



ภาควิชาเทคโนโลยีการบรรจุและวัสดุ
คณะอุตสาหกรรมเกษตร มหาวิทยาลัยเกษตรศาสตร์
ขอเชิญร่วมฟังบรรยาย

เรื่อง RECOVERING LIQUID LIGNINS FROM KRAFT BLACK
LIQUORS: SOLVATION AND CHARACTERIZATION

โดย Prof. Mark C. Thies

Dow Chemical Professor

Department of Chemical and Biomolecular Engineering

Clemson University

ในวันจันทร์ที่ 6 มกราคม 2557 เวลา 11.00-12.00 น.

ณ ห้อง AI 5312 อาคารอุตสาหกรรมเกษตร 5 ชั้น 3

RECOVERING LIQUID LIGNINS FROM KRAFT BLACK LIQUORS: SOLVATION AND CHARACTERIZATION



Mark C. Thies, Ph.D., P.E.
Dow Chemical Professor
Department of Chemical and Biomolecular Engineering
Clemson University, SC, USA
Email: mcths@clemson.edu

ABSTRACT

In this work, a set of softwood lignins were recovered from a Kraft black liquor using a novel pH-based fractionation process involving sequential CO₂ acidification and separation of the solvated aqueous lignin fraction. These recovered lignin fractions were characterized with respect to properties that may be responsible for their phase-partitioning behavior as well as properties that may render the lignins more suitable for materials applications. Lignin fractions were recovered between a pH range of 12.8 and 9.5, with the bulk of the lignin (90%) recovered between a pH of 11.1 and 10.0. While all the fractions were found to consist primarily of lignin as validated by sample methoxyl content, the first fractions to phase separate were found to be especially enriched in aliphatic extractives and polysaccharides. From the bulk of the lignin that was recovered between a pH of 11.1 and 10.0 a number of noteworthy trends were discernible from the data. Specifically, the phenolic hydroxyl content was found to exhibit a strong negative correlation to the fractionation pH and exhibited a nearly 50% increase with recovery at decreasing pH, while the GPC-estimated molecular weight showed strong positive correlations to the pH at recovery. The aliphatic hydroxyl content exhibited minimal differences between recovery conditions. Overall, these results suggest that this fractionation approach can generate lignin fractions enriched in select physical or structural properties that may be important for their application as feedstocks for renewable chemicals or materials.

Mark C. Thies, Ph.D., P.E.

Dow Chemical Professor, P.E.
Department of Chemical and Biomolecular Engineering
Clemson University, SC, USA
Email: mcths@clemson.edu
Phone: 1-864-656-5424



CURRICULUM VITAE

Education

Ph.D., University of Delaware, 1985
B.S., Georgia Tech, 1977

Research Interests: Separations, Thermodynamics, and Supercritical Fluids

The focus of Dr. Thies's work is on separation processes where thermodynamics and phase equilibria play a major role, with an emphasis on dense gases and supercritical fluids as the separating agents. Energy- and materials-related applications are of particular interest. Projects of current interest include thermochemical cycles for the large-scale, "carbon free" production of hydrogen by water-splitting; dense-gas extraction for the molecular design of carbonaceous pitches for advanced carbon materials; the development of an equation of state for predicting liquid crystal formation in carbonaceous oligomers; and rapid expansion of supercritical fluids for the synthesis of polymeric and organic nanoparticles.

Selected Publications

Velez, J.; Thies, M.C. pH-based Fractionation and Physical Characterization of CO₂-Precipitated Lignin. Submitted for publication in *Bioresour. Technol.*, 2013.

Tekinalp, H. L.; Cervo, E. G.; Fathollahi, B.; Thies, M. C. The Effect of Molecular Composition and Structure on the Development of Porosity in Pitch-Based Activated Carbon Fibers, *Carbon*, in press.

Klett, A. S.; Mena, S. E.; Bruce, D. A.; Thies, M. C. Liquid-Liquid Equilibrium Tie-Line Compositions at Elevated Temperatures and Pressures for the I₂-H₂O and HI-I₂-H₂O Systems of the Sulfur-Iodine Cycle, *Int. J. Hydrogen Energy* 2012, 37, 15020-15028.

Tapriyal, D.; Fan, X.; Heintz, Y.; Morsi, B.; Beckman, E.; Enick, R.; Sane, A.; Thies, M.; Schutte, G.; Niederst, J. Micronization of Polyethylene Terephthalate via Freezing of Highly Sheared Emulsions of Polyethylene Terephthalate in Saturated Liquid Tetrahydrofuran. *J. Appl. Polym. Sci.* 2012, 125, 4034-4040.

