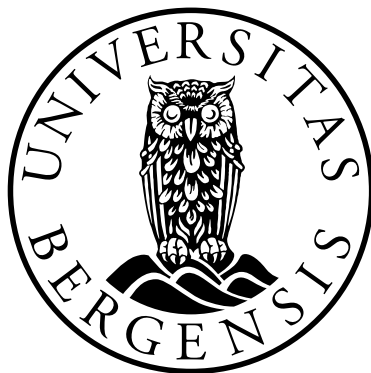


Solvolytic lignin degradation in an alcohol / formic  
acid medium

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Analysis of the reaction system and products by  
means of kinetic modelling and chemometrics

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Thesis for the degree of Philosophiae Doctor (PhD)  
at the University of Bergen

2012

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*"Life ... is a relationship between molecules."*

*- Linus Pauling (1901 - 1994)*



---

# PREFACE

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This thesis, submitted for the degree of Philosophiae Doctor at the University of Bergen, consists of two parts. The first includes an introduction, a summary of the work and main results from the papers in the second part, an overall conclusion and future work suggestions. The second part consists of six research papers and manuscripts, and one conference proceedings paper.

The main part of the work has been performed at the Department of Chemistry, University of Bergen in the period 2010 - 2012, including several guest research stays at Statoil Research Centre Rotvoll in Trondheim, Luleå University of Technology, and Karlsruhe Institute of Technology. The project was funded by VISTA - a basic research programme funded by Statoil, conducted in close collaboration with The Norwegian Academy of Science and Letters.

The aim of the work conducted was to identify critical parameters in solvolytic conversion of lignin with regard to efficient, simultaneous depolymerisation and hydrodeoxygenation, using formic acid as a hydrogenation agent. The project contained two integrated work packages on experimental process optimisation and analytical protocol development. The latter aimed both to aid in the analysis of complex mixtures in general, as well as to increase the understanding of the lignin degradation reaction system.

Relevant work by the author conducted prior to the PhD project has been included in this thesis.



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# ACKNOWLEDGMENTS

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First and foremost I would like to thank Tanja Barth for her excellent supervision as well as support both in professional and personal matters during all my time at the University of Bergen. She has given me the freedom to build my professional competences both within chemistry, but also beyond.

I would further like to thank my co-supervisor Ingvar Eide for always showing a considerable interest in my project and enabling my research stays at Statoil Research Centre Rotvoll. A big thank you also goes to my other co-supervisor Johan E. Carlson, both for investing time and effort in a research approach far from his own field as well as personal guidance. Andrea Kruse I would like to thank for her numerous open armed welcomes at Karlsruhe Institute of Technology. Mike Kleinert deserves my thanks for initially giving me the chance to come to Norway and to work and get involved in this very exciting field.

My sincerest gratitude further goes to two people without whom I doubt I would have retained my nerves to finish this thesis. Georgi Genov and Djurdjica Corak, I will hold both good and bad times together with you in the warmest of memories.

Working together with my good friend Daniel Forchheim has been a true pleasure. Especially considering the way he so brotherly would give up half of his desk space during my quite extensive stays in Karlsruhe. Further, I thank Ekrem Sahin for bearing out together with us on those long evenings and nights in the lab. Ann-Mari Hilmen, Gunhild Neverdal, Bjarte Holmelid, Lucia Liguori, Kolbjørn Zahlsen, Ursel Hornung and Tatjana Sutter are furthermore thanked for some great work together on various papers, presentations and posters.

I further want to express my thanks to Rianne Harmsen, Gregory Johnson, Guro Aspenes and Dagfinn Sleveland for adding colour to the daily work environment. A special thanks goes to Mikel Oregui for proof reading of this work.

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Most of all I thank my parents for their trust, belief and nerves of steel, as I know that they have been accompanying every step of mine in both their hearts and minds and have lived through all my emotional ups and downs together with me.



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# ABSTRACT

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Lignocellulosic biomass has been identified as an abundant renewable resource to produce sustainable alternatives for conventional fossil fuels for the transport sector as well as selected bio-materials and chemicals. Bio-ethanol production from the cellulose and hemicellulose components of this biomass type is already largely established. The remaining 20-30 % of polyphenolic residual matter could be a valuable source of revenue for lignocellulosic biorefineries. Novel fuel components and lignin derived platform chemicals, such as phenols, can be obtained by controlled depolymerisation and deoxygenation.

In this thesis, a novel high temperature and pressure solvolysis of lignin-rich residual material in a formic acid / alcohol mixture has been explored. The reaction products were seen to be comprised of several substituted phenols in addition to long chained hydrocarbons, esters and ketones in a pH neutral non-viscous bio-oil. The O/C ratio was found to be so largely decreased, that a phase separation in the liquid could be observed with selected reaction parameters. In-situ generated gaseous products from formic acid are seen to enhance the lignin depolymerisation and decrease the oxygen content of the liquid products. First evaluation attempts for fuel blending were undertaken. It was found that lignin derived phenolics as the major product fraction should be concentrated upon. Other constituents were seen to be merely byproducts of other reactive components present.

Several experimental series exploring reaction conditions and parameters were performed. Based upon the conclusions found from this work, the kinetics of the main reaction pathways including the deoxygenation reaction steps of monomeric phenolics were modelled. It was shown that both molecular level formation and degradation rates of various phenolics, as well as global bulks, could be correctly described by a simplified lump model. The model, which was further validated, has been shown to be applicable also at varied temperatures and for different reactor types. It will therefore form a significant basis for future scale-up work. Results showed that depolymerisation of lignin is

quickly achieved and that the rate determining step of the conversion process lies within the deoxygenation reactions. These require a somewhat higher activation energy than alternative routes, the latter contributing strongly to gasification and charring reactions.

Further, a new analytical data analysis method based on observed compound class variations between different analysed samples in a novel ESI-MS fingerprint approach was developed. This statistical based tool can be applied as a complement to PCA and highlights the variations based upon extraction of repetitive 14 Da spaced signals (resembling -CH<sub>2</sub>- groups) that can be used to isolate and describe the total variance of single compound classes.

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# ABBREVIATIONS

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AA	Anti agglomerant
AR	Alternating regression
ASTM	American Society for Testing and Materials
CI	Chemical ionisation
CSTR	Continuous stirred tank reactor
DCM	Dichloromethane
EH	Enzymatic hydrolysis
EI	Electron ionisation
ESI	Electrospray ionisation
FID	Flame ionisation detector
FT	Fischer-Tropsch
FT-IR	Fourier transform - infrared spectroscopy
GC	Gas chromatography
IR	Infrared spectroscopy
KI	Kinetic inhibitor
LC	Liquid chromatography
LDHI	Low dosage hydrate inhibitor
LtL	Lignin-to-Liquid
MALDI	Matrix assisted laser desorption / ionisation
MON	Motor octane number
MS	Mass spectrometry
MSD	Mass spectrometry detector
NIC	Natural inhibiting compound
NLPCA	Non-linear principal component analysis
PCA	Principal component analysis
PCR	Principal component regression
PLS-(R)	Partial least squares - (regression)
RON	Research octane number
SAH	Strong acid hydrolysis

TAN	Total acid number
TCD	Thermal conductivity detector
TDI	Thermodynamic inhibitor
UCM	Unresolved complex mixture
UV/VIS	Ultra violet / visible spectroscopy
WAH	Weak acid hydrolysis

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# Part I



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# CHAPTER 1

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## Introduction

### 1.1 Crude oil - a finite resource

Earth's growing population is estimated to reach 9 billion by 2050. Due to the striving towards an ever increasing better quality of life, natural resource demand is increasing even more rapidly around the world. Doubling of the world's population in the second half of the 20<sup>th</sup> century has lead to a tripled demand in food and a quadrupled demand in energy consumption as a consequence.[1]

Crude oil has displaced coal as one of the most important benefactors in development of industrial and post-industrial countries, acting as both liquid energy source but also resource for vital chemical building blocks for production of various products. Its unbalanced geographical distribution in partially politically unstable regions has lead to both the rise and fall of local economies and global markets. The developed countries dependency on this resource has further lead to military conflicts and exploitation of resource-rich but underdeveloped regions.

The awareness of rising energy consumption, the currently declining amount of newly discovered oil-wells for exploitation,[2] and finiteness of crude oil reserves as well as the impact on the atmosphere by combustion of fossil carbon have been recognised as important indicators for the necessity of sustainable alternatives in the energy and fuels

market. Crude oil is a unique resource for higher market price platform chemicals, however, a large percentage of this resource is used for the production of bulk combustion fuels.

A sector heavily dependent on fossil-based energy is the transport sector. Liquid energy carriers have here long been the only resource for storable and on-demand energy, which is not trivial to substitute without implications to our daily habits. Alternative technologies are largely still in their infancy and supply networks, especially on an international level, require further development to become competitive.

On an intermediate time scale, biomass derived drop-in fuels are possibly the only option to bridge the gap between existent transportation infrastructure and long-term carbon neutral ways of transportation. The general idea of using alternative sources to produce petroleum like fuels is, however, not new. One example, although fossil-based but with significant historical bearing, is the production of coal based Fischer-Tropsch diesel. This resource was heavily developed and exploited during the Second World War to ensure liquid fuel independence from imports, which were vulnerable. Today, ethanol or ethanol blended petrol, as well as bio-diesel from locally produced energy crops are the main fuel substitutes gaining increasing market percentages.

