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Towards a Lignocellulosic Biorefinery: Direct One-Step Conversion of Lignin to Hydrogen-Enriched Biofuel

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This paper reports a novel liquefaction process that is capable of depolymerizing the natural biopolymer lignin into a liquid bio-oil with a very low oxygen content, suitable as a blending component to be combined with conventional fossil fuels for motor fuel applications. During the conversion, both depolymerization and removal of oxygen by formation of water occur in a single step. Formic acid serves as both the hydrogen donor and reaction medium in the pyrolysis/solvolytic process. Using an alcohol as cosolvent can improve the liquid yields and H/C ratios. Very little coke (5%) is produced. The liquids produced comprise two easily separable phases, where the lighter organic phase consists mainly of low molecular weight alkylphenols and C₈–C₁₀ aliphatics. The process is developed to be combined with ethanol production from lignocellulosic carbohydrates in a biorefinery concept aimed at converting all fractions of the wood into renewably sourced liquid fuels.

Introduction

Use of biomass as a resource for energy production is increasingly a focus in both research and development projects of alternative energy. The need for exploiting energy resources that are renewable, globally available, and do not contribute to adverse climate effects is generally accepted;¹ however, the specific solutions are still in a process of development, and the list of options is still open—and expanding.

Producing renewable liquid fuels that are suitable for use in motor vehicles is perhaps the greatest challenge in the biofuel area. The quickest route to a widespread use of renewable biofuels would be to produce a fuel that is compatible with the existing motor technology and infrastructure, so that direct substitution and mixing of conventional and renewable fuel types would be possible. Fuels like hydrogen and electricity will not be as simple to implement because they require major changes at several levels of technology. Ethanol, biodiesel (FAMES), and biogas are well-known examples of renewable, petroleum compatible fuels, but the amounts produced based on present day resources and technology will only cover a fraction of the total needed on a global basis.²

In the development of new processes for the production of second-generation renewable motor fuels from biomass,³ wood is the preferred raw material based on resource and process evaluations. Natural wood is a large resource in many areas of the world, and increased exploitation is sustainable. In addition, short rotation forestry may increase the available resources without competing with food production.⁴ This is strongly in contrast to the increased use of vegetable oil and sugar crops since the use of lignocellulosic biomass avoids the negative side

effects of intense farming of, e.g., soya, rapeseed/canola, corn, or sugar cane.

Sustainable use of biomass must include using all components of the raw material, not just the most easily converted fractions. For wood, this would mean converting all parts of the raw material into value-added products, in this context preferably in the form of transport fuels. Ethanol production from the carbohydrate fractions of wood is already close to commercial application. However, the lignocellulosic raw material also contains other components: the average composition of a Norway spruce (*Picea abies*) log (grown in Norway) is 41% cellulose, 28% hemicellulose, 27% lignin, and 4% resins. Thus, the use of the carbohydrate fractions leaves around one-third of the material as a low-value byproduct or waste. This is a significant drawback both for the efficiency of conversion and for the economy of the whole process. Altogether, the lignin should be considered as the second most abundant source of renewable and sustainable carbon next to cellulose and exploited as such.

For optimal use of the renewable resources, it is constructive to think in terms of a biorefinery,^{5–7} where the raw material coming into the refinery is completely transformed into a number of different products. The product slate can then be designed to give the best possible overall economy. Within this concept, the lignin and extractives that are “left over” from ethanol production should be processed to give value-added products, rather than just being burned as a process energy source.

Pyrolysis is a central technique in many biorefinery concepts. Pyrolysis has been widely investigated as a process for converting solid wood and vegetable biomass to liquids, termed, e.g., “bio-oils”, “pyrolysis oil”, “pyrolysis liquids”, or “bio-crude oil”,

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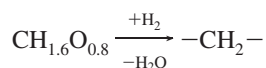
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and is defined as the thermal degradation of organic material compounds in the absence of air.⁸ A general problem encountered when applying pyrolysis to biomass or biomass fractions is that the resulting "oil" contains a high level of oxygen, including water and water-soluble components, and is not miscible with petroleum-based liquids. This is typically the case when using fast or flash pyrolysis, which is the most intensively investigated pyrolysis process at present. In this technology, a very high heating rate is applied to small, dry wood chips over a short time to produce a maximum volume of liquid with a low level of chemical conversion of the biomonomers. These bio-oils are very acidic and corrosive and often chemically unstable over time. In spite of a considerable amount of research on upgrading, no efficient route for the upgrading needed to produce a motor fuel has been established, so a biorefinery based on fast pyrolysis oil is still problematic.^{9–11}

This work addresses the conversion of lignin to liquids with the aim of obtaining liquid fuels also from this part of the raw material.¹² However, the high oxygen content and the dominance of aromatic structures in lignins require a high degree of chemical transformation and incorporation of additional hydrogen to give stable, nonpolar, petroleum soluble liquid products. Simple pyrolysis technologies that only apply heating will result in conversion of lignin mainly to solid coke and gas in a disproportionation process, just as lignin-rich material in nature would be transformed into coal, not petroleum, during natural transformation processes.^{8,13}

If the aim of the process is defined in terms of chemical composition rather than volume of product, the fundamental goal would be to achieve a conversion of lignocellulosic biomass into liquid biofuels that are physically and chemically compatible with petroleum-based hydrocarbon fuels, stoichiometrically expressed by the formula



This requires that hydrogen is added in the process to increase the H/C ratio of the product and to remove excess oxygen as water. Such conversion methodologies should be termed alternatively pyrolysis, solvolysis, or liquefaction, as they involve heating the solid lignin in a solvent-based reaction medium to convert it into a liquid.

