TCS
2016

Symposium on Thermal and Catalytic Sciences for Biofuels and Biobased Products

November 1-4, 2016

The Friday Center, University of North
Carolina, Chapel Hill, NC

RTI
INTERNATIONAL

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Welcome

It is my pleasure to welcome you to Chapel Hill, NC, for TCS 2016—A Symposium on Thermal and Catalytic Sciences for Biofuels and Biobased Products. A lot has happened in the 2 years since TCS 2014. New oil and gas reserves are being tapped with innovative new technology that has transformed the United States into a net natural gas exporter and led the nation toward energy independence. More recently, falling oil prices have challenged the economic competitiveness of advanced biofuels. Nevertheless, there is an increasing realization that reducing the carbon intensity of transportation is needed to slow the effects of global climate change. This year's symposium provides a forum to reinforce the impact that biofuels, bioproducts, and biopower will have in the developing bioeconomy to provide sustainable, low-carbon options for future global energy needs.

This symposium is the fourth in this series since 2010 with the goal of focusing on recent accomplishments in thermochemical biomass conversion research and development. It is also designed to provide early career scientists and engineers a forum to present their research and interact with the senior researchers in the community. The 2016 symposium will spotlight recent technical advances while providing a showcase for networking, collaboration, and mentoring.

A diverse, international group of experts from industry, academia, U.S. national laboratories, and global research institutes has been assembled to present their latest results in thermochemical biomass conversion and upgrading. We are honored to have three distinguished keynote speakers—Dr. Jonathan Male, USDOE-BETO; Dr. Akwesi Boateng, USDA-ARS-ERC; and Professor George Huber, University of Wisconsin–Madison. We have an additional 56 oral presentations and nearly 80 poster presentations. We hope you find the technical program scientifically stimulating and informative.

I want to express my deep appreciation to RTI International for underwriting this conference and to our many sponsors and supporters who have helped make this game-changing event possible, especially Iowa State University's Bioeconomy Institute, NC A&T State University's Center for Energy Research and Technology and the NSF CREST Bioenergy Center, Frontier Laboratories USA, and the RTI Fellows Program.

Most Sincerely,

David C. Dayton

David C. Dayton, Chairman
RTI International

RTI International

For more than 55 years, RTI has provided our government and private-sector clients with independent, objective, and scientifically rigorous research, development, and technical services. We deliver high-quality results and work products that you, our clients, can trust. We routinely publish our research findings in peer-reviewed journals, enhancing the reach and credibility of our work on behalf of clients.

At RTI, we combine the intellectual talents of leading scientists and researchers in more than 250 disciplines to form world-class project teams. Building teams using our own expert staff members lowers project management costs and facilitates collaboration. The results are creative, cost-effective solutions to meet your specific project needs.

We have significant experience managing complex national, international, and multipartner/multisite research studies and projects. For example, RTI is the prime contractor for some of the nation's largest studies and longitudinal research programs, including the National Survey on Drug Use and Health. In addition, we lead a USAID-funded program to support ministries of health in several countries to treat adults and children for seven neglected tropical diseases. Since the program's inception, RTI has supported the delivery of more than 1 billion treatments through national programs.

Headquartered in Research Triangle Park, North Carolina, we maintain offices in the United States and around the world to support our ongoing projects and changing client needs. We have conducted projects in more than 140 countries and have more than 50 years of international experience.

RTI is an independent, nonprofit research institute dedicated to improving the human condition. We believe in the promise of science, and we are inspired every day to deliver on that promise for the good of people, communities, and businesses around the world. As one of the world's leading independent research organizations, we pride ourselves in solving critical social and scientific problems. Access to and availability of sustainable energy is one of those grand challenges that we are addressing in our Energy Technology Division (ETD).

ETD's innovative energy research is committed to solving the national and global concerns to find efficient, economic, and sustainable energy solutions. A key to ETD's continued success in advancing step-out technologies is employing an integrated technology development approach. Such development requires integration of process and materials innovation along with a detailed understanding of economic feasibility and key cost drivers. Because process economics are proactively incorporated in the development process, the development process remains focused on achieving the maximum economic success and potential for successful commercial deployment.

Our scientists and engineers have worked in the industries of power, chemical, petroleum, gas processing, and transportation to produce novel technologies from ideation to pilot scale to commercialized systems. RTI's state-of-the-art facilities and laboratories are equipped to provide high-quality results for process technology licensors, gas processing companies, oil refiners, chemical manufacturers, clean fuels developers, catalyst manufacturers, and other commercial clients, as well as government agencies.

Technical Agenda

Tuesday, November 1—Day 1

8:00–10:00	**Continental Breakfast** (Friday Center)	**Registration/Poster Setup** (Friday Center)
10:00–10:15	**Welcome** (Auditorium)	
	David Dayton, *RTI International*	
10:15–10:45	**Opening Remarks** (Auditorium)	
	Wayne Holden and Terri Lomax, *RTI International*	
10:45–12:00	**Plenary Session** (Auditorium) Session Chair: David Dayton, *RTI International*	
10:45–11:30	**Keynote Presentation: Overview of the U.S. Department of Energy's Bioenergy Technologies Office** Jonathan Male, *DOE Bioenergy Technologies Office*	
11:30–12:00	**Techno-economic and Sustainability Analysis for Co-processing Fast Pyrolysis Oil with Vacuum Gas Oil in an FCC for Second Generation Fuel Production** Mike Talmadge, *NREL*	
12:00–1:00	**Lunch**	
1:00–3:00	**Session 1.1: Techno-economic Analysis (TEA)** Session Chair: Mark Wright, *Iowa State University*	**Session 1.2: Pyrolysis I** Session Chair: Darren Daugaard, *Cool Planet*
1:00–1:30	**Screw Pyrolysis of Sewage Sludge: A Techno-economic Analysis** Marco Tomasi Morgano, *Karlsruhe Institute of Technology*	**Catalytic Biomass Pyrolysis Studies at Pilot-Scale** Ofei D. Mante, *RTI International*
1:30–2:00	**Techno-economic Analysis of Phenolic Compounds Extraction from Pyrolysis Bio-Oil as Drop-In Fuels for Diesel Engines** Sunkyu Park, *NC State University*	**Determination of Impact of Feedstock Composition on Fast Pyrolysis Oil Yield and Quality Using Multiple Linear Regression Modeling** Tyler Westover, *INL*
2:00–2:30	**Techno-economic (TEA) and Life Cycle Analysis (LCA) of the Pyrolysis-Bioenergy-Biochar Pathway for Carbon-Negative Energy** Wenqin Li, *Iowa State University*	**Ex-situ Catalytic Fast Pyrolysis in a DCR—Effect of Pyrolysis Conditions** Mark Jarvis, *NREL*
2:30–3:00	**Finished Fuel Blending Models for Assessing Integration of Biomass-Derived Products with Petroleum Refinery Products** Michael Talmadge, *NREL*	**Process Intensification of a Fluidized Bed Pyrolyzer via Autothermal Operation** Joseph P. Polin, *Iowa State University, Bioeconomy Institute*
3:00–3:30	**Break**	

Tuesday, November 1—Day 1 *(continued)*

3:30–5:30	**Session 1.3: ThermoChemistry** Session Chair: Mark Nimlos, *NREL*	**Session 1.4: Pyrolysis II** Session Chair: Sunkyu Park, *NC State University*
3:30–4:00	**Establishing Elementary Reactions of Hemicellulose Torrefaction** Charles McGill, *NC State University*	**Biomass Pyrolysis Vapor Deoxygenation over Mo_2C to Produce Paraffinic and Aromatic Molecules: The Deactivation and Reactivation of Mo_2C** Calvin Mukarakate, *NREL*
4:00–4:30	**Effect of Torrefaction Temperature on Lignin Macromolecule and Product Distribution from Fast Pyrolysis** Ravishankar Mahadevan, *Auburn University*	**Ex-situ Catalytic Fast Pyrolysis in a DCR—Catalyst Effects** Jessica Olstad, *NREL*
4:30–5:00	**Formate-Assisted Pyrolysis of Biomass** William J. DeSisto, *University of Maine*	**Reactive Catalytic Fast Pyrolysis of Biomass into Hydrocarbon-Rich Bio-crude** Kaige Wang, *RTI International*
5:00–5:30	**Chemical Activation of Fast Pyrolysis Biochar for the Production of Electrically Conductive Carbon** Seunghyun Yoo, *NC State University*	**Co-pyrolysis of Biomass and Polyethylene over HZSM-5: Effects of Plastic Addition on Coke Formation and Catalyst Deactivation** Charles A. Mullen, *USDA-ARS Eastern Regional Research Center*
5:30–6:00	**Break**	
6:00–8:00	**Opening Reception/Posters**	

Wednesday, November 2—Day 2

7:30–8:30	**Continental Breakfast** (Friday Center)	
8:30–10:15	**Plenary Session** (Auditorium) Session Chair: Abolghasem Shahbazi, *NC A&T State University*	
8:30–9:15	**Keynote Presentation: On-Farm Pyrolysis Biorefining at the USDA** Kwesi Boateng, *USDA-ARS Eastern Regional Research Center*	
9:15–9:45	**Drop-In Potential of Upgraded Fuels Produced at Pilot Scale via Hydrothermal Liquefaction of Different Biomass Feedstocks** Patrick Biller, *Aarhus University*	
9:45–10:15	**Highly Selective FT Synthesis for Production of JP-8 Jet Fuel from Biomass, Coal, or Coal/Biomass Mixtures** Andrew Lucero, *Southern Research*	
10:15–10:30	**Break**	
10:30–12:00	**Session 2.1: Future Technology Development** Session Chair: Craig Brown, *NREL*	**Session 2.2: Pyrolysis (Analytical)** Session Chair: Ofei Mante, *RTI International*
10:30–11:00	**Preparing for Scale: IH^{2}® Technology** Alan Del Paggio, *CRI Catalyst Company*	**Functionality and Molecular Weight Distribution of Red Oak Lignin before and after Pyrolysis and Hydrogenation** Daniel J. McClelland, *University of Wisconsin–Madison*
11:00–11:30	**Biomass—Future Source of Renewable Hydrogen or Carbon?** Tim Schulzke, *Fraunhofer UMSICHT*	**Characterization and Upgrading of Catalytic Flash Pyrolysis Oils from Pine Trees** Sylvain Verdier, *Haldor Topsøe*
11:30–12:00	**Low-Temperature Catalyst for Biomass Tars Decomposition and Conversion in Fuel Gas** Hans Leibold, *Karlsruhe Institute of Technology*	**Standardization of Chemical Analytical Techniques for Pyrolysis Bio-Oil** Jack R. Ferrell, *NREL*
12:00–1:00	**Lunch**	
1:00–3:30	**Session 2.3: Gasification** Session Chair: Sushil Adhikari, *Auburn University*	**Session 2.4: Reactor Modeling** Session Chair: Thomas Foust, *NREL*
1:00–1:30	**Influence of Co-gasification Agents on Fluidized Bed Steam Gasification of Biomass for Biofuel Production** Felix Fischer, *Technical University of Munich*	**Towards a Multi-scale Modeling Framework for Fluidized Bed Reactor Simulation** Addison K. Stark, *DOE/ARPA-E*
1:30–2:00	**Research on Small-Scale Biomass Gasification in Entrained Flow and Fluidized Bed Technology for Biofuel Production** Sebastian Fendt, *Technical University of Munich*	**Micro-Ratcheted Surfaces for a Heat Engine Biomass Conveyor** Saurabh Maduskar, *Universtiy of Minnesota*

Wednesday, November 2—Day 2 *(continued)*

2:00–2:30	**Ru Promoted Mono-and Bi-metallic Fe-Cu, Fe-Co and Cu-Co Nano-Catalysts, Coated in Microchannel Si-Microreactor for Biosyngas Conversion to Fuels** Tim Davis, *NC A&T State University*	**Computational Study on Biomass Fast Pyrolysis Oil Yield, Effects of the Bubbling-to-Slugging Transition in a Laboratory-Scale Fluidized Bed** Emilio Ramirez, *ORNL*
2:30–3:00	**Detailed Measurement of Sulfur Compounds in Producer Gas from Fluidized-Bed Gasifier** Reinhard Seiser, *University of California–San Diego*	**Thermal DEM Simulation of Particle Heat Transfer in a Lab-Scale Double Screw Reactor** Fenglei Qi, *Iowa State University*
3:00–3:30	**Sustainable Production of Renewable Hydrogen in Biorefinery via Integrated Bioelectrochemical Systems** Abhijeet P. Borole, *ORNL*	**Modeling the Impact of Biomass Particle Size Distribution and Shape on Heating Behavior During Fast Pyrolysis** Gavin Wiggins, *ORNL*
3:30–5:30	**Poster Session**	
6:00–9:30	**Conference Dinner**	

Thursday, November 3—Day 3

7:30–8:30	**Continental Breakfast** (Friday Center)	
8:30–10:15	**Plenary Session** (Auditorium) Session Chair: Robert Brown, *Iowa State University*	
8:30–9:15	**Keynote Presentation: Commodity Chemicals from Biomass: Catalytic Conversion of Biomass into α,ω-diols** George Huber, *University of Wisconsin–Madison*	
9:15–9:45	**Elucidation of the Type of Chemical Reactions in Primary Stage of Biomass Fast Pyrolysis** Marion Carrier, *Aston University*	
9:45–10:15	**Catalytic Fast Pyrolysis for Chemical Products** Mark Nimlos, *NREL*	
10:15–10:30	**Break**	
10:30–12:00	**Session 3.1: Pyrolysis Fundamentals** Session Chair: Charles Mullen, *USDA-ARS*	**Session 3.2: Upgrading** Session Chair: Catherine Brewer, *New Mexico State University*
10:30–11:00	**Kinetics of Cellulose Pyrolysis via Pulse-Heated Analysis of Solid Reactions (PHASR)** Saurabh Maduskar, *University of Minnesota*	**Production of Hydrocarbon Liquid Fuel from Biocrude by Hydroprocessing** Ofei D. Mante, *RTI International*
11:00–11:30	**Thin-Film Fast Pyrolysis of Isotopically-Labeled Glucose for the Analysis of Primary Reaction Pathway** Young-Jin Lee, *Iowa State University*	**Continuous Hydrotreatment of Hydrofaction™ Oil to Drop-In Diesel** Claus Uhrenholt Jensen, *Steeper Energy ApS*
11:30–12:00	**Pyrolysis of Two- and Three-Carbon Monosaccharides to Understand Hemicellulose and Cellulose Pyrolysis** Phillip R. Westmoreland, *NC State University*	**Novel Bio-Oil Hydrodeoxygenation Catalysts based on Strong Electrostatic Adsorption** Yaseen Elkasabi, *USDA-ARS Eastern Regional Research Center*
12:00–12:45	**Lunch**	
12:45–1:00	**Presentation of Poster Awards** (Auditorium)	
	Winner: Jake Lindstrom, *Iowa State University*, P18s: **Thermal Deconstruction of Cellulose with Subsequent Hydrolysis to Fermentable Sugars**	
	Runner-Up: Rui Li, *NC A&T State University*, O5s: **Syngas Production by Dry Reforming of Biogas over Biochar Supported Molybdenum Carbides**	
	Runner-Up: Sabyasachi Das, *Michigan State University*, U6s: **Renewable Transportation Fuels via Fast Pyrolysis and Electrocatalytic Hydrogenation**	
1:00–1:30	**Presentation: Catalyst Activity Management in the Anellotech Bio-TCat™ Process** (Auditorium)	
	Chuck Sorensen, *Anellotech*	

Thursday, November 3—Day 3 *(continued)*

1:30–4:30	**Session 3.3: Hydrothermal** Session Chair: Nichole Fitzgerald, *DOE-BETO*	**Session 3.4: Upgrading and Products** Session Chair: Amit Goyal, *Southern Research*
1:30–2:00	**Development of ZrO$_2$-based Hydrothermally Stable Catalysts for the Catalytic Upgrading of Biomass-Derived Aqueous Streams** Juan A. Lopez-Ruiz, *PNNL*	**Methylation of Carboxylic Acids and Phenols from Fast Pyrolysis Bio-Oil** Suh-Jane Lee, *PNNL*
2:00–2:30	**Fecal Sludge to Energy in a Prototype Supercritical Water Oxidation Reactor** Marc A. Deshusse, *Duke University*	**Thermocatalytic Process for Biomass Conversion to Acrylonitrile for Production of Carbon Fibers** Jadid E. Samad, *Southern Research*
2:30–3:00	**Continuous Pilot-Scale Loblolly Pine Liquefaction to a Partially Deoxygenated Bio-Oil** Taylor Schulz, *Iowa State University*	**Upgrading of the Bio-Oil Model Compounds by a Two-Step Process Combining Hydrogenation-Esterification and Cracking** Junhao Chen, *State Key Laboratory of Clean Energy Utilization, China*
3:00–3:15	**Break**	
3:15–3:45	**Comparing Quantitative Characterization of Bio-crude and Aqueous Phase from Hydrothermal Liquefaction of Biomasses** René B. Madsen, *Aarhus University*	**Purification of Pyrolytic Sugar from Bio-Oil Fractions** Patrick Hall, *Iowa State University, Bioeconomy Institute*
3:45–4:15	**Design, Fabrication, and Testing of the Modular Hydrothermal Liquefaction System (MHTLS)** Justin M. Billing, *PNNL*	**Steam Reforming of Bio-derived Oxygenates: Coupling Ketonization for Greater Stability** Stephen D. Davidson, *PNNL*
4:15–4:45	**Production of Soluble and Hydrolyzable Carbohydrates from Biomass Using THF/Water Co-solvent in the Presence of Acid Catalyst** Arpa Ghosh, *Iowa State University*	**Analysis and Catalytic Upgrading of Pyrolysis Oils from Various Biomass Feedstocks** Mariefel V. Olarte, *PNNL*
4:45–5:00	**Conference Wrap-Up** (Auditorium)	

Friday, November 4

Optional Facility Tour: RTI Headquarters

9:00 am to 12:00 pm

Keynote Speakers

Jonathan Male, PhD

Director, DOE Bioenergy Technologies Office

Overview of the U.S. Department of Energy's Bioenergy Technologies Office

Abstract: The Bioenergy Technologies Office is one of the ten technology development offices within the Office of Energy Efficiency and Renewable Energy at the U.S. Department of Energy. The Bioenergy Technologies Office's mission is to develop and transform our renewable biomass resources into commercially viable, high-performance biofuels, bioproducts, and biopower through targeted research, development, and demonstration, supported through public and private partnerships. The Office aims to enable sustainable, nationwide production of biofuels that are compatible with today's transportation infrastructure, can reduce greenhouse gas emissions relative to petroleum-derived fuels, and can displace a share of petroleum-derived fuels to reduce U.S. dependence on foreign oil, while encouraging the creation of a new domestic bioenergy and bioproduct industry. This presentation will provide an overview how the Office carries out this mission and its strategic direction for the future, while describing the challenges and opportunities this emerging bioeconomy presents. Highlighted will be interagency collaborations, the status of recent funding opportunities, and successes from its cutting-edge project portfolio.