## **1.2 Biomass - a further exploitable resource**

Biomass comprises the largest renewable carbon source on earth and if calculated purely on energy basis, the amount of carbon synthesised by plants amounts to roughly ten times the world consumption.[3] Biomass has long been seen as an option for the production of liquid fuels and thus offers one of the basic properties necessary to substitute fossil-based fuels.[4]

The promotion of the development and use of biofuels or other renewable fuels has been established by law since 2003 in form of the EU directive 2003/30/EC for EU

member states [5]. The directive supports the creation of a new agricultural raw materials market and aims to further reduce emissions in the transport sector. Amendments to the fuel quality directive were announced in 2009, thus enabling the blending of a minimum percentage of bio-based fuel with fossil derived fuels for the transport market.[6]

In the ideal case, energy crop cultivation, i.e. those crops solely produced for energy use, can increase the independence from imported energy, and especially oil imports. National economies which have suitable agricultural settings can furthermore increase their trade balance by involving themselves in global biomass markets.

Typical energy crops for the production of bio-ethanol are sugar-rich plants, such as sweetcorn, sugar beet or sugarcane. For the production of bio-diesel (fatty acid methyl esters, FAMES), rapeseed and soy bean are typical examples.[7] However, the use of these biomass types face heavy criticisms, as they compete with alternative food and feed use. Further, clearance of woodland in combination with single-crop farming in some areas have caused a devastating impact on the environment. Excessive use of limited water resources and fertilisers for the production of these crops and their export to other countries where they are then used as feed material for biofuels furthermore questions the sustainability within this approach.[8, 9]

To avoid some of the mentioned aspects, so-called second generation biofuels are attracting more and more attention from researchers, industry and policy makers. These fuels comprise various feedstocks, ranging from algae to lignocellulose biomass. However, the production of fuels from these resource materials is generally more complicated and demands further research efforts.[10]

### **1.3 Lignocellulosic biomass for fuels and chemicals**

A very abundant resource both for a potential fuel and chemical production is the lignocellulosic material found in both wood and forestry residues. In a Norwegian and European

context, there is a strong tradition for sustainable forestry to provide feedstock for both large-scale paper production and building materials. However, the market for paper is shrinking, and a considerable part of the yearly production could be used for biofuels with no competition with food.[11] In addition to this, additional feedstocks could be provided in terms of waste wood from sawmills, builders, or other waste streams.[12]

Lignocellulosic biomass consists of the two polymeric sugars cellulose and hemicellulose, and the polyphenolic component lignin in plant-specific ratios.[13] In comparison to sugar-rich energy crops, lignocellulosic material has a lower percentage of free sugars, which can be easily hydrolysed and later fermented to ethanol. The necessary initial separation of cellulose from lignin and hemicellulose can be achieved by a wide variety of pre-processing approaches such as Organosolv, Kraft, enzymatic, as well as strong and weak acid hydrolysis.[13] However, although the production of bio-ethanol from the sugar components derived from lignocellulose material has been deemed to be economically viable, the increasing quantities of isolated residual lignin with its potentially valuable aromatic structure, see Figure 1.1, largely go unused.[14]

In petroleum refinery models, 96 % of the raw material is converted to liquid transportation and bunker fuels, as well as other low-value products.[16] Only 4 % of the raw material is converted to chemicals, rubbers and plastics, which in turn generate 42 % of the revenue.[17] It is thus, also for biomass, attractive to think within the perspective of a refinery approach.[12] Within the different models of lignocellulose biorefineries, a large variety of feedstock and product streams are suggested, see Figure 1.2.

Current product lines from lignocellulosic biorefineries could further be extended to include value-added products such as aromatic platform chemicals (e.g. phenols), novel liquid biofuels and biomaterials based on lignin, next to the existant gross bulk ethanol output, see Figure 1.3.[19, 18, 20, 21] Especially the potential for the production of phenols in terms of market demand is high, as phenols play a vital role in the chemical

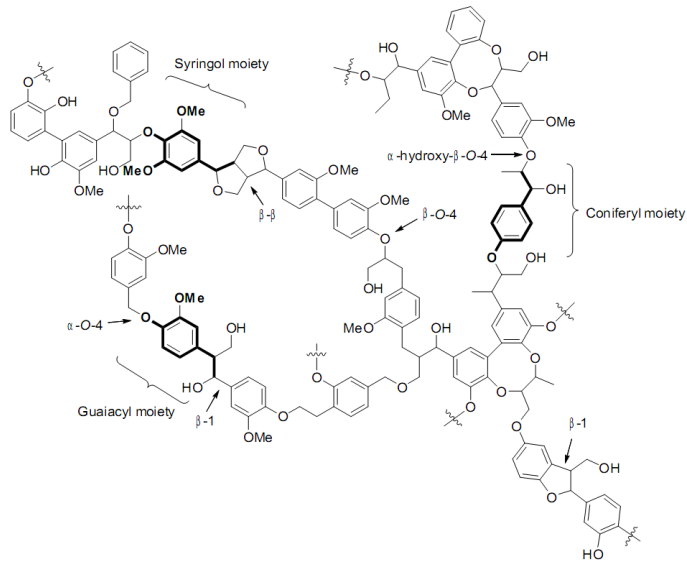


Figure 1.1: Schematic representation of a typical softwood lignin macro structure.[15]

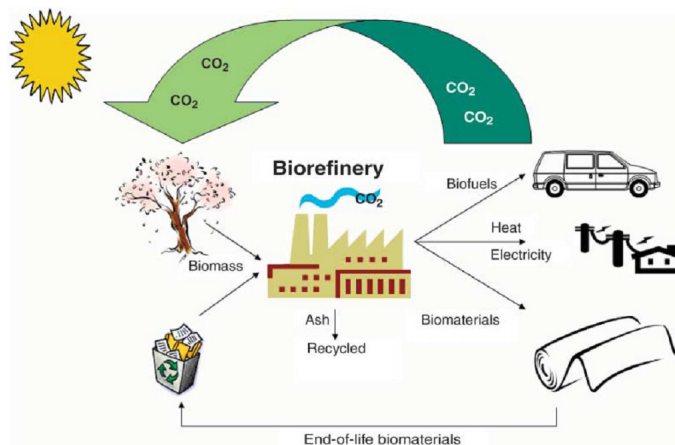


Figure 1.2: The fully integrated agro-biofuel-biomaterial-biower cycle for sustainable technologies.[18]

industry already today as building blocks for synthesis of herbicides and pharmaceuticals as well as for plastics and phenolic resins. Further reactions, e.g. by hydrogenation of phenol yields cyclohexane, which in turn is a precursor of nylon. Indeed, lignin offers the only potential direct production pathway for phenolics and could thus contribute to a sustainable production of both industrial chemicals and novel fuel blending components.[22] New building blocks derived both from lignin, but also from sugars will largely benefit the overall economics of such lignocellulosic biorefineries and could be the initial starting point for a novel sustainable industrial chemical production approach.[23]

## 1.4 Thermochemical treatment of lignin

Various different pathway options have been explored for the conversion of lignin-rich residual material to both fuels and phenols. Biological or biochemical treatment methods are mostly not applicable or aim at degrading the aromatic rings.[24] The degradation of lignin is thus widely performed using thermochemical / pyrolysis methods. These range from gasification for syn-gas purposes to the direct degradation to a liquid of variable quality. The latter enables the retention of a large amount of the abundant aromatic structures present in lignin in form of a mixture of different monomeric phenolics of different oxygenation degrees in the bio-oil product.

The liquid products which can be produced by pyrolysis methods vary largely according to experimental conditions and target applications. These cover pure energy compaction in terms of density reduction and transportability for later gasification or co-firing, upgrading to fuels or the production of platform chemicals.[25, 26, 27] A wide variety of pyrolysis techniques exist and are categorised by applied heating rate, residence time, temperature and medium in which the reaction is performed, i.e. in a gaseous atmosphere or in a solvent medium.[25]



## 1.5 Lignin-to-Liquid concept

In comparison to atmospheric pyrolysis, solvolysis provides the advantages of milder conditions and a single phase environment due to the miscibility of the organic products in the (supercritical) solvent. Anthracene, water and ethanol have been shown to have suitable solvent properties in this context. Especially ethanol has been reported to have a very high solvency for biomass and a low critical temperature which makes it attractive for lignin depolymerisation.[28] Further advantages of solvolysis performed in polar solvents, such as ethanol or iso-propanol,[29] over fast pyrolysis are a lower O/C ratio in the oil fraction and almost no solid residue ( $< 5\%$ ).[25, 30, 31, 32]

The use of hydrogen in solvolysis can further benefit process results. Hydrogenolysis in a supercritical solvent environment is to a large degree able to suppress the competing charring and gasification processes which are encountered under high temperature conditions in alcoholic media. This is the most promising approach for a high conversion rate and subsequent high yield of mono-phenolics from lignin.[27] Indeed, a hydrogen rich environment has been found to aid both in depolymerisation lignin and hydrodeoxygenation of its degradation products.[33, 34, 31] Next to the use of molecular hydrogen in combination with various catalysts, shown e.g. by Forchheim et al.,[35] hydrogen-donor solvents have also been seen to accelerate the depolymerisation process and give higher yields of mono-phenolics.[36]

