofuel seems attractive. Previous attempts in that direction have failed, however,[6]and it was found only recently that lignin can be efficiently depolymerized and deoxygenated if the pyrolysis is carried out in the presence of formic acid with an alcohol as the co-solvent.[7]

Thus, a one-step pyrolysis of lignins at about 380 °C in the presence of formic acid and an alcohol, such as ethanol, results in almost complete degradation of the material to a liquid bio-oil.[7] This can easily be separated from the water that is simultaneously formed because almost no coke (<5%) is formed in the process. Preliminary analytical data have shown that the bio-oil (1) has no structural resemblance with the starting material, (2) contains alkylated phenols together with alkane and alkene structures, and (3) has a low O/C ratio, thus making it interesting as a biofuel. The heating value was also found to be similar to that of petroleum-based fuel oils.

In the present work, the bio-oil produced from different lignin sources has been further analyzed to obtain insight into the degradation mechanism and to obtain further structural information. The molecular-mass distribution has been analyzed using size-exclusion chromatography (SEC) as well as electrospray mass spectrometry (ESI−MS).[8] The presence of hydroxyl and carboxyl groups was quantified using phosphorus nuclear magnetic resonance (NMR), and the types of carboxylated structures were identified using gas chromatography−mass spectrometry (GC/MS) of the silylated bio-oil. For a general analysis of functional groups, Fourier transform infrared spectroscopy (FTIR) and ^{13}C NMR were used.

Experimental Section

Starting Materials. Two bio-oils, obtained from a commercial spruce sodium lignosulfonate (Borregaard Ind., Norway) (MK79) and from isolated lignin from steam-exploded birch wood[9] (MK84), were used. In addition, several of the previously produced bio-oils have been included in some of the analyses. The procedure for making the bio-oils has been described elsewhere.[7] Despite the large difference in lignin origin, the two bio-oils (MK79 and MK84) were similar in composition, with O/C ratios of 0.08 and 0.09 and H/C ratios of 1.36 and 1.32, respectively. The corresponding values for the original lignins were O/C ratios of 0.84 and 0.53 and H/C ratios of 1.31 and 1.21.

SEC. The sample (2 mg) was dissolved in 2 mL of tetrahydrofuran (THF) and filtered with a 0.2 μm filter to remove any particles. The solution (20 μL) was injected into a SEC system consisting of three polystyrene−divinylbenzene columns connected in series, with cutoff values of 1000, 500, and 100 Å (Waters). A flow rate of 0.8 mL/min at room temperature was used, and the detection was performed with UV at 254 and 280 nm, as well as with RI. The set

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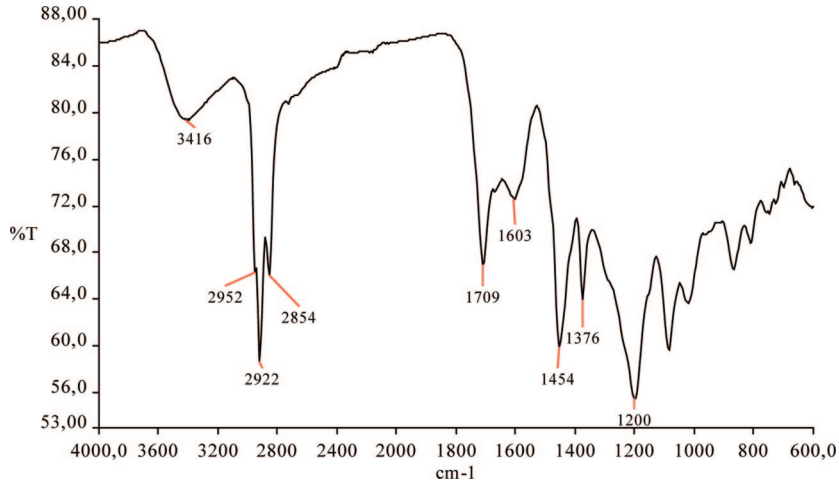

Figure 1. FTIR spectrum of the bio-oil MK84.