Bio: Dr. Jonathan Male is the Director for the Bioenergy Technologies Office (BETO) in the Office of Energy Efficiency and Renewable Energy (EERE). In this role, he leads the Office's work to lower costs, reduce technical risk, and accelerate deployment of bioenergy and renewable chemicals technologies. Before joining the U.S. Department of Energy, he was the laboratory relationship manager for biomass at PNNL. Previously, he worked at the GE Global Research Center in Niskayuna, New York, and developed programs in heterogeneous and homogeneous catalysts. In total, he has more than 17 years of research experience in catalysts, inorganic materials, high throughput experimentation, greenhouse gas emissions reduction technologies, production of chemicals, and biofuels. Dr. Male received a BS in applied chemistry from the University of Greenwich, England, and his PhD in organometallic chemistry from Simon Fraser University in Canada.

Akwasi (Kwesi) A. Boateng, PhD

USDA-ARS Eastern Regional Research Center

On-Farm Pyrolysis Biorefining at the USDA

Abstract: In 2012, USDA-NIFA funded the "Distributed On-Farm Bioenergy, Biofuels and Biochemicals (FarmBio3) Development and Production via Integrated Catalytic Thermolysis" under the DOE-USDA Biomass Research and Development Initiative (BRDI) as directed by Section 9008 of the Farm Security and Rural Investment Act of 2002. FarmBio3 is a government-university-industry partnership led by ARS with an overarching objective of leveraging existing synergies among partners to address some of the barriers confronting the optimization of pyrolysis pathways to commodity fuels and chemicals at various scales. Part of the logic model was the construction of a 2 metric ton per day fluidized bed, combustion-reduction integrated pyrolysis unit (CRIPS) to be equipped with robust catalysts having appropriate chemical selectivity designed for on-the-farm operation. The talk will provide an overview of the status of the program and the CRIPS 4 years into the project.

Bio: Dr. Boateng is the Lead Scientist of the thermochemical biomass conversion program at ARS, the principal research arm of USDA. He is located at the USDA's Eastern Regional Research Center in Wyndmoor, PA, near Philadelphia and functions within the Sustainable Biofuels and Coproducts Research Unit of this U.S. research landmark. He leads the ARS research project that is developing pyrolysis processes to enable the commercial production of marketable, partially deoxygenated pyrolysis oil intermediates toward on-farm or in-forest biorefineries. Dr. Boateng is also the project director of the NIFA-funded DOE-USDA BRDI project FarmBio3, comprising 14 university-industry partnership in a consortium to address barriers facing on-farm pyrolysis biorefining. Prior to joining ARS in 2003, Dr. Boateng held engineering faculty positions at two universities followed by a 10-year tenure in the high-temperature mineral/materials processing industry where he held various positions in process/product development rising to chief process engineer. He is the author of the book Rotary Kilns: Transport Phenomena & Transport Processes (Butterworth-Heinemann Publishers), a single-source reference and instructional guide for the design, use, and maintenance of rotary kilns. Dr. Boateng received his PhD from the University of British Columbia; he is a fellow of the American Society of Mechanical Engineers and a senior member of the American Institute of Chemical Engineers. He has authored over 100 peer-reviewed publications including five patents.

George W. Huber, PhD

University of Wisconsin-Madison

Commodity Chemicals from Biomass: Catalytic Conversion of Biomass into α,ω-diols

Abstract: The low cost of petroleum and large capacity of petroleum refineries, combined with challenges in implementing technologies at scale, have made it difficult to commercialize technologies to produce liquid transportation fuels from lignocellulosic biomass. An alternative, economically viable approach that could help transition society to a more sustainable society is to synthesize high-volume oxygenated commodity chemicals from biomass. In this presentation we describe a multi-step catalytic approach for conversion of cellulose into 1,6-hexanediol and hemicellulose into 1,5 pentanediol. These α,ω-diols are high-volume (2.6 million tons/year), high-value ($2,000–4,600/ton) commodity chemicals used in the production of polyurethanes, coatings, acrylates, adhesives, polyesters, and plasticizers. Cellulose is first converted to levoglucosan, which is then dehydrated into levoglucosenone (LGO) in the condensed phase with dilute acid using a polar, aprotic solvent. The product selectivity is a function of the water concentration, the solvent type, and the cellulose loading. Increasing the water content leads to the production of 5-hydroxymethylfurfural. The LGO is then hydrogenated into dihydrolevoglucosenone, levoglucosanol, and tetrahydropyran-2-methanol (THPM). The THPM then undergoes selective C-O-C hydrogenolysis to produce 1,6-hexanediol using a bifunctional (reducible metal with an oxophilic promoter) catalyst with > 90% selectivity to 1,6 hexanediol. The hemicellulose is converted into furfural, which then undergoes a series of reactions to produce 1,5 pentanediol. We will outline the catalytic chemistry that happens in each of these steps and estimate the economic viable of our approach to produce infrastructure-compatible biomass-based commodity chemicals.

Bio: George Huber is the Harvey Spangler Professor of Chemical Engineering at University of Wisconsin-Madison. His research focus is on developing new catalytic processes for the production of renewable liquid fuels and chemicals. He has authored over 120 peer-reviewed publications, including three publications in *Science*, and over 15 issued patents. In 2015, Thomson Reuters listed George as a “highly cited researcher” a title given to “the “world’s most influential scientific minds” who rank in the top 1% most cited. He has been named one of the top 100 people in bioenergy by *Biofuels Digest* for the past 4 years. He is co-founder of Anellotech (www.anellotech.com). He obtained his PhD in chemical engineering from University of Wisconsin-Madison (2005). He obtained his BS (1999) and MS (2000) degrees in chemical engineering from Brigham Young University.

Session Speakers

Patrick Biller

Aarhus University

Drop-In Potential of Upgraded Fuels Produced at Pilot Scale via Hydrothermal Liquefaction of Different Biomass Feedstocks

Patrick Biller[1,2], Yinlong Yu[1], René B. Madsen[1], Jacob Becker[1], Bo B. Iversen[1], Ib Johannsen[3], and Marianne Glasius[1]

[1]Department of Chemistry and iNano, Aarhus University, Aarhus, Denmark
[2]Aarhus Institute of Advanced Studies, Aarhus University, Aarhus, Denmark
[3]Department of Engineering. Aarhus University, Aarhus, Denmark

Abstract: Hydrothermal liquefaction (HTL) is an emerging technology for the production of drop-in biofuels from biomass and organic wastes. Aqueous slurries are processed in hot-compressed water to produce a high energy density bio-crude. The resulting HTL bio-crude requires upgrading via catalytic hydrotreating and distillation to produce fuels resembling gasoline, diesel, and kerosene. The technology has been shown to result in high mass, carbon, and energy yields to upgraded fuel for a variety of feedstocks such as lignocellulosics, wastes, and algae. A major bottleneck of the technology is its demonstration on large-scale continuous reactors. Furthermore, the effect of different feedstocks on final fuel yields, composition, and quality after upgrading is currently unclear.

In the current work, a state-of-the-art pilot-scale continuous HTL facility with a throughput of up to 100 L/h was used to produce bio-crude. The reactor system employed innovative pumping, mixing, and pressure release systems to pump high solids (20wt.%) containing slurries to 250 bar and 350 °C. The reactor is designed for scalability and energy efficiency, achieving ~80% heat recovery. Continuous operation of three different HTL plants was successful for a variety of feedstocks and high yields of bio-crude were achieved. Bio-crude was catalytically hydrotreated in batch reactors to reduce heteroatom contents (O and N), lower the viscosity and density, and increase the higher heating value. Different biomasses ranging from lignocellulosics to high-protein feedstocks were employed to assess the effect of feedstock on drop-in fuel potential. Upgrading of bio-crude improved the fuel quality significantly toward drop-in fuel specifications. The analysis of compounds in upgraded fuels revealed a large abundance of aliphatic and aromatic fuel components ranging from C8 to C20.

The different fuel cut—gasoline, diesel, and kerosene—were quantified for each biomass and compounds quantified via GC-MS to elucidate fuel production pathways from biomass to final fuels.

This work demonstrates continuous HTL at large scale for a variety of feedstocks successfully, a major step toward the commercialization of the technology. The fuel upgrading study

revealed yields of gasoline, diesel, and kerosene for each feedstock. These data allow the assessment of the HTL technology for a wide range of biomasses and fuel products, which will allow more realistic and accurate life-cycle and techno-economic assessments of the HTL technology for different feedstocks.

Bio: Dr. Patrick Biller obtained his PhD at the Energy Research Institute, University of Leeds, UK, in 2013. During his PhD, he investigated the conversion of microalgae to bio-crude via hydrothermal liquefaction. Patrick obtained an EPSRC fellowship to continue some of the work developed during his PhD studies. In this 2-year fellowship, he worked, among other things, on the design and construction of continuous HTL facilities. In 2015, he started a postdoc position at the Department of Chemistry, Aarhus University, Denmark. During this period, he worked on optimizing the HTL technology on batch- and pilot-scale HTL reactors as well as catalytic upgrading of bio-crude. On October 1st Patrick commenced a Marie Curie, Co-fund fellowship at Aarhus University to further pursue his own research ideas within the HTL technology.

Justin Billing

Research Engineer, Chemical and Biological Process Development Group, Pacific Northwest National Laboratory

Design, Fabrication, and Testing of the Modular Hydrothermal Liquefaction System (MHTLS)

Justin M. Billing, Daniel B. Anderson, Richard T. Hallen, Todd R. Hart, Gary D. Maupin, Andrew J. Schmidt, and Douglas C. Elliott

Pacific Northwest National Laboratory, Richland, WA, USA

Abstract: Hydrothermal liquefaction (HTL) has emerged as a leading thermochemical conversion process for biomass feedstocks. The simplicity of the design and the use of sub-critical water as a reaction medium permit the use of low-cost feedstocks that are generally not compatible with other conversion processes such as fast pyrolysis due to high moisture and mineral content. At PNNL, scores of continuous HTL tests with diverse feedstocks have been performed in bench-scale reactor systems. In addition to screening feedstocks, the bench-scale tests have served to identify and address engineering challenges related to process scale-up.

A third-party engineering assessment of PNNL's HTL technology was provided by the Harris Group in 2013. Key recommendations were made concerning pump selection, heat integration, phase separations, reactor costs, and materials of construction. In addition, PNNL has participated in several consortia and industrial partnerships and has used the insight gained from these interactions to best position the technology for success at larger scales. These efforts have culminated in the design, fabrication, and delivery of the engineering-scale Modular Hydrothermal Liquefaction System (MHTLS) that is sized for slurry feed rates that are 5–10× greater than the bench-scale systems. The engineering design and process improvements incorporated into the MHTLS will be discussed and initial testing data will be presented if available.

Bio: Mr. Billing earned his BS in chemical engineering from Montana State University in 2001. He has process engineering experience in biofuels, nuclear waste remediation, semiconductor fabrication, and petrochemicals. In his current position with PNNL's Chemical and Biological Process Development Group, he is working with both thermochemical and biological conversion pathways, specializing in physical and chemical separations, applied process engineering, equipment selection, scale-up, and process troubleshooting.

Abhijeet Borole

Research Scientist, Oak Ridge National Laboratory and Professor, Chemical and Biomolecular Engineering Department, University of Tennessee, and Energy Science and Engineering, Bredesen Center for Interdisciplinary Research and Education

Sustainable Production of Renewable Hydrogen in Biorefinery via Integrated Bioelectrochemical Systems

Abhijeet P. Borole[1,2], Alex Lewis[2], Xiaofie Zeng[3], Lydia Park[3], Shoujie Ren[2], Nicole Labbe[2], Spyros Pavlostathis[3], Philip Ye[2], and Costas Tsouris[1,3]

[1]Oak Ridge National Laboratory
[2]University of Tennessee, Knoxville
[3]Georgia Institute of Technology

Production of renewable hydrogen from biorefinery wastes and wastewater generated during biofuel production can contribute to energy efficiency and resource recovery to improve biorefinery economics. This talk will discuss production of hydrogen from switchgrass-derived bio-oil aqueous phase generated in a thermochemical biorefinery process and potential for bioelectrochemcial systems (BES) such as microbial electrolysis cells (MECs) to improve the biomass-to-product conversion efficiency and sustainability of the processes. Production of bio-oil via pyrolysis, followed by oil-water separation and conversion of the bio-oil aqueous phase to hydrogen using electroactive biofilms enriched on biomass pyrolyzate, will be discussed.

The performance of the MECs achieving rates up to 20 A/m^2 will be presented demonstrating the potential for commercial consideration of this technology. Additionally, production of hydrogen from multiple waste streams including catalytic pyrolysis bio-oil aqueous phase as well as use of other biomass feedstocks will be discussed to demonstrate the feedstock-agnostic nature of this technology. Production of hydrogen is essential in all biorefinery operations; therefore, these characteristics are considered very important to develop a universal hydrogen production method in biorefineries.

Preliminary techno-economic and life cycle analysis will also be presented to compare MEC technology with existing mature hydrogen production alternatives.

In a thermochemical process, enrichment of a diverse biofilm consortia was shown to achieve removal of more than 100 compounds derived from biomass, delivering hydrogen or electricity production rates > 10 A/m^2. Integration of the bioelectrochemical processes in biorefineries requires consideration of upstream and downstream separations. A discussion of potential alternatives for developing a continuous, streamlined biorefinery-BES operation will be presented. Utilization of membrane systems for enabling recycle of bioanode effluent will be discussed. The sustainability parameters of interest will be highlighted and presented for the integrated system.

Bio: Dr. Borole is a chemical engineer with expertise in biomass conversion, waste to energy. and bioelectrochemical systems. He is currently a Research Scientist at Oak Ridge National Laboratory and holds a Joint Faculty Professor appointment at the University of Tennessee, Knoxville in the Chemical and Biomolecular Engineering Department as well as in Energy Science and Engineering program at the Bredesen Center for Interdisciplinary Research and Education. He is involved in R&D focused on fermentation, microbial fuel cells and electrolysis cells, and application of bioelectrochemical systems in the biorefinery and the oil and gas industry. He has published over 50 peer-reviewed publications and holds 4 patents. He has also contributed to three books in the area of biocatalysis and bioenergy. His interests lie at the interface of biology, electrochemistry and engineering, which are targeted toward increasing energy efficiency during electrosynthesis of fuels and chemicals from biomass and waste.

Marion Carrier

Marie Curie Research Fellow, European Biomass Research Institute, Aston University

Elucidation of the Type of Chemical Reactions in Primary Stage of Biomass Fast Pyrolysis

M. Carrier and A.V. Bridgwater

Aston University, Bioenergy Research Group, European Bioenergy Research Institute, Birmingham, United Kingdom

Abstract: The overall degradation scheme of biomass “fast” pyrolysis can be seen as a combination of parallel and competing reactions through non-ionic and ionic mechanisms, whose occurrence depends on the physical states of pyrolysis products and gaseous and condensed phases. The presence and dominance of these phases obey the thermodynamic laws of transport (mode) and transfer (limitations), mainly controlled by the design of the reactor. As a result, the pyrolysis regime must be controlled to allow the description of biomass degradation patterns in real-world reactors and under “fast” conditions. An ongoing discussion on the importance and dominance of the ionic and/or non-ionic character of pyrolysis reactions[1] provides clues that could be used to rationalize the degradation mechanisms. If radical mechanisms are assumed and are dominant in coal pyrolysis, experimental evidence[2,3] and theoretical calculations[4,5] for biomass fast pyrolysis (FP) until recently invoked the presence of radical/concerted mechanisms during the primary “fast” pyrolysis stage.

By combining the use of analytical pyrolysis (Py-GC/MS) and carbon-13 enriched materials, this study reveals important information on degradation pathways and the type of chemical reactions occurring during the primary stage of “fast” pyrolysis of extracted biopolymers (i.e., cellulose and technical lignin). The inspection of good prediction of mass spectrometric

fragmentation patterns (Fig. 1) for key pyrolysis organic compounds confirmed the absence of scrambling during the primary pyrolysis stage, thus indicating the dominance of unimolecular mechanisms such as internal molecular rearrangements and H-abstraction as only bimolecular reaction.

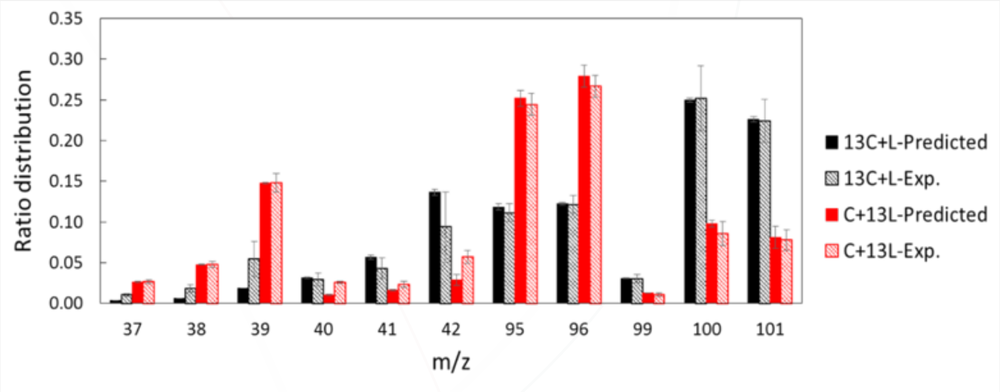

Figure 1. Confirmation of the product identity (e.g., furfural as example) and lack of scrambling by comparing experimental and predicted MS fragmentation patterns (ratio distribution vs mass/charge ratio-m/z) of "fast" pyrolysis products from mixtures of unlabelled cellulose (C), lignin (L) and carbon-13 enriched cellulose (13C) and lignin (13L).

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Bio: Dr. Carrier is a Marie Curie Research Fellow at the European Biomass Research Institute of Aston University, Birmingham (UK). She obtained degrees in chemical engineering from CPE Lyon (MEng in 2004), in analytical science (MSc 2004), and in chemistry (PhD 2007) from Claude Bernard University in Lyon (France). Trained as an interdisciplinary researcher, she has been applying her current skills and knowledge in the field of pyrolysis for the last 8 years at leading research organisations in France, South Africa, Chile, and England. Her research contributed to a wide range of research fields such as chemical mechanistic, pyrolysis chemical analysis, bioprocessing, thermochemical processing and soil sciences. She is author or co-author of 30 peer-reviewed publications and 2 chapter books. In October 2015, she joined Prof. Bridgwater's team to pursue her research on molecular engineering of fast pyrolysis using fractionation and isotopic characterization techniques along with molecular dynamics calculations.