Using such strategies, a number of conversion processes that utilize heating of the biomass in different types of reaction media with the aim of producing higher quality oil have already been explored, e.g., hydroprocessing in which water or steam acts as the reaction medium and also as a hydrogen donor to some degree.¹⁴ The HTU process is a prominent example of this approach. It utilizes wet biomass as feedstock, which also removes the need for drying.¹⁵ However, this approach has not incorporated conversion of the carbohydrate fractions into ethanol, as the whole biomass is used as raw material for the pyrolysis. Some processes have also been developed that specifically convert lignin to transportation fuel components based on hydrodeoxygenation. They utilize gaseous hydrogen

and different catalysts, e.g., zeolites, to remove the covalently bound oxygen as water.^{2,16} Other techniques involve a two- or three-step procedure in which first the natural polymer is depolymerized by strong bases at elevated temperatures, and subsequently, the respective mono- or oligomers are hydrotreated in the presence of heavy and/or transition metals and their oxides.^{17–19} In this way, a high-quality product is obtained, but the multistep conversion is not optimal for large-scale use.

In this work, formic acid/alcohol mixtures are used as the reaction medium for converting lignin to liquid "oils" in a pyrolysis/solvolysis process. The composition of the produced oils has been analyzed using gas chromatography combined with mass spectrometry (GC-MS) to determine the overall boiling point range of the produced "oil" and identify major components. Nuclear magnetic resonance (NMR) is used to show the average distribution of aromatic vs aliphatic structures in the liquid, and elemental analysis is used to give information on the removal of oxygen and incorporation of hydrogen in the product. The scope and applicability of the conversion process has been explored and validated through a large number of laboratory experiments of which representative examples are given here. The investigation has been done with raw materials ranging from lignin model compounds to an assortment of softwood and hardwood lignins. Their preparation ranges from precipitated lignin after steam explosion,^{20,21} through waste material from industrial wood-based bioethanol production, to commercial liginosulfonate and organosolv lignin.

Experimental Section

Starting Material. Fresh and chipped Norway spruce, NS (*Picea abies*), Scots pine, SP (*Pinus sylvestris*), birch, BI (*Betula verrucosa*) and aspen, AS (*Populus tremula*), were provided by several Norwegian companies. The wood chips were screened to a chip size between 3 and 13 mm (pine), 7 and 13 mm (aspen and birch), or 13 and 45 mm (spruce) before use.

Lignin fractions were prepared as described by Li et al.²² A short summary of the process is given here: The wood chips were steam impregnated at 2 bar steam for 30 min. Sulfur dioxide impregnation was performed at room temperature by introducing SO₂ gas to reach a charge of 4 to 8% with respect to the wood mass and kept for 30 min before ventilating out the gas. Steam explosion was carried out at 205 to 225 °C using equipment consisting of a 10 L pressure vessel and a flash tank to collect the steam-exploded materials as described elsewhere.²³

The steam-exploded fibers were subjected to an alkaline extraction by 1.5 M NaOH at 70 °C for 120 min followed by a filtration. The solid residues were washed to neutral pH and dried to obtain extracted steam-exploded fibers for further analysis. The liquid was neutralized to pH 4 by addition of sulfuric acid, and the precipitates were isolated by filtration followed by drying at 40 °C to obtain alkaline extractable lignins.

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Table 1. Elemental Composition of Biomass Types and Model Compounds

lignin	wt %					molar ratio	
	C	H	N	S	calcd O	O/C	H/C
Lignins isolated after steam explosion of wood and milled wood lignin							
BI	54.1	5.5	0.2	2.2	38.0	0.53	1.21
NS	61.2	5.8	0.2	1.1	31.7	0.39	1.13
AS mwl	58.7	5.9	0	0.1	35.3	0.45	1.20
NS mwl	59.2	6.0	0.1	0.1	34.6	0.44	1.21
Industrial lignin sources							
AL: alkali lignin ^a	48.2	3.4	0	1.1	47.3	0.74	0.84
OS: organosolv lignin ^a	66.3	5.3	0.2	0.3	27.9	0.32	0.95
LS: liginosulfonate ^b	42.0	4.6	0	6.3	47.1	0.84	1.31
HL: hydrolysis lignin ^b	47.6	4.3	0	0.4	47.7	0.75	1.07
lignin from ethanol plant ^c	55.2	6.0	0.1	0.1	38.6	0.52	1.30
lignin from ethanol plant ^d	63.3	4.7	0	0.6	31.3	0.37	0.88
Commercially available standards							
G: guaiacol	67.7	6.5	0	0	25.8	0.29	1.14
S: syringol	62.3	6.5	0	0	31.1	0.38	1.25
GGE: guaiacylglyceryl ether	60.6	7.1	0	0	32.3	0.40	1.40
cellulose	43.8	6.3	0	0	49.9	0.83	1.67
Plain wood for comparison							
AS wood, <i>Populus tremula</i>	39.0	4.0	0.1	5.5	51.4	0.99	1.21
NS wood, <i>Picea abies</i>	44.6	6.4	0	0.6	48.4	0.82	1.70
BI wood, <i>Betula verrucosa</i>	46.6	6.4	0.1	0.1	46.9	0.76	1.63
SP wood, <i>Pinus sylvestris</i>	41.8	6.7	0.1	0.4	51.1	0.92	1.90

^a Sigma-Aldrich Co.. ^b Borregaard Ind. ^c Lund, SE. ^d Bergen, NO.

Commercial lignins were also used within this study. The elemental compositions of all used starting materials are given in Table 1.

All chemicals were purchased from Aldrich and used without further purification or drying.

Pyrolysis/Solvolytic. Closed system nonstirred stainless steel batch reactors of the 4740 series from Parr Instruments (with 25 and 75 mL volume, respectively) were used. Lignin, formic acid, and alcohol, and in some cases water or DMC (dimethyl carbonate), were added to the reactor in the required proportions before closure and heated in a Carbolite LHT oven for periods of 2–54 h. The heating time from room temperature to 300 °C was tested to be ca. 15 min, giving an approximate heating rate of 20 °C/min.