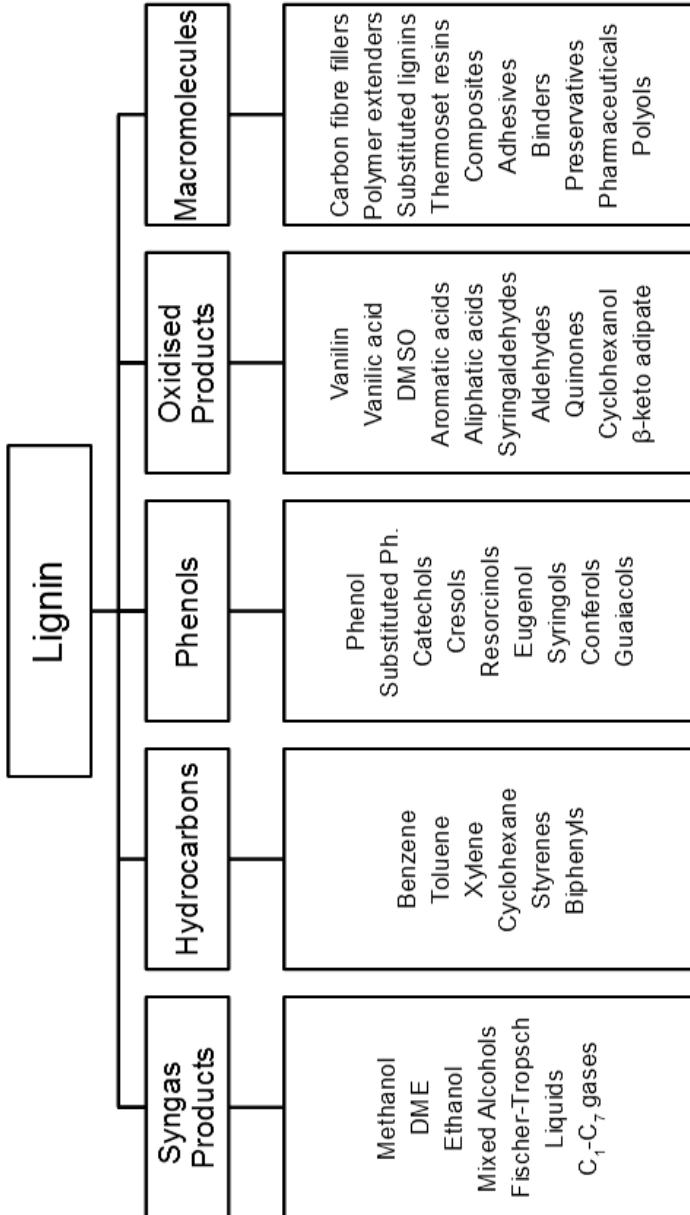


Figure 1.3: Potential products from lignin. [adapted from [21]]

Within this context, a new solvolytic conversion process for lignin based on heating solid lignin in a solvent medium consisting of a mixture of alcohols and formic acid as in-situ hydrogen donor has been reported, see Figure 1.4.[31]

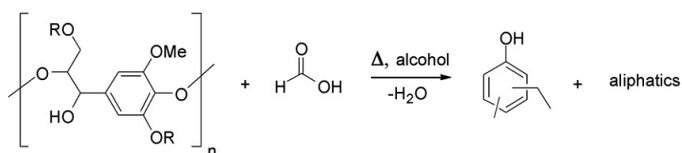


Figure 1.4: Lignin and its degradation products in the LtL reaction approach.[37]

The formic acid used within the LtL approach decomposes to hydrogen and CO<sub>2</sub>, and CO and H<sub>2</sub>O.[38] The in-situ produced hydrogen has been deemed to be a very active atomic hydrogen species,[39] and shows a unique hydrogenation capacity, also without any catalyst present. Overall, the reaction system comprises combined depolymerisation, deoxygenation and hydrogenation in one step and is in short referred to as Lignin-to-Liquid (LtL). The liquid fraction can be divided into an organic phase and an aqueous phase. The organic phase has a high H/C and a low O/C ratio and is a complex mixture of compounds derived from the lignin monomers, typically alkylated phenols, together with a range of mostly low molecular weight hydrocarbons, esters and ketones that are thought to be derived from the bridging units of the polymer together with the solvents. The quantitative distribution between hydrocarbons and oxygenated compounds is strongly influenced by the reaction conditions, and there is thus the potential to tailor the composition relative to the demand for potential fuel blending or for the production of phenols.[40, 41]



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## CHAPTER 2

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### Methods

#### 2.1 Introduction

The following chapter shortly introduces some of the analytical methods and tools used in this thesis. Further information is given in the individual papers in Part II of this thesis. In the first section of this chapter, three selected analytical chemical techniques are introduced, which have found extensive use in different papers.. Further, the application of statistical tools is given in the second section with a focus on experimental design and a short introduction to common evaluation and analysis tools such as principal component analysis (PCA) and partial least squares - regression (PLS-R), as used in papers **A** and **B**. The third section is dedicated to the implementation and exploitation of raw analytical data by chemometric means, as reported in papers **D** and **E**. The final section deals with the modelling of reaction kinetics, as used in the simplified lump model, which was developed and further validated in papers **F** and **G**.

#### 2.2 Chemical characterisation

Although physical properties play a vital role in the evaluation of complex mixtures such as fuels, molecular level knowledge is vital to aid in being able to tailor products in an

economical fashion. It is, for example, necessary to identify the oxygen containing species and functional moieties through which these are bound so as to be able to reduce the O/C and increase the H/C ratio in crude bio-oils, as is required for conventional fuel applications. Only if these are known, can these be targeted and efficiently converted.

A number of methods to characterise the reaction products from biomass degradation reactions have been used in this thesis, of which the three most important are introduced below.

### 2.2.1 Gas chromatography

Gas chromatography techniques are widely used in various chemical analysis applications. Here, the components in a mixture are separated based on both their volatility and their affinity to a stationary phase and a mobile phase, which in this case is a gas. The most common stationary phase used for complex mixtures are capillary columns, although also molsieve columns find wide applications.[42] The mobile phase is a chemical inert gas. The column, which is inside a column oven, is on the one side connected to an injector system and on the other to a detector. The injection system is heated to an individual high temperature and thus ensures volatilisation of the different components in the sample, prior to introduction into the gas stream. Variable programming of oven temperature ramps enables an increased chromatographic separation of the compounds in the mixture and a time-efficient analysis.

Typical detectors used in gas chromatography are the flame ionisation detector (FID), the thermal conductivity detector (TCD) and the chemical or electron ionisation (CI and EI) mass spectrometry detector (MSD). FID and TCD are non descriptive detectors and although these are widely used, as in this work, for quantitative data collection, require calibratory standards to identify the single components. The characteristic retention times at which the single components elute are used to identify these same components

in other samples.

Mass spectrometry detectors are descriptive detectors and consist of an ionisation source, a mass separator and a mass analyser. When using hard ionisation techniques, such as CI and EI, the ionised (charged) molecules fragment to give characteristic fragmentation patterns, the study of which can aid in identification of the parent molecules. In GC applications, the molecules are ionised when they elute from the column after chromatographic separation. Large databases, enabling matching of such fragmentation patterns to parent molecules in a library based approach have been widely established. GC-MS is probably the most widely used analytical method for the characterisation of compound mixtures.[43]

### 2.2.2 Infrared spectroscopy

Fourier transform infrared spectroscopy (FT-IR) can be used to visualise the abundance of various functional groups in a sample. Absorption of characteristic infrared wavelengths by the different chemical functionalities is transformed into vibrational energy. Classical IR spectrometers are operated in either transmission or absorption modus. For specific applications, attenuated total reflectance measurements are a further option. The infrared sample spectrum obtained is subtracted from a baseline measurement, thus visualising the characteristic absorption wavelengths, which can be allocated to the specific functional groups. Various sample preparation options for both liquid and solid samples exist.[44] The application of Fourier transformation has further enhanced the speed and sensitivity of analysis, making FT-IR a reliable and also quantitative measurement for functional group abundances, also in mixtures.

### 2.2.3 Fingerprint mass spectrometry

In comparison to the prior presented chemical and electron ionisation methods in mass spectrometry, which aim to fragment ionised molecules for further identification, soft ionisation techniques aim to retain the analysed molecule as a whole in form of a molecular ion. These methods also enable ionisation directly from atmospheric conditions without necessitating prior sublimation or evaporation. This has had major impact on macro- and biomolecule analysis, which largely disintegrate already during the harsh sublimation or evaporation conditions. Furthermore, the largely very small fragments produced during EI or CI do not enable any means of identification for such large molecules.

Another application for these soft ionisation techniques is the analysis of mixtures without or only minor prior chromatographic separation, as the ionised molecules are not (largely) fragmented and can be directly identified, given sufficient resolution. Recent developments of such applicable high resolution mass analysers have led to the addition of the field of "petroleomics" to the so called "-omics" sciences.[45, 46] Herein the aim is to simultaneously analyse many components in a sample by a single or a low number of analysis runs.

Typical and widely applied soft ionisations are electrospray ionisation (ESI) and (matrix assisted) laser desorption / ionisation ((MA)LDI). In ESI, the soluted analyte is injected via a capillary into a chamber with slightly reduced pressure. A high positive voltage, if operated in positive mode, is applied to the capillary tip thus removing electrons from the analyte and solvent molecules, causing highly charged drops, see Figure 2.1 for illustration. The repulsion between the identically charged ions causes so-called Coulomb explosions, by which ions are expelled from the droplets. This mechanism is supported by a dry gas flow, which disperses the droplets, causing a higher charge to surface ratio. In addition, the dry gas flow together with a skimmer removes a large proportion of the solvent analyte mixture which is pumped out of the system. The desol-



vatisation of the analyte is concluded after passing the skimmer and entering the vacuum chamber after which ion optics channel the ionised molecules towards the mass analyser and detector.