Junhao Chen

PhD Candidate, State Key Laboratory of Clean Energy Utilization, Institute for Thermal Power Engineering, Zhejiang University

Upgrading of the Bio-Oil Model Compounds by a Two-Step Process Combining Hydrogenation-Esterification and Cracking

Junhao Chen, Shurong Wang, Liang Lu, Fan Zhang, and Zhongyang Luo

State Key Laboratory of Clean Energy Utilization, Zhejiang University, Hangzhou, China

Abstract: Biomass can be converted into bio-oil by fast pyrolysis, which is substituted for conventional fossil fuel. However, the inferior properties of crude bio-oil, including high oxygen content, high water content, strong acidity, and low heating value, limit its direct utilization. Therefore, the proper upgrading techniques are needed for the high-grade utilization of bio-oil, including catalytic cracking, esterification, and hydrogenation, etc. With regard to the conventional cracking, heavy coke tends to be formed during cracking because of the inherent low effective hydrogen-to-carbon ratio ($(H/C)_{eff}$) of bio-oil, resulting in severe catalyst deactivation. In particular, the bio-oil would exhibit strong corrosivity in the high-temperature reaction. In this study, a two-step process was proposed involving hydrogenation-esterification over a supported Cu catalyst as a stabilization step under mild conditions, followed by cracking over HZSM-5. In the first stage, oxygenated model compounds were converted into alcohols via hydrogenation-esterification or direct hydrogenation, which significantly increased the corresponding $(H/C)_{eff}$ ratio and reduced the corrosivity of reactants. Afterward, the upgraded products were converted into light olefins and aromatic hydrocarbons over HZSM-5. By improving the conventional single cracking, the two-step process remarkably inhibited coke formation and thus promoted the stability of the catalyst. Meanwhile, the influences of hydrogenation temperature, hydrogen pressure, and feedstock weight hourly space velocity (WHSV), as well as the catalyst regeneration, were investigated to achieve an excellent performance under an optimized reaction condition.

Bio: Mr. Chen received his bachelor's degree from Zhejiang University in June 2014, majoring in energy and environment system engineering in the Department of Energy Engineering. He entered the State Key Laboratory of Clean Energy Utilization as a PhD candidate in Prof. Shurong Wang's group in September 2014. He received a second scholarship for freshmen in 2014. His work focuses on the catalytic hydrogenation and cracking of bio-oil produced by biomass fast pyrolysis, and his paper titled "The Effect of Mild Hydrogenation on the Catalytic Cracking of Bio-oil for Aromatic Hydrocarbon Production" has been accepted in the *International Journal of Hydrogen Energy* in 2016.

Stephen D. Davidson

Postdoctoral Researcher, Pacific Northwest National Laboratory

Steam Reforming of Bio-derived Oxygenates: Coupling Ketonization for Greater Stability

Stephen Davidson, Kurt Spies, Igor Kutnyakov, Vanessa Dagle, Karl Albrecht, and Robert Dagle

Pacific Northwest National Laboratory, Richland, WA, USA

Abstract: Over the last few decades, steam reforming of bio-derived compounds has gained a great deal of attention as a possible alternative to the industry standard of natural gas steam reforming. While there are a variety of potential feedstocks, the aqueous phase derived from bio-oils obtained from processes such as fast pyrolysis and hydrothermal liquefaction are among the most viable. These aqueous phases consist of a wide variety of compounds ranging from alcohols and carboxylic acids to sugars and ring compounds. Of the components, the carboxylic acids pose an interesting perplexity in that they are relatively easy to convert but also generate large amounts of coke deposition. An alternative approach for utilization of bio-derived carboxylic acid compounds is direct ketonization and using those ketones as platform molecules to achieve higher value products. In this work, we investigate the steam reforming of acetic acid and its ketonization product acetone over catalysts of 15wt% Co supported on $MgAl_2O_4$, CeO_2, and ZnO. Similar to prior work, we found large amounts of coke deposition following the steam reforming of acetic acid and relatively low amounts of coke deposition following acetone steam reforming. We demonstrate that a two-bed system, coupling the direct ketonization of the acetic acid in the first bed with the steam reforming occurring in the second bed, can significantly reduce total coke formation and improve catalyst stability. Finally, we demonstrate utility of this approach using aqueous phase feedstock derived from hydrothermal liquefaction.

Bio: Stephen is presently studying the catalytic conversion of bio-oil aqueous fractions to hydrogen and other value-added products. In 2015, he completed his doctorate degree in chemical engineering at Washington State University under Professor Yong Wang where his work focused on the steam reforming of ethanol over cobalt-based catalysts. Stephen completed his BS at University of Colorado in 2007. Between his undergraduate and graduate studies, Stephen worked at Sundew Technologies LLC. in Broomfield, CO, where he worked on development and application of atomic layer deposition films.

Tim Davis

Chemistry Candidate and Research Associate CREST Bioenergy Center, NC A&T State University, Greensboro, NC

Ru Promoted Mono-and Bi-metallic Fe-Cu, Fe-Co and Cu-Co Nano-catalysts, Coated in Microchannel Si-Microreactor for Biosyngas Conversion to Fuels

Tim Davis[1], Richard Abrokwah[2], Vishwanath Deshmane[1,3], Smith Woosley[4], Shyam Aravamudhan[4], and Debasish Kuila[1]

[1]Department of Chemistry, CREST Bioenergy Center, NC A&T State University, Greensboro, NC, USA
[2]Department of Energy and Environmental Systems, CREST Bioenergy Center, NC A&T State University, Greensboro, NC, USA
[3]Department of Chemical & Biological Engineering, CREST Bioenergy Center, NC A&T State University, Greensboro, NC, USA
[4]Joint School of Nanoscience & Nanotechnology, CREST Bioenergy Center, NC A&T State University, Greensboro, NC, USA

Abstract: The primary aim of our NSF-CREST Bioenergy Center is the thermochemical conversion of biomass to fuels. It is well known that the high oxygen content of most biomass feedstocks promotes the conversion of a large fraction of carbon to CO-rich bio-syngas ($CO:H_2$) during gasification. Biomass based Fischer-Tropsch (F-T) fuels is a viable option for transportation since it could be blended with conventional fuel in any concentration. Recently, the use of microreactors as a tool to screen various catalysts for F-T reaction has received enormous attention due to its efficient mass transfer, high heat dissipation for exothermic reaction, high throughput, precise control of hydrodynamics, portability, lab on chip analysis, and easy scale-up. Furthermore, microreactors are convenient in terms of fast fabrication, installation, and maintenance. In this study, cobalt, iron copper, and ruthenium nanocatalysts supported on TiO_2 and SiO_2 have been prepared by the sol-gel method. Solid state mechano-chemistry approach (using ball mill) has also been used to synthesize bimetallic catalysts. These catalysts are coated into the channels of a Si-microreactor and tested for F-T activity. The catalysts have been characterized by TGA-DSC, SEM, EDX, BET, and XRD techniques. The surface areas of the powder Co-TiO_2, Ru-TiO_2, and Fe-TiO_2 catalysts are 48.2, 118.9, and 117.1 m^2/g, respectively. Preliminary testing showed that while 12%Ru-TiO_2 produced mostly methane and a small amount of butane, I2% Co-TiO_2 yielded predominantly butane and traces of methane. 20%Cu/MCM-41 exhibited impressive stability, 86% CO conversion, and produced only methane and ethane. All testing was performed at 220 °C, 1 atm and CO: H_2 molar ratio of 1:2. Catalysts performance testing is ongoing and we shall present our findings.

Bio: Mr. Davis is a native of Winston Salem and graduated from Winston-Salem State University in 2013 with a BS in chemistry. He has since been working at T.W. Garner Company in Winston-Salem as a food processing scientist. Tim Joined NC A&T State University in 2014 to pursue his advanced education in chemistry. He works under the supervision of Professor Debasish Kuila in the area of catalyst development, optimization, and testing for conversion of various types of biomass to biofuels.

Alan Del Paggio

Vice President, CRI Catalyst Company

Preparing for Scale: IH$^{2®}$ Technology

Alan Del Paggio[1] and Vann Bush[2]

[1]CRI Catalyst Company, Houston, TX, USA
[2]Gas Technology Institute, Des Plaines, IL, USA

Abstract: Routes to affordable, low-carbon "drop-in" hydrocarbon fuels directly from forestry, agricultural, and municipal residues have drawn considerable interest for the past several years. IH$^{2®}$ technology, a continuous catalytic thermochemical process, has the potential to be among those in the first wave of commercial-scale technologies to provide such fuels. IH$^{2®}$ technology, invented by Gas Technology Institute in early 2009 and jointly developed with CRI Catalyst Company (CRI) since 2010, is now preparing for demonstration-scale operations in India. CRI would like to share its perspectives on commercialization and its model for de-risking the IH$^{2®}$ technology in preparation for commercial deployment.

Bio: Dr. Del Paggio is currently Vice President of CRI Catalyst Company, a fully owned subsidiary of Royal Dutch Shell, plc, located in Houston, Texas. Dr. Del Paggio has 30 years of experience in catalytic petrochemical and refinery processes with a current focus on delivering commercial catalysts for fossil whole crude and unconventional heavy oil processing and the Shell Gas-To-Liquids process. Dr. Del Paggio is currently leading the effort to commercialize the low carbon intensity biomass-direct-to-hydrocarbon fuel IH$^{2®}$ technology invented by Gas Technology Institute. Dr. Del Paggio received his BS in chemistry from Purdue University in 1982 and his PhD in inorganic chemistry from UC Berkeley in 1986 as an NSF Predoctoral fellow.

Marc Deshusses

Professor, Department of Civil and Environmental Engineering, Duke University

Fecal Sludge to Energy in a Prototype Supercritical Water Oxidation Reactor

Mark Deshusses

Department of Civil & Environmental Technology, Duke University, Durham, USA

Abstract: Our team has designed and built a technical-scale prototype supercritical water oxidation system to treat the fecal waste produced by roughly 1,000–1,200 persons daily. The unit is housed in a standard 20 ft shipping container and has been undergoing testing at Duke since early 2015. The process calls for moderate preheating of the waste slurry, which is then mixed with supercritical water (~600 °C) and air (which serves as oxidant), which rapidly brings the waste undergoing treatment to supercritical conditions (~400 °C, 240 bars). Under these conditions, all organics are rapidly (i.e., few seconds) oxidized to CO_2, with the corresponding heat of combustion released in the reaction medium. In our

prototype, the reactor has a 19 mm ID and is 4.2 m long. After the reaction, heat recovery follows in a 39 m long heat exchanger. The system is well instrumented and operation is controlled using a programmable logic controller. Experiments were first conducted with isopropanol (IPA), prior to treating secondary sludge, first as a slurry mixed with IPA as a co-fuel. Detailed system performance including conversion of organics, process kinetics, and energy balances will be presented and discussed at the conference. The project is funded by the Bill & Melinda Gates Foundation.

Bio: Dr. Deshusses holds degrees in chemical engineering from the Swiss Federal Institute of Technology. He was a professor and department chair at the University of California, Riverside, prior to joining Duke University. He is now a professor in the Department of Civil and Environmental Engineering and has a secondary appointment in the Duke Global Health Institute. He also serves as the Director of the Energy Engineering Program. Dr. Deshusses is a fellow of AAAS, an Associate Editor for *Biotechnology and Bioengineering*, and was Editor for the *Chemical Engineering Journal*. His research interests are related to the design, analysis, and optimization of processes for waste treatment. Applications include treatment of air toxics, biogas production, waste to energy, and novel sanitation technologies for less developed countries.

William DeSisto

Professor, Chemical and Biological Engineering, University of Maine

Formate-Assisted Pyrolysis of Biomass

William J. DeSisto[1,2], M. Clayton Wheeler[1,2], Mayank Patel[1], Anushka E. Vithanage[3], and William M. Gramlich[3]

[1]Department of Chemical and Biological Engineering, University of Maine, Orono, ME, USA
[2]Forest Bioproducts Research Institute, University of Maine, Orono, ME, USA
[3]Department of Chemistry, University of Maine, Orono, ME, USA

Abstract: Pyrolysis is a viable candidate for the conversion of biomass into liquid transportation fuels. During this conversion, a primary challenge is to remove oxygen while maintaining high liquid yields. This oxygen removal, either through dehydration or decarboxylation, can favor secondary pyrolysis reactions that produce either char or permanent gas and reduce liquid and energy yield. Adding hydrogen over a catalyst during pyrolysis has been effective at maximizing deoxygenated liquid yield.

In this work, we present results utilizing calcium and magnesium formate as a hydrogenating agent during pyrolysis. We have co-pyrolyzed pine sawdust with calcium formate, along with other calcium salts including calcium sulfate, calcium carbonate, calcium hydroxide, and calcium oxide, in a laboratory-scale, continuous, fast pyrolysis unit (1 g/min feed). Mass balance and oil composition results will be presented for all salt/pine feedstocks. The calcium formate/pine generated oils showed improved carbon yields and improved hydrogen-to-carbon ratios relative to other oils generated.

In addition to our work with pine sawdust, we applied formate-assisted pyrolysis to lignin feedstock. The addition of formate salts improved the feeding of lignin to the reactor,

essentially eliminating plugging issues due to lignin swelling. Both liquid and carbon yield improved 41 and 34 percent, respectively, relative to non-formate lignin pyrolysis. In addition, the oxygen content of the oil was significantly reduced while the hydrogen content increased during formate-assisted pyrolysis of lignin. The addition of formate also generated oil more rich in phenol and cresols. Extraction of phenolic fraction of the FAsP lignin oil isolated 21.7% phenols, substituted phenols and catechols. The phenolic fraction was used to synthesize novolac resins. Results confirmed that extracting a mixture of substituted aromatics from FAsP lignin bio-oil could synthesize resins with properties similar to those from phenol and improved over the parent bio-oil.

Bio: Dr. DeSisto is currently a Professor of Chemical and Biological Engineering at the University of Maine. His current research interests are focused on the conversion of woody biomass to fuels and chemicals, with a particular emphasis on pyrolysis and catalytic hydrodeoxygenation processes.

Yaseen Elkasabi

Research Chemical Engineer, Eastern Regional Research Center, USDA-ARS

Novel Bio-Oil Hydrodeoxygenation Catalysts based on Strong Electrostatic Adsorption

Y. Elkasabi[1], Q. Liu[2], Y. Choi[1], A.A. Boateng[1], and J.R. Regalbuto[2]

[1]Eastern Regional Research Center, USDA-ARS, Wyndmoor, PA, USA
[2]Department of Chemical Engineering, University of South Carolina, Columbia, SC, USA

Abstract: Fast pyrolysis of biomass produces an intermediate crude oil ("bio-oil") with potential to become fungible transportation fuel. Catalytic hydrodeoxygenation (HDO) has currently gained attention as a technique for bio-oil upgrading, due to its ability to convert highly oxygenated and reactive species to hydrocarbons. Most studies of HDO catalysts are process and not catalyst oriented; noble metal catalysts are typically used in conjunction with common supports, and important variables that affect catalyst performance are often not decoupled during preparation, including catalyst particle size, hydrothermal stability, and precision of bimetallic formations.

Experiments were designed to test the hypothesis that a precisely synthesized combination of bimetallic base metal catalysts can possess requisite activity and selectivity for pyrolysis oil HDO. We studied the hydrotreatment of bio-oil from switchgrass in a batch reactor, using a series of active and hydrothermally stable HDO catalysts. Strong electrostatic adsorption was used to prepare single and bimetallic combinations (Pt, Ru, PtRu, Ni, Cu, NiCu) on carbon and mesoporous alumina supports. Particle size was determined by XRD to fall within 3–5 nm with narrow distribution and, in many cases, as small as 1.0 nm. Catalyst stability was determined by examining the support crystal structure before and after reaction. The selectivities of each catalyst toward deoxygenation, hydrogenation, and coke inhibition were compared, and this information was used to identify optimum HDO catalysts.

Bio: Dr. Elkasabi earned a BS in chemical engineering from Michigan State University, and PhD/postdoctoral experience at the University of Michigan, where he designed vacuum pyrolysis processes for producing polymers. He joined the USDA-ARS in 2013, where he develops post-pyrolysis bio-oil upgrading technologies; specifically, he leads efforts in the areas of catalytic hydrotreatment, separation processes, and coproduct development.

Emilio Ramirez

PhD Candidate, Energy Science and Engineering, University of Tennessee

Computational Study on Biomass Fast Pyrolysis Oil Yield, Effects of the Bubbling-to-Slugging Transition in a Laboratory-Scale Fluidized Bed

E. Ramirez[1,2], C.E.A. Finney[1], S. Pannala[3], C.S. Daw[1], and J. Parks[1]

[1]Oak Ridge National Laboratory, Oak Ridge, TN, USA
[2]University of Tennessee, Knoxville, TN, USA
[3]Saudi Arabia Basic Industries Corporation Americas, Sugar Land, TX, USA

Abstract: Fast pyrolysis is a leading candidate process for converting biomass to liquid fuels. During fast pyrolysis in bubbling bed or circulating bed reactors, biomass particles are rapidly heated through contacting with hot gases and solids, and their constituent components decompose into volatiles, ash, and char. The product vapor/gas composition, which determines the yield of fuel-compatible molecules, is highly dependent on the bubbling intensity, which promotes heat and mass transfer within the biomass particles and at the particle surfaces as they transit through the reactor. Fluidized bed hydrodynamic characterization at bench scale is vital for scaling up to pilot and industrial scales.

In this study, we simulate a bubbling fluidized bed biomass fast pyrolysis process with emphasis on the effects of the bubbling-to-slugging transition on oil yield. All variables were held constant while fluidizing air was adjusted to increase the bubbling intensity from free bubbling up to fully developed slugging. We employ MFiX, an open-source software package supported by DOE, which utilizes a continuum (two-fluid) approach for modeling the reactor hydrodynamics. Bubbling intensity was evaluated utilizing pressure and bubble statistics. The output of our simulations include oil yield along the reactor height for the expected bubbling intensities.

For validation, we compare our computational results with an experimental laboratory biomass pyrolysis fluidized bed using Geldart Group B particles. Lab measurements include oil yield at the reactor exit. Comparisons reveal close similarity between the simulations and experimental measurements for a range of fluidizing gas flows.

Bio: Emilio is a PhD candidate in energy science and engineering in the Bredesen Center, a joint program between the University of Tennessee, Knoxville, and ORNL. He earned his bachelor's in mathematics from the University of California, Santa Barbara. Before joining the Bredesen Center, he operated and maintained an industrial 24 MWe biomass combustion fluidized bed, where he created empirical models to optimize and increase plant reliability.

