DEVELOPING SOLVOLYTIC CONVERSION OF LIGNIN-TO-LIQUID (LtL) FUEL COMPONENTS: OPTIMIZATION OF QUALITY AND PROCESS FACTORS

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Wood-based biorefineries are focussed on providing ethanol from the carbohydrate fraction of biomass, which generates large amounts of lignin as a major by-product. The thermo-chemical conversion of such residual lignin materials to low molecular mass oil by solvolysis in a formic acid/alcohol reaction medium has been further investigated to provide access to value-added products. Subsequent optimisation attempts showed that the amount of the *in situ* hydrogen source (formic acid) can be reduced in relation to lignin, with small effects on the yield of the product oil. The impact of other experimental factors has been explored, their influence on the phase separation properties and the proportion of phenols related to hydrocarbons in the produced oil have been evaluated. The work shows that further reduction in solvent use will be possible, thus paving the way for more efficient production of oxygen-depleted bio-oils: suitable liquid transport fuel components from solid lignin.

Keywords: lignocellulosic biomass resources, liquid biofuels, chemicals from biomass, lignin-to-liquid (LtL)

INTRODUCTION

Establishing biorefineries based on the conversion of woody biomass into bioethanol is attracting wide interest, the lignocellulosic ethanol production being already implemented at an industrial scale in some paper mills and dedicated ethanol production sites. In a forestry-based biorefinery, the processes for converting carbohydrates into renewable fuels like bio-ethanol need to be complemented by providing value-added products from the lignin fraction, which makes up to 25-35% of the dry wood mass.[1,2]

For the development of a successful process, an efficient separation of the biomass polymers, namely cellulose, hemice-lluloses and lignin, is required. Currently, processes such as organosolv pulping, steam explosion and acid hydrolysis are being explored for this purpose.[3] Irrespective of the process used, a large quantity of lignin will always be generated as a by-product. Considering the substantial production scale required in future ethanol biorefineries, a simultaneous thermo-chemical conversion of the lignin stream into a liquid biofuel seems attractive. Previous attempts in this direction have failed.[4] Just recently, it has been found out that lignin can be depolymerised and de-oxygenated efficiently if pyrolysis is carried out in the presence of formic acid with an alcohol as co-solvent.[5] Hence, solvolytic

conversion could provide a critical additional profit to make the biorefinery concept economically feasible, thus providing a broad range of products compatible and suitable for use as fuel blending components in the existing motor technology, on also producing other high-value components – like phenols for bio-plastics.[6,7]

The strategy of the solvolytic liquefaction of solid lignin into versatile products includes simultaneous depolymerisation and deoxygenation through hydrogenation, to yield compound mixtures of low molecular mass, low oxygen content and polarity, and enhanced H/C ratio.[8] Serving as an active hydrogen source, formic acid is added to the solvent. However, it is degraded during the process, leading to a net consumption of this reactant. In addition, 2-propanol has been used as a moderately strong hydrogen source and co-solvent, besides ethanol, even if it cannot be recovered in sufficient amounts. This leads to an unacceptable overall atom efficiency of solvolysis. This paper describes the initial work performed to reduce the negative side effects of solvent and co-solvent consumption, while maintaining the desired product quality, along with the investigation of product composition as a function of process conditions, exploring the potential for tailoring the product properties by selecting appropriate process conditions. A complete report on total optimisation by the chemo-metric approach will be published elsewhere in due course.

Background

Producing renewable liquid fuels for the transportation sector is a great challenge in the biofuels area, requiring sustainably managed source materials with no adverse socio-economic side effects. Technically, the liquid products have to be fully compatible with the existing fuel technology and to supply infrastructure, which demands unpolar, low-viscous liquids with very low oxygen content. Biomass deoxygenation is a core element which cannot be simply and efficiently accomplished by means of high pressure hydrogen supply, for reasons of reactivity and of the demanding process conditions – which exclude many theoretically suitable catalysts. Within the solvolytic approach, formic acid acts as an effective hydrogen donor. However, at present, the chemical mechanisms for conversion are not clearly understood. Since the application of gaseous hydrogen does not lead to the described simultaneous depolymerisation and deoxygenation, it is an acceptable hypothesis that the active hydrogen formed (*in statu nascendi*) from the formic acid is a relevant agent. Considering the harsh reaction conditions, this seems also reasonable, since radical reactions are likely to take place. However, at present, no firm evidence of such reaction pathways has been identified.