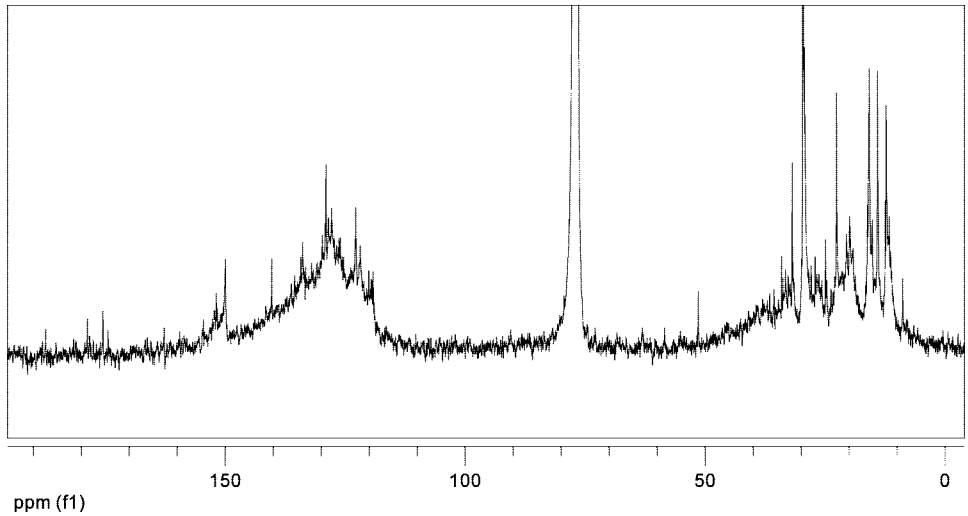

Figure 2. ^{13}C NMR in chloroform-*d* (77.2 ppm) of the bio-oil MK84.

of columns was calibrated with toluene and a series of polystyrene standards covering a molecular-mass range of 580−915 000 Da.

ESI−MS. Each sample (2 mg/mL) was dissolved in dichloromethane and analyzed by full-scan mass spectrometry (*m/z* range from 65 to 1300 with 1 scan/s) on an Agilent 1100 Series LC/MSD system (Agilent Technologies, Inc., Palo Alto, CA). The system consisted of a G1322A mobile phase degassing unit, a G1311A quaternary pump with a gradient mixer for up to four mobile-phase constituents, a G1367A autosampler, and a G1946D single quadropole mass spectrometer. Samples of 2 μL were injected by the autosampler and led into the mass spectrometer by 70 cm of PEEK tubing (i.d. of 0.18 mm) without separation on a chromatographic column. Each sample was analyzed 5 times. The mobile phase consisted of 9:1 acetonitrile/aqueous ammonium acetate (50 mM), using a flow rate of 0.2 mL/min. The fragmentor voltage was 100 V. Both positive and negative electrospray ionization was used to detect different compounds. Details of the methodology have been described elsewhere.[8,10]

Multivariate data analysis was performed with Simca P+ 11.5 (Umetrics, Umeå, Sweden). Prior to analysis, the data were normalized and mean-centered. Principal component analysis (PCA) was used to evaluate similarities and differences between the spectra illustrated as score plots.[8,10,11]

Phosphorus (^{31}P) NMR.[12,13] The sample (30 mg) was mixed with 100 μL of dimethylformamide/pyridine (1:1, v/v) and 100 μL of an internal standard solution consisting of 1.5131 g of cyclohexanol in 100 mL of pyridine. The sample solution was mixed in a NMR tube with a solution of 100 μL of derivatization reagent (2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane) in 400 μL of $CDCl_3$. The mixture was analyzed in a Bruker Avance 400 MHz spectrometer.

GC/MS. The sample was silylated with 250 μL of *N*,*O*-bis(trimethylsilyl)-trifluoroacetamide containing 5% trimethyl chlorosilane (TMCS) and 150 μL of pyridine at room temperature for 1 h. The analysis was performed on a Thermo Finnigan Trace GC/MS 2000 series, using helium as the carrier gas (0.5 mL/min), an initial temperature of 60 °C, and a ramp rate of 5 °C/min to 240 °C, followed by 15 °C/min to a final temperature of 320 °C. The mass spectrum was recorded at 70 eV.

FTIR. The FTIR spectra were recorded by applying an attenuated total reflectance (ATR) crystal. The main measurement features were a spectral range from 4000 to 600 cm^{-1}, 16 scans, and a resolution of 4 cm^{-1}.

Carbon (^{13}C) NMR. The sample was dissolved in 600 μL of $CDCl_3$ (77.2 ppm) and analyzed using the Bruker standard pulse program for ^{13}C NMR.