He also interned at NREL, where he developed a pilot-scale biomass gasification catalytic reactor model using ANSYS Fluent. Currently, he is using MFIX, an open source Fortran CFD code, to improve mixing, heat transfer, and chemistry in fluidized bed biomass fast pyrolysis reactors. He works with experimentalists at NREL and NETL to validate fluidized bed simulations. He is a member of the Computational Pyrolysis Consortium, a multi-laboratory, multi-scale, computational modeling collaboration to improve bio-oil quality, upgrading catalyst, process integration, and scale-up (http://cpcbiomass.org/).

Sebastian Fendt

Group Leader, Institute for Energy Systems, Technical University of Munich, Germany

Research on Small-Scale Biomass Gasification in Entrained Flow and Fluidized Bed Technology for Biofuel Production

Sebastian Fendt[1], Felix Fischer[1], Reinhard Seiser[2], Michael Long[3], and Hartmut Spliethoff[1,4]

[1]Technical University of Munich (TUM), Institute for Energy Systems, Garching, Germany
[2]UC San Diego, CA, USA
[3]UC Davis, CA, USA
[4]Bavarian Center for Applied Energy Research (ZAE Bayern), Garching, Germany

Abstract: Biomass, especially low-grade, lignocellulosic feedstock raises increasing interest for sustainable fuel production in Europe. However, fuel logistics and investment risks seem to favor small-scale applications in order to overcome remaining technological hurdles and limit plant complexity.

Different gasification technologies and process designs are investigated focusing on entrained flow and fluidized bed technology. Comparing the technologies concerning efficiencies, economics, and technological readiness, research and development needs are carved out and put in relation to current research projects at TUM as well as other European activities.

The test rigs for bubbling fluidized bed gasification and autothermal entrained flow gasification at TUM can handle various biogenic feedstocks with thermal inputs up to 100 kWth, pressures of 5 bar, and temperatures of up to 1600 °C. The focus of the experiments is a technological evaluation in relevant scale including heat management, long-term experiences, slagging and fouling behavior, and plant operations and control.

Hot gas cleaning technology for tar reforming, as well as adsorptive removal of trace substances, is tested in long-term experiments downstream of the fluidized bed gasification. Syngas conversion reaction like methanation for SNG (synthetic natural gas) production allows not only the investigation of catalytic conversions under well-defined conditions but also long-term catalyst testing regarding poisoning effects, degradation mechanisms like sintering, or carbon formation on the catalyst surface.

Furthermore, elaborate fuel and gas analysis measures ensure the evaluation of the gasification processes at a scientific level. Additional process simulation studies and CFD modeling enable process evaluation including biomass pre-treatment and product gas upgrading options.

Bio: Sebastian Fendt graduated from TUM in 2010 with a diploma (master's degree) in chemical engineering. During his master's studies, he did a research stay abroad at UC Berkeley, CA (group of Prof. Prausnitz). After receiving his diploma, he started his PhD studies at the Institute for Energy Systems (Prof. Spliethoff) with the topic "Small-scale biogenic SNG production with optional excess power integration." Since 2015, Mr. Fendt has been a group leader at the Institute for Energy Systems at TUM active in the research field of energetic biomass utilization and conversion technologies. His work includes the coordination of research projects both nationally and internationally (e.g., EU projects) as well as teaching (e.g., "Energy recovery from biomass and residues").

Jack Ferrell

Research Engineer, National Bioenergy Center, National Renewable Energy Laboratory

Standardization of Chemical Analytical Techniques for Pyrolysis Bio-Oil

Jack R. Ferrell III[1], Earl D. Christensen[1], Mariefel V. Olarte[2], Asanga B. Padmaperuma[2], and Raynella M. Connatser[3]

[1]National Renewable Energy Laboratory, Golden, CO, USA
[2]Pacific Northwest National Laboratory, Richland, WA, USA
[3]Oak Ridge National Laboratory, Oak Ridge, TN, USA

Abstract: There has been a recent surge in interest in the production of fuels and renewable chemicals from biomass feedstocks. The pyrolysis pathway produces a liquid "bio-oil" product, which must be processed further, or upgraded, to ultimately produce fuels or chemicals. Bio-oil is an extremely complex mixture, and research and development on upgrading processes require reliable analyses of bio-oil. In particular, chemical characterization techniques are needed that quantify both functional groups and individual compounds present in bio-oil. Reliable chemical characterization of bio-oils will enable upgrading research and allow for detailed comparisons of bio-oils produced at different facilities. Reliable analytics are also needed to enable an emerging bioenergy industry, and processing facilities often have different analytical needs and capabilities than research facilities. Furthermore, data from reliable bio-oil analyses are needed to define the *quality* of bio-oils. Quality metrics are needed to assign a value to raw bio-oil, and will help inform process conditions for bio-oil upgrading.

While analytical standardization for bio-oils has a rich history, the majority of standardization efforts to date have tested only physical characterization techniques (e.g., elemental analysis, viscosity). In this presentation, results will be presented from an international round robin on the validation of chemical characterization techniques for pyrolysis bio-oils. Techniques tested include carboxylic acid titration (CAN/TAN analysis), carbonyl titrations using two different methods, ^{31}P NMR for determination of hydroxyl groups, and a quantitative GC-MS method. The round robin results presented are one of the first examples of successful validation of chemical characterization techniques for bio-oils. In particular, for the first time, carbonyl titration and carboxylic acid titration methods have yielded acceptable inter-laboratory variabilities. The Faix carbonyl titration method and the carboxylic acid number (CAN) are especially reliable, with variabilities of less than 5%

between participating laboratories. An NMR technique has never been tested in an interlaboratory study on bio-oil analysis, and the ^{31}P NMR technique here produced acceptable variabilities among the labs. With variabilities less than 10%, aliphatic and phenolic OH groups can be reliably quantified using this method, but carboxylic OH groups were prone to larger variabilities, on the order of 15%. As has been shown in previous round robin studies, GC-MS results were more variable. The method quantified 31 volatile compounds in bio-oil, and 21 compounds had variabilities of less than 20%. Detailed analytical protocols of the methods presented will be shared with the bioenergy community and will be free and publicly available.

Bio: Dr. Ferrell holds degrees in chemical engineering, with a BS from the University of Virginia and a PhD from the Colorado School of Mines. Prior to joining NREL, Jack held a postdoctoral fellowship at the NETL. At NREL, he leads research on the development and standardization of analytical techniques for pyrolysis bio-oils and also on kinetic modeling for syngas to fuels processes. The analytical standardization research project is a collaborative effort between NREL, PNNL, and ORNL. The standardized methods developed in this project are publicly available as Laboratory Analytical Procedures and can be found at this website: http://www.nrel.gov/bioenergy/bio-oil-analysis.html.

Felix Fischer

Research Assistant and PhD Candidate, Institute for Energy Systems, Technical University of Munich

Influence of Co-gasification Agents on Fluidized Bed Steam Gasification of Biomass for Biofuel Production

Felix Fischer, Stephan Herrmann, Sebastian Fendt, and Hartmut Spliethoff

Institute for Energy Systems, Technical University of Munich, Garching, Germany

Abstract: Fluidized bed gasification of biomass is mostly performed using superheated steam as the fluidizing and gasification agent. While the gasification properties of superheated steam are good, it requires large amounts of heat to produce it. Hence, the influence of alternative co-gasification agents will be discussed in this presentation. Ideally, these co-gasification media have lower heat capacities and a positive effect on the gasification process. Furthermore, the applied methods for syngas cleaning should not be negatively affected, and the produced syngas should at least be of the same quality and suitability for its final utilization (e.g., synthesis reactions). One possible option is using waste gas streams (e.g., from biogas plants) or gas streams that have high contents of CO_2. By using CO_2 as a co-gasification agent, the carbon content in the produced syngas can be increased. Additionally, the S/C-ratio as well as the $H_2/(CO+CO_2)$-ratio for the synthesis of biofuels can be adjusted to required values in order to achieve high yields and selectivity.

This presentation will be based on experimental results, obtained at the Institute for Energy Systems of the Technical University of Munich. The complete process chain from biomass to substitute natural gas is built up in a small-scale test rig of 5 kW. It consists of an allothermal fluidized bed gasifier, hot gas cleaning, and a fixed bed methanation reactor.

Superheated steam is fed through nozzles at the bottom of the gasifier and fluidizes the bed material (quartz sand). Additionally, co-gasification agents can be added and mixed with the steam. The effects of combined steam- and co-agent-gasification on the gas composition, the tar level, and the efficiency are analyzed in long-term experiments with parameter variations (e.g., steam/biomass-ratio, pressure, temperature).

The main gas composition (H_2, CO, CO_2, CH_4) of the produced syngas is measured online using different gas analyzers. The addition of co-agents in the gasification zone influences the carbon conversion of the biomass; hence, the produced amount and distribution of tar components is analyzed at two different measuring points using the offline SPA method. First results show reduced tar concentrations with CO_2-addition in the gasification zone.

The results of the experimental investigations are compared with detailed process simulations using Aspen Plus, as partially presented before.

Bio: Mr. Fischer has a BSc in mechanical engineering and an MSc in energy and process engineering both from the Technical University of Munich. Since July 2014, he has worked at the Institute for Energy Systems on biomass gasification, hot gas cleaning, and fuel synthesis.

Arpa Ghosh

Graduate Research Assistant, Chemical and Biological Engineering, Bioeconomy Institute, Iowa State University

Production of Soluble and Hydrolyzable Carbohydrates from Biomass Using THF/Water Co-solvent in the Presence of Acid Catalyst

Arpa Ghosh[1] and Robert C. Brown[2]

[1]Department of Chemical and Biological Engineering, Iowa State University, IA, USA
[2]Department of Mechanical Engineering, Iowa State University, IA, USA

Abstract: Non-enzymatic sugar production from lignocellulosic biomass using polar aprotic solvents is drawing increasing attention. In this study, two-step solvent liquefaction of red oak was investigated. In the first step, biomass was pretreated at 120 °C in a mixture of tetrahydrofuran (THF) and water (80/20 vol%) with 10 mM sulfuric acid to remove lignin as a THF-soluble by-product and recover the pretreated solids as a polysaccharide pulp. The solubilized lignin was easily precipitated out by adding water to the pretreatment liquid followed by recovery of THF. In the second step, the polysaccharide pulp was further solubilized and decomposed in a mixture of THF and water with 1.25–5 mM sulfuric acid at a higher temperature (e.g., 250 °C). The yield of solubilized products from the polysaccharide pulp was 71 wt% within only 8 min of reaction. HPLC analysis indicates that the solubilized product primarily consists of water-soluble C_6 and C_5 monosaccharides and oligosaccharides. The total yield of solubilized and hydrolyzable C_6 and C_5 carbohydrates from pretreatment and solvent liquefaction steps combined was as high as 42 wt% (in the form of glucose and xylose), based on initial raw red oak. Future work includes quantification of the hydrolyzable solubilized oligosaccharides. In addition to being an effective solvent for deconstructing biomass, THF can be easily separated from water and the sugars by simple distillation due to its low boiling point (66 °C). Additionally, it would be important to evaluate the performance

of other low-boiling polar aprotic solvents for developing the most effective and economically feasible solvent liquefaction process for producing solubilized carbohydrates from biomass.

Bio: Ms. Ghosh is a third-year chemical engineering PhD student working in Prof. Robert C. Brown's research group at the Bioeconomy Institute at Iowa State University. She completed her master's and undergraduate degrees in chemical engineering from the Indian Institute of Technology, Kharagpur and West Bengal University of Technology, India, respectively. Her research interest is solvent liquefaction of biomass, sugar and platform chemical production from biomass, the role of solvents in biomass conversion, and reaction kinetics and energetics.

Patrick Hall

Thermochemical Research Scientist, Bioeconomy Institute, Iowa State University

Purification of Pyrolytic Sugar from Bio-Oil Fractions

Patrick H. Hall[1], Marjorie R. Rover[1], Patrick A. Johnston[1], Ryan G. Smith[1], and Robert C. Brown[1, 2]

[1]Bioeconomy Institute, Iowa State University, Ames, IA, USA
[2]Department of Mechanical Engineering, Iowa State University, Ames, IA, USA

Abstract: Productive use of all streams of fractionated bio-oil will be important to the development of a bio-refinery based on the fast pyrolysis of biomass. Fractionation technology separates bio-oil into water-soluble sugars, water-insoluble phenolic monomers, dimers, and oligomers and aqueous phases containing water-soluble, light oxygenates. The major species in our first two-stage fractions are water-soluble sugars and water-insoluble phenols. We can separate the sugar from the phenolics with a simple water extraction. However, phenolic monomers are slightly water soluble, and some of them get carried over in the pyrolytic sugar stream, which can be inhibit fermentation or interfere with catalytic upgrading.

The primary goal of this research is to investigate purification of the sugar stream using resins. We have discovered an adsorbent resin that sufficiently purifies the sugar mixture to allow its crystallization or use for biological or catalytic upgrading. Our results show an increase of sugar purity to 80.75 ± 9.5 wt. % on a dry basis (db) from 52.34 ± 3.66 wt. % in the original pyrolytic sugar syrup. The resin has high selectivity (affinity) for phenols and other bioactive compounds, high adsorption capacity, low cost, and ease of regeneration. Phenol concentrations of the pyrolytic sugar syrup have been reduced from 20.94 ± 1.01 wt. % to 1.08 ± 0.24 wt. % utilizing this resin technology. Some sugar is adsorbed by the resin (12.81 ± 1.9293 wt. % db) but can easily be reobtained by regeneration. Resin purification of the pyrolytic sugar stream has shown favorable results with almost complete removal of the sugar impurities.

Bio: In addition to working as a scientist, Mr. Hall is a PhD candidate in Dr. Robert Brown's research group in Biorenewable Resources and Technology. Mr. Hall received a BA in chemistry with ACS certification from Grinnell College. He has 3 years of experience in organic synthesis in industry. His research interests are bio-oil separation, purification, and upgrading.

Mark Jarvis

Thermochemical Process Engineer, National Renewable Energy Laboratory

Ex-situ Catalytic Fast Pyrolysis in a DCR—Effect of Pyrolysis Conditions

Mark Jarvis, Jessica Olstad, Yves Parent, and Kim Magrini

National Renewable Energy Laboratory, Golden, CO, USA

Abstract: Integration of biomass feedstocks into petroleum refinery operations is an important step towards energy independence, growth of the bio-economy, and proper management of the global carbon cycle. Successful deployment of biomass technologies at the commercial scale requires rigorous investigation of numerous process variables that are only feasible at smaller scales. W.R. Grace developed the Davison Circulating Riser (DCR) to match the conditions of a commercial FCC unit in the laboratory. In particular, it is widely used to develop and test new FCC methods and catalysts for the petroleum industry, so we developed a front-end pyrolyzer to deliver fast pyrolysis vapors to a DCR Mark IV to explore biofuel integration into petroleum refinery operations. Our hypothesis is that fresh vapors will contain fewer oligomers and thus be more amenable to upgrading when compared to re-volatilized pyrolysis oil. In this work, we investigated the impact of fast pyrolysis conditions on the efficiency, oxygen reduction, and hydrocarbon yield of the upgrading process. The fast pyrolysis of biomass was carried out in a 2" fluidized bed reactor for 1.5s at 500 °C and 37 psia, employing nitrogen as the primary fluidization gas in a sand bed. Upgrading in the riser was nominally 1s, and the reactor was operated adiabatically at 550 °C and 32 psia. First, the impact of hardwood vs. softwood was tested at a 0.5 biomass to nitrogen ratio (mixed hardwoods and clean loblolly pine) over a metal-modified ZSM5-based catalyst. Second, the concentration of pyrolysis vapor in nitrogen was increased to determine the role of vapor density on the upgrading process. Average yields from the pyrolyzer system showed ~65 wt% liquid, ~18 wt% gas, and ~18 wt% char. Pyrolysis oils had a density of 1.12 g/mL. NREL's unique molecular beam mass spectrometry (MBMS) system was employed to provide real-time analysis of the vapor stream entering the DCR to ensure the fast pyrolysis conditions were consistent as possible and that cracking to light gases (CO, CO_2, and CH_4) was minimized. Primary oxygenates in the stream were typical for fast pyrolysis and were attributed to guaiacol (124 amu) and other methoxyphenols, sugars, furans, and acetic acid. A hot filter (~400 °C) was employed to remove inorganic materials from the vapor before proportioning the stream between the quench system and the DCR riser (metered, 0.5–1.5 kg/hr).

Bio: Dr. Jarvis earned his doctorate in mechanical engineering from the University of Colorado at Boulder in 2009. His dissertation involved studying pyrolysis mechanisms with lignin model compounds in a microtubular reactor and whole biomass using a laminar entrained flow reactor (LEFR) via MBMS employing both electron impact and photo-ionization methods. He has worked with NREL's 4" FBR to study the effects of particle size on pyrolysis and gasification reactions and began pilot-scale work with the mixed alcohol synthesis laboratory for the 2012 demonstration. Under the National Advanced Biofuels Consortium, he began studying catalytic hydropyrolysis systems at the bench scale while continuing to develop the LEFR system as an automated bench-scale vapor phase upgrading (VPU) unit. His work the past 2 years has focused on developing engineering solutions for NREL's DCR to study the effects of mixed liquid and vapor feeds, novel catalysts, and pyrolyzer conditions on the VPU process.

Claus Uhrenholt Jensen

Industrial PhD Student, Steeper Energy ApS, Denmark

Continuous Hydrotreatment of HydrofactionTM Oil to Drop-In Diesel

Claus Uhrenholt Jensen[1], Julie Katrine Rodriguez[2], Sergios Karatzos[2], and Lasse Rosendahl[3]

[1]Steeper Energy ApS, Copenhagen, Denmark
[2]Steeper Energy Canada Ltd., Calgary, Canada
[3]Aalborg University, Aalborg, Denmark

Abstract: Thermochemical conversion of lignocellulosic biomass residues through continuous hydrothermal liquefaction and subsequent upgrading represents the Hydrofaction™ pathway for production of sustainable transport biofuels. Over the past few years, Steeper Energy has significantly progressed technology intellectual property and detailed commercial engineering and economic validation as it progresses through the stages of the commercialization pathway, focusing on all aspects of the value chain from feedstock flexibility validation to process efficiency, market acceptance, process scale-up, and economic feasibility, Steeper has engaged in strategic collaborations and targeted activities in order to prove its unique value proposition. Hydrofaction's high conversion efficiencies result in compelling economic returns and over 80% greenhouse gas emission reductions over conventional energy. This is achieved by a unique platform that exploits supercritical water chemistry while maximizing oil yield and oil quality.

