



The effect of solvent and input material pretreatment on product yield and composition of bio-oils from lignin solvolysis



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ABSTRACT

Solvolytic conversion of lignin from wood with formic acid as a hydrogen donor can provide a renewable source of aromatic compounds, especially phenols. In this paper, lignin or lignin-enriched fractions from Norway spruce and white birch are compared with regard to yields of bio-oil in solvolytic conversion. Water as a green solvent is also compared to ethanol as the reaction medium, and the yields and composition of the produced oils are presented. Maximum yields by weight are inversely connected to the oxygen content of the feedstock, showing that pure lignins give the highest yields while carbohydrate-containing feedstocks undergo more deoxygenation and thus give lower yields. The overall composition of the bio-oils produced is quite stable and independent of the feedstock type and pretreatment, though some difference in the quantitative distribution of the individual components is observed. The use of water or ethanol as reaction media has a significant impact on the bio-oil yields and composition due to the alkylation of the aromatic rings by the ethyl group from the solvent.

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1. Introduction—purpose of the work

Lignin is the third most abundant biopolymer in nature, and a promising feedstock for production of aromatic fuels and chemicals. Solvolysis with formic acid is an innovative conversion method for producing aromatic compounds from the lignin. A considerable amount of work has been completed to establish this conversion pathway [1–5]. However, lignins from different plants have differences in their structural and monomeric composition. The lignin concentration within lignocellulosic biomass varies from species to species and even in samples from different parts of the same tree [6,7]. Guaiacyl lignin is dominated by coniferyl monomeric units and found predominantly in softwoods, while guaiacyl-syringyl lignin is typically found in many hardwoods. The copolymer consists of both the coniferyl and sinapyl phenylpropane units, and the fraction of sinapyl units is therefore higher in hardwood lignin than in softwood lignin [8]. The structural abundance of each monomeric unit in the raw material could thus have a strong influence on the aromatic compounds being produced during lignin solvolysis.

Previous literature on lignin liquefaction with formic acid focused on the utilization of ethanolic solvent systems. In order to investigate the use of a more readily available solvent, with the aim

of incorporation of the technique in a biorefinery concept, water was selected as an alternative to ethanol in the majority of the following investigation of lignin conversion to bio-oils. The overall reaction system for thermochemical conversion of solid lignin in a solvent system of formic acid (FA) as hydrogen donor in ethanol is shown in Fig. 1 [1].

FA delivers reactive hydrogen upon degradation, together with CO₂, in a more reactive form than for H₂ gas [9]. This hydrogen combines with oxygen stemming from methoxy groups from the lignin to form water, resulting in a reduced oxygen content of the phenolic fraction of the complex product mixture [2]. The degradation of FA to carbon dioxide and hydrogen ensures that there is no acid remaining to lower the pH of the formed product mixture [10]. Formic acid in itself can be produced by thermal treatment of biomass, which gives perspectives for a biorefinery approach with production of all of the ingredients in an integrated biorefinery concept [11].

The quantitative results from experiments using the Lignin-to-liquid-technique (LTL), with formic acid as hydrogen donor, depend largely on the reaction conditions [5]. The known variations in structural composition and monomeric distribution affects depolymerisation rates and conversion rates, and experience with the LTL-system, indicates that each new lignin quality needs to be screened through systematic experimental designs to obtain the maximum conversion conditions and ratios [1]. In our experiences, to treat all lignins only at one set of conditions and ratios does not

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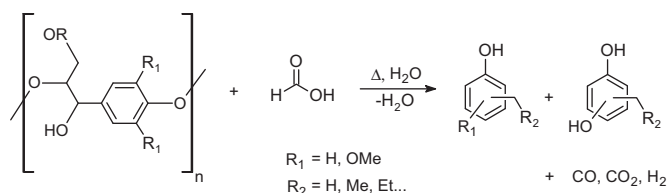


Fig. 1. Overview of the main conversion route; lignin is a methoxylated, phenolic polymer which in course of the solvolytic reaction is degraded to phenol monomers with different substitution patterns and aliphatic compounds. Simultaneously a hydrodeoxygenation occurs in which formic acid (FA) serves as the hydrogen donor. Water is generated during the reaction [1].

necessarily result in a correct or justified determination of optimal oil yields.