The concept of using formic acid and especially formates together with different co-solvents or other hydrogen donating agents in a solvolysis process has been previously suggested for use in coal liquefaction.[9] The separate application of these compounds has been investigated,[10,11] and much effort has been made to elucidate the actual reaction pathway of, *e.g.*, thermal decomposition of formic acid and of its hydrogen donating properties,[12] either under hydro-thermal conditions[13] or in the context of catalytic transfer hydration.[14,15] The mechanisms discussed include ionic, free-radical, surface-catalysed or molecular reaction steps, but no clear mechanistic understanding has been reached. The different degradation reactions of formic acid as a hydrogen donating agent, during its thermal degradation with and without water, are illustrated in Figure 1. In a kinetic study of Savage *et al.*, it was concluded that decomposition at high pressure and high temperature yields CO_2 and H_2 as major products, so that decarboxylation is the preferred reaction path.[13]

During the solvolytic treatment of biomass or plain lignin in the liquid reaction medium, a complex mixture of products is formed: some minor amounts of solid char/coke are, in most cases, accompanied by a well-separated liquid-liquid two-phase system, along with a gas phase. All products have been analyzed thoroughly; in this research, however, stress has been laid on gas phase composition and phase separation of the two liquid products. The fact that phase separation occurs in the LtL-oils is an interesting phenomenon, and a combination of two separate experimental setups has been used to explore the conditions required for obtaining separation. One approach views separation as a function of the reaction time (*T*-experiment series), the other one shows

the effect of varying the solvent ratios, as well as temperature (*F*-experiment series).

In addition, up to 10% water on molar basis was added as a variable, to view the possible influences on the degradation pathway of formic acid, as suggested by Savage. If this does occur, it would allow the use of lower quality ethanol, which is a vital point for continuous reactions at an industrial scale, such as reusing the unreacted solvents with limited technical efforts of purification.

The essential function of alcohols is to solubilize the depolymerized lignin fragments effectively, hence serving as a classical solvent and remaining inert, thus allowing full recovery after solvolysis. This involves no additional reactions with the other solvents, the hydrogen donor or the depolymerized biomass. Preferably, thermal stability and no side reactions following evaporation into the gas phase are desired, as important properties of an ideal inert low-cost solvent.

Interestingly, some of the previously produced oils[5] contained hydrocarbon structures not expected to be found in depolymerised lignin fragments, since lignin is a complex, highly oxygenated polyphenolic polymer. Such hydrocarbons include both linear and branched aliphatic chains, up to a C-12 backbone, and also some esters. Fischer-Tropsch reactions were considered to be responsible for the formation of such compound classes, which explains why the authors preferred the evaluation of the pure solvent system without additional biomass.

The aim of the present work was threefold, as shown in Table 1: i) B-Series: to elucidate the composition of the produced gases as a function of the selected ratios of formic acid, ethanol and *iso*-propanol, and to evaluate the origin of the straight chain hydrocarbons occurring in the LtL-oils in the absence of lignin; ii) T-Series: Retention time experiments, to elucidate the phase separation characteristics; iii) F-Series: Statistical (fractional factorial) reaction design, to create models for the influence of the investigated process parameters on product composition.

EXPERIMENTAL
General

Different combinations of the selected experimental parameters were used, as specified in Table 1. In the initial series of runs, only the retention time (T-series) of the experiments was varied. The blank runs (B-series) consisted solely of different input amounts of the used fluids, without any biomass added. For the major series here reported (F-series), a multivariate design was used, to generate statistically-based experimental data, permitting to identify the influence of the different variables on the response factors. A two-level fractionated factorial design of ($2^{4-1} = 8$) eight experiments plus two duplicate center point runs was chosen, which uses a statistically spread half of all possible variable combinations, as shown in Table 2. All chemicals and reagents were purchased from Aldrich and used without further purification or drying. Commercial residual lignins from an ethanol plant were provided by SEKAB, Sweden. Two types of hydrolysis lignin were used in the experiments: weak acid hydrolysis lignin (F-series) and enzymatic hydrolysis lignin (T-series).