Results

In the presence of formic acid and using ethanol as a cosolvent, lignin can be efficiently degraded at high temperature

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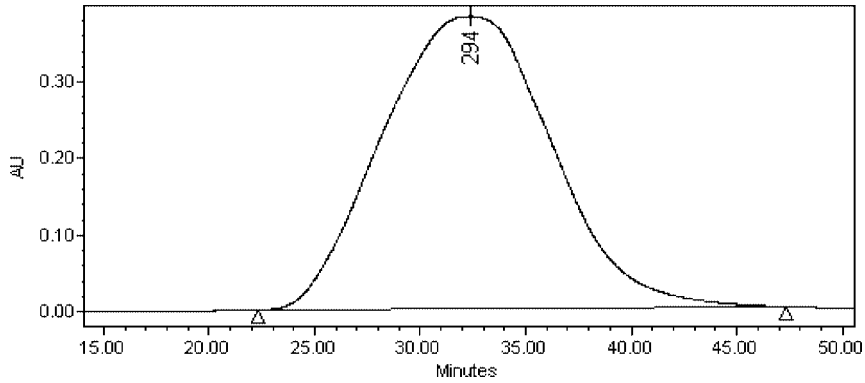

Figure 3. SEC in THF of the bio-oil MK84.

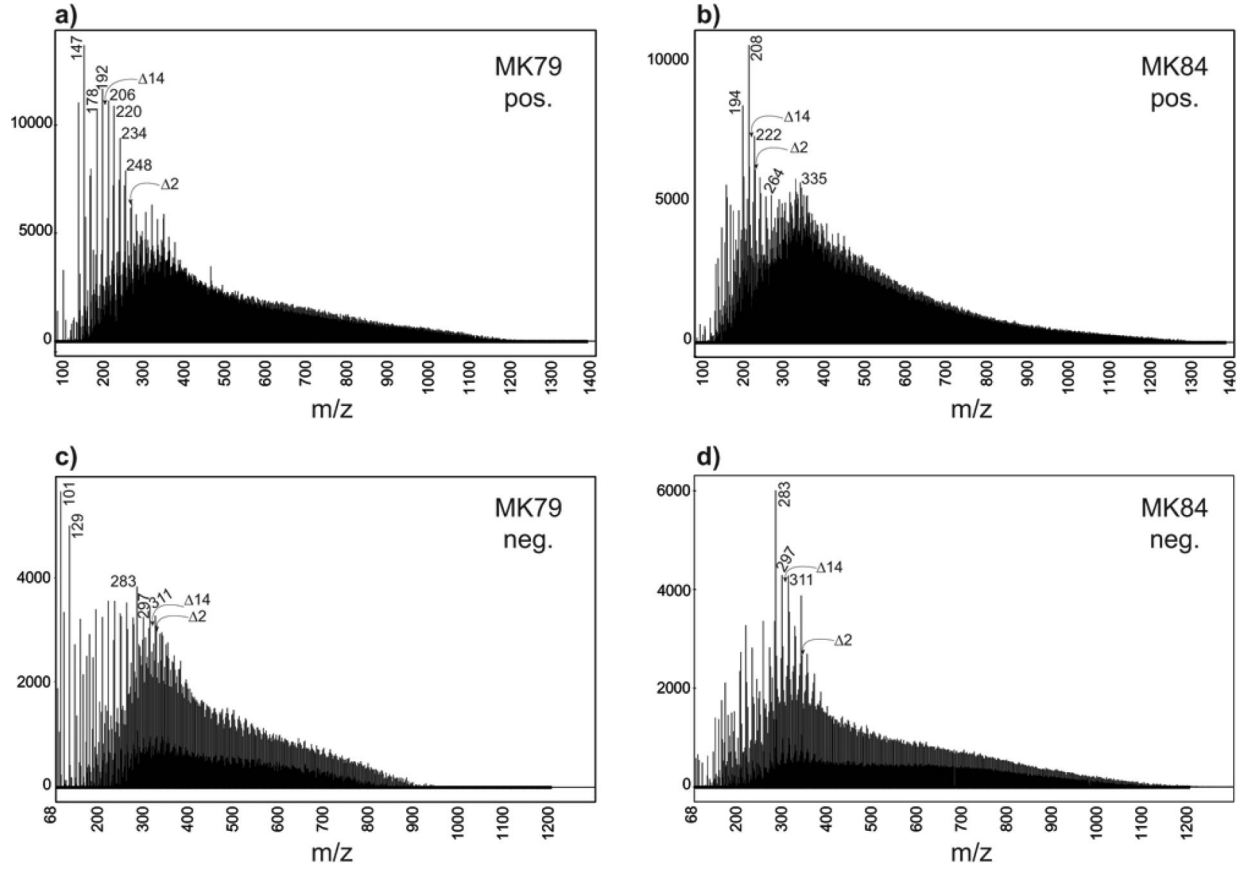

Figure 4. Positive and negative ESI−MS spectra of the two bio-oils MK79 (a, positive ESI), MK84 (b, positive ESI), MK79 (c, negative ESI), and MK84 (d, negative ESI).