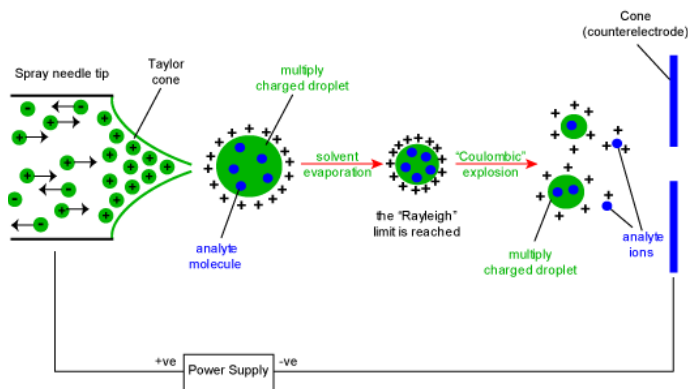


Figure 2.1: A schematic of the mechanism of ion formation in ESI.[adapted from [47]]

Hughey et al. showed that coupling an ESI source with high resolution mass spectrometry ion cyclotron analysers allowed to distinguish between up to 11.000 components in a single analysis of a crude oil sample.[48] The soft ionisation from liquid or solid state ideally ionises compounds without fragmentation, yielding solely one molecular ion, in addition to possible adducts or clusters. Based on the elemental composition, which can be deduced given sufficient resolution, and significant patterns within the so called fingerprint mass spectra, compound classes and their varied abundance in different samples were analysed.

Although high resolution analysers are of course superior in this context, modifications to a ESI LC-MS bench-top analyser by Eide and Zahlsten in combination with a novel chemometric implementation of the resulting mass spectra showed a surprisingly good ability to differentiate between various crude and bio oils.[49, 50] Also here, the dominance of compound class variance was shown to be one of the major differences between samples.

## 2.3 Chemometric supported reaction system evaluation

### 2.3.1 Use of experimental design

A common strategy in the exploration and optimisation of reaction systems is the "one-factor-at-a-time" approach. Herein, reaction parameters are singularly altered from selected starting points, showing an increase in, e.g. the total yield of a compound. However, this approach can lead to false yield maxima, see Figure 2.2. Furthermore, several combinations of parameters may give rise to multiple local yield maxima in the experimental plane, which a linear optimisation approach does not consider. The approach also does not take the interaction between parameters into account and thus implies that the chosen parameters have a defined single effect, which is not necessarily true. Complex reaction systems, such as biomass pyrolysis reactions are governed by a multitude of reactions of various components and the interaction effects in these complex systems are of major importance.

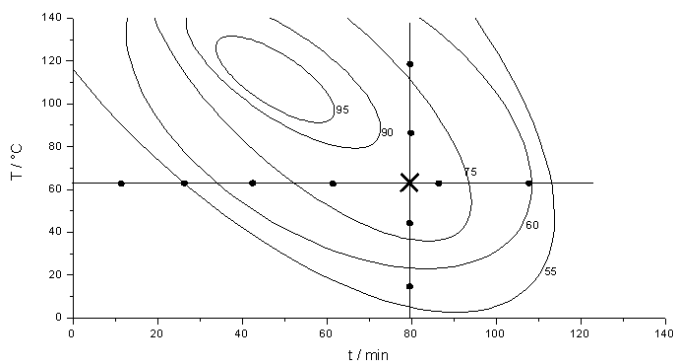


Figure 2.2: An unsuccessful "one variable at a time" optimisation approach.[adapted from [51]]

Screening of many variables with a limited amount of experimental resources and to

extract the maximum possible amount of information from these, is the first step in a sequential chemometric approach. For best performance, experiments are carried out on the basis of an experimental design, which ensures the statistic value of the collected data.[52]

For this purpose, a wide range of experimental designs have been developed.[53, 51] Factorial or space-filling designs offer a consistent (statistical) spread over the experimental space, whereas other designs, such as the D-optimal design, offer a higher degree of flexibility if a corner of the experimental space is not accessible. The selection of a suitable design is highly dependent on the reaction system and the focus of the investigation.[54] Coupled with statistical evaluation, the results can be considerably helpful during the exploration of boundaries, interaction and parameter effect characterisations as well as reaction optimisation. These have been shown to be especially successful in complex mixtures.[55]

Within this thesis, fractional-factorial designs were chosen for screening purposes, as these offer a good spread over the experimental space, after having performed a number of corner experiments. The factorial design utilizes a number of factors with discrete levels, in this case a minimum and maximum level. A full factorial approach studies the effect of all minimum and maximum level combinations of the individual factors. So as to reduce the number of experiments performed, a statistical balanced half of all combinations and thus experiments are omitted. This approach is also called a half-factorial design.[51]

### 2.3.2 Principal component analysis

A first statistical evaluation basis of the varied experimental parameters and logged results can be carried out using PCA. PCA aims to reduce the dimensionality of the data while retaining most of the variation therein.[56] Thus aiding in visualising correlations between sets of independent and dependent variables. Herein, a new set of linear com-

binations of orthogonal vectors with suitable vector parameters describe the variance present in the dataset. The new vectors, or principal components are orientated along the maximal residual variance in the data. Hence, the largest variance is described by the first principal component, the largest remaining variance by the second and so forth, see Figure 2.3.[57, 58, 59] Residual variance, which is deemed of no importance in the evaluation, can thus be discarded and the interpretation of results limited to the basis of a restricted number of components.

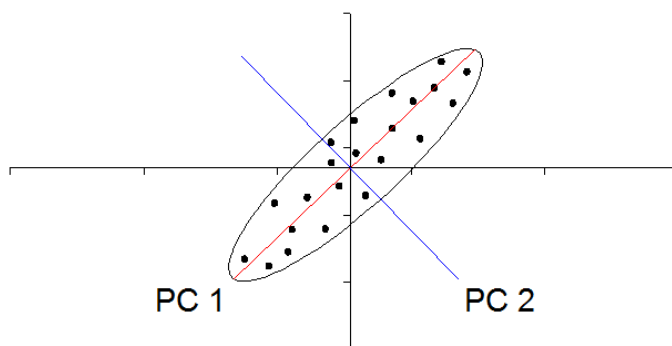


Figure 2.3: Determination of the first two orthogonal principal components based on describing maximum variance in a dataset.[adapted from [59]]

### 2.3.3 Partial least squares regression

Chemometrics does not only aim to aid the user in terms of visualising relationships between independent variables such as experimental parameters, and dependent variables such as the collected responses from the reaction system, but also to predictively model these dependent variables quantitatively. PLS-R is the most used form of PLS in chemistry and technology and has thus been chosen for modeling in this work. PLS can be considered as an extension of PCA, aiming to model the relationship between two matrices,  $\mathbf{X}$  and  $\mathbf{Y}$ . In the case of a large number of independent variables ( $\mathbf{X}$ ), which

are often very highly correlated, PLS-R is used to produce a small number of linear combination of the two original sets of variables,  $\mathbf{X}$  and  $\mathbf{Y}$ , which are then used as input for the regression model.[52] It can thus be said, that PLS-R models the "structure" of both  $\mathbf{X}$  and  $\mathbf{Y}$ , thus enhancing the results in comparison to traditional multiple regression approaches.[60] The result from PLS-R are described by several regressions equations for each dependent variable  $y$ .

## 2.4 Chemometric supported product analysis

Increased computerisation of analytical data collection has further enabled the quantitative introduction of typical chemical analytical methods such as FT-IR, UV-Vis, GC and MS data. Thus, not only allowing bulk prediction based on quantitative data, but direct implementation of raw analytical data in the chemometric evaluation process. These can be further used also for process control in on-line methods.[61]

Within complex mixtures however, FT-IR or UV-Vis are however not always suitable to discriminate between different compound classes, whereas in simple mixtures, this can indeed be achieved.[62] In the depolymerisation and deoxygenation of lignin it is, however, vital to be able to trace the (relative) quantities of very specific changes in the monomeric phenolic compound classes.

### 2.4.1 Gas chromatography

Chromatography based approaches are able to separate different components even in a mixture as complex as crude or biomass derived oils. Combining this versatile technique with chemometrics is especially valuable in combination with complex mixtures. For chemometric evaluation and interpretation of this kind of data, the retention time of individual compounds is used to identify identical compounds in different samples. This

method is widely applied in form of liquid and gas chromatography methods and several (commercial) methods are available to overcome typical issues such as retention time shifts or variable injection quantities.[63, 64] When investigating complex mixtures however, the variable contents in different samples can lead to mismatching of compounds at similar retention times, which can falsify results and complicate interpretations. The complexity of samples makes a manual correction after systematic data processing nearly impossible.

Furthermore, alterations to the analytical method or to the hardware may deem older collected data no longer comparable, or require large modifications to the data handling to compensate for alterations. In recent years, chromatographic methods have advanced considerably. However, the separation of compounds by boiling point and / or polarity is time consuming and can only depict a select fraction of compounds in very complex samples. E.g., in gas chromatography, compounds are required to be vaporised prior to separation and analysis, thus introducing limitations in terms of the molecular weight of compounds which can be analysed.