In this work we compare bio-oils, from different lignins stemming from various pretreatment techniques and wood species. Most of the oils are produced in a water-based LtL-solvent system, but some ethanol-based experiments are included for comparison. The results provide a basis for evaluation of variation due to feedstock relative to product distribution and product composition. Selected experiments have been duplicated to screen the reproducibility of the conversion method.

2. Experimental

2.1. Lignin starting materials and chemicals

The different lignin types used in this work are given in Table 1.

SEH and SAH lignins were produced at SEKAB for Statoil ASA. The carbohydrate content was determined by supplier. SKL lignin was kindly supplied by Innventia Sweden and SSEH and BEH were received from the Norwegian University of Life Sciences in the context of the LignoRef research project. The raw materials are of different degrees of purity and some of them have carbohydrate residues depending on the pretreatment applied.

Samples of SEH, SAH and SKL were not sieved or exposed to any other preparation steps after they were received as dry powder of <500 μm particle size. SSEH and BEH were received as wet samples and were dried at ambient temperature until constant weight before use.

All other reagents and solvents were purchased from Sigma-Aldrich and used without further purification (≥99.5%).

Table 1
Lignin feedstock types and characteristics.

Feed-stock	Characteristics	Ratio		Lignin Content (%)	Ash Content (%)
		H/C	O/C		
SEH	Norway Spruce (<i>Picea abies</i>)— 30% cellulose, Enzymatic Hydrolysis —bioethanol production process	1.20	0.45	~70%	NA
SAH	Norway Spruce— 30% cellulose, weak Acid Hydrolysis, SO ₂ -treated —bioethanol production process	1.37	0.57	~70%	<1.0
SKL	Norway Spruce— cleaned lignin from paper production —lignin from Kraft pulp mill black Liquor (Lignoboost)	1.10	0.36	95–98% [12]	<1.5
SSEH	Norway Spruce— Steam exploded, Enzymatic Hydrolysis —bioethanol production process	1.40	0.70	~60% ^a	1.16
BEH	Birch (<i>Betula pubescens</i>)— Enzymatic Hydrolysis, tempered at 210 °C for 10 min —bioethanol production process	1.31	0.51	~70% ^a	1.25

^a Estimated from the elemental composition.

2.2. Solvolysis system and conditions

Biomass and solvent was added to a 25 mL high pressure Parr reactor from the 4740-series without stirring, closed directly and placed in a preheated Carbolite Laboratory High Temperature oven. After the completed reaction time, the reactor was taken out of the oven and cooled by an air stream to ambient temperature. The resulting products after solvolysis included a gas phase, a liquid phase and a small solid phase. The amount of gaseous product was determined by weighing the reactor before and after venting the gas.

In the water system the liquid phase consisted of a single aqueous phase. The dark brown LtL-oil was not present as a separate phase, but adsorbed to the solid residue due to its hydrophobic character. The LtL-oil was miscible in dichloromethane (DCM) and therefore separated from the solid phase using DCM and filtered through a 0.45 μm Puradisc™ 25 NYL filter. The entire liquid phase was then extracted with DCM three times and the organic phases were combined and dried over Na₂SO₄. The aqueous phase was in addition extracted with a mixture of ethyl acetate (EtAc) and tetrahydrofuran (THF) in 90:10 v/v ratios respectively to increase the recovery of the most polar compounds. The organic phases were combined and dried over Na₂SO₄.

In the ethanol system, the liquid phase consisted of two immiscible layers; a dark brown organic phase representing the LtL-oil and a small clear aqueous/ethanol phase. The two layers were separated using the same workup procedure as in the water system.

DCM in the first extraction step was removed from the LtL-oil on a rotary evaporator at a temperature of 40 °C and a pressure of 175 mbar for removal of ethanol. These conditions were replicated for all LtL-oils to ensure the same work-up protocol. EtAc:THF in the second extraction step was left for evaporation under atmospheric conditions. The two organic phases adds up to the total oil yield. The oil yields were determined by weight after solvent evaporation. The char yield was determined by weight after drying.

2.3. Mass spectrometry

The LtL-oil was analysed shortly after workup using GC–MS on a Trace Ultra GC coupled with a DSQ II quadrupole MS detector from Thermo Scientific. DCM and EtAc:THF were used as solvents for the respective product fractions and the samples were analysed using splitless injection at 260 °C (injector temperature) on a 25 m Ultra 2 Silica capillary column ((5% phenyl)-methylpolysiloxane),

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