The presentation will cover recent advances in continuous hydrotreatment of wood-based Hydrofaction biocrude. The study includes catalyst and parametric screening with a focus on deoxygenation and catalyst stability. Analysis of the upgraded products cover fractional distillation, Py-GCxGC-MS, as well as conventional diesel fuel specifications. The results will also cover yield figures and carbon balances for the overall conversion of wood to drop-in biofuel.

Bio: Claus is an industrial PhD at Steeper Energy ApS and associated with the University of Aalborg, Denmark. His research focuses on conditioning and upgrading biocrude from hydrothermal liquefaction into drop-in biofuel blend stocks. Claus has more than 4 years of experience with the Hydrofaction technology and in particular with upgrading of HTL biocrudes.

Suh-Jane Lee

Energy and Environmental Directorate, Pacific Northwest National Laboratory

Methylation of Carboxylic Acids and Phenols from Bio-Oil

Suh-Jane Lee, Evgueni Polikarpov, and Karl Albrecht

Chemical and Biological Process Development Group, Pacific Northwest National Laboratory, Richland, WA, USA

Abstract: Carboxylate ester, such as methyl acetate, and aryl ether, such as anisole, are considered effective anti-knock additives and substantially increase the octane number for motor fuel. We anticipate the great increase in value of bio-oil by methylation of both carboxylic acids and phenolics, which are rich species in bio-oil. Two major challenges for methylation of both carboxylic acid and phenolics in bio-oil are 1) how to make chemistry work for acid catalytic esterification of carboxylic acid and base catalytic etherification of phenols and 2) how to selectively target carboxylic acids and phenolics in bio-oil feed.

Unlike a model compound study, direct methylation of acids and phenols using bio-oil may not be efficient owing to its complexity and undesired properties. We demonstrated a proficient liquid-liquid fraction to obtain target compounds, acetic acids, and phenols from pyrolysis bio-oil and developed a two-step methylation for carboxylic acid and selectively O-methylation of phenols. Bio-oil was first washed with adequate water; then the acids and phenols were recovered with the recyclable solvents, MtBE, EtOAc, and Cyanex with which the partition coefficient of acid and phenol in two phases was investigated. We also learned how other factors such as sugar and polyols affect the esterification and etherification. A flow system was designed to accommodate a first acid catalyst bed at 200 °C and a second basic catalyst bed at 300–400 °C. An overall methylation of carboxylic acid and phenols from bio-oil will be presented.

Bio: Dr. Lee joined PNNL's Energy and Environmental Directorate in 2008 after her postdoctoral training in PNNL's Fundamental Sciences Directorate. She is currently focusing on development and syntheses of heterogeneous catalysts for chemical process of stabilizing and upgrading bio-oil and valuable bio-based chemicals.

Young Jin Lee

Associate Professor, Chemistry, Iowa State University

Thin-Film Fast Pyrolysis of Isotopically-Labeled Glucose for the Analysis of Primary Reaction Pathway

Young Jin Lee and Carolyn Hutchinson

Department of Chemistry, Iowa State University, Ames, IA, USA

Abstract: There has been a lack of molecular-level understanding in reaction mechanisms and kinetics in fast pyrolysis of lignocellulosic biomass. Bulk sum models, most commonly represented by the Broido-Shafizadeh model, cannot delve into molecular-level complexity that would be necessary to control the final product distribution. Recently, Broadbelt group

developed a mechanistic model by dissecting cellulose pyrolysis into over 300 elementary reactions. Reaction parameters for each elementary reaction were either quantum mechanically derived or obtained by fitting into micropyrolysis-GC-FID/MS data. While the Broadbelt model provides the first comprehensive approach, it has two critical limitations: verification of each elementary reaction mechanism and uncertainty of reaction parameters.

Our group has recently developed a novel instrumentation to monitor the molecular products of fast pyrolysis in virtually real-time. A drop tube micropyrolyzer is directly connected to a fast scanning high-resolution time-of-flight mass spectrometer, enabling the immediate detection of pyrolyzate products with only 0.5s dead time and in 0.1s time resolution. In the current study, we use this instrumentation to trace each molecular product and validate the reaction pathways by the fast pyrolysis of glucose with select carbon isotopically labeled.

Glucose labeled at carbon position 1, 3, or 6 was used for this study. Each thin film of glucose, 0.5µg with ~1µm thickness, spotted outside of the pyrolysis cup was individually pyrolyzed at 500 °C along with 0.05µg $^{13}C_6$-levoglucosan spotted on the opposite side of the cup as a time calibrant and an internal standard. Because of very short reactor residence time, 0.2s, we observe only primary pyrolyzates, well suited for the primary reaction analysis. Chemical compositions are determined for each compound from the accurate masses, and their temporal profiles are monitored. Comparing the ratios of non-labeled and labeled pyrolysis products of three isotopically labeled glucose, we can validate each chemical reaction pathway.

All C_6 products exhibit only labeled peaks as expected, validating the methodology. $C_4H_8O_4$ is predicted to contain carbons 3-6. Only non-labeled $C_4H_8O_4$ is detected in the pyrolysis of C1 labeled glucose, and ^{13}C-$C_4H_8O_4$ is detected in C_3 or C_6 labeled glucose, agreeing with the proposed reaction pathway. The major product in thin-film pyrolysis, $C_3H_6O_3$, should contain only carbons 1-3 according to the Broadbelt model; however, our data show there are at least two pathways leading to $C_3H_6O_3$, with one-third of them containing carbons 1-3 and two-thirds containing carbons 4-6. When GC separation is combined with thin film fast pyrolysis, there are actually three pathways leading to $C_3H_6O_3$. One of them is glyceraldehyde, a compound never before characterized by traditional Py-GC-MS analysis due to thermal instability, observed only for C6 labeled glucose, whereas dihydroxyacetone has two reaction pathways containing carbon 1-3 and carbon 4-6. Two carbon products (e.g., $C_2H_4O_2$) show fairly even distributions regardless of which carbon is labeled; i.e., 1/3 are labeled and two-thirds are non-labeled. This suggests that the existence of multiple reaction pathways leads to fairly even distribution, in line with the Broadbelt model. Reaction pathways of other products will also be discussed in comparison with Broadbelt model.

Bio: Dr. Lee has over 25 years of expertise in various fields of mass spectrometry, from fundamentals and instrumentations to diverse applications including proteomics, metabolomics, and mass spectrometry imaging. His group first adopted high-resolution mass spectrometry for complex bio-oil analysis. Recently, his group developed a drop-tube micro-pyrolyzer time-of-flight mass spectrometer system for real-time monitoring of thin film pyrolysis. Another major focus of his group is mass spectrometry imaging of plant metabolites where five micron high-resolution chemical imaging capability is developed for single cell, subcellular resolution in situ direct analysis. He received his BS, MS, and PhD from Seoul National University, Korea, and postdoctoral training at Indiana University. Before joining Iowa State, he was a staff scientist at University of California at Davis.

Hans Leibold

Karlsruhe Institute of Technology

Low-Temperature Catalyst for Biomass Tars Decomposition and Conversion in Fuel Gas

H. Leibold and G. Straczewski

Institute of Technical Chemistry, Karlsruhe Institute of Technology (KIT),
D-76344 Eggenstein-Leopoldshafen, Germany

Abstract: Tar is a complex mixture of hydrocarbons derived from biomass gasification or pyrolysis processes. The presence of tar in the product gas can effect fouling and reduces the overall efficiency of processes and may also cause blockage and corrosion of equipment like gas engines, gas turbines, or fuel cell–based power generation. Therefore, the successful implementation of gasification technology depends largely on effective and efficient tar removal from the product gas. One of the most promising methods to overcome the addressed problems is the catalytic decomposition of the tar species, where the energy content of the tar is completely converted into the fuel gas and the heating value, respectively. Proprietary Pt-based catalysts already provide the complete conversion of tars above 600 K[1] depending on the respective Pt content. Those temperature conditions enable catalyst operation in the synthesis gas downstream of a gasifier without additional reheating of the gas. Besides the low temperature operation a preceding hot gas filter prevents the catalyst against syngas-related deposits of ash and coke or soot particles. S and Cl compounds can be effectively removed by mineral sorbents upstream of the catalyst.

In our basic approach, a Ni-based catalyst is loaded with precious metals for the decomposition of the tar in biomass gasification processes. The low-temperature Ni-based catalyst was optimized with respect to the support material, the metal content, and the final pellet size. The compositions of transition metals were adjusted to minimize problems related to catalyst coking. A precious metal (Pt, Pd, or Rh) was added to the catalyst only in small quantities. Both the transition metals and the noble metal were co-impregnated on a porous cylindrical pellet support. A mixture of Al_2O_3 and montmorillonite (Mg, Al-silicates) in a different mass ratio was used as the pelletized support material.

Regarding performance tests of the catalysts, a laboratory-scale test facility was used. A tubular fixed bed reactor was operated with model synthesis gases corresponding to the outlet of downdraft fixed bed gasifiers. Naphthalene was used as the most relevant tar model compound. A complete CH-conversion was already measured at temperatures above 750–840 K depending on the respective catalyst composition, the pellet size, and the space velocity. All the prepared catalysts showed longtime activity (naphthalene conversion greater than 80%) between 70 and 110 hours without regeneration except for a catalyst on a commercial Al_2O_3 support. With regard to the future long-term operation downstream of

small fixed bed gasifiers the in-situ regeneration of Pt-doped catalysts was also carried out. The thermal regeneration with short-term O_2 addition, the reforming with variable H_2O vapor contents, and the deactivation performance were examined.

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Wenqin Li

Graduate Student and Research Assistant, Mechanical Engineering, Iowa State University

Techno-economic (TEA) and Life Cycle Analysis (LCA) of the Pyrolysis-Bioenergy-Biochar Pathway for Carbon-Negative Energy

Wenqin Li[1], Qi Dang[1,2], M.M. Wright[1], R.C. Brown[1,2], and D. Laird[3]

[1]Department of Mechanical Engineering, Iowa State University, Ames, IA, USA
[2]Bioeconomy Institute, Iowa State University, Ames, IA, USA
[3]Department of Agronomy, Iowa State University, Ames, IA, USA

Abstract: The objective of this project is to evaluate the economic and environment impacts of the pyrolysis-bioenergy-biochar pathway for carbon-negative energy. Biochar, a carbon-rich coproduct of pyrolysis, has the potential to improve soil quality by sequestering carbon, thus helping to achieve a carbon-negative energy goal. In addition to biochar, fast pyrolysis of biomass can also produce biofuels, bio-power, and chemicals. Techno-economic analysis (TEA) and life cycle analysis (LCA) results will vary with the selection of pyrolysis products, feedstock materials, and facility locations.

Economic analysis was conducted on two pyrolysis product utilization scenarios: biochar & biofuel and biochar & bio-power. In the biochar & biofuel scenario, we estimate that the minimum fuel-selling price varies between $2.91 and $3.03 per gallon if biochar can be sold for $60 to $20 per tonne. On the other hand, if the biofuel can be sold at market prices of $2.00 to $5.00 per gallon, the biochar can be sold for $364 to –$637 per metric tonne. The biochar & bio-power scenario yields minimum electricity-selling prices of 9.85 to 10.07 ¢/kWh for biochar prices of $60 to $20 per tonne. Biochar can be sold for –$336 to $400 per tonne at electricity prices of 12 to 8 ¢/kWh. These prices do not include environmental credits or incentives. More pyrolysis product combination scenarios will be assessed and compared.

Biochar properties and yields vary from different types of biomass. Regression models of the relationship between biochar & biofuel yield and biomass carbon, ash & oxygen contents have been built based on a series of fast pyrolysis experimental yields data. The regression model was validated for different types of feedstock and used to predict the yield for various feedstocks. Process models for fast pyrolysis of various feedstocks will be built in Aspen Plus^{TM}, with the products' prediction data. Mass and energy balance and subsequent TEA will be assessed and compared to elect the best economic performance feedstock.

The pyrolysis facility locations might affect various factors, such as feedstock cost, feedstock type, capital cost, and operating cost. Biochar type and the demand for biochar will also vary with the plant locations. Three specific U.S. land areas are investigated depending on the selection of pyrolysis facility locations: Upper Mississippi River Basin, California, and U.S. Southeast. The capital cost, operating cost, and minimum fuel selling price were estimated to indicate the economic benefits of employing an integrated pyrolysis-bioenergy-biochar pathway in various regions. LCA will also be conducted using GREET to evaluate the greenhouse gas emissions of the integrated pyrolysis-bioenergy-biochar production facility in different regions.

Bio: Ms. Li is a graduate student and research assistant in Mechanical Engineering, Iowa State University. Her research focuses on chemical processing modeling, TEA, and LCA of biorenewable pathways.

Juan A. Lopez-Ruiz

Research Associate, Chemical and Biological Process Development Group, Pacific Northwest National Laboratory

Development of ZrO_2-based Hydrothermally Stable Catalysts for the Catalytic Upgrading of Biomass-Derived Aqueous Streams

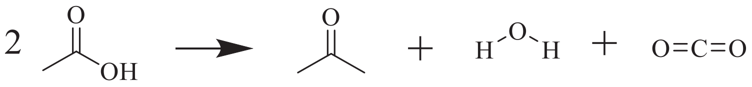
Juan A. Lopez-Ruiz[1], Luis Estevez[2], Alan R. Cooper[1], Yunhua Zhu[1], and Karl O. Albrecht[2]

[1]Chemical and Biological Process Development Group, Pacific Northwest National Laboratory, Richland, WA, USA
[2]Transportation Energy Storage Group, Pacific Northwest National Laboratory, Richland, WA, USA

Abstract: The technologies involving the conversion of biomass into fuels and chemicals generate aqueous streams that may contain a high fraction of biogenic carbon. For example, the hydrothermal liquefaction (HTL) of biomass has about 30% of the total carbon fed to the HTL process report to an aqueous stream. A large portion (up to 70%) of the biogenic carbon consists of short chain carboxylic acids such as acetic acid and propionic acid. Hence, the recovery and transformation of the biogenic aqueous carbon have the potential to greatly improve the feasibility of the biomass conversion technologies.

The ketonization reaction represents an attractive route to upgrade these carboxylic acids into intermediate ketones (Scheme 1), which are platform molecules for further conversion to fuels and chemicals. Furthermore, the ketonization reaction may be adventitiously performed under hydrothermal reaction conditions (in the presence of condensed H_2O at temperatures above its boiling point) in order to eliminate the need to supply a large amount of energy to vaporize the aqueous stream. However, common ketonization catalysts such as TiO_2, CeO_2, ZrO_2, and $Ce_xZr_{(1-x)}O_2$ have been reported to change physical structure and lose catalytic activity when exposed to hydrothermal conditions.[1-4] For example, ZrO_2 restructures under hydrothermal reaction conditions to a monoclinic phase while gradually losing catalytic activity. Hence, hydrothermally stable heterogeneous catalysts are needed for the upgrading of biomass-derived aqueous streams.

SESSION SPEAKERS



Scheme 1. The ketonization of two equivalents of acetic acid to produce acetone, water and carbon dioxide is an example of the ketonization reactions being investigated in this work.

In this work, we successfully synthesized a series of hydrothermally stable ZrO_2-based mixed-metal oxides with ketonization activity increased by nearly 25 times compared to pure ZrO_2, 0.78 and 0.031 mmol g_{cat}^{-1} h^{-1}, respectively. The improved catalysts maintain 100% selectivity to the ketone products. In particular, the effect of catalyst composition on the catalyst activity and stability was explored. Carbon-supported mixed-metal oxides were synthesized to significantly increase the catalyst active surface area and maximize the catalytic activity on a per gram of active phase basis. The hydrothermally stable material was used to upgrade several biomass-derived aqueous streams and understand the effect of contaminants on the catalyst activity and stability. Furthermore, a techno-economic analysis was used to assess the impact of this technology when coupled to biomass conversion processes such as HTL.

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Bio: Dr. Lopez-Ruiz is currently doing his postdoctorate at PNNL in the Chemical and Biological Process Development group working with Karl O. Albrecht. He has a double major in chemical engineering and industrial engineering from the Universitat Rovira i Virgili in Tarragona, Spain; obtained a masters in chemical engineering from Bucknell University in Lewisburg, PA; and received his PhD in chemical engineering from the University of Virginia in Charlottesville, VA, where he worked with Robert J. Davis. His research areas are catalytic transformation of biomass- and waste-derived molecules into fuels and chemicals, synthesis and characterization of hydrothermally stable heterogeneous catalysts, and rational catalyst design by combining kinetic, characterization, and computational studies.

Andrew Lucero

Manager, Process Development and Engineering, Energy and Environment Division,
Southern Research

Highly Selective FT Synthesis for Production of JP-8 Jet Fuel from Biomass, Coal, or Coal/Biomass Mixtures

Andrew Lucero, Brittany Koob, Brandon Cline, Kevin McCabe, and Santosh Gangwal

Southern Research, Durham, NC, USA

Abstract: An indirect liquefaction process employing advanced process intensification approaches is being developed to reduce costs and accelerate commercialization of a process for converting biomass, coal, and coal-biomass mixtures to JP-8 jet fuel. In this Air Force- and DOE-sponsored cooperative agreement, Southern Research is leading a team consisting of IntraMicron, Inc., Southwest Research Institute, and Nexant, Inc., along with Chevron as selective Fischer-Tropsch (FT) catalyst supplier and the National Carbon Capture Center (NCCC) as the host site. The process reduces the number of parasitic syngas cleaning steps and eliminates costly upgrading of wax produced in conventional indirect liquefaction processes, resulting in improved economics and lower life-cycle greenhouse gas emissions for CTL-based jet fuel production. These improvements directly reduce capital costs of indirect CTL processes, resulting in significantly improved economics and cost competitiveness of CTL when compared to petroleum refining. Specific objectives for FT experiments are to demonstrate a selective and active second generation cobalt-zeolite hybrid FT catalyst from Chevron that predominantly produces liquid range C5–C20 hydrocarbons with high productivity (5X conventional FT catalysts) and jet fuel selectivity while eliminating the production and associated handling of solid C21+ wax. In fall 2015, Southern fed simulated syngas to a bench-scale FT reactor with a 2" diameter heat exchange reactor tube using IntraMicron technology in a nominal 5 gallons per day skid-mounted fixed-bed installed at NCCC. In those experiments, both productivity and selectivity goals were achieved during a 300-hour experiment. In fall 2016, another experiment is planned with the reactor diameter increased to 4". This work will compare the results from the two long-term tests of the hybrid FT jet-selective catalyst using the skid-mounted fixed-bed FT reactor system.

Bio: Dr. Lucero is a senior chemical engineer with over 25 years of experience conducting laboratory , bench-, and pilot-scale R&D. His expertise includes designing, constructing, commissioning, operating, troubleshooting, evaluating, and improving a variety of fuel and energy technology processes for conversion of gas, coal, biomass, and other feedstocks to energy or fuels. He has a broad technical background in applied catalysis including FT and related processes, methanol synthesis, mixed alcohol synthesis, and steam reforming. Dr. Lucero's experience also includes gasification, CO_2 capture, a variety of separation processes, and process safety planning and evaluation (HAZOP).