Solvolytic conversion procedures and workup

The autoclave reactor used in these experiments was a 75 mL high temperature and high pressure non-stirred stainless steel (SS 316) batch reactor of the 4740 series, from Parr Instrument Co. The reactor was filled with solvents and lignin, if applicable, and sealed, optionally with an attached Autoclave Engineers gas valve for subsequent gas sampling. The sealed reactor was placed into a preheated Carbolite LHT oven, at a given temperature. After complete reaction time, the reactor was removed and placed into an air stream for cooling, until room temperature was reached. The reactor was weighed before and after ventilation. After gas ventilation, the liquids were removed from the reaction vessel, most often in two liquid component phases. Effervescence was sometimes noticed due to solute gases. The denser phase comprised mainly alcohols and water and was of clear translucent or yellowish appearance. The top phase, namely the oil phase, was of a dark reddish-brown, non-viscous nature. Due to the complete decomposition of formic acid to gaseous products, the liquids recovered had a pH close to neutral. The oil had a pungent smell and burned with a sooty flame. In the case of the one-phase product, its appearance resembled a mixture of the two single phases. Phase separation was rated upon a subjective basis from -2 (no separation) till +2 (perfect separation with a clear bottom phase), to allow PCA and PLS regression analysis for the response factor, too. Sometimes, the recovered char had a true black gleaming charcoal-like appearance; however, moist char of sticky consistency was also recovered.

A small sample of the top liquid layer was directly analyzed by GC-MS. The ESI-MS samples were also taken from the top layer or, if not separated, from the single liquid phase. The liquid phases were separated by decanting. The volume and/or weight of the resulting phases were recorded. Residual char was weighed directly after recovery from the reactor, after 10 min drying at 60 °C, to account for volatile liquid loss.

Gas phase-GC analysis

Gas phase analysis was carried out on a HP 6890 GC System operated with two columns set up in parallel, controlled by a Chromeleon software system. The initial temperature was 35 °C for a time period of 5 min, after which the heating rate was set to 15 °C/min till reaching a final temperature of 180 °C. This temperature was held for a duration of 22 min. The inlet temperature was set to 200 °C. The FID and TCD detectors were set at temperatures of 250 and 230 °C, respectively. The detection of the hydrogen amount in the gas mixture was permitted through injection on one of the two columns, a 3 m Porapack Q-packed column, whose eluting products were detected *via* a TCD detector. The compounds could be detected by a FID detector on the other column, a 30 m Hp-Plot Q-capillary column, whose eluting products were first channeled over a nickel catalyst, which reduced both carbon monoxide and carbon dioxide to methane.

GC-MS analysis

GC-MS liquid analysis was performed on a GC-MSD (HP 5890-II with HP Auto 5890) with 25 m WCOT fused silica column (CP-Sil 8 CB) equipped with both FID and an HP5971 MSD detector, controlled by an HPChem laboratory data system. The heating program was as follows: the initial temperature was 50 °C for 2 min, being further increased at a rate of 6 °C/min up to 320 °C, for 10 min. The injection port had a temperature of 320 °C, the FID was at 350 °C and the MSD had a temperature of 280 °C. The program included a solvent cut-off at 3.1 min run time, to avoid overloading of the MS detector. The compounds were identified with an Agilent MSD software suite and a NIST 05 library. The samples were diluted with an appropriate amount of ethyl acetate, to give a preferably good signal quality, then injected *via* the autosampler system.

Electrospray mass spectrometry (ESI-MS)

Each sample from the F-series was dissolved in dichloromethane (2 mg/mL) and analyzed by full scan mass spectrometry (*m/z* range from 65 to 1300 with one scan/sec), on an Agilent 1100 Series LC/MSD system (Agilent Technologies Inc., Palo Alto, CA, USA). The system consisted of a G1322A mobile phase degassing unit, a G1311A quaternary pump with gradient mixer for up to 4 mobile phase constituents, a G1367A autosampler and a G1946D single quadropole mass spectrometer. 2 μL samples were injected by the autosampler and led into the mass spectrometer by 70 cm of PEEK tubing (I.D. 0.18 mm), without separation, on a chromatographic column. Each sample was analyzed 5 times. The mobile phase consisted of acetonitrile–aqueous ammonium acetate (50 mM) 9:1, using a flow rate of 0.2 mL/min. The fragmentor voltage was of 100 V and positive ionization was used. Details on the methodology have been described elsewhere.[16,17]

Multivariate data analysis (general considerations)

Multivariate data analysis was carried out with the macroscopic results (oil and gas yield, phase separation, etc.) presented in Table 1. For visualisation and other data treatment, the ESI-MS data excepted (see below), the software program Sirius 8.0, Pattern Recognition Systems AS, was used. The data obtained were standardized and mean centered prior to acquiring the presented results.