## 2.4.2 Fingerprint mass spectrometry

Although chromatography based analysis for many chemical products is common practice, chemometric implementation of collected data especially from complex mixtures still inherits unique challenges, as mentioned above. Modern mass analysers have enabled the development of direct-injection fingerprint MS methods, which avoid some of the typical complications, such as chromatographic and peak matching issues, which demand complex curve resolution approaches.[65] Here, the complete or a fractionated part of the sample is directly ionised and analysed in its totality under near atmospheric conditions without any chromatographic separation. The analysis of the single components in the mixture is carried out on a molecular weight basis, and thus largely avoids any neces-

sary complex peak matching algorithms. Based on the different ionisation methods, a selectivity for different heteroatomic containing species can be chosen, making modern fingerprint MS methods a highly versatile and fast alternative to chromatographic based approaches.

## 2.5 Modelling reaction kinetics

Biomass conversion processes combine a wide diversity of competing and parallel reactions to yield char, gas and liquids with largely varying components of both intermediate and stable nature. A kinetic understanding of the degradation processes and formation of products is an essential step in increasing yields and achieving product requirements. For this, the development and evaluation of kinetic models are a very useful approach. Modelling of these key processes can be classified into micro- and macro-particle models. For identification of kinetic schemes, the kinetically controlled micro-particle models are desirable. The requirements for the application of a micro-particle model are fulfilled, when particle sizes are sufficiently small, so that diffusion and heat capacity effects can be ignored. This is especially relevant in processes, where reactions with the solid particles are a necessity, such as the penetration of active components from formic acid into the lignin matrix for depolymerisation. To satisfy these conditions, the critical particle size estimates have been reported to lie between circa. 100 - 1000  $\mu\text{m}$ .<sup>[66]</sup>

In formal kinetic modelling, a scheme with all reaction pathways is developed by the user and rate coefficients are fitted to match experimental results. According to the quality of results obtained, i.e. the quality of agreement of the rate coefficients with literature values and the fit quality of modelled results with obtained experimental values, the user adds or removes pathways or components in the model.

A large number of models describing lignin degradation concentrate on global bulk yields and individual compound classes. Although Jegers and Klein have concluded that

modelling of the monomeric phenolic classes could be accomplished by a simple lump model,[34] no attempts to implement this suggestion in an overall kinetic reaction model and the influence of experimental parameters or feedstock has been explored.[67] The deoxygenation of phenolics in the LtL approach are a vital parameter and the implementation of a formal kinetic lump model including both monomeric aromatics as well as global bulks has been deemed largely relevant.[68]

The validation of the model and its transfer to another reactor system,[69] as well as determination of the reactions with major impact under variable conditions were further investigated using sensitivity and flux analysis.[70]



# Summary & main results

### 3.1 Introduction and outline

This chapter summarises the main results of the attached papers in Part II of this thesis. To simplify the reader's understanding of the overall work approach strategy, the papers have been grouped and their presentation subdivided into three sections in this chapter.

The first section deals with initial screening approaches and boundary testing of the LtL bio-oil approach and includes papers **A**, **B** and **C**. These deal with the experimental design supported exploration of operational parameters and their influence on the product compositions, as well as the identification of new potential chemical characterisation methods.

The second section deals with the chemometric supported exploitation of conventional chromatographic GC-FID analysis and a novel ESI-MS fingerprint analysis method, as documented in papers **D** and **E**. Herein, the usefulness of using statistical supported evaluation of complex analytical data is shown on the basis of (a) the detection of natural gas-hydrate inhibitors in a set of GC crude oil data, and (b) the extraction of homologous series as an orthogonal basis vector set in a novel fingerprint MS analysis method of a set of LtL bio-oils.

The third section summarises the results from papers **F** and **G**. Within this work, the

lignin degradation and deoxygenation processes that produce demethoxylated phenols, a major product fraction from the LtL conversion, is investigated by developing a formal kinetic best-fit model based on data from one experimental series. The model is further tested for experiments conducted in a continuous reactor and at different temperatures, to ensure its validity for future scale-up approaches. The impact of the changed conditions are discussed on the basis of the derived kinetic parameters which are further evaluated with the help of flux and sensitivity analysis.

## 3.2 Screening & exploration

Based on the complex reaction system making up the LtL approach and the limited amount of knowledge present since it was first reported in 2008, a wide range of parameter testing was necessary, and multivariate methods were applied to help identify crucial parameters, critical loading ratios and their influence on products. For this purpose two half-factorial designs comprising a total of 16 experiments plus centre points were devised, which are presented in paper **A**. In these experiments, the ratios of the two co-solvent alcohols ethanol and iso-propanol, the ratio of the hydrogen donor formic acid to alcohols and the loading level of solvents as well as lignin were tested. All experiments were conducted for roughly 16 h duration and at 380 °C. Valuable information was gathered concerning the reactivity and role of the input formic acid, which markedly contributes on the one hand to the high conversion of lignin to phenols, but on the other hand strongly contributes to the amount of excess gas produced. The complete degradation of formic acid therefore does not lower the pH of the neutral liquid product oil phase, which contains roughly twice as much hydrogen (by weight) as the initial lignin, while oxygen values are halved. Variations within the product oil phases show that the composition can be influenced to yield a larger degree of hydrocarbons or alkyl substituted demethoxylated phenols, or a mixture of both, see Figure 3.1.

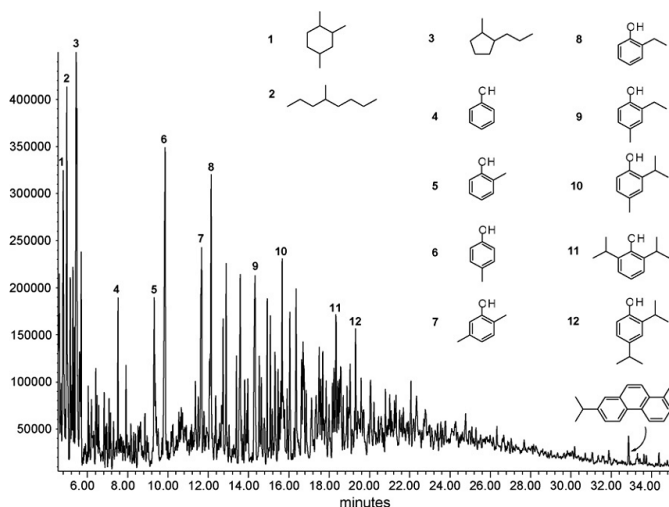


Figure 3.1: GC/MS chromatogram of a sample of aliphatics and phenols being almost equally abundant. Reaction conditions: 6 g SAH lignin, 15 ml formic acid, 15 ml iso-propanol, 75 ml reactor, 380 °C, 15h.[37]

Chemometric analysis further indicates that this variation can largely be controlled by altering the ratio of iso-propanol to ethanol and the ratio of formic acid to alcohols. The high alkylation degree of phenols is most likely a product of reactions of the phenolic rings with the alcohols, whereas the produced hydrocarbons are most likely products from the reactions of the bridging chain carbons from lignin / possibly residual carbohydrates in the lignin with other compounds from the reaction medium. However, a close correlation between alcohols and aliphatics was found, which leads to the conclusion that these strongly contribute to the aliphatic yields by being initially gasified and later condensate possibly by a Fischer-Tropsch type mechanism. The volatile compositional fraction would suggest itself for both fuel blending or the production of phenols. Analysis showed no presence of polyaromatic compounds in the product liquid.

The PCA showed that although an increase or decrease of specific parameter values correlate well with product variations, no ideal setting with solely beneficial effects could

be found. PLS models, for example, showed that an increase of temperature would yield a better separation between liquid phases, however, as a consequence gas and char yields would increase.

Screening experiments were continued in three further separate approaches, partially supported by experimental design and chemometric evaluation. These are presented in paper **B**.

For the first approach, a series of experiments (F-series) was conducted with the aim of reducing amounts of iso-propanol, formic acid and the reaction temperature. In addition, water was added to evaluate its influence on depolymerisation and solubility properties. For the half-factorial design, molar ratios of the alcohols iso-propanol / ethanol, the hydrogen donor formic acid / alcohols and water / alcohols were varied. In addition, the reaction temperature influence was evaluated between 370 and 390 °C. The results and data treatment gave conclusive PLS models for gas composition as well as for the separation and overall amounts of gas, liquids and char. The established models may be used as a basis for further experimental approaches so as to improve the overall efficiency of the process as based on these equations. The PCA biplots allow the conclusion that formic acid as well as iso-propanol contribute to the conversion of the educts to a product of higher diversity. However, it is not possible to link the addition of iso-propanol to the conversion of lignin to phenols. A novel fingerprint analysis method using ESI-MS analysis was further tested on this experimental design set of produced LtL oils. Initial chemometric evaluation showed that differentiation between the characteristic mass spectra is based upon consecutive series with 14 Da spacings, which are characteristic of homologous series. This is especially visible in the loading line plots, see Figure 3.2, and it is suggested that the analysis technique should be further explored and utilised.