René Madsen

PhD Fellow, Aarhus University

Comparing Quantitative Analysis of Bio-crude and Aqueous Phase from Hydrothermal Liquefaction of Biomass

René Madsen, Patrick Biller, Mads Jensen, and Marianne Glasius

Department of Chemistry and iNANO, Aarhus University, Langelandsgade 140, 8000 Aarhus C, Denmark

Abstract: Gas chromatography coupled to mass spectrometry (GC-MS) is often applied to bio-crude and the aqueous phase from the hydrothermal liquefaction (HTL) of biomass. The complexity of the chromatograms means that most studies rely on tentative peak identifications and report relative peak areas based on integration of the total ion chromatogram. This means that faulty assigned peaks and overestimation of peak areas are highly prevalent, and comparison of literature values is impossible due to different analytical methods. Quantitative analysis of bio-crude will provide input needed for further processing into liquid bio-fuels. Many uses of the aqueous phase have been proposed, including anaerobic digestion and catalytic hydrothermal gasification, for which quantitative characterization is important.

This study subjected 11 different biomasses, including waste products, lignocellulosics, and aquatic biomasses, to HTL in batch reactors at the same conditions. Furthermore, mixtures of biomasses were evaluated to investigate potential interactions among biomass components. The bio-crude and aqueous phase were extensively quantitated by GC-MS with prior derivatization with *N*-methyl-*N*-(trimethylsilyl) trifluoroacetamide and methyl chloroformate, respectively, using validated methods. Results were explored with principal component analysis (PCA) to identify latent variables that could be of importance for selective reaction pathways influencing further processing.

A total of 96 compounds of the bio-crude and 65 compounds of the aqueous phase, which included all major compound classes identified in the literature, were quantitated with the methods. Acetic acid remained the most abundant compound detected in the aqueous phases, while bio-crudes were more highly varied. Aqueous phase and bio-crude of high lipid microalgae strains were most abundant in fatty acids and fatty acid amides. The 11 samples were clearly separated both in the bio-crude and aqueous phase with PCA, which was explained by their differences in biochemical content. Changes in reaction pathways of especially nitrogenates were explained and provide a mode for tuning of product composition with potential utilization in further processing.

This is the most extensive quantitative study to have been reported on bio-crude and the aqueous phase from HTL and the first study to compare compositions from a wide variety of biomasses with validated methods. The methods provide a framework for comparison with literature values and provide new information for techno-economic assessments that have previously not been available. Furthermore, it will be of use for further processing technologies relying on microbes or catalysts.

Bio: Dr. Madsen got his master's degree in medicinal chemistry in 2012 from Aarhus University, Denmark. His master's project was done within the field of metabolomics at DuPont. He went on to work as an analytical chemist in the pharmaceutical industry and is currently a PhD fellow at Aarhus University. René has taken part in the commissioning of a novel continuous flow reactor for hydrothermal liquefaction at Aarhus University through analysis of the different product fractions. His main analytical focus is derivatization methods for analysis with gas chromatography coupled to mass spectrometry along with multivariate data analysis.

Saurabh Maduskar

Graduate Research Assistant, Chemical Engineering and Materials Science, University of Minnesota

Kinetics of Cellulose Pyrolysis via Pulse-Heated Analysis of Solid Reactions (PHASR)

Saurabh Maduskar, Christoph Krumm, Cheng Zhu, and Paul J. Dauenhauer

Department of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, MN, USA

Abstract: Cellulose is a major constituent of biomass and the most abundant biopolymer in the world. During high temperature pyrolysis, it transforms into a liquid intermediate before depolymerizing and volatilizing into condensable bio-oil products for upgrading into fuels and chemicals.[1] The underlying pyrolysis chemistry has been studied for decades, and numerous conflicting mechanisms and kinetics models have been proposed. A major challenge in the experimental verification of such kinetic models is the complexity of the analytical problems—hundreds of products are formed on a millisecond timescale and reaction kinetics are convoluted by heat and mass transfer.[2]

To overcome the challenge of reaction complexity, Pulse-Heated Analysis of Solid Reactions (PHASR), an experimental microreactor system, was developed. The PHASR reactor rapidly heats and cools (~10^6 °C/min) thin film solid samples (10–50 µm thick) at millisecond timescales to control reaction progression, allowing for quantification of vapor, gas, and intermediate products as a function of reaction time.[3]

The PHASR reactor system was used to measure millisecond-resolved evolution of cellulose and its volatile pyrolysis products over a wide range of temperature (370–550 °C). By comparison of cellulose conversion and product formation kinetics, a mechanism of cellulose fragmentation, unifying the long-debated models of end chain versus intrachain scission, during initial stages of pyrolysis was proposed. The transition from chain-end scission to intrachain scission mechanism was found to occur at around 467 °C termed as "Reactive melting point" of cellulose.[3] Kinetic parameters including apparent activation energy (E_a) were measured by analyzing cyclodextrin, a demonstrated surrogate of cellulose for pyrolysis reactions.[1] In addition, kinetics of the reaction were measured in the presence of alkaline earth metal calcium to quantify its catalytic effect on pyrolysis reactions.

Product distributions obtained by PHASR were compared with that obtained by conventional analytical systems to understand the effects of sample preparation, heating rate, crystallinity

of cellulose, heat, and mass transfer limitations on observed product distribution. The kinetic parameters extracted out of the product evolution profiles obtained by PHASR will be useful in understanding the mechanism of formation of important pyrolysis products like levoglucosan.

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Micro-Ratcheted Surfaces for a Heat Engine Biomass Conveyor

Saurabh Maduskar, Christoph Krumm, and Paul J. Dauenhauer

Department of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, MN, USA

Abstract: Difficult-to-handle solid feedstock, heat transfer limitations, and complexity of product mixture are the major design challenges of bio-reactors. The condition of heat transfer to lignocellulosic biomass particles during thermal processing at high temperature (>400 °C) dramatically alters the yield and quality of renewable products. High temperature bio-reactors commonly utilize energy-intensive moving augers or conveyors to transport and inject lignocellulosic particles for gasification, torrefaction, pyrolysis, and combustion for energy and biofuels applications.

In this work, crystalline cellulose particles were discovered to lift off heated surfaces by high speed photography similar to the Leidenfrost effect in hot, volatile liquids.[1] Order of magnitude variation in heat transfer rates and cellulose particle lifetimes was observed as intermediate liquid cellulose droplets transitioned from low temperature wetting (500–600 °C) to fully de-wetted, skittering droplets on polished surfaces (>700 °C). Introduction of macroporosity to the heated surface was shown to completely inhibit the cellulose Leidenfrost effect, providing a tunable design parameter to control particle heat transfer rates in industrial biomass reactors.[2]

Cellulosic particles were shown to spontaneously move on a patterned metal surface of microstructured, asymmetric ratchets (100 by 400 μm) at reactor temperatures with limited resistance to flow. The spontaneous motion of particles orthogonal to ratchet wells was analyzed using high speed photography. Evaluation of the accelerating particles supported the mechanism of propelling viscous forces (50–200 nN) from rectified pyrolysis vapors. Ratcheted metal surfaces utilize heat to propel particles without moving parts while creating a lubricating layer of gas/vapor between the particle and hot surface. The ability to control the movement of organic solid particles and fibers within high temperature systems provides a simple alternative for transporting and processing difficult-to-handle solid feedstocks.

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Bio: Mr. Maduskar is a fourth-year PhD student working under Prof. Paul Dauenhauer in the Chemical Engineering and Materials Science Department at the University of Minnesota. He completed his B.Tech in chemical engineering from the Institute of Chemical Technology, Mumbai, in 2011. Later, he worked as a process engineer at Reliance Industries Limited for 2 years before entering graduate school. His doctoral research is focused on understanding chemical and physical processes during biomass pyrolysis using novel analytical techniques. He is a co-inventor of the Quantitative Carbon Detector (QCD), now sold as PolyARC^{TM} by Activated Research Company, which eliminates calibration in gas chromatography analysis. Currently, he is studying kinetics of biomass pyrolysis using the PHASR technique.

Ravishankar Mahadevan

PhD Student, Department of Biosystems Engineering, Auburn University

Effect of Torrefaction Temperature on Lignin Macromolecule and Product Distribution from Fast Pyrolysis

Ravishankar Mahadevan[1], Sushil Adhikari[1], Rajdeep Shakya[1], Kaige Wang[2], and David Dayton[2]

[1]Department of Biosystems Engineering, Auburn University, Auburn, AL, USA
[2]Energy Technology Division, RTI International, Research Triangle Park, Durham, NC, USA

Abstract: Torrefaction is a low-temperature process considered as an effective pretreatment technique to improve the grindability of biomass as well as enhance the production of aromatic hydrocarbons from catalytic fast pyrolysis (CFP). This study was performed to understand the effect of torrefaction temperature on structural changes in the lignin macromolecule and its subsequent influence on in situ CFP process. Lignin extracted from southern pine and switchgrass (via organosolv treatment) was torrefied at four different temperatures (150, 175, 200, and 225 °C) in a tubular reactor. Between the two biomass types studied, lignin from pine appeared to have greater thermal stability during torrefaction when compared with switchgrass lignin. The structural changes in lignin as a result of torrefaction were followed by using FTIR spectroscopy, solid state CP/MAS ^{13}C NMR, ^{31}P NMR spectroscopy and it was found that higher torrefaction temperature (200 and 225 °C) caused polycondensation and de-methoxylation of the aromatic units of lignin. Gel permeation chromatography analysis revealed that polycondensation during torrefaction resulted in an increase in the molecular weight and polydispersity of lignin. The torrefied lignin was subsequently used in CFP experiments using H^+ZSM-5 catalyst in a micro-reactor (Py-GC/MS) to understand the effect of torrefaction on the product distribution from pyrolysis. It was observed that although the selectivity of benzene-toluene-xylene compounds from CFP of pine improved from 58.3% (torrefaction temp at 150 °C) to 69.0% (torrefaction temp at 225 °C), the severity of torrefaction resulted in a loss of overall aromatic hydrocarbon yield from 11.6% to 4.9% under same conditions. Torrefaction at higher temperatures also increased the yield of carbonaceous residues from 63.9% to 72.8%. Overall, torrefying lignin caused structural transformations in both type of lignins (switchgrass and pine), which is ultimately detrimental to achieving a higher aromatic hydrocarbon yield from CFP.

Bio: Ravishankar received his BS in chemical engineering at Anna University, India, and is currently studying for his PhD in biosystems engineering at Auburn University. His research is focused on the thermochemical conversion of lignocellulosic biomass and algae for the production of fuels and chemicals.

Nii Ofei Mante

Research Chemical Engineer, Energy Technology Division, RTI International

Production of Hydrocarbon Liquid Fuel from Biocrude by Hydroprocessing

Ofei Mante, David C. Dayton, David Barbee, Kaige Wang, and James Shumaker

Energy Technology Division, RTI International, Research Triangle Park, NC, USA

Abstract: Upgrading of pyrolysis bio-oil by catalytic hydrotreating (HDT) to produce transportation fuels continues to be challenging due to the chemical complexity and thermal instability of bio-oil. Typically, rapid catalyst coking/deactivation reactions are commonly experienced. Besides, there is a lack of understanding of the impact of each class of oxygenated compound present in the bio-oil on the HDT process.

In contrast to the traditional approach for the production of hydrocarbon-based biofuels from pyrolysis derived bio-oil, RTI is developing an advanced biofuels technology that integrates the catalytic biomass pyrolysis process and hydrotreating. It is hypothesized that the biocrude could be hydrotreated fairly well without the usual preprocessing or the stabilization step. In this work, several well-characterized biocrudes produced from catalytic pyrolysis of loblolly pine were hydrotreated over a sulfided catalyst using a single-stage approach. The goal of this research effort is to gain insight on the HDT performance in terms of product yields, liquid product quality, and hydrogen consumption.

The presentation will discuss in detail the effect of biocrude composition and process condition (temperature, H_2 pressure, H_2/oil ratio, and LHSV) on product yield/quality and hydrogen consumption. One of the significant findings from this work is that biocrude produced by catalytic biomass pyrolysis could be successfully upgraded into hydrocarbon liquid fuels without a stabilization step. A detailed knowledge of the impact of biocrude composition and process conditions could result in innovative technology solutions to control reaction selectivity and minimize hydrogen demand.

Catalytic Biomass Pyrolysis Studies at Pilot-Scale

Ofei Mante, David C. Dayton, David Barbee, James L. Shumaker, and Kaige Wang

Energy Technology Division, RTI International, Research Triangle Park, NC, USA

Abstract: Catalytic fast pyrolysis is the direct liquefaction process used by RTI to produce a hydrocarbon-rich biocrude that can subsequently be upgraded by hydrotreating to make refinable intermediates and "drop-in" advanced biofuels. As part of the technology development, the process has been scaled up from bench-scale to 1 ton per day pilot-scale. Evaluation of the process at the pilot-scale is one of the critical steps being taken by RTI to

address a number of technical challenges facing catalytic pyrolysis and to collect required processing and engineering data to support the demonstration and commercialization of the technology.

To date, several experimental campaigns have been conducted to optimize the catalytic biomass pyrolysis process to achieve a high degree of deoxygenation while maximizing biocrude production and improving the biocrude thermal stability. A commercially available spray dried, non-zeolite, alumina-based catalyst has been exclusively studied so far. The quality and biocrude yield have been evaluated at different temperatures and other process conditions. Typically, partially deoxygenated biocrude with oxygen contents between 20 and 25 wt% is produced. Gas chromatography mass spectrometry analysis has shown high amounts of oxygenated aromatics in the partially deoxygenated biocrude. Current results from RTI's 1 ton per day pilot-scale catalytic pyrolysis unit show a biocrude yield up to 19.2 wt% is achievable. This presentation will be used to discuss in detail the results that have been obtained from several studies and highlight the progress that has been made.

Bio: Dr. Mante is currently a Research Chemical Engineer in RTI International's Energy Technology Division. He has more than 10 years of experience in thermochemical conversion of biomass and his research efforts are geared toward addressing technical barriers and challenges related to processing and conversion of biomass. Dr. Mante is interested in the use of thermal, chemical, and innovative catalytic processes based on a biorefinery concept, but analogous to the existing petroleum refinery to produce a wide variety of biomass-derived intermediates that can be used in today's processing infrastructures for liquid fuels, bioproducts, and other essentials of modern life.

Daniel McClelland

Graduate Student, Huber Research Group, Department of Chemical and Biological Engineering, University of Wisconsin-Madison

Functionality and Molecular Weight Distribution of Red Oak Lignin before and after Pyrolysis and Hydrogenation

D.J. McClelland[1], A.H. Motagamwala[1,2], Y. Li[2,3], M.R. Rover[4], A.M. Wittrig[6], C. Wu[6], J.S. Buchanan[6], R.C. Brown[4,5], J. Ralph[2,3], J.A. Dumesic[1,2], and G. W. Huber[1]

[1]Department of Chemical and Biological Engineering, University of Wisconsin-Madison, Madison, WI, USA
[2]Great Lakes Bioenergy Research Center, Wisconsin Energy Institute, Madison, WI, USA
[3]Department of Biochemistry and Department of Biological Systems Engineering, University of Wisconsin-Madison, Madison, WI, USA
[4]Bioeconomy Institute, Iowa State University, Ames, IA, USA
[5]Department of Mechanical Engineering, Iowa State University, Ames, IA, USA
[6]ExxonMobil Research and Engineering, Annadale, NJ, USA

Abstract: Three red oak–derived lignin samples—1) lignin extracted from red oak chips using γ-valerolactone (GVL lignin), 2) lignin extracted from the pyrolysis oil of red oak chips by fractionation followed by washing with water (pyrolytic lignin), and 3) pyrolytic

lignin hydrogenated over Ru/C at 423 K (hydrogenated pyrolytic lignin)—were analyzed with Fourier-transform ion cyclotron resonance mass spectrometry (FT-ICR MS), nuclear magnetic resonance spectroscopy (NMR), and gel-permeation chromatography (GPC). The average molecular weight of the lignin determined by GPC decreased from 4660 Da to 831 Da after pyrolysis and further to 726 Da after hydrogenation. More than 1100 distinct molecular weights were observed with FT-ICR MS of the lignin streams. The O/C and H/C ratios, obtained from FT-ICR MS, decreased from 0.33 and 0.94 to 0.25 and 0.90 after pyrolysis, suggesting dehydration of sidechain –OH to alkenes during pyrolysis. The O/C ratio decreased to 0.23, and the H/C ratio increased to 1.11 after hydrogenation, indicating that the compounds are at least partially saturated during the hydrogenation. Quantitative ^{13}C NMR reveals a large decrease in the C-O aliphatic carbons (from 35.0% to 11.4% of carbons) during pyrolysis accompanied by an increase in carbonyl and C-C aliphatic carbons (from 0% and 1.3% to 4.2% and 15.4% of carbons respectively). The hydrogenation decreases the carbonyl and aromatic carbons (from 4.2% and 69.0% to 2.6% and 37.0%) and increases the C-C and C-O aliphatic carbons (from 15.4% and 11.4% to 41.3% and 19.2%, respectively). The methoxy region, a subregion of the C-O aliphatic region, decreased from 13.3% to 6.3% of carbons after pyrolysis and 4.2% of carbons after subsequent hydrogenation. Changes in the C-C aliphatic, C-O aliphatic, aromatic, and aldehyde functionalities for the three different types of lignin studied were observed using HSQC NMR. Benzaldehyde and cinnamaldehyde are seen for the lignin and pyrolytic lignin but completely disappear after hydrogenation. These aldehyde functionalities are highly reactive during hydrogenation and are potentially responsible for coke formation. Correlations between C-C aliphatic and aromatic functionalities were observed using HMBC NMR. These correlations increased after both pyrolysis and hydrogenation, while C-C to C-O aliphatic correlations increase after hydrogenation. Quaternary aromatics to aromatics and C-C aliphatic to carboxylic acid/ester correlations are seen in lignin, pyrolytic lignin, and hydrogenated pyrolytic lignin. Ketone correlations appear after pyrolysis but, similarly to the aldehydes, disappear after the hydrogenation.

Bio: Mr. McClelland is a fourth-year graduate student who got a BS in chemical engineering from the Illinois Institute of Technology in 2012. His work focuses on the catalytic upgrading of biomass-derived feedstock to fuels and chemicals. He has worked on cellulose conversion as well as upgrading of pyrolysis oils. His current work focuses on the use of NMR to elucidate chemical compositions and reaction products for biomass conversion, which are unable to be identified by traditional means such as gas chromatography, high performance liquid chromatography, or mass spectrometry.