Multivariate data analysis (ESI-MS data)

An average spectrum was obtained from each individual analysis. The process of background subtraction and processing of spectra was performed by a post-run macro, to ensure identical data collection between different injections, as described in previous papers. Each average spectrum was tabulated as mass and intensity, with rounding of the decimal mass to an integer. Matrix construction was performed by a specially designed macro in Microsoft Access. Details have been described previously.[3,16,17] Multivariate data analysis was performed with the Simca P+ 11.5 software (Umetrics, Umeå, Sweden). A mass number range of 65-600 was used exclusively, since background noise occurred mostly in the 600-1300 range. Prior to analysis, the data were normalized to a constant sum and mean centered. Principal Component Analysis (PCA) was used to evaluate similarities and differences among spectra.[18]

RESULTS AND DISCUSSION
Effects of residence time

Lignin conversion into liquids in one-step depolymerisation and hydro-deoxygenation reactions is plotted in Figure 2 as a function of time. The results show that, under the conditions applied (380 ºC, fixed lignin-to-solvent ratios, as given in Table 1 for experiments T01-T07), the degree of lignin conversion and the properties of the product phases develop over a time scale of hours. A

minimum residence time of 6 h is needed to obtain sufficient phase separation into oil and residual solvent liquid phase. In terms of oil phase yields, the best results are obtained at 12 h duration, as longer reaction times tend to increase the gas phase and residual coke yields, indicating the onset of cracking and disproportionation reactions.

The results demonstrate the feasibility of lignin-to-liquid conversion, but also highlight the need for improving the applied conditions, to make the process technically viable in a biorefinery context.

The dependence of oil yields and composition on the reaction conditions must be explored and adjusted to minimize the consumption of the reaction medium components and provide the most suitable product composition for use as biofuel or "green" industrial bulk chemicals. The increase in the reaction rate is also meant at reducing the time needed for conversion.
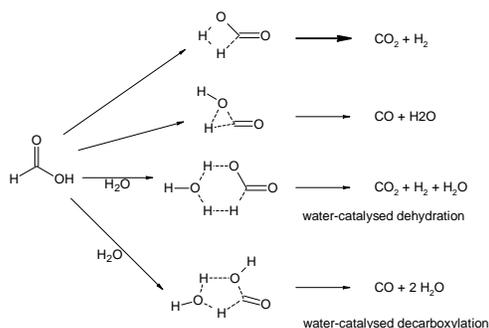
Figure 1: Thermal degradation of formic acid. Under LtL conditions, the formation of H_2 and CO_2 is the preferred pathway[13]
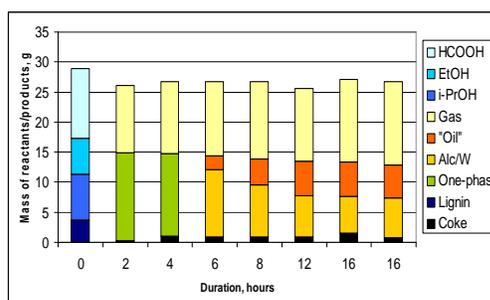
Figure 2: Results from time series experiment: column 0 describes the input of lignin, formic acid, ethanol and iso-propanol into the reactor; columns 2-16 show the distribution of product phases at a given duration; "One-phase" – a single liquid phase, "Oil" – a separate, lipophilic oil phase as a top layer relative to the residual alcoholic solvents as bottom layer