to a liquid bio-oil, with only minor amounts of coke being formed. The bio-oil has been found to contain 5−10% of oxygen, with the rest being carbon (∼76−83%) and hydrogen (∼9−14%). After pyrolysis, the bio-oil can be efficiently separated from the water layer that is formed simultaneously. The aqueous phase contains a portion of the solvent (an alcohol) together with some phenol and inorganic impurities. During the course of the reaction, all formic acid decomposes, thus resulting in the aqueous phase having a pH close to neutral (about 6.5).

FTIR analysis of the two bio-oils originating from a spruce lignosulfonate (MK79) and a birch lignin resultant from steam explosion (MK84), respectively, revealed strong similarities between the samples despite the difference in the original lignin structure.[14,15] Thus, an intense signal cluster, centered around 2900 cm^{-1} and accompanied by signals at 1455 and 1375 cm^{-1}, was found in both samples. Together with signals around 1200 cm^{-1}, these strongly indicate the presence of hydrocarbons containing, at least in part, geminal dimethyl and/or tert-butyl groups. In both FTIR spectra, a strong signal at ∼1710 cm^{-1} showed the presence of carboxyl groups. Furthermore, signals originating from hydroxyl groups and aromatic rings were present (Figure 1). These data strongly support the predominance of hydrocarbon structures together with smaller amounts of phenols and carboxyl groups.

Further support for the suggested types of compounds was

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obtained by ^{13}C NMR analysis of the bio-oils. As shown in Figure 2, a substantial portion of the carbons were located below 40 ppm, thus belonging to carbons without any oxygen attachment; a result in good agreement with the ^{1}H NMR that was reported earlier, where the majority of protons were found at chemical shift values <2 ppm.[7] In the ^{13}C NMR spectrum, major signals were, however, also found in the aromatic region, with the highest concentration centered about 130 ppm, indicating alkyl-substituted aromatic (and olefinic) structures. Furthermore, the signal cluster at ~150 ppm showed the presence of phenolic structures. Minor carboxyl and carbonyl signals (>160 ppm) were also present in the spectrum. From the spectrum, it was obvious that the mixture of compounds present in the bio-oil was of low-molecular-mass origin because the spectral width of the individual signals was small and in the order of 2−5 Hz. Furthermore, the signal at ~56 ppm, typical of lignin-derived methoxyl groups, was completely absent, demonstrating that a comprehensive chemical modification of all aromatic structures takes place in the pyrolysis reaction.

The molecular-mass distribution of the bio-oils was further analyzed using SEC as well as ESI−MS. From SEC in THF, calibrated with polystyrene standards and with toluene, rather uniform distribution curves were obtained as shown in Figure 3. The peak mass weight was calculated to be less than 300. The data from positive and negative ESI−MS analyses showed peak values around 320 and with mass distribution ranging from ~100−1100 mass units (Figure 4), in excellent agreement with the SEC data. Although the mass spectra may appear unresolved, there is one distinct line per integer mass number (*m*/*z*). The lines represent those parent compounds (unfragmented) that have become ionized. Electrospray ionization (ESI) typically occurs by the addition or loss of a proton, but sometimes positive ionization occurs by adducts. Positive ESI−MS detects polar compounds, such as nitrogen-, oxygen-, or sulfur-containing heterocycles, amines, ethoxylates, glycerides, esters, etc.[8,10,16,17] Negative ESI−MS detects naphtenic and other organic carboxylic acids, sulfonates, phosphonates, etc.[10,16] Nonpolar hydrocarbons, such as paraffins and aromatics, are largely not ionized by ESI.