Charles J. McGill

PhD Graduate Student, Chemical and Biomolecular Engineering, North Carolina State University

Establishing Elementary Reactions of Hemicellulose Torrefaction

Charles J. McGill, Arnab Bose, and Phillip R. Westmoreland

North Carolina State University, Raleigh, NC, USA

Abstract: Torrefaction kinetics of xylose, mannose, and other monomer components of hemicelluloses are being measured over the temperature range of 200 °C to 300 °C. Torrefaction provides a potential method for preconditioning biomass, improving it as a feedstock for pyrolysis and gasification. A more precise understanding of the chemical mechanism of torrefaction is needed so the optimal reaction conditions can be chosen.

Simultaneous thermogravimetric analysis and calorimetry (SDT Q600, TA Instruments) provide overall kinetics during linearly ramped temperature increase such as 20 °C/min, while pyrolysis products at different temperatures are analyzed using flash pyrolysis (Pyroprobe 5200, CDS Analytical) with product analysis performed using two-dimensional gas chromatography and time-of-flight mass spectroscopy (Pegasus 4D, Leco). Major products of pentose reactions were shown to include glycolaldehyde, furfural, and dihydroxyacetone. Hexose reactions included many of the same products as the pentose reactions but with the addition of 5-hydroxymethylfurfural and bicyclics such as 1,6-anhydro-D-mannopyranose. Thermogravimetric analysis of the reactions showed that there are two different stages of reaction for the monomers, a primary stage peaking at roughly 210 °C and a secondary one peaking at roughly 300 °C.

In parallel, computational quantum chemistry (Gaussian 09 and GaussView) has been used to predict transition states for reactions involved in torrefaction. The transition states have been initially modeled at a B3LYP/6-311++G(d,p) level of theory. This modeling will be used to build reaction pathways leading to the major observed products and to describe the reaction observations made with thermal analysis.

Bio: Charles J. "Chas" McGill is a PhD student and ChE graduate research assistant, conducting research with Prof. P.R. Westmoreland on pyrolysis chemistry of hemicellulose and related sugars. He earned his BSChE in 2011 from Clemson University, and he subsequently worked at Corning Inc. in Wilmington, NC, from 2011 to 2013.

M. Tomasi Morgano

PhD Student, Department Pyrolysis/Gas Treatment, Institute for Technical Chemistry, Karlsruhe Institute of Technology

Screw Pyrolysis of Sewage Sludge: A Techno-economic Analysis

M. Tomasi Morgano, H. Leibold, F. Richter, H. Seifert, and D. Stapf

Institute for Technical Chemistry, Karlsruhe Institute of Technology (KIT), D-76344 Eggenstein-Leopoldshafen, Germany

Abstract: Sewage sludge is the by-product of wastewater treatment processes before its discharge in rivers. The introduction of the European Directive (UWWTD 91/271/EEC) on the treatment of municipal wastewater increased the amount of sewage sludge in Europe, where more than 10 million tons (dry matter) are produced annually. In Europe, the thermal treatment of sewage sludge, i.e., mono-incineration or co-firing in large waste to energy, coal power plants, and cement rotary kilns plays a major role. Substantial investment and operational costs characterize such facilities. Besides, the number of large wastewater and sewage sludge treatment plants, respectively, is relatively small compared to the total number of plants. Small-scale wastewater treatment in rural areas also requires thermal sludge treatment. Moreover, alternative technologies are arising, and the main target is nutrients recovery with a special focus on phosphorus. The recovery of valuable nutrients is affected by the mineral structure of the ashes, which is controlled by its temperature history. The char from pyrolysis processes may have advantages in comparison to the ash from the direct combustion of sewage sludge. The aforementioned issues, i.e., the small scale (below 1 MW) and the nutrients recovery, suggest that pyrolysis in screw reactors may become an attractive alternative technology for the efficient and effective thermal conversion of sewage sludge and nutrient recovery and recycling.

In this work, about 100 kg of dried sewage sludge from a municipal wastewater treatment plant in Germany were processed at temperatures between 350 °C and 500 °C in the newly developed STYX pyrolysis reactor at KIT. Well-defined pyrolysis char was produced; the integrated hot gas filtration with online re-cleaning enables the production of particle-free vapors and condensates, respectively. The mass, elemental, and energy balances will be presented. The pyrolysis products were characterized into detail with a focus on the pyrolysis char (BET analysis, phosphorus availability, etc.). The heavy metals issue will be addressed. Finally, an innovative concept for combined heat and power generation from the pyrolysis condensates and gases in a multistage process will be presented. The process is based on a micro gas turbine for power generation and char production for further material utilization. On the basis of the process flow sheet, a techno-economic analysis is carried out for a 500 kW_T pyrolysis reactor.

Bio: Mr. Morgano has been a PhD student at the Karlsruhe Institute of Technology, Institute for Technical Chemistry since 2013. He graduated in energy engineering, advanced power plants from Polytechnic of Milan in 2013. His research focuses on the development of intermediate pyrolysis reactors for the upgrading of low-rank feedstocks, characterization of pyrolysis products, design of pyrolysis-based process chains in decentral systems, and development of a mathematical model for pyrolysis of wood in screw reactors.

Calvin Mukarakate

Senior Scientist, National Bioenergy Center, National Renewable Energy Laboratory

Biomass Pyrolysis Vapor Deoxygenation over Mo_2C to Produce Paraffinic and Aromatic Molecules: The Deactivation and Reactivation of Mo_2C

Calvin Mukarakate[1], Josiah McMillen[1], Mengze Xu[2], Kristiina Iisa[1], Mark R. Nimlos[1], Daniel A. Ruddy[1], and Joshua A. Schaidle[1]

[1]National Bioenergy Center, National Renewable Energy Laboratory, Golden, CO, USA
[2]Department of Chemistry and Geochemistry, Colorado School of Mines, Golden, CO, USA

Abstract: Catalytic fast pyrolysis (CFP) of biomass is an attractive technology for producing renewable liquid transportation fuels. Zeolites, especially HZSM-5 catalysts, are used during CFP because of their ability to almost completely deoxygenate biomass pyrolysis vapors to form hydrocarbons; however, these materials suffer from low yields due to high light gas production and coke formation. In order to address the barriers associated with zeolites, catalysts effective at both deoxygenation and hydrogenation of biomass pyrolysis vapors should be explored. Bifunctional materials possessing metallic sites and acidic sites, for example, molybdenum carbide (Mo_2C), have demonstrated promising performance in the deoxygenation of biomass pyrolysis model compounds such as guaiacol and acetic acid. In this study, we explored the hydrodeoxygenation of biomass pyrolysis vapors using Mo_2C with low-pressure hydrogen to produce hydrocarbon molecules. These studies were carried out using cellulose, lignin, and pine in a pyrolysis molecular beam mass spectrometer (py-MBMS) and a py-GCMS/FID/TCD system. The results show that Mo_2C upgrades biomass pyrolysis vapors to form paraffins and aromatics with comparable yields to ZSM-5. The experiments conducted with extracted lignin and cellulose feeds demonstrated that fresh Mo_2C converted the lignin vapors to aromatic compounds and small paraffins and the cellulose vapors exclusively to paraffins. After pyrolysis of a couple of biomass samples, the product selectivity changed from paraffinic and aromatic molecules to furan and alkyl furans and phenol and alkyl phenols. This decrease in deoxygenation ability of Mo_2C is attributed to adsorption of multi-ring aromatics on the catalyst surface. The deactivation and reactivation of this catalyst will also be discussed. The results from this work will open attractive new avenues for converting biomass into intermediates for liquid transportation fuels.

Bio: Dr. Mukarakate's research efforts focus on thermochemical conversion of biomass into hydrocarbon fuels and chemicals. He has published over 30 technical papers and government reports. His research includes catalytic fast pyrolysis of biomass vapors for fuels, conversion of biomass to monomers for renewable polymers, and reforming of aqueous waste streams to produce value-added chemicals and hydrogen. Dr. Mukarakate joined NREL in June 2008. He received his PhD in physical chemistry from Marquette University, Milwaukee, WI, and a BSc honors in engineering from the University of Zimbabwe.

Charles Mullen

Research Chemist, USDA-ARS, Eastern Regional Research Center

Co-pyrolysis of Biomass and Polyethylene over HZSM-5: Effects of Plastic Addition on Coke Formation and Catalyst Deactivation

Charles A. Mullen, Christina Dorado, and Akwasi A. Boateng

U.S. Department of Agriculture's Agricultural Research Service, Eastern Regional Research Center, Wyndmoor, PA, USA

Abstract: Fast pyrolysis processes are among the most effective methods for liquefaction of lignocellulosic biomass to energy carrier intermediates and chemical precursors. Conducted in the presence of a zeolite catalyst such as HZSM-5, fast pyrolysis of biomass can promote the rejection of problematic oxygen from the organic liquid products by initiation of dehydration, decarbonylation, and aromatization reactions. These pyrolysis oils are composed of mostly aromatic hydrocarbons and some phenolic compounds. Unfortunately, these reactions remove hydrogen from the already hydrogen-deficient biomass starting material, limiting the yield of hydrocarbons and leading to coke formation that ultimately results in catalyst deactivation. While these carbon deposits or coke can be removed by burning them out, combustion leads to reduction of catalyst activity. Recently co-pyrolysis of biomass and plastic has been studied as a means of mitigating hydrogen-deficiency issues that lead to coking with an added benefit of disposing of waste plastics effectively. Previous studies have shown an enhancement of aromatic yields when polyolefins were copyrolyzed with biomass over fresh HZSM-5,[1-3], but the effect of catalyst deactivation with repeated use of the catalyst has not been studied. In this study, we used a py-GC/MS system with an external catalytic reactor to perform ex situ co-catalytic pyrolysis of switchgrass and polyethylene (1/1 w/w). Results showed that blending of the hydrogen-rich polyethylene with biomass led to a slower rate of catalyst deactivation as measured by the production of aromatic hydrocarbons over repeated uses of the catalyst. Total coke yield was also measured and compared. Furthermore, changes in selectivity to various hydrocarbon and oxygenated products with polyethylene blending and catalyst use will also be discussed.

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Bio: Dr. Mullen is a Research Chemist with USDA-ARS at the Eastern Regional Research Center in Wyndmoor, PA. He holds a BA in chemistry from the University of Pennsylvania (2002) and a PhD in chemistry from the University of North Carolina–Chapel Hill (2007). He has 9 years of experience in biomass pyrolysis chemistry and related research. Currently, he is the primary chemist on ARS's congressionally appropriated Farm Scale Pyrolysis Biorefining project and a co-PI on the competitively funded FarmBio3 project. He has over 50 published articles, including 48 peer-reviewed, 2 issued U.S. patents, and over 20 abstracts for presentation at national and international meetings.

Mark R. Nimlos

Principal Scientist, National Renewable Energy Laboratory

Catalytic Fast Pyrolysis for Chemical Products

Mark R. Nimlos[1], Calvin Mukarakate[1], Lintao Bu[1], Nolan Wilson[1], Peter Ciesielski[2], Ruoran Zhang[2], Mike Himmel[2], and Danniel Ruddy[1]

[1]National Bioenergy Center, National Renewable Energy Laboratory, Golden, CO, USA
[2]Biosciences Center, National Renewable Energy Laboratory, Golden, CO, USA

Abstract: Catalytic fast pyrolysis (CFP) of biomass is a recognized conversion technology for producing hydrocarbon fuels from lignocellulosic biofuels, but it is less regarded as an approach for making higher value chemical products. Producing chemicals can positively impact the economics of biofuel production much as they do in existing petrochemical refineries. In this presentation we will discuss our work on improving the selectivity of CFP to make high value chemical products, their separation, and synthesis of bio-based polymers. Work on several chemical products will be discussed. 1) Phenol is often formed from CFP and can often be found in the aqueous phase of the product liquid. As such, it must be removed before the water can be discharged, which adds significant cost to a biofuels process. Furthermore, producing phenol from petroleum chemicals (benzene) is an energy-intensive process. Isolating phenol from wastewater may decrease the cost of biofuels production and the amount of greenhouse gas emissions. We have worked on improving the selectivity for phenol formation, isolating it from CFP liquids and using it to prepare polymers. 2) Cyclopentenone is another prominent molecule in the CFP aqueous streams, though there is no apparent direct use of this compound in existing commodity polymers. However, we have found that it can be used with nanocrystalline cellulose to form strong composite films. 3) Methylphenols and 2-naphthol produced from CFP could be used to form carbonate resins or polymers with different physical properties from those obtained from phenol.

In addition to these products from microporous zeolites, we are also investigating the selective formation of oxygenates such as furans, which are thermodynamically favored in acidic catalysts. We are investigating catalysts that are weaker than ZSM-5 for the formation of furans and will report on the results using some mesoporous alumina silicates, such as MCM-41.

Bio: Dr. Nimlos is a Principal Scientist in the National Bioenergy Center at the National Renewable Energy Laboratory, where he has worked for more than 27 years on a variety of renewable energy projects. In biomass conversion, the bulk of his work has focused on thermochemical processes and the utilization of biofuels. He has authored or co-authored over 100 peer-reviewed scientific papers/book chapters. His areas of expertise are chemical and physical processes, including chemical kinetics, reaction mechanisms, and molecular modeling.

Mariefel V. Olarte

Senior Research Engineer, Pacific Northwest National Laboratory

Analysis and Catalytic Upgrading of Pyrolysis Oils from Various Biomass Feedstocks

Mariefel V. Olarte[1], Alan H. Zacher[1], Daniel (Miki) Santosa[1], Huamin Wang[1], Esther Wilcox[2] and Corinne Drennan[1]

[1]Pacific Northwest National Laboratory, Richland, WA, USA
[2]National Renewable Energy, Golden, CO, USA

Abstract: The cost of biomass feed impacts heavily the overall cost of converting biomass into renewable liquid transportation fuels. Currently, achieving the $80 per metric ton target will require sourcing and blending together cheaper feedstocks other than the typical woody biomass source such as pine. Since there are fundamental differences in the chemical makeup of these feedstocks, pyrolysis oil quality is expected to be impacted. The impact of pyrolysis oil quality on the robustness of the subsequent catalytic bio-oil hydrotreating needs to be determined. Here, we report the result of compositional analysis and subsequent bio-oil upgrading of several pyrolysis oils sourced from clean pine, oak, and a blend consisting of clean pine and construction and demolition waste. Pyrolysis was done at two different temperatures (480 °C and 500 °C) and two residence times (~2.9 and ~3.5 seconds) at NREL. These oils were analyzed and upgraded at PNNL. Preliminary results suggest that upgraded product oil density did not vary much between tested bio-oils from different feedstock and pyrolysis conditions using a 60-mL continuous trickle bed reactor for about 80 hours. The upgrading was done using two sulfided catalyst beds: RuS/C (170 °C, 2000 psig H_2) and sulfided commercial HT catalyst (400 °C, 2000 psig). However, low-temperature pre-treatment is still necessary to enable longer time-on-stream processing.

Bio: Dr. Olarte joined PNNL in 2011. Since then, she has worked on thermochemical upgrading of biomass focusing on the catalyst development and processing of pyrolysis oils for hydrocarbon production. She also has interest in the development and standardization of techniques used to characterize pyrolysis oils. Aside from catalytic upgrading of pyrolysis oils, she had earlier worked on catalytic hydrothermal gasification, hydrothermal liquefaction, fast pyrolysis, aqueous phase reforming, and lignin depolymerization. She earned her BS in chemical engineering, major in paper science and technology from the University of the Philippines Los Baños and her MS in paper science and engineering and PhD in chemical engineering at the Georgia Institute of Technology in Atlanta.

Jessica Olstad

Thermochemical Process Engineer, National Bioenergy Center, National Renewable Energy Laboratory

Ex-situ Catalytic Fast Pyrolysis in a DCR – Catalyst Effects

Jessica Olstad, Mark Jarvis, Kimberly Magrini, and Yves Parent

National Renewable Energy Laboratory, Golden, CO, USA

Abstract: Ex-situ catalytic upgrading of vapors was performed on NREL's coupled pyrolyzer/Davison Circulating Riser (DCR) systems. The DCR, a pilot-scale FCC unit that was designed by W.R. Grace for evaluating FCC catalysts and upgraded products, is ideal for providing refinery-relevant information about turning bio-based materials into energy-dense liquid fuels and high-value chemicals. The objective of this work was to study the effect of using different catalysts (equilibrium Y-type zeolite, destabilized ZSM-5, and metal-modified ZSM-5 catalysts) to upgrade mixed hardwood pyrolysis vapors. The pyrolysis vapors were produced in a 2" i.d. fluidized sand bed at 500 °C, 37psia, with nitrogen as the primary fluidization gas (biomass to nitrogen ratio of 0.5). The pyrolysis vapors were hot filtered (400 °C), and then a split stream was sent to the DCR for upgrading. The DCR was run adiabatically, with upgrading reactions occurring at 500 °C and 32 psia, and a residence time of approximately 1s, and product stripping and catalyst regeneration occurring at 500 °C and 600 °C, respectively. The effect of catalyst on the upgraded products, including catalyst circulation, coke rate, liquid compositions, and light gas compositions, will be discussed.

Bio: Ms. Olstad earned her bachelor's degree in chemical and biochemical engineering from the Colorado School of Mines in 2009. After graduating, she joined NREL working for the Concentrated Solar Program and the National Bioenergy Center. During her time in the solar program, she worked on heat transfer material development, characterization, and compatibility; she also performed a study using a distributed temperature sensing system to determine possible use in concentrated solar power plants. In 2012, Jessica left the solar program and concentrated all of her attention to the National Bioenergy Center. She worked on NREL's 4" fluidized bed reactor, studying how different feedstocks and catalysts affect the gasification product composition. Jessica performs analytical work, specifically on bio-based materials and catalyst characterization. Currently, Jessica is the lead engineer on the FCC unit of NREL's pilot-scale tandem pyrolysis-DCR system, where the research focuses on pyrolysis vapor phase upgrading.

Sunkyu Park

Associate Professor, Department of Forest Biomaterials, North Carolina State University

Techno-economic Analysis of Phenolic Compounds Extraction from Pyrolysis Bio-Oil as Drop-In Fuels for Diesel Engines

Sunkyu Park, Hoyong Kim, Carlos Aizpurua, Camilla Abbati de Assis, Tiegang Fang, Stephen Kelley, and Ronalds Gonzalez

Department of Forest Biomaterials, North Carolina State University, Raleigh, NC, USA

Abstract: Interest in pyrolysis bio-oil as a potential renewable and sustainable alternative for transportation fuels has increased. However, low heating value and low miscibility make direct application of bio-oil difficult. It is generally agreed that upgrading of bio-oil is a prerequisite despite the high capital and operation costs. Among the bio-oil components, however, phenolic compounds exhibit relatively higher miscibility and have higher heating values compared to carbohydrate-derived compounds. There are a few studies related to phenolics recovery from bio-oil, but most of them used organic solvent (e.g., methyl isobutyl ketone or ethyl acetate), which requires additional evaporation and mixing steps. In this study, we develop a process that included direct extraction of phenolics from bio-oil into diesel.