Table 1
List of experiments

Exp	FA, mmol	EtOH, mmol	iPrOH, mmol	H2O, mmol	Lig., g	T, °C	T, h	Gas, g	Org., g	Alc/Aq., g	Sep., -2 – +2	One, g	Dry chr., g
F01	65.9	359.2	35.9	4.0	3.75	370	16.25	5.1			-2	17.5	1.1
F02	59.2	177.7	177.7	3.6	3.75	390	16.25	7.7	8.6	6.6	+2	-	1.3
F03	268.2	243.8	24.4	2.7	3.75	390	16.25	15.4	4.4	7.0	+2	-	0.4
F04	249.3	124.6	124.6	2.5	3.75	370	16.00	13.1	5.2	8.1	+1	-	0.6
F05	64.3	350.7	35.1	38.6	3.75	390	16.00	8.0	3.1	12.0	+1	-	1.2
F06	58.0	173.9	173.9	34.8	3.75	370	16.25	5.6	-	-	-2	17.3	1.2
F07	263.8	239.8	24.0	26.4	3.75	370	16.25	13.2	-	-	-2	14.4	0.6
F08	245.5	122.8	122.8	24.6	3.75	390	16.00	15.2	5.3	6.2	+2	-	0.6
F09	112.4	224.8	112.4	16.9	3.75	380	16.00	8.7	3.3	12.1	0	-	1.0
F10	112.4	224.8	112.4	16.9	3.75	380	16.00	8.6	3.2	12.4	0	-	1.0
B01	47.7	0.0	24.1	-	-	380	4.0	21.6	5.8	9.1	+2	-	-
B02	19.9	19.5	20.1	-	-	380	4.0	11.3	0.6	18.3	+2	-	-
B03	31.0	30.8	0.0	-	-	380	4.00	12.4	-	-	-2	16.0	-
B04	0.0	24.0	24.1	-	-	380	4.00	2.3	-	-	-2	23.3	-
T01	242.3	121.4	120.4	-	3.75	380	2	11.2	-	-	-2	14.7	0.2
T02	242.3	121.4	120.4	-	3.75	380	4	11.9	-	-	-2	13.8	1.0
T03	242.3	121.4	120.4	-	3.75	380	6	12.4	2.3	11.2	+2	-	0.8
T04	242.3	121.4	120.4	-	3.75	380	8	12.8	4.4	8.6	+2	-	0.9

T05	242.3	121.4	120.4	-	3.75	380	12	12.1	5.7	6.9	+2	-	0.9
T06	242.3	121.4	120.4	-	3.75	380	16	13.8	5.7	6.2	+2	-	1.5
T07	242.3	121.4	120.4	-	3.75	380	16	13.8	5.5	6.5	+2	-	0.8

Experimental series: F = fractional factorial design, B = blank solvent runs, T = retention time experiments. Input of formic acid (FA), ethanol (EtOH), *iso*-propanol (iPrOH) and water (H_2O) are given on a molar basis. Input of lignin (Lig.) and the yield of product phases (Gas, Org. (separated organic phase), Alc/Aq. (separated residual solvent phase), one-phase liquid phase (One) and char (Dry chr.) are given as mass, in grams. Presence of a separate oil phase is given on a qualitative scale of separation: -2 to +2, from one phase (-2) to a well-separated oil and clear alcohol/aqueous phase (+2)

Table 2
Experimental design variables X1-4

	$-$	0	$+$	
X1	0.1 : 1	0.5 : 1	1 : 1	mol ratio *i*PrOH/EtOH
X2	1 : 6	1 : 3	1 : 1	mol ratio FA/Solvents (alc)
X3	0.01 : 1	0.05 : 1	0.1 : 1	mol ratio water/Solvents (alc)
X4	370	380	390	Temperature, °C

Molar ratios of the different solvents used as variables for the fractionated factorial design ($2^{(4-1)} = 8$ experiments), together with the temperature variable

Solvent medium reactions

The reaction medium in itself is not inert and has been found to react and degrade under the conditions used. This has been further investigated in a separate set of experiments, using no lignin input, but only different mixtures of solvents and formic acid. The experimental conditions are specified in Table 1 (experiments B01-B04). Two liquid phases are obtained in 2 of these experiments, showing that the reaction medium in itself has the potential for polymerising and providing a separate phase with typical organic phase properties. The composition of the non-polar (upper) organic phase is illustrated in Figure 3, which shows that a range of alkanes, from octane to decane, together with some substituted cyclohexanes, form the major components of this complex mixture of products. A Fischer-Tropsch-type reaction mechanism is suggested, based on the gas phase composition – rich in both hydrogen and carbon monoxide, actually comprising almost a synthesis gas mixture, as shown in Figure 4. Carbon dioxide and homologous series of hydrocarbon gases include the remaining components. Although the products of the components in the reaction medium would be quite suitable for a motor fuel, they are only by-products in relation to lignin conversion and should be consequently minimized to reduce solvent and formic acid consumption in the process.