After the completed reaction time, the reactors were taken out of the oven and cooled in an air stream to ambient temperature. The reactor was opened, and a small sample of the organic top layer was saved for GC/MS analysis in ethyl acetate as solvent. The reaction mixture was separated by simple decanting, and the aqueous layer was extracted with dichloromethane (ca. 10 mL) twice. The recombined organic phases were concentrated in reduced pressure (ca. 100 mbar) to yield a dark brown to black liquid. The yield was determined by weight. It was necessary to remove residual solvents before quantification even though this will lead to loss of volatile products. The evaporation step is only essential to exactly measure and characterize the lignin-derived liquid products. However, in process scale, the evaporation step is not necessary.

Elemental Analysis. All samples were analyzed for their elemental composition in the CHNS mode with a Vario EL III machine using helium as the carrier gas. The amount of oxygen was calculated by difference.

GCMS Analysis. The liquid samples were analyzed on a GC-MSD (HP 5890-II with HP Auto 5890) and a 25 m WCOT fused silica column (CP-Sil_8_CB) equipped with both FID and an HP5971 MSD detector and controlled by an HPChem laboratory data system. The run started at 50 °C for 2 min and then was heated at a rate of 6 °C/min up to 320 °C. The final temperature was held for 10 min. The injector temperature was 300 °C; the FID was at 350 °C; and the MSD had a temperature of 280 °C. Compounds were identified using the Agilent MSD software and the NIST 05 library. The gases were analyzed on a GS (HP 6890 Series GC Plus) and a HP Plot Q-capillary equipped with an FID. The run started at 35 °C for 5 min and then was heated at a rate of 10

°C/min up to 180 °C. The final temperature was held for 22 min. The injector temperature was 150 °C, and the FID was at 250 °C.

NMR Analysis. Nuclear magnetic resonance: NMR spectra were recorded on Bruker AV500 (500 MHz for ¹H, 125.47 MHz for ¹³C) and AV600 instruments (600 MHz for ¹H, 150.47 MHz for ¹³C). Standard pulse programs for 1D experiments of proton and carbon (broadband decoupled and dept 135) nuclei were applied, and the spectra were calibrated to the signal of TMS: 0.00 ppm.

Results

The elemental compositions of the lignin samples used in this study are given in Table 1. A considerable degree of variation is found, depending on the type of wood used as raw material and the separation process applied. One liginosulfonate lignin contains significant levels of sulfur (6.8%). The lignins also contain a certain amount of inorganic salts (up to ca. 10%), which are mainly derived from the process of separation or precipitation (data obtained from TGA-based ash analysis). These inorganics are found mostly in the aqueous phase after the pyrolysis and therefore do not seem to cause any problems in the oils. It should be noted that the yields of the products given below are based on the total mass of lignin used as starting material, so that if the calculations were based on the dry organic matter content of the lignin the yields would be even higher.

Yields and Elemental Composition of the Product. The conditions used and the quantitative yields and elemental compositions of the oils for some selected experiments are given in Table 2. The volume ratio of formic acid to alcohol has been varied over a wide range and has in most cases given good yields of an oil phase with a high hydrogen content and very low oxygen content. The C₁–C₄ low molecular weight alcohols can all be used in the reaction medium, but the emphasis in these experiments has been on ethanol as the primary product from fermentation and 2-propanol which gives the highest yields and is also known to serve as a moderate hydrogen donor.²⁴ Adding DMC as a methylating agent changes the product composition to some degree by methylating acidic sites and also increasing the number of methyl substituents attached to the aromatic ring. However, it has only a limited capacity of changing the molecular composition. In general, water-free alcohols have been used, but adding water to correspond to the use of 96% ethanol does not reduce the yield but causes slightly higher oxygen content (Table 2, entry 9). 380 °C is used as the standard temperature, but higher and lower temperatures have also been tested, with comparable results above a minimum of 350 °C. For reasons of convenience, most experiments were run overnight, corresponding to durations of 14–17 h, but residence times down to 4 h (at $T \geq 350$ °C) have also given moderate to satisfactory results of 60–80% yield of liquids.

Chemical Composition. The molecular composition of the lignin-to-liquid (LtL) oil has been analyzed using gas chromatography combined with mass spectrometry (GC/MS), and nuclear magnetic resonance spectroscopy (NMR) has been used to determine the ratio of aromatic vs aliphatic protons.

The gas chromatograms of the oil from experiments 4 and 9 in Table 2 are shown in Figures 1 and 2, respectively, where the identification of some major peaks and an overlay of plain diesel fuel are included for comparison. The assigned peaks from experiments 4 and 9 are also presented in terms of elemental composition in Tables 3 and 4, respectively.

With lignin as the starting material, the product consists of a complex mixture of components with mono- to oligo-alkylated

Table 2. Typical Pyrolysis Conditions and Results^a

exp. #	SM [g]	acid [mL]	alcohol [mL]	additive [mL]	T [°C]	t [h]	yield ^b [%]	molar ratio	
								H/C	O/C
1	2.3 G	5 HCO ₂ H	1 MeOH	-	380	14	95	1.21	0.16
2	2.0 GGE	5 HCO ₂ H	5 <i>iso</i> PrOH	-	380	17	130	1.66	0.17
3	0.7 NS	6 HCO ₂ H	6 EtOH	-	380	8	92	1.48	0.12
4	0.7 NS	6 HCO ₂ H	6 EtOH	-	380	54	90	1.50	0.07
5	0.7 NS	6 HCO ₂ H	6 EtOH	2 DMC	380	14	90	1.39	0.11
6	0.7 NS	8 HCO ₂ H	4 <i>iso</i> PrOH	-	380	14	90	1.69	0.05
7	0.7 NS	2 HCO ₂ H	10 EtOH	2 DMC	380	32	90	1.50	0.05
8	2.5 BI	12 HCO ₂ H	24 <i>iso</i> PrOH	-	380	16	85	1.65	0.06
9	1.0 BI	6 HCO ₂ H	6 EtOH	0.2 H ₂ O	380	14	99	1.56	0.17
10	6.0 HL	12 HCO ₂ H	18 <i>iso</i> PrOH	-	380	17	93	1.49	0.15
11	5.0 LS	15 HCO ₂ H	20 EtOH	-	380	14	82	1.41	0.12

^a SM, Starting material; G, guaiacol; GGE, guaiacolglyceryl ether; NS, Norway spruce lignin; BI, Birch lignin; DMC, dimethyl carbonate; HL, hydrolysis lignin; LS, liginosulfonate. ^b Wt % of SM.