The second approach aimed at understanding the influence of reaction duration on

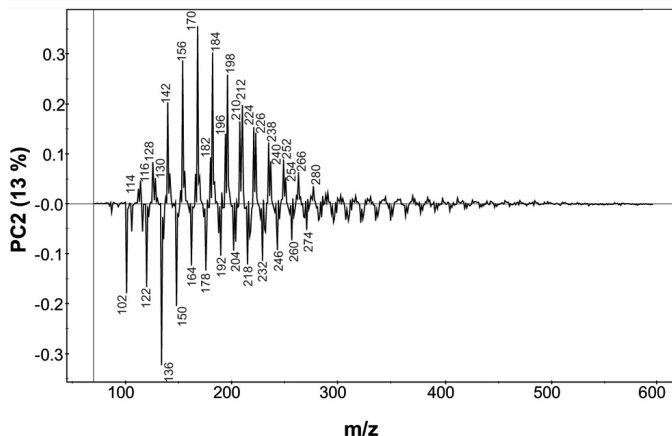


Figure 3.2: Loading line plot for the second principal component obtained after PCA of positive ESI-MS data. The plot is largely dominated by 14 Da spaced signal series.[adapted from [71]]

the bulk product groups. For this, six experiments (T-series) with varying reaction durations between 2 and 16 h were conducted with identical loadings. Results show that an increased reaction duration yields more solid residue and gas. In addition, the observed two-phase separation of liquids does not occur at low reaction durations, but, under given loadings, requires a minimum of 6 h. This suggested that some of the reactions in the process take considerable time to occur, as the phase separation occurs based upon the separation of polar and unpolar species. Even above 6 h, the liquid oil phase continues to increase with further reaction duration, suggesting that polar components are deoxygenated, reducing their solubility and thus increasing the non-polar fraction of the total liquid product. It can be concluded that a maximum reaction duration of 12 h should not be exceeded to avoid excess gas and char formation.

In the final approach, experiments without lignin (B-series) were conducted, aimed at better understanding the degradation product ratios of formic acid under LtL conditions and to assess the possible degradation of iso-propanol and ethanol. The alcohols, especially iso-propanol, were seen to be quite reactive, and to degrade not only to their

analogue gaseous components, but to further react to produce long chained esters, ketones and hydrocarbons up to a  $C_{12}$  backbone, see Figure 3.3. Due to presence of syn-gas components in the reaction atmosphere and typical Fischer-Tropsch catalyst elements in the reactor material, a Fischer-Tropsch type mechanism is assumed.

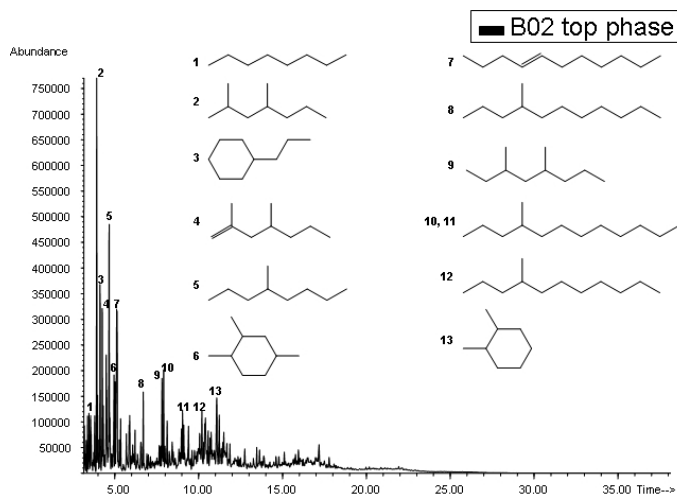


Figure 3.3: Gas chromatogram of the organic phase obtained from experiment B02, showing the predominant aliphatic components.[37]

The high degree of degradation of the input alcohols, especially of iso-propanol, and the lack of contribution to the phenol yield, suggest it should be removed from the input. In addition, the evaluation criteria of the LtL product should be more concentrated on the yield and the deoxygenation degree of phenolic species, as other components seem to largely arise from the solvent medium and not from the lignin. They are thus only byproducts, and should in the due course of optimisation be reduced.

Initial scale-up work is reported in paper C, summarising the efforts made to review the impact of scale on the products found from the LtL concept. A small number of representative experiments using solely ethanol and formic acid, exempting the use of

iso-propanol based on the findings in previous work, were performed in both in a 5 ml batch and 1 l shaken batch reactor and their results compared. The removal of iso-propanol and the higher dilution yielded a single phase liquid product. A dominance of phenols is found in the GC analysis. The scale-up experiments showed that the liquid composition did not vary to any great degree, but that solid recoveries could be minimised and that the large scale experiments gave gas with lower values of carbon dioxide. This lead to the conclusion that the larger scale does not lead to loss of quality or significant variations in the product.

The upscaled experiments supported additional measurements, allowing more insight into the potential of blending the LtL oil with motor fuels. Octane numbers were determined based on blending-measurements of crude LtL oils mixed with petrol of a known octane value. The high RON values (105.8 - 110.7), although benefiting from the high octane number of the solvent medium ethanol which was still present in the crude product, suggest that LtL oils rich in substituted phenols might be used as a fuel-blend product. However, since scale-up approaches are aimed at recycling the solvent, a focus on the isolation of phenols should be prioritised.

### 3.3 Chemometric supported product analysis

Chemometrics can be a very powerful tool to help visualise complex connections in chemical systems. Further, the application to complex analytical data can allow the extraction of important components, which a mere visual comparative inspection may fail to see. The application of statistical tools is reported for two very different research approaches using GC-FID and ESI-MS data in the following. The first of which was largely aimed at also gaining first hand experiences with the complications that retention time based data inherit, yielding a basis for comparison with the later presented fingerprint ESI-MS data approach in paper **E**.

Chemometric evaluation of a routinely collected GC-FID data is used to relate to compounds which inhibit natural gas hydrate plugs in a set of crude oils in paper **D**. Gas hydrate plugs in subsurface crude oil pipelines can pose a costly issue for exploitation and recovery operations. The tendency of selected oils to form plugs, whereas others transport gas hydrates within a harmless dispersion has been connected to the presence of natural gas hydrate inhibitors in the latter. The separated unresolved complex mixture (UCM) background in the GC-FID data was treated separately, see Figure 3.4, and detected peak times were matched by a simple binning approach. PCA showed that both UCM and peak data could be used to distinguish between biodegraded and non-biodegraded oils and also plugging from dispersion forming oils. The peak data furthermore showed strong correlation of branched components within the  $nC_9$ - $nC_{13}$  range. Comparison with structural proposals in literature confirm that the volatile fraction of crude oils contains compounds which can be correlated to the gas hydrate plugging potential. It can be concluded that the use of a simple GC-FID database approach could possibly be used to categorise oils of high plugging potential. The reported approach could thus be used complementary or as a pre-screening to the usually costly carried out plugging potential loop measurements.

In paper **E** the relevance of 14 Da spaced signal series, which were reported to describe a majority of the variation in the PCA of fingerprint ESI-MS data of a set of bio-oils in paper **B**, were further investigated. Within the loadings of PCA, several of the 14 Da spaced series, 14 Da corresponding to a  $-CH_2-$  group, representing different compound classes are described by one single loadings vector and isolation and impact of single series cannot be achieved, see Figure 3.2. The separation and visualising the variation of these series is however necessary to be able to make chemical interpretations. The isolation and assessment of description power by using these single series as loading vectors in a sample set of bio-oil ESI-MS data was reported.



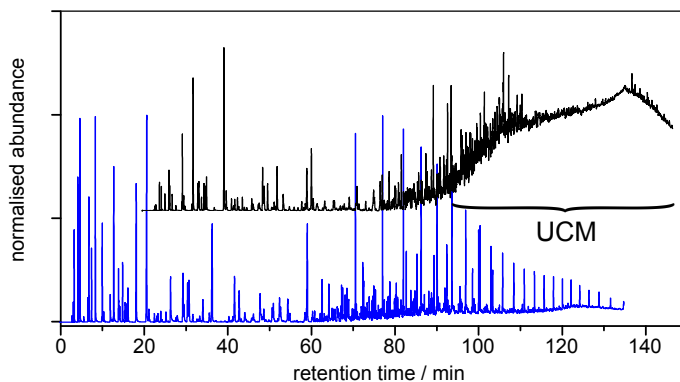


Figure 3.4: FID traces of the heavily biodegraded oil B2c (top) and the non-biodegraded oil S5b (bottom) illustrating the spread of sample-set as seen in GC-FID. The unresolved complex mixture (UCM) area is indicated for B2c.[72]

Positive ESI-MS data, obtained from the F-series bio-oil samples in paper B, were projected onto a pre-defined set of equally spaced sequences, in this case 14 Da, see Figure 3.5. Compensating for minor peak shifts, these individual series were used as orthogonal loading vectors and compared with the discrimination and descriptive performance of PCA.

Discrimination between samples was largely satisfactory. Based on the sample-set, 71 % of the total variation (of the scores) could be described by the first three 14 Da basis vectors, showing that a large amount of variation can indeed be expressed by a few homologous series in this dataset. Complementary analysis on GC-MS showed that the two first isolated vectors with largest variation represent non-methoxylated phenols and substituted ketones, respectively. Coupled with the the fast analysis accomplished by the fingerprint ESI-MS, this novel method can largely support fast screening approaches to monitor variation on a compound class series basis in complex mixtures.