Identification of individual compounds has not been performed in the present study because the major purpose with the ESI−MS analysis was to verify the existence of compounds that can be ionized with ESI and to obtain a molecular-mass distribution. In addition, the detailed fine structure has been systematically explored by the use of multivariate data analysis.[8] In Figure 5, the score plot is shown after PCA of the ESI−MS data obtained from five analytical runs of each of the two oils MK79 and MK84, each ionized by both positive and negative ionization. The first principal component explains 68% of the variation in the data (the difference between the ionization techniques), and the second explains 16% (the difference between the two bio-oils). The score plot illustrates the very high repeatability of the ESI−MS data, and in addition, it shows that the spectra from the two bio-oils are different from each other despite the obvious similarities. The major differences were found to occur in the lower mass range dominated by lines with repetitive spacing of 14 Da (CH_2) and 2 Da (saturated versus unsaturated analogues) as indicated in Figure 4.

By reaction with a 2-chlorophosphalone derivative, compounds with labile hydrogens, such as hydroxyl groups, can be quantitatively derivatized and the amount of phosphorus can be conveniently determined by ^{31}P NMR (Figure 6 and Table 1).[12,13] Analytical data on several phenol, alcohol, and carboxylic acid reference compounds are available and show that even small changes in the chemical structure give rise to characteristic changes in the chemical-shift value.[12] Some examples are shown in Table 2.

The three clusters of peaks between 138 and 144 ppm, shown in Figure 6, therefore indicate that the bio-oils contain phenolic compounds with several distinctly different substitution patterns.

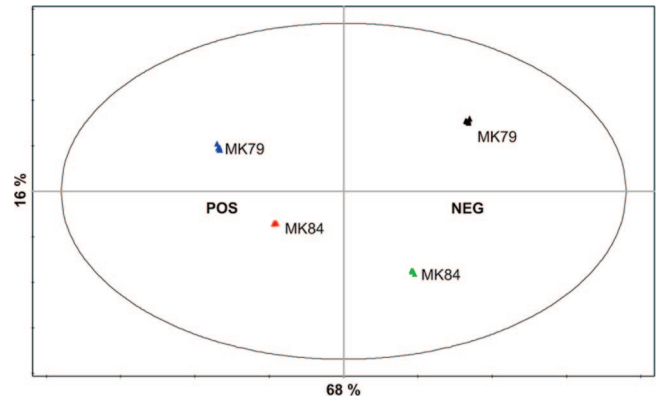

Figure 5. Score plot obtained from PCA of both positive and negative ESI−MS data of the two bio-oils MK79 and MK84.

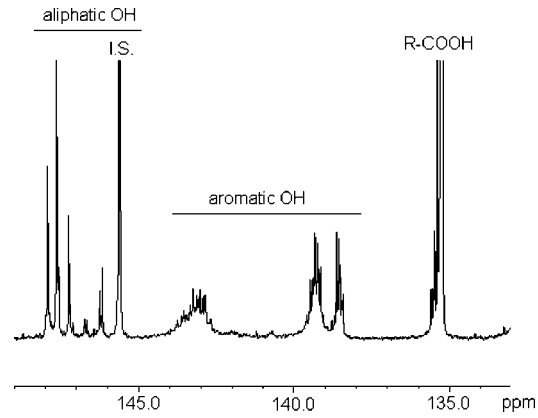

Figure 6. ^{31}P NMR of the bio-oil MK84.

Table 1. Amounts (mmol/g) of Aliphatic Hydroxyl, Aromatic Hydroxyl, and Carboxyl Groups in the Bio-oils MK 79 and MK 84 Together with the Corresponding Values Obtained from Steam-Exploded Birch Wood Lignin (Reference) after Analysis with ^{31}P NMR

	mmol/ g of sample				
		phenolic OH			
sample	aliphatic OH	142−144 ppm	139−140 ppm	138−139 ppm	carboxyl
reference	0.99	1.65	0.54	0	0.40
MK 79	0.07	0.55	0.02	0.65	0.93
MK 84	0.40	1.54	0.09	0.12	0.42

Table 2. ^{31}P NMR Shifts of Some Phenols Derivatized with 2-Chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane[a]

compound	^{31}P NMR shift (ppm)
phenol	138.7
p-cresol	138.8
o-cresol	139.3
2,4-xylenol	139.5
2,6-xylenol	143.0
2,4,6-trimethylphenol	143.4

[a] Data from ref 12.