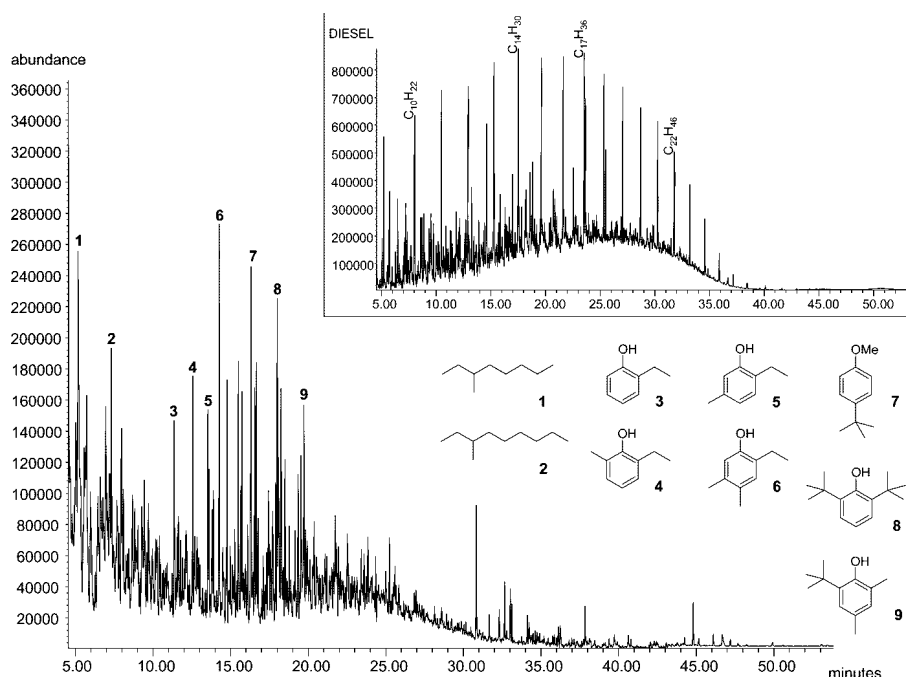


Figure 1. GC/MS chromatogram of experiment 4 and diesel spectrum for comparison. Some major peaks are assigned (see Table 3). No biphenyl ($R_t = 17.43$ min), diphenyl methane ($R_t = 18.67$ min), or polyaromatic compounds such as naphthalene ($R_t = 12.83$ min), α -naphthol ($R_t = 20.29$ min), or anthracene ($R_t = 25.98$ min) can be detected.

phenols as major compounds. The substituents mainly are C₁–C₄ alkyl groups, as shown in Figures 1 and 2. The products contain almost no methoxy groups even though they predominate in the original lignin.²⁵ This contributes to the low levels of oxygen in the LtL oils and demonstrates that effective hydrodeoxygenation is occurring, instead of the previously reported substitution processes that produce mainly aromatic ethers.¹⁹

The degree of methylation on the aromatic rings can in some cases be increased even further by adding methylating agents such as dimethyl carbonate. The oils also contain a certain amount of saturated alkyl components, either as branched, linear, or cyclic alkanes or as alkyl esters. The presence of polyaromatic hydrocarbon structures (PAHs), which are a serious concern due to health and environmental risks, has been checked by comparing with standards, and these compound types are either not present or present in very small amounts (Figure 1). The chromatograms also illustrate the molecular weight range obtained after the conversion. Comparing with the chromatogram of diesel run at the same conditions, the retention times

and hence the volatility of LtL oils are in the same range. Additional checks on the molecular weight range of the components in the liquid by means of ESI-MS show the absence of high molecular weight lignin fragments over 400 *m/z*, so the GC traces give a correct representation of the complete oils with no repression of higher boiling components.

Proton NMR spectra show the high proportion of hydrogen atoms attached to saturated aliphatic carbon chains as compared by aromatic protons (Figure 3).

Though the core aromatic rings of the lignin monomers are still present and provide signals in the aromatic region, the alkyl chains dominate and give very low aromaticity factors. This is also confirmed by carbon spectra in broadband decoupled and dept135 experiments (data not shown). However, quantitative integration of protons in a multicomponent mixture cannot be done accurately, and further investigation with carbon inverse gated experiments is ongoing.