Experimental design approach, quantitative yields

To determine the effect of different experimental factors on the yield and composition of oils, a systematic experimental design approach has been used, combined with multivariate interpretation of the complete table of results. The variables included are the ratios of the three solvents and the temperature (Table 1, experiments F1-F10, and Table 2). The addition of up to 10% water on molar basis was included as a variable, to determine the possible influence of low water levels on the degradation pathway of formic acid.

A PCA plot, showing the relationship among the experimental variables, the yields of the different product phases and the degree of phase separation, is given in Figure 5. The first principal component (PC1) explains 52% of the total data variance, while the second component explains 23% of it, which illustrates the high degree of systematic variation in the data. The PCA plot only contains the total yield of liquids, since the lack of separation into two phases in some experiments makes the statistical data set incomplete and unsuitable for analysis, if the values for each separate phase are included.

The most obvious relationship seen in the plot is the clear positive correlation between formic acid and the amount of gas produced, which can be understood as reflecting the

thermal decomposition of excess formic acid to gas phase products. Correspondingly, the input of formic acid is negatively correlated to the total yields of liquids and solid products. A moderate positive effect of ethanol on the liquid yields can be seen. The separation into two phases is strongly and positively related to temperature during the experiment, and also to the formic acid input on PC1and the *iso*-propanol content on PC 2. The addition of water does not significantly influence product distributions, indicating that the presence of some water in the initial solvents could be acceptable. The relationships between the experimental variables and the products can be numerically modeled with PLS (Partial Least Squares/Projection to Latent Variables).[19] The regression models for the selected product phases and parameters are given in Table 3. The explained variance in regression analysis for the selected independent/dependent subsets lies at 82.7 and 90.0%, respectively, for the two components used for this model. Predictions of residual char, as well as the mass percentage of gas and total liquids, are given, showing a high degree of accuracy, when predicting center-point experiments without data input from them. As separation was rated on a subjective basis, the predicted model was not expected to be very precise.
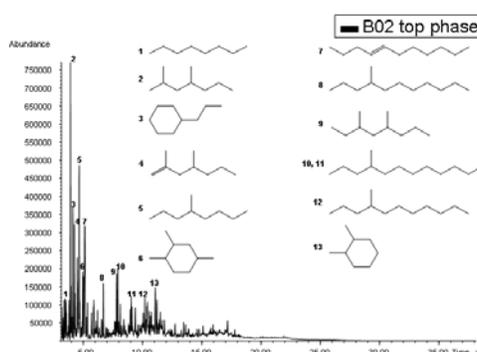
Figure 3: Gas chromatogram of the organic phase obtained from experiment B02, showing the predominant aliphatic components
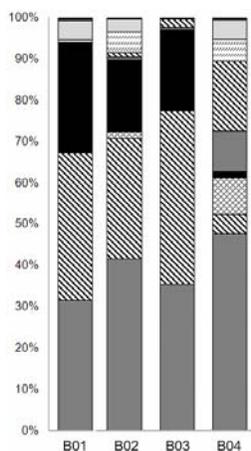
Figure 4: Gas phase analysis of the different blank solvent samples, showing the percentage of each identified gas component in relation to the sum of identified gases – hydrogen (H), carbon monoxide (CO), carbon dioxide (CO2), methane (C1), and C2-C6 saturated (an) and unsaturated (en) hydrocarbons
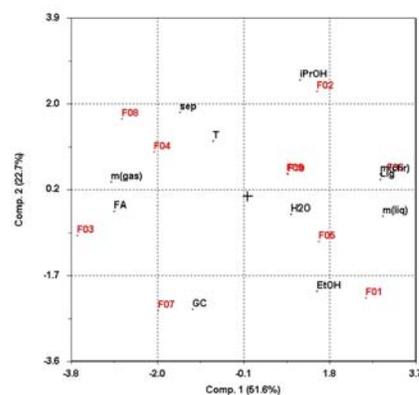
Figure 5: Principal Component Analysis (PCA) biplot of the lab results from the *F*-experiment series. Before analysis, the data set was standardized and mean centered. The objects (experiments F01-F10) are shown grey and the design variables (experimental conditions) and responses (yields and the qualitative separation indicator) are shown in black. The variable names are given in Table 1