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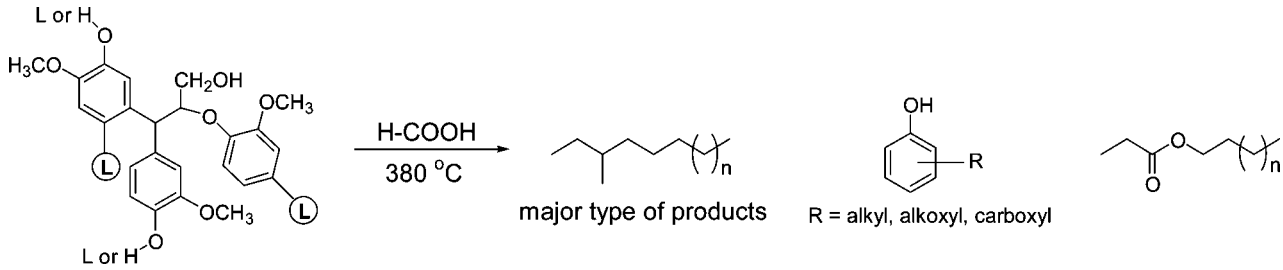

Figure 7. Schematic picture of the products formed upon the pyrolysis of lignin in the presence of formic acid.

Bio-oils with different lignin origins, when derivatized and analyzed by ^{31}P NMR, showed that only a minor portion of aliphatic hydroxyl groups remains after the pyrolysis, in agreement with the other analytical data. Phenolic structures with different degrees of substitution as well as carboxyl groups were found to be quite frequent, however, as shown by the data in Table 1.

The presence of carboxyl groups in the bio-oils as revealed by ^{13}C and ^{31}P NMR as well as by FTIR analysis was further characterized by silylation and GC/MS analysis of the resulting mixture. In addition to several previously identified aliphatic and aromatic compounds,[7] a series of aromatic carboxylic acid structures was found. All identified compounds (on the basis of the MS fragmentation pattern) contained a benzoic acid structure, with one or two other substituents, such as hydroxyl, alkyl, alkoxy, or carboxyl, attached to the same aromatic ring.

Discussion

From the analytical data obtained, it is obvious that the pyrolysis of lignin in the presence of formic acid is a powerful way of completely changing the chemical structure. The original macromolecule, containing phenylpropane units interconnected by ether and carbon−carbon linkages and with oxygen content in the order of 30−35%, is broken down to a mixture of aliphatic hydrocarbons of low molecular mass, as schematically illustrated in Figure 7. A substantial number of phenolic structures are also present, with some units carrying carboxyl substituents in addition to alkyl groups. The possibilities of further optimizing the pyrolysis reaction toward a biofuel composition seem, however, to be good, and a further decrease of the content of aromatics as well as of oxygen should be possible. Alternatively, the product composition might be tailored toward the production of value-added products, such as phenols.[18]

From a mechanistic point of view, the function of formic acid as a reducing agent at high temperature is well-known, and recent examples include the reduction of acetone to isopropanol[19] and benzaldehyde to benzyl alcohol.[20] Furthermore, the presence of an alcohol can be assumed to increase the solubility of the lignin to a great extent, thus promoting a more homogeneous reaction than would otherwise occur.[21] Thus, it seems logical to assume that the formic acid is cleaved with the formation of atomic hydrogen and a carboxyl radical. The former is an efficient scavenger of any radical species formed in the lignin, whereas the latter seems to give stable end products upon addition to a phenyl-type of radical, with minor amounts being incorporated as ester groups in alkyl chains. By successive homolytic cleavage of the covalent linkages in the lignin, including aromatic rings (presumably in structures of the ortho-quinone type), most of the oxygen is removed as water and hydrocarbons are formed. The aromatic methoxyl groups present in the original lignin can be assumed to be a supplier of methyl radicals during pyrolysis, thus giving rise to structures having two or three methyl groups linked to the same carbon atom. Furthermore, alkyl groups might be formed through Fischer−Tropsch-type reactions between carbon monoxide and hydrogen, both known degradation products from formic acid.

Conclusions

The pyrolysis of lignins in the presence of formic acid and an alcohol results in the complete conversion of the original macromolecular phenylpropane structure with the formation of a complex mixture of low-molecular-mass compounds. The majority of these seem to be aliphatic hydrocarbons, although a substantial number of phenolic structures are also present. A minor portion of the latter has been converted to oxygenated benzoic acid structures. By further optimization of the pyrolysis reaction, a complete conversion of lignin to biofuel should be feasible.

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