Working with pure compounds that represent lignin structural units, a key discovery in our investigation was that 2-methoxyphenol^{26,27} can be quantitatively transformed into a mixture of phenol and

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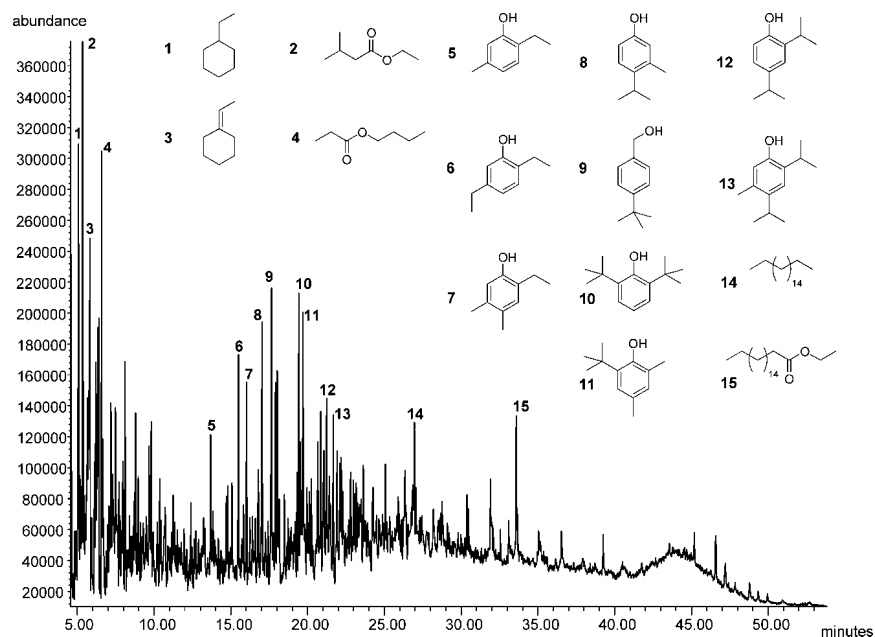


Figure 2. GC/MS chromatogram of experiment 9. Some major peaks are assigned (see Table 4).

Table 3. Molecular Formula and Elemental Ratios for Some Major Product Components of Experiment 4 (Figure 1)

peak	formula	O/C	H/C
1	C ₉ H ₂₀	-	2.22
2	C ₁₀ H ₂₂	-	2.20
3	C ₈ H ₁₀ O	0.13	1.25
4	C ₉ H ₁₂ O	0.11	1.33
5	C ₉ H ₁₂ O	0.11	1.33
6	C ₁₀ H ₁₄ O	0.10	1.40
7	C ₁₁ H ₁₆ O	0.09	1.45
8	C ₁₄ H ₂₂ O	0.07	1.57
9	C ₁₂ H ₁₈ O	0.08	1.50

Table 4. Molecular Formula and Elemental Ratios for Some Major Product Components of Experiment 9 (Figure 2)

peak	formula	O/C	H/C
1	C ₈ H ₁₆	-	2.00
2	C ₇ H ₁₄ O ₂	0.29	2.00
3	C ₇ H ₁₄	-	1.75
4	C ₇ H ₁₄ O ₂	0.29	2.00
5	C ₉ H ₁₂ O	0.11	1.33
6	C ₁₀ H ₁₄ O	0.10	1.40
7	C ₁₀ H ₁₄ O	0.10	1.40
8	C ₁₀ H ₁₄ O	0.10	1.40
9	C ₁₁ H ₁₆ O	0.09	1.45
10	C ₁₄ H ₂₂ O	0.07	1.57
11	C ₁₂ H ₁₈ O	0.08	1.50
12	C ₁₂ H ₁₈ O	0.08	1.50
13	C ₁₃ H ₂₀ O	0.08	1.54
14	C ₁₈ H ₃₈	-	2.11
15	C ₂₀ H ₄₀ O ₂	0.1	2.00

alkylphenols upon pyrolysis in formic acid and an alcohol, as illustrated in Figure 4.

This product distribution can only be explained by the replacement of the methoxy group by a methyl group, eliminating the ether oxygen most probably as water. The generated water comprises a separate layer in the bottom of the reactor after the reaction, and excess hydrogen together with formed carbon monoxide are found in the produced gases. Further

experiments with labeled ¹³C solvents are currently in process and will give further insight into the reaction pathways.

The consistent retention of the phenol group in all the products emphasizes the difficulty of generating a pure hydrocarbon product that is completely analogous to crude oil. However, the low level of oxygen remaining in the products in the form of phenolic groups does not cause any problems for its use as a motor fuel additive, but may rather have a positive effect on fuel quality due to the presence of these compounds that are known to be octane increasing agents.

Discussion

Elemental Composition. The results given above clearly show that the chemical composition of the products from the lignin to liquid conversion in the formic acid–alcohol reaction medium is completely different from other one-step pyrolysis products of lignin or biomass and especially different from flash pyrolysis liquids. This is illustrated in Table 5, which gives the elemental composition and some physical properties of relevant products. The table shows that fast pyrolysis processes do not change the molar ratios of hydrogen to carbon and oxygen to carbon from feedstock to product very much. Although termed “bio-oil” these liquids are not miscible with hydrophobic, petroleum-derived products such as diesel or gasoline. They also always contain a considerable amount of water accompanied by organic acids such as acetic acid, which results in a very low pH value. In comparison, the LtL oil is much less polar and has solvent properties much more similar to petroleum products, which makes it fully miscible with petroleum-based fuels. The low oxygen content also results in an estimated higher heating value (HHV) that can be double that of the flash pyrolysis bio-oil and in the best cases lies in the same range as that for the hydrocarbon-based products such as diesel/light fuel oil (Table 5).

The similarity between the bulk composition of LtL oil and petroleum is clearly shown when plotted in a Van Krevelen plot (Figure 5) which shows the relation of the ratio of H/C vs O/C of biomass and fossil materials. A high H/C and a low O/C value characterize the energetically most valuable products, and the improved quality of the LtL oils compared to fast pyrolysis oils is easily seen. Figure 5 also illustrates the “ideal”