Table 3
Regression coefficients for PLS models of individual product yields (unweighed)

Variable Response	FA 0.105-0.428	EtOH 0.198-0.647	iPrOH 0.051-0.420	H$_2$O 0.002-0.027	T 370-390	Constant	R	Predictive quality
m(gas) 0.212-0.563	0.511	-0.288	-0.167	-2.787	0.004	-0.975	0.970	very good
m(liq) 0.418-0.726	-0.440	0.259	0.131	2.272	-0.004	1.933	0.971	very good
m(chr) 0.014-0.051	-0.061	0.027	0.029	0.244	2.3E-05	0.022	0.979	very good
liq sep. -2-+2	1.704	-3.048	1.975	-33.768	0.140	-52.079	0.931	good
GC rating -1 (aliphatic) - +1 (phenolic)	1.694	1.083	-3.237	-1.381	-0.019	6.529	0.825	guidance

Coding of variables: FA, EtOH, iPrOH are given in wt%, temperature in °C. R: correlation coefficient between modelled and predicted values for all data, representing a value for goodness-of-fit. The figures give the regression coefficients of each process parameters (**in bold**) and for each of the response factors (*in italics*). The shaded figures represent the variable variation range of both variables and responses, respectively

However, the predictive quality given in the table indicated a high correlation, so that it can be used for evaluating the conditions leading to phase separation.

Another qualitative indicator is also included, describing the range of compositions of oils on a scale from dominantly aliphatic to dominantly phenolic, as shown by the GC variable in the plot (Fig. 5 and Table 3). Phenolic-type spectra are achieved with an increase in formic acid and ethanol. An increase in the aliphatic-type compounds correlates positively with the amount of iso-propanol.

Table 3 illustrates the challenges in the optimization of such a complex reaction system; if the amount of formic acid is reduced to prevent a major loss factor from thermal decomposition into gas phase products, separation efficiency will be reduced. Similarly, increasing the water content of the solvent system increases the char yields, which is not optimal, decreases the separation efficiency and increases the liquid yields – which is most probably a positive effect. Thus, positive and negative effects on product composition and properties must be balanced, and a compromise between costs of the inputs and the value and quality of the output needs to be reached. Further development of experimental designs is ongoing, to find the optimal balance among parameters.

Experimental design approach, oil compositional effects observed using ESI-MS

The very complex composition of the lignin conversion products makes the analytical challenges comparable to that of petroleum analysis. ESI-MS combined with multivariate interpretation is a very powerful tool in such analysis.[3]

Figure 6 shows the score plot obtained after PCA of the ESI-MS data obtained from the 5 repeated analyses of the 10 samples from the F-series. The first principal component explains 82% of the variation in the data, while the second explains 13% of it, implying that altogether 95% of the variation is systematic and can be explained by two principal components (another 2% part being explained by a third component). The score plot illustrates the very high repeatability of the ESI-MS data. The three samples obtained from one-phase liquid (marked "o" – the final digit) are located in the right part of the score plot. F07o is significantly different from all the other samples. Figure 7 shows the spectra of the 4 F-samples that span variation in the spectra. Although mass spectra may appear unresolved, there is one distinct line per integer mass number (*m/z*). The lines represent the parent compounds (unfragmented) that have become ionized. Positive electrospray ionization (ESI) typically occurs by the addition or loss of a

proton (+1), but sometimes positive ionization occurs by the addition of ammonium or sodium adducts (+18 or 23, respectively).[3,16,17] The positive ESI-MS detects primarily polar compounds containing nitrogen, oxygen, or sulphur. Non-polar hydrocarbons, such as paraffins, are generally not ionized by ESI.