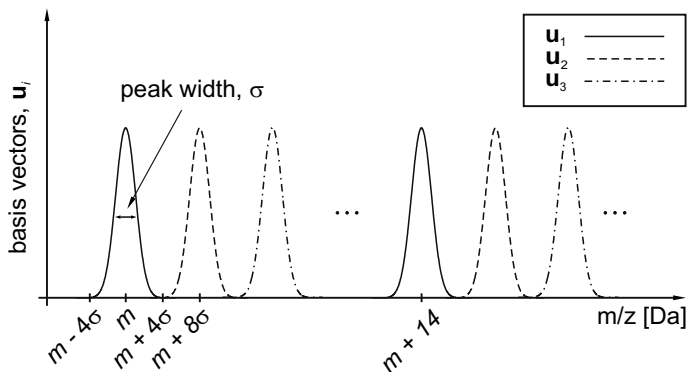


Figure 3.5: Definitions of the basis vectors used in the analysis. The figure shows a section of the three first vectors only.[73]

### 3.4 Modelling major reaction pathways

Performed experiments to produce bio-oils based on the LtL concept were commonly performed with long reaction durations to achieve a high degree of deoxygenation of the phenolic products. In order to identify both bottleneck reactions, causing this necessary long durations and main competing reactions yielding both char and gas, a kinetic best-fit lump model was developed, which is reported in paper **F**. The model combines both global bulk and key compound lumps and bases itself on a series of 10 experiments with varied experimental durations. These were all conducted in batch reactors using a wheat straw lignin at 360 °C. Both the use of ethanol as solvent and formic acid as hydrogen donor were taken into account and are represented in the reaction pathways of the model. Ranks of the different quantified phenolic species were determined by Delplot analysis, for which the solid residue was characterised by FT-IR, so as to describe the necessary conversion, see Figure 3.6.

The lump model using both a small number of selected phenolic lumps and global bulks, as shown in Figure 3.7, is able to describe the experimental values from lignin degradation experiments under LtL conditions correctly and determined rate constants

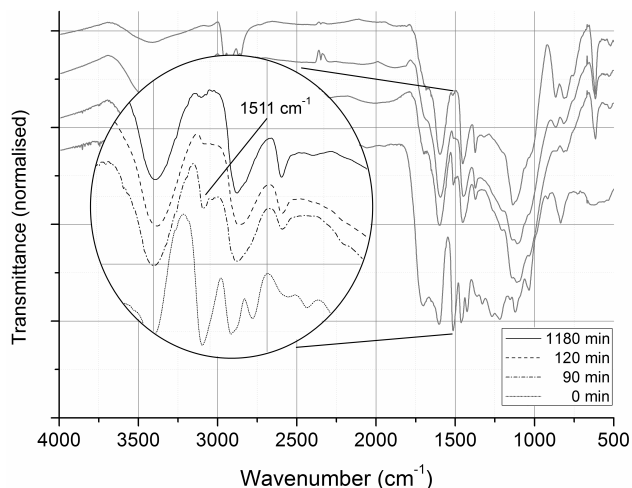


Figure 3.6: Zoom of the FT-IR region around the functional aromatic ring vibration band at  $1511\text{ cm}^{-1}$ , which is used for identification of the transition period from largely lignin dominant structures to polyaromatic char of the solid residue.[74]

are largely in very good accordance with literature values, where available. The model results show that the depolymerisation of lignin is accomplished quickly and that the typical consecutive deoxygenation reactions of the first monomeric intermediate phenolics documented in the literature also take place under LtL conditions. The prevalence of ethyl substituted phenolics is linked both to the use of ethanol as solvent, but is also suggested to be dependent on the type of lignin used, as 4-ethylphenol was found to be highly dominant at shorter reactions durations. Gasification and charring reactions are the main competing pathways to this route, which are however only loosely linked to the monomeric phenolics produced. A large degree of intermediate products from lignin in liquid phase could not be quantified. This lump is largely coupled to the ongoing charring and gasification processes and depolymerisation resistant oligomeric structures may be suggested to represent major components therein.

The model was further validated and its applicability beyond development conditions in a batch reactor tested in a continuous stirred tank reactor at temperatures ranging

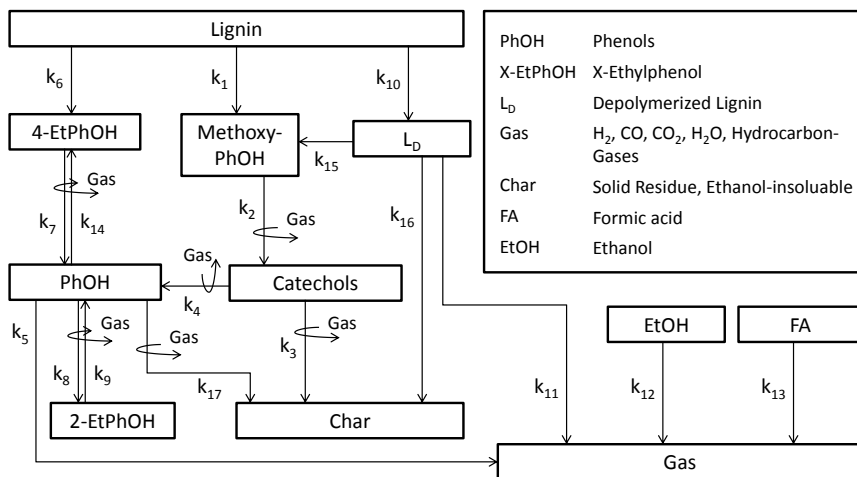


Figure 3.7: The simplified formal-kinetic lump-model uses lumped mono-phenolic components as well as global bulks to describe the main pathways and characteristic reactions taking place under LtL conditions with a focus on the deoxygenation reactions of the mono-aromatic components.[68, 74]

between 360 and 400 °C. The results for these experiments were evaluated in paper **G**. Rate constants of the single reactions and activation energies were used as a basis to extensively discuss the impact of the variation in experimental conditions. This was further supported by sensitivity and flux analysis.

Results showed that the model can be successfully transferred to a continuous operated reactor and can also be used to describe the reaction kinetics in the temperature range of 360 - 400 °C. Increased reaction rates for several key reactions including depolymerisation were found for the continuous reactor. Further, a preference for the production of monomeric products and their consecutive deoxygenation opposed to the production of solid residue by repolymerisation was found. Produced gas yields are severely decreased and are strongly coupled to the gasification of ethanol and formic acid, opposed to lignin as a source in the batch reactor model. The temperature increase was further seen to decrease solid residue yield and increase the yield of deoxygenated phenols. This is due to

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the overcoming of the somewhat higher activation energy barrier for the deoxygenation reactions. However, the formation rate of methoxyphenols, which are stipulated to be primary products from lignin depolymerisation in the model, were found to be insensitive to temperature variation within the range tested.



# Conclusion & outlook

## 4.1 Screening & exploration

Formic acid / alcohol solvolysis of lignin-rich residual material under high temperature and pressure conditions was explored. In paper **A**, it could be shown that the use of formic acid benefits an increased yield of deoxygenated phenols, and largely reduces solid residues in comparison to typical flash pyrolysis approaches. Formic acid was seen to be positively correlated with the O/C ratio found for this product fraction. However, a large excess amount of gas is produced during the thermal degradation, which is undesired. Experiments performed, yielded a two-phase product liquid. The hydrophobic top layer was mainly comprised of hydrocarbons, esters, ketones and phenols. The ratios between the four major compound classes in this fraction could be altered according to chosen experimental parameters. The hydrophilic bottom layer contained a large degree of the solvents, process water and further water soluble components.

Minor amounts of solid residue (circa. 5 %) could not be further decreased during optimisation, even when using an increased amount of formic acid. It might therefore be assumed that the solid residue obtained consists of non degradable non-lignin components in the feed material. From an economical point it was deemed necessary to reduce the amounts of formic acid to try and find an optimal ratio of minimum amounts of formic

acid to lignin, which still yield a suitable liquid product. This was further investigated in paper **B**. A series of experiments were conducted with equal loadings but varied reaction times. Here, it was seen that the deoxygenation processes require a relatively long time, which was confirmed by a separation of liquid phases into a hydrophobic and a hydrophilic layer after 6 h reaction duration. It was concluded that a maximum reaction duration of 12 h should not be exceeded to avoid excess gas and char formation. To further reduce the amount of formic acid, based on the assumption of reactive atomic hydrogen,[75] a partial replacement with hydrogen gas was attempted, however, the amount of solid residue as well as the yield of phenols was seen to be solely correlated with the amount of formic acid, deeming a partial replacement not possible.[76] Further reports suggested that although the hydrogen from formic acid is seen to be vital for the deoxygenation processes, the successful depolymerisation of lignin might be aided by the high concentration of carbon dioxide, which is produced during the thermal degradation of formic acid.[77]

Although the alcohol mixture displayed a high solvency, their reactivity was identified to be of critical issue. Iso-propanol was found to be largely contributing to the production of various non-aromatic components in the product mixture, and no significant influence of the mild hydrogen donor towards increased phenol recovery could be found. The analysed esters, ketones and hydrocarbons found, were originally assumed to be derived from the bridging units in the lignin structure after possible reaction with the present alcohols. Reactions performed without lignin however displayed a similar composition of non-aromatic volatiles as in experiments where lignin material was used. It can thus be assumed that these components are largely formed by the reactive solvents in the system. Both due to the degradation and lacking contribution to the yield of recovered phenolics, iso-propanol was hence removed from the reaction system in further work.