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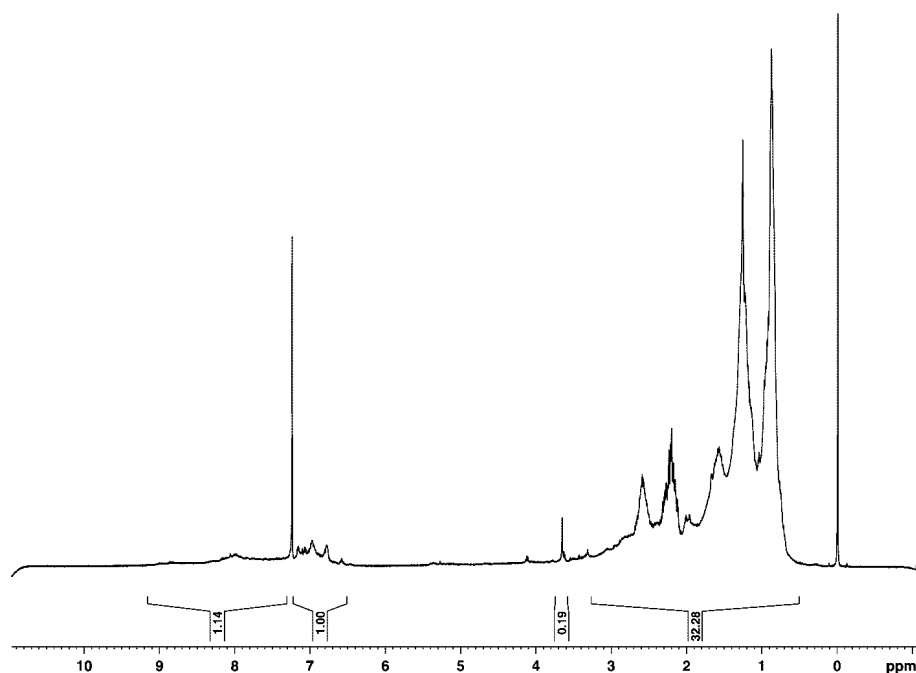


Figure 3. ^1H NMR spectrum of the product of experiment 7 in deuterated chloroform. The integration of the aromatic region (6.5–8.5 ppm) as compared by the aliphatic region (0.5–3 ppm) shows the larger proportion of aliphatic protons. Peaks at 7.26 ppm and 0.00 ppm are derived from the solvent and the reference TMS, respectively.

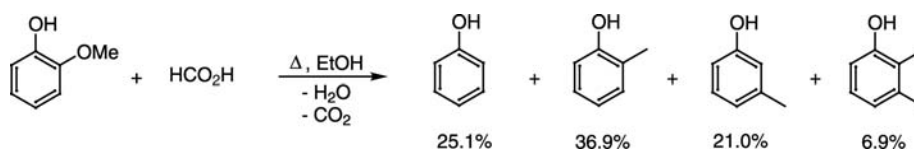


Figure 4. Deoxygenation of guaiacol by formic acid and ethanol in the described solvolytic process. Main pyrolysis products are phenol (25.1%), 2-methylphenol (26.9%), 3-methylphenol (21.0%), and 2,3-dimethylphenol (6.9%). Conditions: 380 °C, 14 h, high pressure.

Table 5. Physical Properties of Typical Milled Wood Lignin (MWL), Flash Pyrolysis Product of Biomass,¹⁰ Fossil Fuels, and the LtL Oil^a

property	MWL	flash pyrolysis oil	heavy fuel oil	light fuel oil	LtL oil
elemental composition ^b					
carbon	59.2	54–58	85	85	76–83
hydrogen	6.0	5.5–7.0	11	13	9–13.5
oxygen	34.5	35–40	<1.0	0.4	5–10
sulfur	<0.2	<0.2	1.0	1.0	<0.2
molar ratio					
H/C	1.2	1.15–1.55	1.55	1.8	1.3–1.8
O/C	0.44	0.6–0.73	0.01	0	0.05–0.1
ash [wt %]	2–3	0–0.2	0.1	0	0–0.2
pH	—	2.5	—	—	—
density [g/mL]		1.2–1.3	0.9	0.9	0.94–1.0
HHV [MJ/kg]	24.2	21–25	42.5	44.5	35.6–44

^a Higher heating values (HHV) calculated after Parikh et al.²⁸ ^b Wt %.

conversion path that would be needed to transform oxygen-rich raw material like wood into hydrocarbon-like products. At present, no such conversion route exists, either in nature or in the laboratory. When lignin is the raw material for conversion, the oxygen-rich carbohydrate fractions are already removed and used for ethanol production, and the elemental composition of the remaining lignin is improved. The LtL process then adds hydrogen and removes oxygen to a degree that gives a product with an elemental composition close to crude oil.

Effect of the Experimental Conditions. When working with lignin as starting material (and other complex raw materials and conversion processes), we meet the problem of defining the criteria for a “good” experimental result.

As seen in the chromatograms (Figures 1 and 2), the product composition is very complex—just as a crude oil fraction is—and complete molecular analysis is neither realistic nor necessarily very useful. We have chosen to evaluate the performance of the conversion process in terms of (a) the yield of liquids, (b) their boiling-point distribution as seen by GC, (c) their elemental composition, (d) their phase or solvent properties with respect to separation into a stable two-phase system relative to water, (e) the absence of significant amounts of coke in the product, and (f) their solubility in nonpolar solvents.

Using these criteria, we have tested a wide range of conditions regarding temperature, duration, reactor size, solvent combinations, and proportions of solvent to lignin to explore the range of process conditions that can be used. After testing a number of combinations of formic acid and other acids with C₁–C₃ alcohols as well as their esters as reaction media, we have found that formic acid or formates are the critical factor for obtaining the combined depolymerization and hydrodeoxygenation of the lignin. If formic acid or formate is not present, the product slate after pyrolysis resembles the products obtained in flash pyrolysis processes, and the amount of char produced is high. Maximum yields of oils with low oxygen contents are obtained when combining formic acid with 2-propanol as cosolvent, and in this case, some propyl chains from the alcohol are incorporated into the products to a degree where the yields may exceed 120% of the original lignin by weight. 2-Propanol also donates hydrogen and is converted into acetone, which was observed in NMR spectra of the products. Aromatic esters are not observed, and there is little to no formation of biphenylic or polyaromatic systems.