Kulkarni, S. U.; Thies, M. C. Quantitative analysis of polydisperse systems via solvent-free matrix-assisted laser desorption/ionization time-of-flight mass spectrometry. *Rapid Commun. Mass Spectrom.* 2012, 26, 392-398.

Cervo, E. G.; Kulkarni, S. U.; Thies, M. C. Isolating Polycyclic Aromatic Hydrocarbon (PAH) Oligomers via Continuous, Two-Column Supercritical Extraction. *J. Supercrit. Fluids* 2012, 66, 120-128.

Kulkarni, S. U.; Esguerra, D. F.; Thies, M. C. Isolating Petroleum Pitch Oligomers via Semicontinuous Supercritical Extraction. *Energy Fuels* 2012, 26, 2721-2726.

Kulkarni, S. U.; Räder, H. J.; Thies, M. C. The effects of molecular weight distribution and sample preparation on MALDI mass spectrometry analysis of petroleum macromolecules. *Rapid Commun. Mass Spectrom.* 2011, 25, 2799-2808.

Burgess, W. A.; Thies, M. C. Molecular Structures for the Oligomeric Constituents of Petroleum Pitch. *Carbon* 2011, 49, 636-651.

Burgess, W. A.; Pittman, J. J.; Markus, R. K.; Thies, M. C. Structural Identification of the Monomeric Constituents of Petroleum Pitch. *Energy Fuels* 2010, 24, 4301-4311.

Mena, S. E.; Cervo, E. G.; Crosthwaite, J. M.; Thies, M. C. Phase equilibrium measurements for the I₂-H₂O and I₂-HI-H₂O systems of the sulfur-iodine cycle using a continuous-flow apparatus. *Int. J. Hydrogen Energy* 2010, 35, 3347-3357.

Cervo, E. G.; Thies, M. C. Control of molecular weight distribution of petroleum pitches via multistage supercritical extraction. *J. Supercrit. Fluids* 2010, 51, 345-352.

Wang, Y.; Hong, L.; Tapriyal, D.; Kim, I.-C.; Paik, I.H.; Crosthwaite, J. M.; Hamilton, A. D.; Thies, M. C.; Beckman, E. J.; Enick, R. M.; Johnson, J. K. Design and Evaluation of Nonfluorous CO₂-Soluble Oligomers and Polymers. *J. Phys. Chem. B* 2009, 113, 14971-14980.

Cristadoro, A.; Kulkarni, S. U.; Burgess, W. A.; Cervo, E. G.; Räder, H. J.; Müllen, K.; Bruce, D. A.; Thies, M. C. Structural characterization of the oligomeric constituents of petroleum pitches. *Carbon* 2009, 47, 2358-2370.

Tapriyal, D.; Wang, Y.; Enick, R. M.; Johnson, J. K.; Crosthwaite, J.; Thies, M. C.; Paik, I. H.; Hamilton, A. D. Poly(vinyl acetate), poly((1-O-(vinylloxy) ethyl-2,3,4,6-tetra-O-acetyl-beta-D-glucopyranoside) and amorphous poly (lactic acid) are the most CO₂-soluble oxygenated hydrocarbon-based polymers. *J. Supercrit. Fluids* 2008, 46, 252-257.

Wu, X.; Gallego, N. C.; Contescu, C. I.; Tekinalp, H.; Bhat, V. V.; Baker, F. S.; Thies, M. C.; Edie, D. D. The effect of processing conditions on microstructure of Pd-containing activated carbon fibers. *Carbon* 2008, 46, 54-61.

Burgess, W. A.; Zhuang, M. S.; Hu, Y., Hurt, R. H.; Thies, M. C. SAFT-LC: An Equation of State for Predicting Liquid Crystalline Phase Behavior in Carbonaceous Pitches. *Ind. Eng. Chem. Res.* 2007, 46, 7018-7026.

Sane, A.; Thies, M. C. Effect of Material Properties and Processing Conditions on RESS of Poly(L-lactide). *J. Supercrit. Fluids* 2007, 44, 134-143.

Brunner, E.; Thies, M. C.; Schneider, G. M. Fluid mixtures at high pressures: phase behavior and critical phenomena for binary mixtures of water with aromatic hydrocarbons. *J. Supercrit. Fluids* 2006, 39, 160-173.