

## Final report VISTA September 2012

### **Project title: Analytical aspects of optimisation of the one-step production of high-quality bio-oil – a petroleomics approach**

Project director:	Barth, Tanja, University of Bergen
Post-doc/ scholar:	Gasson, James R.
Project duration:	15.08.09 – 25.09.12
Technical contact person in Statoil:	Eide, Ingvar
Division head:	Grislingås, Arne
Project number:	6455

#### **Objectives:**

The main objective of the project was to develop analytical protocols for bio-oil analysis, using amongst other techniques also advanced mass spectrometry in a petroleomics like approach. The analytical protocols that were developed have been used to support the optimisation of solvolytic conversion of lignin and other refractory biopolymers, especially for simultaneous depolymerisation and hydrodeoxygenation using formic acid as a hydrogenation agent, i.e. the Lignin-to-Liquid (LtL) approach. The project cooperated with complimentary projects that emphasise the organic synthesis and process optimisation aspects.

#### **Results:**

Results of good impact and significance were produced within the different areas of the project, and methods and approaches for further follow-up research have been developed. The results have been documented in a number of journal papers, presentations as well as in the scholar's Ph.D. thesis entitled "Solvolytic lignin degradation in an alcohol / formic acid medium - Analysis of the reaction system and products by means of kinetic modelling and chemometrics", which was submitted in June 2012.

A high number of experiments have been performed to explore and optimise the LtL reaction system, providing the basis for evaluation of product composition as a function of experimental conditions and lignin input. Since phenols are a major product under all conditions, the focus was placed on following the variation in the abundance of the different phenolic species in the bio-oil. The stepwise depolymerisation and deoxygenation of the polyaromatic structures to produce high-value phenols was explored using kinetic lump model approaches, aiming to understand the bottleneck reactions in the one-step production. The resulting formal kinetic values, which were further subjected to extensive sensitivity and flux analysis, were used in the transfer of the reaction system from a batch reactor setup to a continuous stirred tank reactor. The results suggested that lower initial temperatures could aid in making the LtL process more economically viable. Investigation of catalysts that could facilitate the final deoxygenation steps is also indicated to give less severe reaction conditions and decrease secondary reactions.

To decipher between the different compound classes in the oils, gas chromatographic analysis that require analysis times of 1-2 hours was substituted by the use of a novel mass spectrometry fingerprint method already developed by I.Eide at Statoil, which was further enhanced by a new statistical data evaluation approach. This approach showed to allow a clear distinction of effects of the different compound classes in a set of samples and further quantitative applications are to be explored as a follow-up to this project.

The co-operations between Ingvar Eide (Statoil Research Centre Rotvoll), Johan E. Carlson (Luleå University of Technology) as well as several researchers at Karlsruhe Institute of Technology has been critical for the success of the interdisciplinary approach used in this work, and we intend to continue these collaborations.

A list of publications which were produced during the project period by the scholar, or were included in the final Ph.D. thesis work, is given below. In addition, all conference contributions which included work of the scholar during the VISTA project are also listed.

## List of publications and conference contributions

### Ph.D. thesis (1)

"Solvolytic lignin degradation in an alcohol / formic acid medium - Analysis of the reaction system and products by means of kinetic modelling and chemometrics",

**J.R. Gasson**, University of Bergen June 2012, submitted.

---

### Journal papers and manuscripts (6)

"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. Hornung, A. Kruse, T. Barth, *Industrial & Engineering Chemistry Research* 2012, submitted.

---

"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. Hornung, A. Kruse, T. Barth, *Industrial & Engineering Chemistry Research* 2012, 51 (32), 10595-10606. ([DOI: 10.1021/ie301487v](https://doi.org/10.1021/ie301487v))

---

"Comparison of the gas hydrate plugging potential 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 & Engineering* 2012, submitted.