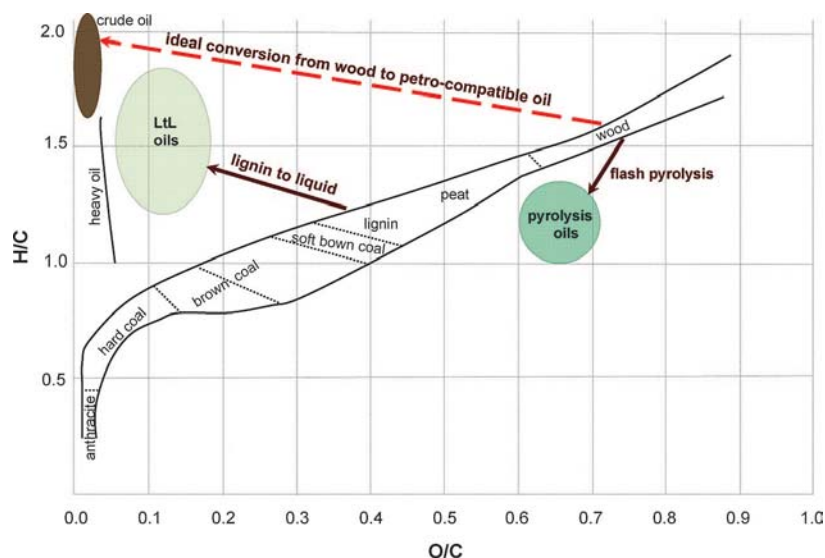


Figure 5. Van Krevelen diagram showing the H/C vs O/C ratios of different biomass and fossil materials. The arrows indicate conversion pathways for the flash pyrolysis and the lignin to liquid process as described here as well as the “ideal” theoretical conversion from wood to crude petroleum (dashed arrow). Areas of LTL and flash pyrolysis oils are drawn in.

A considerable range of combinations of solvent systems, temperatures, and durations of the pyrolysis step yield good results. Formic acid, however, is the single necessary component, and the temperature should be higher than 350 °C to obtain both good conversion and low levels of char. The product composition changes with the time–temperature conditions and proportions of solvent to lignin, varying from alkylphenols as the major products to mixtures also containing C₈–C₁₂ cyclic and branched alkanes. The conversion process thus has the potential for tailoring to provide optimal product slates depending on the requirements. Further optimization can be based on economic and process considerations to give a practical process in a biorefinery application. As previously reported for hydrothermal processing in nonstirred reactors,²⁹ we have seen that the best product composition is obtained with low concentrations of lignin in the solvent systems, and this may be a major challenge in the upscaling of the LTL process. However, all our experiments have been done under nonstirred conditions which may have limited the availability of reactive hydrogen due to diffusion restraints. Using other reactor configurations may therefore improve the results, as also suggested for water gasification reactions.

Mechanisms of Conversion. The chemical mechanisms for the conversion are at present not clearly understood. The concept of using formic acid together with different cosolvents such as iso-propanol or other hydrogen donating agents in a solvolysis process is entirely new in the area of biomass or lignin conversion, though formates have previously been suggested for use in coal liquefaction.³⁰ However, application of these compounds separately has been investigated,^{24,31} and much effort has been put into elucidating the actual reaction pathway of, e.g., the thermal decomposition of formic acid and its hydrogen donating properties,³² either at hydrothermal conditions³³ or in the context of catalytic transfer hydration.^{34,35} The mechanisms

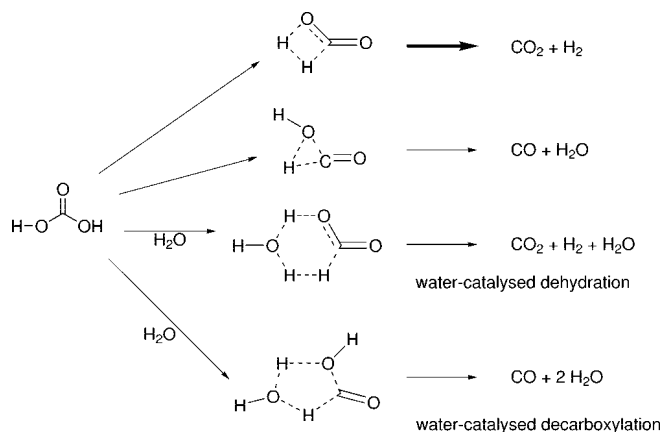


Figure 6. Molecular elimination mechanisms for formic acid decomposition at high temperatures.³³

that have been discussed include ionic, free-radical, surface-catalyzed, or molecular reaction steps, but no clear mechanistic understanding has yet been reached. The different reactions of formic acid as a hydrogen-donating agent in its thermal degradation with and without water present are depicted in Figure 6. In a kinetic study by Savage et al. it was concluded that the decomposition at high pressure and high temperature yields CO₂ and H₂ as the major products, so decarboxylation is the preferred reaction path.³³

After the solvolysis experiments reported here, no formic acid remained in the reaction mixture, as observed using carbon NMR experiments of the untreated crude product. Thus, a complete decomposition of the formic acid in the solvent mixture occurred over the whole range of experimental conditions.