The reduction of formic acid in combination with the use of either a reduced amount of iso-propanol or complete replacement by solely ethanol as a solvent yielded only a single



liquid phase product, the volatile fraction of which was seen to be mainly composed of phenolics, see papers **B** and **C**. The gasification of ethanol is, in respect to its use as a solvent still considered problematic. Comparisons with water systems have shown that although a decreased amount of solid residue and a higher recovery of phenolic compounds in ethanol can be achieved, the overall benefits of a low solvent cost and its recovery, as well as the possibility of using wet biomass strongly suggests the use of water as a solvent. Work in aqueous medium further shows a preference for a product of lower diversity, which is of interest, if the production focus lies on selected phenols. This is due to lacking post-depolymerisation alkylations by the alcohols.[68, 78]

In terms of the consecutive alterations to the product spectrum throughout the screening papers **A**, **B**, and **C**, it can be concluded that the main lignin-derived products are largely a mixture of various substituted phenolics. Depending on reaction conditions, a very low degree of oxygenation based on demethoxylation and dehydroxylation reactions down to (alkyl substituted) phenols can be achieved, which, within the initial aim of the production of fuel components, is highly relevant. The reaction pathways involved were the focus of the kinetic lump model. The development of which is reported in paper **F** and was further validated and discussed in paper **G**.

## 4.2 Chemometric supported product analysis

Using chemometric tools such as experimental design and PCA to evaluate complex reaction parameter correlations already proved to yield valuable results in the exploration of the LtL concept, as reported in papers **A** and **B**. Chemometric aided evaluation was further used to identify crucial components in a crude oil GC-FID dataset in paper **D**. This dataset was used to gain first experiences with the implementation of raw analytical data as an initial step to the development of a novel approach describing the variation of homologous series in a mass spectrometry fingerprint approach of a set of LtL-oils in

paper **E**.

In paper **D**, the use of routinely collected GC-FID data of a set of 11 crude oils were analysed using a simple binning approach to identify gas hydrate inhibiting components, which are deemed to aid in the dispersion of gas hydrates present in crude oil in sub-sea pipelines. The discrimination between high and low risk plugging potential oils by routine analysis such as GC-FID, is a highly relevant alternative to the costly gas hydrate measurements which are otherwise performed. Using further analytical means, a successful identification of such compounds could aid in their isolation and their possible use as additives to replace current inhibitors, which are both costly and have partially caused environmental concern. The results showed that a clear distinction between bio- and non-biodegraded oils using the separate UCM and peak analysis data could be made. Further, the analysis of peak data enabled also a separation of oils with a high and low plugging potential, pointing towards the presence of branched molecules in the  $nC_9$  to  $nC_{13}$  range, which display an inhibiting function. This coincides with prior results, which suggested that ester or other carbonyl moieties in these components can inhibit clathrate hydrate plug build-up.

Use of chemometrics aiding the interpretation of fingerprint ESI-MS data was already exemplified in paper **B**. A satisfactory reproducibility and degree of data compaction was shown to be achieved by PCA. Differentiation between samples was found to be largely linked to variations in compound classes. However, the solely statistical approach did not allow separation of the observed dominant 14 Da spaced homologous series describing these compound classes, which during the analysis were compacted into single loading vectors. Hence, chemical limitations, based on the observed patterns and in form of pre-defined 14 Da spaced sequences, were introduced already during the data processing stage in paper **E**. The measured spectra were thereupon projected onto this set of individual sequences, contributing a novel evaluation approach based on homologous series

as a complement to PCA. The method developed allows to visualise the abundance of whole homologous series, and characterisations are thus linked to all constituents of a compound class instead of selected components only, which are most commonly used in the case of retention time based data approaches. In light of the recent advances in high resolution mass analysers, new data handling approaches such as the one presented have become absolutely vital to be able to handle and interpret the amounts of data collected. Especially in the analysis of crude oils by such methods, so called petroleomics,[46] the significance of identifying the relevance of various homologous series in samples cannot be highlighted enough. A further step would thus be to combine the benefits of high resolution analysis methods with the data interpretation method presented here.

### 4.3 Modelling major reaction pathways

During the exploration of the LtL concept in this work, a preferred aim for the production of phenols was found. A more in-depth investigation into the degradation processes and formation of products was deemed to be an essential step to gain valuable insights into the main reaction pathways and their individual sensitivities. A formal kinetic model combining both chemical compound lumps as well as global bulks based on an experimental series of reactions with varying residence times was developed and is documented in paper **F**. Derived rate constants for different reactions in the model were found to be in very good accordance with literature values.

The robustness of the model was further proven, when validated for different temperatures carried out in a CSTR, as documented in paper **G**. The analysis of the model showed that the main reaction pathways and significant products of interest in the LtL approach can be modelled by such a simplified formal kinetic lump model. The basis approach will certainly, with certain modifications, also be transferable to other solvolysis approaches. The comparison between batch and continuous operation showed that the

depolymerisation of lignin considerably faster in the continuous system. Furthermore, a higher amount of phenolics could be obtained, whilst both gasification and charring processes were suppressed.

The validated kinetic lump model describing the different reaction pathways, especially between monomeric phenolics, will largely aid in developing the reaction process design in scale-up work. A fast depolymerisation of lignin which was seen to be insensitive to temperature variations, within the range tested, was found. Coupled with the found rate determining reaction steps describing the successive deoxygenation, which show an increased rate with higher reaction temperatures, suggest a possible two-stage reaction process, by which temperature and thus necessary energy input can be decreased. Competing reaction pathways during depolymerisation of lignin were found. The selectivity towards the direct degradation to the monomeric units of guaiacols and 4-ethylphenol needs to be increased to avoid the alternate pathway to possibly oligomeric ethanol soluble components ( $L_D$ ), which strongly contributed to both charring and gasification reactions. In light of the relatively low yield of monomeric phenols by comparison to reactions with other lignins,[78], it may be assumed that different lignins are more easily degradable than others, or that certain parts of the lignin matrix are more easily penetrable by the active formic acid degradation products. Both catalyst work on the deoxygenation reactions as well as more detailed lignin characterisations are currently under further investigation.[79]

## 4.4 Concluding remarks

In this work, a new formic acid / alcohol solvolysis approach to degrade lignin to a phenol enriched bio-oil was explored. Within this exploration, a new method for the chemometric supported compound class specific analysis of fingerprint MS data was developed. The degradation mechanisms were further investigated in detail by the development of a

kinetic lump model combining both monomeric phenolics and global bulks.

The results show that the depolymerisation and deoxygenation to produce phenols is largely enhanced by formic acid as a hydrogen donor. The solvent medium originally suggested in prior work, however, inherits some drawbacks and substitution to an inert solvent such as water is preferential. The evaluation of biomass reaction systems poses a considerable degree of challenges, due to the complexity of both reactions and subsequent products. New fast evaluation methods in combination with chemometrics can support the understanding of variations in these complex products. The multitude of reactions taking place further require a good understanding of major reaction pathways to be able to steer the overall conversion to a higher yield of desirable products.

Overall, it can be concluded that lignin is a promising resource material, which can be used to further enhance the current lignocellulosic biorefinery models. A mixed palette of proven chemicals as well as new readily available chemicals will be developed from which subsequently new products will be produced. These will aid in the establishment of a competitive market for alternative fuels, chemicals and materials.



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## Part II



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## LIST OF PUBLICATIONS

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- Paper A** Optimizing solvolysis conditions for integrated depolymerisation and hydrodeoxygenation of lignin to produce liquid biofuel. M. Kleinert, J.R. Gasson, and T. Barth, *Journal of Analytical and Applied Pyrolysis* **2009**, Vol. 85, 108-117.
- Paper B** Developing solvolytic conversion of Lignin-to-Liquid (LtL) fuel components: Optimization of quality and process factors. M. Kleinert, J.R. Gasson, I. Eide, A.-M. Hilmen and T. Barth, *Cellulose Chemistry and Technology* **2011**, Vol. 45, No. 1-2, 3-12.
- Paper C** Lignin solvolysis: Upscaling of the Lignin-to-Liquid conversion process towards technical applicability. J.R. Gasson, M. Kleinert, T. Barth, D. Forchheim, E. Sahin, A. Kruse and I. Eide, In *Proceedings of the 19<sup>th</sup> European Biomass Conference and Exhibition*, 3-7 May **2010**, Lyon, France, 10-13.
- Paper D** Comparison of the gas hydrate plugging potentials of a set of crude oils from the Norwegian continental shelf using chemometric decomposition of GC-FID data. J.R. Gasson, T. Barth, G. Genov, *Journal of Petroleum Science and Engineering* **2012**, submitted.
- Paper E** Extracting homologous series from mass spectrometry data by projection on predefined vectors. J.E. Carlson, J.R. Gasson, T. Barth, I. Eide, *Chemometrics and Intelligent Laboratory Systems* **2012**, Vol. 114, 36-43.
- Paper F** Modeling the lignin degradation kinetics in a ethanol / formic acid solvolysis approach - Part I: Kinetic model development. J.R. Gasson, D. Forchheim, T. Sutter, U. Horning, A. Kruse, T. Barth, *Industrial & Engineering Chemistry Research* **2012**, 51 (32), 10595-10606.
- Paper G** Modeling the lignin degradation kinetics in a ethanol / formic acid solvolysis approach - Part II: Validation and transfer to variable conditions. D. Forchheim, J.R. Gasson, U. Horning, A. Kruse, T. Barth, *Industrial & Engineering Chemistry Research* **2012**, submitted.