---

"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, 114, 36-43. ([DOI: 10.1016/j.chemolab.2012.02.007](https://doi.org/10.1016/j.chemolab.2012.02.007))

---

"Developing solvolytic conversion of lignin to liquid (L<sub>L</sub>) fuel components: Optimisation of quality and process factors",

M. Kleinert, **J.R. Gasson**, I. Eide, A.-M. Hilmen, T. Barth, *Cellulose Chemistry and Technology* 2011, 45, 3-12. ([pdf](#))

---

"Optimizing solvolysis conditions for integrated depolymerisation and hydrodeoxygenation of lignin to produce liquid biofuel",

M. Kleinert, **J.R. Gasson**, T. Barth, *Journal of Analytical and Applied Pyrolysis* 2009, 85, 108-117. ([DOI: 10.1016/j.jaap.2008.09.019](https://doi.org/10.1016/j.jaap.2008.09.019))

---

### Papers in conference proceedings (1)

"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, I. Eide, In *Proceedings of the 18<sup>th</sup> European Biomass Conference*, Lyon 2010, 10-13, ISBN 978-88-89407-56-5. ([DOI: 10.5071/18thEUBCE2010-PB1.3](https://doi.org/10.5071/18thEUBCE2010-PB1.3))

---

### Conference presentations (5 oral and 7 visual)

"Thermochemical valorisation in a wood based biorefinery",

T. Barth, M. Kleinert, B. Holmelid, **J.R. Gasson**, *Renewable Energy Research Conference*, Trondheim, April 16 - 18, 2012. (Oral Presentation)

---

*"A Kinetic Study on Intermediate Species and their Role in the Degradation and Hydrodeoxygenation of Lignin in the Lignin-to-Liquid Process"*,

D. Forchheim, **J.R. Gasson**, T. Sutter, T. Barth, A. Kruse, U. Hornung, *Renewable Energy Research Conference*, Trondheim, April 16 - 18, **2012**. (Oral Presentation)

---

*"Extracting Homologous Series from Fingerprint Mass Spectra Data of Bio-Oils: A Complement to PCA"*,

**J.R. Gasson**, J.E. Carlson, T. Barth, I. Eide, *Renewable Energy Research Conference*, Trondheim, April 16 - 18, **2012**. (Poster Presentation)

---

*"Extracting Homologous Series from Fingerprint Mass Spectrometry Data of Bio-Oils: A Complement to PCA"*,

**J.R. Gasson**, J.E. Carlson, I. Eide, T. Barth, *Joint Conference of German Mass Spectrometry Society and Polish Mass Spectrometry Society*, Poznan, March 4 - 7, **2012**. (Poster Presentation)

---

*"Production of phenols and fuel components from residual lignin: A state of the art report on the LiL concept"*,

**J.R. Gasson**, T. Barth, B. Holmelid, L. Liguori, I. Eide, *242<sup>nd</sup> American Chemical Society National Meeting, Division of Petroleum Chemistry*, Denver, CO, August 28 - September 1, **2011**. (Oral Presentation)

---

*"Comparison of two Lignin Liquefaction Approaches for the Production of Phenols in Aqueous Media"*,

B. Holmelid, D. Forchheim, A. Kruse, T. Barth, **J.R. Gasson**, *19<sup>th</sup> European Biomass Conference*, Berlin, June 6 - 10, **2010**. (Poster Presentation)

---

*"Mass Spectrometry Approaches to Analysis of Lignocellulosic Biomass Conversion supported by modern Data Analysis"*,

**J.R. Gasson**, T. Barth, M. Kleinert, I. Eide, *3<sup>rd</sup> Nordic Wood Biofinery Conference*, Stockholm, March 22 - 24, **2011**. (Poster Presentation)

---

*"Identification of homologous series of organic compounds in bio-oils from lignocellulose"*,

I. Eide, G. Neverdal, **J.R. Gasson**, T. Barth, K. Zahlens, *3<sup>rd</sup> Nordic Wood Biofinery Conference*, Stockholm, March 22 - 24, **2011**. (Oral Presentation)

---

*"Deciphering Complex Bio-Oil Mass Spectra with the Help of Chemometrics"*,

**J.R. Gasson**, J.E. Carlson, I. Eide, T. Barth, *44<sup>th</sup> Annual Convention of the German Society for Mass Spectrometry*, Dortmund, February 27 - March 2, **2011**. (Poster Presentation)

---

*"Characterisation of Bio-oils using Advanced Analytical Techniques and Data Analysis"*,

**J.R. Gasson**, M. Kleinert, T. Barth, I. Eide, *Renewable Energy Research Conference*, Trondheim, June 7 - 8, **2010**. (Poster Presentation)

---

*"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, I. Eide, *18<sup>th</sup> European Biomass Conference*, Lyon, May 3 - 7, **2010**. (Plenary Presentation)

---

*"Developing solvolytic conversion of lignin to liquid (LiL) fuel components: Optimisation of quality and process factors"*,