Even the degradation of pure model compounds proves to be a very complex process, and Mulder et al. have suggested the following reaction sequence for the thermal degradation of guaiacol in an excellent article (Figure 7).³⁶ Further investigation is required, as a clear understanding of the mechanism may suggest ways to improve the process in terms of increasing the

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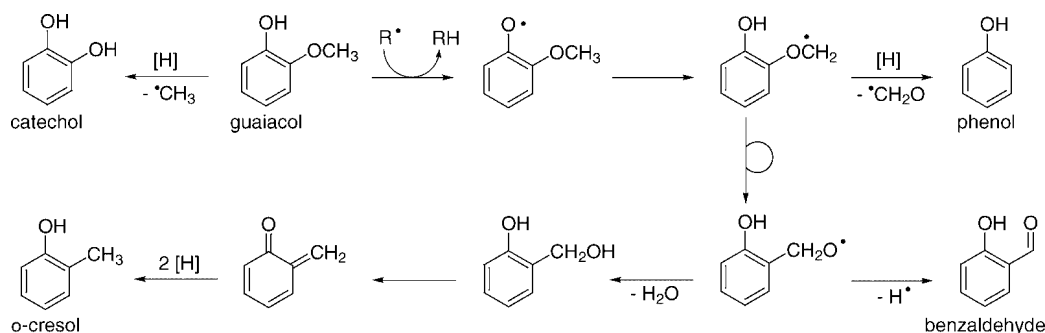


Figure 7. Thermal degradation of guaiacol as suggested by Mulder et al. The radical species are assumed to be present at the given harsh reaction conditions.

reaction rate and reducing the ratio of reaction medium to solid. It is clear that the depolymerization of the lignin is a complex process. The range of molecular types and molecular weights in the product suggests complex reaction pathways and perhaps multistep, potentially competing reactions. This is supported by the observation that a certain duration of the pyrolysis step is necessary. Under the conditions applied here, heating periods of less than 3–4 h do not give a satisfactory degree of conversion. From a large number of experiments (over 80), it is obvious that lower temperature and duration of the pyrolytic step reduce the degree of depolymerization and deoxygenation, and thereby the yield of desirable liquid product is decreased. An optimum is reached at 380 °C and ≥ 8 –10 h regardless of the lignin used. These conditions give complete liquefaction and almost quantitative yields.

It is possible that the stainless steel walls of the reactor may have a heterogeneous catalytic function, though this is at the moment just a speculation. One way this could occur would be by Fischer–Tropsch-type reactions that generate hydrocarbons by polymerizing hydrogen and carbon monoxide, which can be generated by dehydration of the formic acid as a side reaction. This is supported by production of measurable amounts of hydrocarbons in an intermediate molecular weight range in blank runs where the reactor only contained the solvents. A systematic investigation based on statistical experimental designs is ongoing to determine the precise effects of the experimental variables and the optimal conditions for each lignin type. The finding will be reported in subsequent papers.

Perspectives. Lacking a thorough and proven mechanistic understanding of the conversion process, continued development will be pursued using statistical experimental designs and modeling to find the optimal reaction conditions for the conversion of different lignin types. The requirement for product quality must be balanced relative to practical consideration of especially temperature, pressure, and solvent costs for the whole process. This work is under way but is strongly dependent on defining the quality objectives, so we return to the question of what is a sufficiently “good” bio-oil for use as transport fuel. Even after the elimination of obviously negative properties, like high levels of dissolved water or solid particles, too low volatility, corrosiveness, etc., there is a wide range of possible compositions that could function as motor fuels. Further optimization of the process, balancing quality against cost of production, is needed to develop a new motor fuel or fuel component. A close cooperation with especially the oil and gas industry is clearly necessary for efficient progress toward production of a motor fuel that can be put on the market. However, the product from the LtL conversion process is already more suitable as motor fuel, directly or with a limited level of refining, than any other pyrolysis oil available at present.

Though the chemical research on developing new ways of conversion of different natural raw materials into liquids is the

necessary first step in the search for new, renewable motor fuels, the interdisciplinary aspects of such development cannot be overemphasized. In the context of a biorefinery, it is essential to include technical and economical parameters in the continuing optimization work. The concept of a wood biorefinery which produces ethanol from wood carbohydrates and LtL liquids from the lignin is very attractive from a resource point of view. The thermochemical conversion of the lignin could, e.g., be achieved using formic acid produced from CO that is generated by gasification of forestry wastes by way of synthesis gas. A sufficient amount of ethanol as cosolvent could be provided from the established carbohydrate fermentation processes. Gaseous byproducts of the conversion of excess formic acid have been found to contain considerable amounts of hydrogen, which together with the small amounts of coke that may be formed could be used for heat and energy purposes. In addition, value-added minor products like wood turpentine could also easily be produced in the separation steps by steam-distillation. There is also the general option to tailor the product composition toward the production of biomonomers suitable for future bioplastics. Using this concept, an energetically self-sufficient, fuel producing or chemical providing wood biorefinery may be successfully achieved.

Finally, it might be remarked that the concept of producing fuels for the automotive sector from sustainable biomass sources may not be the optimal long-term strategy to overcome future problems of energy supply and use. Alternative technologies may over time turn out to be a better option, and this could influence the optimal product slate of the biorefinery. In this context the LtL process would still be useful for producing chemicals for further industrial use. At present, however, due to market reasons and political issues, there is an urgent need for development of renewable, premium grade fuels which are compatible with current fuels and their supply infrastructure and that also meet the established quality standards, so this must be the initial goal.

Conclusion

In the work presented here, we describe a novel one-step process for converting lignin into nonviscous organic liquids (oil). The lignin has been separated from whole wood as a step in the production of lignocellulose-derived ethanol. The lignin conversion is achieved using closed system pyrolysis in a new type of liquid reaction medium. The novelty in our process is that the conversion is completed in a single-step reaction which comprises depolymerization as well as deoxygenation. The essential factor in the conversion is the presence of formic acid in the solvent system, which functions as a hydrogen source in the reaction.

We assume that the high reactivity of the in situ formed hydrogen “in statu nascendi” is responsible for converting the lignin constituents into hydrogen-rich, oxygen-depleted products with no added catalyst. An alcohol is used as a cosolvent/coreactant, which

improves both the yield of liquids and the H/C (hydrogen to carbon) ratio of the product. Use of dimethyl carbonate (DMC) as an additional methylating reagent has also been tested and can in some cases improve the product quality.

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