Relatively few lines are observed in F07o, whereas especially F08t has a high number of lines. Interestingly, mass spectra are dominated by lines with repetitive spacings of 14 Da (CH_2) and 2 Da (saturated *versus* unsaturated analogues). This becomes even more pronounced in the two loading plots from Figure 8. Instead of a scatter plot, the loadings are shown in line plots, one per principal component, illustrating very nicely that the most important compounds according to PCA appear to be from homologous series with repetitive spacings of 14 and 2 molecular mass units. Future work will focus on the identification of these compounds.
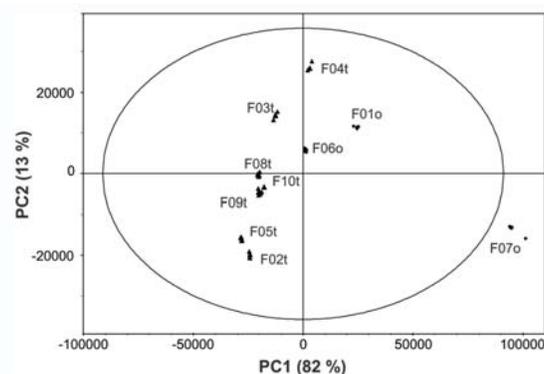
Figure 6: Score plot obtained from PCA of positive ESI-MS data of the F-series
(each sample analyzed 5 times)
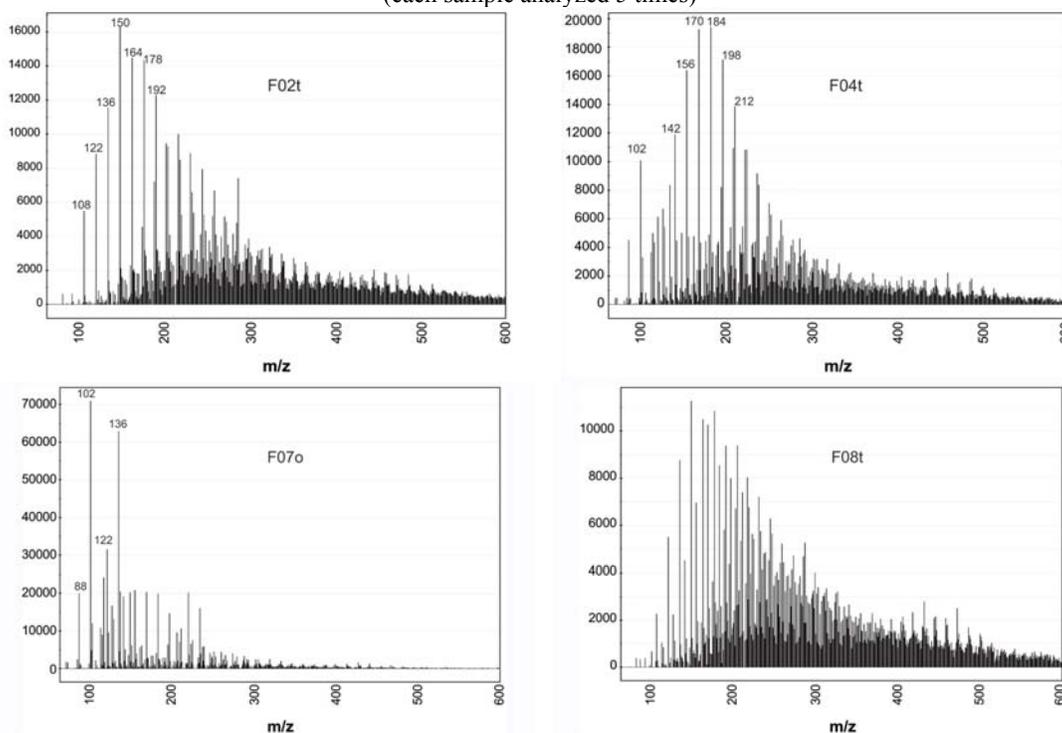
Figure 7: ESI-MS spectra of the 4 F-samples that span spectra variation
(see score plot in Fig. 6)

Figure 8: Loading line plot for the first and second principal component obtained
after PCA of positive ESI-MS data

CONCLUSIONS

Solvolytic conversion of lignin is a complex process, with a number of intriguing subjects of chemical research and development efforts. The reaction mechanism of formic acid as a hydrogenation agent still needs to be explored in greater detail, for providing a basis for the selection of catalyst systems and for improving the reaction efficiency, both in terms of reaction rates and reduction of the use of excess reactant. Pragmatic optimization approaches using an experimental design and the multivariate optimization of the reaction conditions will permit to find the best conditions in terms of reactant and solvent use and physical conditions, as well as to tailor the product, in order to get the preferred range of chemical compositions.

The results obtained confirm the potential of the lignin conversion process of contributing to total valorization of lignocellulosic biomass. However, a considerable amount of chemical research and development work is still needed to provide an industrially applicable biorefinery unit.

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