Pyrolysis bio-oil produced from loblolly pine was extracted with diesel or oleic acid methyl ester (OAME). Diesel extraction yield of bio-oil was 6.7%, while OAME extraction yield was 13.3%. With the simulated pyrolysis capacity of 500 tons dry biomass per day, a process simulation was developed in Aspen Plus and capital/operation cost variables were adapted from NREL 2010 and PNNL 2013 design reports. To enhance process feasibility, remaining bio-oils after extraction were regarded as a heating source for burner fuel, and credit was assigned based on their heating value.

Minimum fuel selling price (MFSP) of crude bio-oil without extraction is 0.9$/gal and it is 60% higher than the price of natural gas. Due to low extraction yield, MFSP of transportation fuel in the diesel extraction case soared 10.2$/gal, which indicates economically infeasible. However, MFSP of transportation fuel in the OAME extraction case was only 2.5$/gal because of the twice higher extraction yield. Actual value determination of the remaining bio-oil after extraction as a burner fuel and engine performance test of transportation fuel produced by diesel and OAME extraction of bio-oil are required to clarify the process feasibility.

Bio: Dr. Park is an associate professor in the Department of Forest Biomaterials, North Carolina State University. He received his PhD in 2006 in the same department and worked in DOE's NREL as a postdoctoral researcher. Since 2009 when he joined the department, he has over 60 journal papers and conducted over 25 research projects. He was recently recognized as a University Faculty Scholar at North Carolina State University.

Joseph Polin

Graduate Research Assistant, Mechanical Engineering Department, Iowa State University

Process Intensification of a Fluidized Bed Pyrolyzer via Autothermal Operation

Joseph P. Polin[1], Lysle E. Whitmer[2], Ryan G. Smith[2], and Robert C. Brown[1,2]

[1]Department of Mechanical Engineering, Iowa State University, IA, USA
[2]Bioeconomy Institute, Iowa State University, IA, USA

Abstract: Fast pyrolysis is a mildly endothermic process, requiring thermal energy to deconstruct and volatilize biomass. Providing this heat from external sources requires either high temperature heat exchange tubes within the reactor or circulation of a solid heat carrier between the reactor and a combustor. We have developed autothermal pyrolysis to internally provide the enthalpy of pyrolysis to a fluidized bed pyrolyzer. Oxygen is admitted to the reactor as part of the fluidizing gas, which combusts part of the biomass or pyrolytic products to support pyrolysis reactions occurring in parallel. Previous researchers have attempted autothermal pyrolysis but found that bio-oil yield and quality suffered. We have found that careful thermal management and control of equivalence ratio can avoid these deleterious effects, allowing air-blown pyrolysis for the production of bio-oil and biochar.

In the present study, red oak and corn stover were chosen as feedstock for pilot-scale experiments in a fluidized bed pyrolyzer in combination with a fractional recovery system consisting of three condensers and three electrostatic precipitators alternating in series. The reactor was enclosed in clam-shell electric heaters to overcome baseline heat losses and allow adiabatic operation to be simulated during autothermal pyrolysis experiments at 500 °C. Changes in electric load to these heaters upon feeding biomass allowed the enthalpy of pyrolysis for the feedstocks to be calculated.

Under autothermal operation, the reactor's biomass throughput increased from 5 kg/h to 25 kg/h, and bio-oil yields were observed to significantly increase, especially the heavy ends of bio-oil (that is, the organics recovered in stage fractions 1 and 2). Both the yield of pyrolytic sugar and phenolic monomers in the heavy ends increased compared to conventional nitrogen-blown pyrolysis. One possible explanation is that oxygen enhanced the depolymerization of the lignin sheath surrounding plant polysaccharides in lignocellulose, which produced more phenolic monomers and helped liberate anhydrosugars. This partial oxidation of lignin is thought to have provided about half of the heat of combustion, with the other half coming from the oxidation of non-condensable gases released during pyrolysis (carbon monoxide, methane, ethane, and ethylene).

Bio: Joseph is a graduate student at Iowa State University working on his PhD in mechanical engineering with a co-major in biorenewable resources and technology. He received an MS in agricultural and biosystems engineering from South Dakota State University and a BS in chemical engineering from the University of Massachusetts–Amherst. His research focuses on autothermal pyrolysis and process intensification using pilot- and lab-scale fluidized bed reactor systems.

Fenglei Qi

PhD Candidate, Mechanical Engineering, Iowa State University

Thermal DEM Simulation of Particle Heat Transfer in a Lab-Scale Double Screw Reactor

Fenglei Qi and Mark Mba Wright

Department of Mechanical Engineering, Iowa State University, Ames, IA, USA

Abstract: Lab-scale double screw reactors have been alternatively developed as biomass fast pyrolysis reactors at Iowa State University. Previous studies showed bio-oil yield in the double screw reactor up to 65%, which is comparable to the performance of fluidized bed reactors. Understanding heat transfer mechanisms within the reactor is necessary for reactor design, scale-up, and optimal operation. In this research, a thermal Discrete Element Method (DEM) model is developed and applied to simulate particulate flow as well as particle heat transfer in the lab-scale double screw reactor. Particle hydrodynamics is resolved with traditional DEM model and thermal conduction by particle-particle contact, conduction through stagnant interstitial fluid, and thermal radiation are considered for the heat transfer between particles. The developed model is successfully validated by comparing simulated temperature profiles with experimental measurements in packed beds. Heat transfer in the screw reactor is modeled and the influences of operating conditions such as screw rotation speed, solid feed rate, and biomass particle size are investigated. It is observed that particle mixing affects temperature profiles in the reactor and particle axial segregation causes the oscillation of the temperature profile in the axial direction. Biomass heating rate is improved because of enhanced transverse recirculation at higher screw rotation speed. At smaller rotation speed, the longer residence time is favorable for achieving a narrow distribution of particle temperature at the outlet of the reactor. At low biomass feed rate (volumetric filling level<0.2), particle mixing has insignificant effects on heat transfer since biomass particles do not require a lot of mixing efforts to have contact with hot sand particles. Smaller particles are heated up faster at low biomass feed rates due to low thermal capacity of small particles, while biomass heating rates are not affected by particle size in the investigated particle size range at high biomass feed rates (volumetric filling level>0.4). The biomass heating rate in the screw reactor (20–50 K/s) is smaller than the reported biomass heating rate in the fluidized bed (usually>100 K/s).

Bio: Mr. Qi is a PhD candidate in mechanical engineering at Iowa State University. He got his master's degree from China University of Petroleum with a focus on CFD modeling of syngas high temperature air combustion. The author's current research mainly focuses on the development of CFD/DEM models for reactive multiphase flows encountered in biomass thermochemical conversion processes.

Jadid E. Samad

Postdoctoral Engineer, Southern Research, Energy and Environment

Thermocatalytic Process for Biomass Conversion to Acrylonitrile for Production of Carbon Fibers

Jadid E. Samad, Zora Govedarica, Lindsey Chatterton, and Amit Goyal

Southern Research, Energy and Environment, Durham, NC, USA

Abstract: Polyacrylonitrile (PAN)-based carbon fibers are gaining rapid traction in automotive applications for their specific mechanical properties (250 ksi tensile strength and 25 Msi Young's modulus). Its monomer, acrylonitrile (ACN), is commercially produced from petroleum-based feedstock (e.g., propylene). An alternate production route is using biomass-derived feedstock (e.g., glycerol is currently being explored). This route enables high selectivity to ACN with an array of valuable by-products but is limited to purified glycerol obtained from biodiesel production. As a result, although promising, this route has yet to become economically attractive.[1]

Southern Research is developing a biomass to ACN (B2ACN) process under a cooperative agreement with the Department of Energy.[2] The goal of this work is to pursue a cost-effective process for ACN production at mild conditions using biomass-derived sugars as raw materials. The entire B2ACN process consists of multiple catalytic reaction steps. In the first step, using novel multi-functional catalysts, single-pass conversion of sugar to C2 and C3 polyols (oxygenates) has been achieved. These oxygenates will be converted to acrolein and acrylonitrile, respectively, in the subsequent steps. Based on preliminary results, significantly reduced cost (~15 –22%), as well as greenhouse gas emissions (~37%), compared to typical ACN processes have been forecasted.

In this presentation, the overall process will be discussed with particular emphasis on the first reaction step (i.e., thermocatalytic sugar conversion to oxygenates).

[1] M. Olga Guerrero-Pérez, Miguel A. Bañares, Metrics of acrylonitrile: From biomass vs. petrochemical route, Catalysis Today, Volume 239, 1 January 2015, Pages 25-30

[2] Department of Energy, Energy Department announces $11 million to advance renewable carbon fiber production from biomass. http://energy.gov/eere/articles/energy-department-announces-11-million-advance-renewable-carbon-fiber-production

Bio: Dr. Samad specializes in heterogeneous catalyst development and characterization and testing for energy- and environment-related applications. As a graduate student, he has worked on multiple academic research projects on rational catalyst design for specific applications. As a postdoctoral engineer at Southern Research, he undertakes research initiatives in the areas of sustainable chemistry and catalyst development. His main focus is the DOE-funded ($6 million), multistep thermocatalytic process to produce acrylonitrile from biomass-derived sugars. Aside from his catalyst development and evaluation works, he also conducts the techno-economic and life cycle analysis and helps in other projects to find novel ways to test materials for specific applications. Dr. Samad completed his BS in chemical engineering at Bangladesh University of Engineering and Technology, Bangladesh.

He received his MS from the University of Alberta, Canada, and his PhD from the University of South Carolina, both in chemical engineering.

Taylor C. Schulz

Postdoctoral Research Associate, Bioeconomy Institute, Iowa State University

Continuous Pilot-Scale Loblolly Pine Liquefaction to a Partially Deoxygenated Bio-Oil

Taylor C. Schulz[1], Martin R. Haverly[1, 2], Lysle E. Whitmer[1], Andrew J. Friend[1], Jordan Funkhouser[1], Ryan G. Smith[1], and Robert C. Brown[1, 2]

[1]Bioeconomy Institute
[2]Department of Mechanical Engineering Iowa State University, Ames, IA, USA

Abstract: We describe a continuous pilot-scale process in which loblolly pine is converted to a partially deoxygenated bio-oil via solvent liquefaction. The primary objective of this project is to convert the pine feed to a bio-oil containing less than 20 wt. % oxygen at a 50 wt. % yield using a recycled wood oil product. This bio-oil is to then be hydroprocessed to bio-crude and upgraded to gasoline and diesel fuels. The pilot-scale system generated three unique cuts of bio-oil (light, medium, and heavy wood oil), an aqueous fraction, non-condensable gaseous products, and bio-char. Biomass and solvent (hydrocarbon and recycled wood oil) were fed to the liquefaction unit at rates of 0.5–1 kg/h and 2–4 kg/h, respectively. The liquefaction unit was operated between 300–400 °C and 27–48 bar. The process described above is an improvement on previous research[1,2] in that it does not require a catalyst/reducing gas and it operates at lower system pressures.

Moisture-free elemental analysis of the biomass resulted in the following distribution: C—52.0 wt. %, H—5.37 wt. %, and O—42.6 wt. %. Concentrations of N and S were negligible in the feedstock. Preliminary experiments utilizing a hydrocarbon solvent resulted in a biomass conversion of 83.5% and mass closure of 99.8 wt. %. The product distribution of bio-oil produced using the hydrocarbon solvent averaged 92.6 wt. % liquid products, 2.22 wt. % gaseous products, and 4.09 wt. % bio-char. The light, medium, and heavy wood oil products contained 0.5 to 1.4 wt. % moisture, as determined via Karl Fischer titration. Operation of the pilot-scale liquefaction unit resulted in a bio-oil yield of 48.0 wt. %, near the project goal of 50.0 wt. %. Initial moisture-free and solvent-free elemental analysis of a mixture of light, medium, and heavy wood oil determined the oxygen content to be 19.7 wt. %. Elemental analysis of recently generated material is ongoing to confirm this oxygen concentration.

The use of recycled wood oil as solvent has not yet been conducted in the pilot-scale system. However, batch conversion of loblolly pine utilizing a surrogate medium wood oil solvent suggests conversion will increase.

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(2) Vanesse, C.; Chornet, E.; Overend, R. P. Liquefaction of Lignocellulosics in Model Solvents: Cresosote Oil and Ethylene Glycol. *Can. J. Chem. Eng.* 1988, 66, 112-120.

Bio: Dr. Schulz has been a postdoctoral research associate in the Bioeconomy Institute at Iowa State University since September 2015. Prior to joining Dr. Robert Brown's group at the Bioeconomy Institute, he earned his PhD in chemical engineering from North Carolina State University. At N.C. State, he studied deoxygenation of cyanobacteria-derived fatty acids over carbon-supported palladium heterogeneous catalysts under the direction of Dr. Henry Lamb. Taylor completed his BS in chemical engineering at Pennsylvania State University. During his time at Penn State, Taylor investigated the diffusivity and solubility of industrial solvents in polyethylenes in the laboratory of Dr. Ronald Danner.

Tim Schulzke

Diploma in Chemical Engineering, Group Manager Thermochemical Processes and Hydrocarbons, Department Biorefinery and Biofuels, Fraunhofer Institute for Environmental, Safety and Energy Technology UMSICHT

Biomass—Future Source of Renewable Hydrogen or Carbon?

T. Schulzke

Fraunhofer Institute for Environmental, Safety and Energy Technology UMSICHT, Oberhausen, Germany

Abstract: To meet the global CO_2 mitigation goals settled in Paris in 2015, the electricity system must be transformed from a fossil basis to renewables, and the use of fossil resources like coal and mineral oil in transportation and materials must be reduced. Biomass could play a role in electricity production, because there are several well-developed conversion technologies available for biomass-based power stations. There are many alternative options for the production of electricity from renewable resources, such as wind and solar power, hydropower stations, and geothermal sources. But biomass is a limited resource for biomass power and perhaps not the best use of biomass.

On the other hand, the chemical industry and (heavy) transportation rely on carbon-containing compounds. The only renewable source of carbon for all these applications is biomass. With the average composition of biomass represented by the molar formula $CH_{1.44}O_{0.66}$, it becomes obvious that biomass itself is deficient in hydrogen, if products like methane, methanol, higher alcohols, gasoline, Fischer-Tropsch-Hydrocarbons, or similar will be produced, as they have a hydrogen-to-carbon ratio of 2:1 and higher. Either carbon dioxide is produced as an inevitable by-product or hydrogen produced from renewable resources (e.g., by electrolysis from wind power) must be added.

Alternatively, carbon dioxide from concentrated sources like cement mills or steel mills can be used for the production of said carbon-containing base chemicals. A source of renewable hydrogen is necessary, which again will be renewable electricity for electrolysis. In the near future, the amount of renewable electricity in the grid will not be sufficient to supply enough hydrogen for CO_2 conversion. If biomass is gasified and the syngas is upgraded with water gas shift, it can supply renewable hydrogen. It can be shown from stoichiometric equations that biomass growth and gasification/shift constitute "solar" water separation to hydrogen and oxygen with a closed carbon dioxide cycle.

On the background of specific German conditions, the “best” utilization of biomass in the short term and long terms will be discussed, especially considering the German “energy transition” pathway for the electricity grid.

Bio: Mr. Schulzke received his diploma in chemical engineering from Dortmund Technical University, Germany, in 1992 and then entered Fraunhofer UMSICHT as an engineer. From 2000 to 2005, he was responsible for installing and operating a 200 kW PEM fuel cell from Ballard on the premises of the institute. Since 2005, he has been a member of the group working on thermochemical biomass conversion mainly focused on fluidized bed gasification with subsequent catalytic tar reforming, which he has led since 2013. An additional topic—fast pyrolysis of straw and the application of pyrolysis condensates—was added to his tasks in 2007. He is involved in the recently started research cluster Carbon2Chem, which is a publicly funded project led by thyssenkrupp aiming to convert carbon monoxide and carbon dioxide–containing waste gases from steel mills into chemicals like methanol, alcohols with longer carbon chains (e.g., ethanol and propanol), polymers, and oxymethylethers.

Reinhard Seiser

Research Scientist, Department of Mechanical and Aerospace Engineering, University of California, San Diego

Detailed Measurement of Sulfur Compounds in Producer Gas from Fluidized-Bed Gasifier

Reinhard Seiser[1], Zach McCaffrey[1], Michael Long[2], Serge Biollaz[3], Robert Cattolica[1], and Bryan Jenkins[2]

[1]University of California at San Diego, San Diego, CA, USA
[2]University of California at Davis, Davis, CA, USA
[3]Paul Scherrer Institute, Switzerland

Abstract: Sulfur compounds play a major role in the deactivation of catalysts for fuel synthesis, such as methanation and Fischer-Tropsch processes. Not only hydrogen sulfide (H_2S), but also thiophenes, thiols, and other organic sulfur compounds are present in producer gas and have to be removed to very low concentrations if catalyst degradation is to be avoided. A measurement campaign of sulfur compounds was undertaken at a 4,400 kg/day (5 tons/day) fast internally circulating fluidized bed gasifier to characterize sulfur compounds in the producer gas at different stages in the gas cleanup. A gas chromatograph with a sulfur chemiluminescence detector (GC-SCD) allowed accurate separation and quantification of sulfur compounds down to the parts per billion range. Apparatus after the gasifier include organic solvent scrubbers, bag house filters, gas compression, and storage equipment. Sulfur compounds decreased along the process train due to absorption and reactivity. In addition to H_2S and carbonyl sulfide (COS) as the major sulfur-containing species, other organic sulfur compounds were measured. Various measurement techniques were compared with each other to verify the integrity of the sulfur compounds during sampling, including direct connection to the gas-sampling valve on the GC-SCD, use of liquid absorption media, and gas capture from remote sampling ports using gas sampling bags.

Bio: Dr. Seiser is a research scientist at UC San Diego. He has a background in chemical engineering and has worked on combustion fundamentals, internal combustion engines, and fluidized-bed gasification. He directs research activities at the Woodland Biomass Research Center, including gasification for the production of power, renewable natural gas, and mixed alcohols.

Charles Sorensen

Chief Technology Officer, Anellotech

Catalyst Activity Management in the Anellotech Bio-TCat™ Process

Charles Sorensen

Anellotech, Pearl River, NY, USA

Abstract: The Anellotech Bio-TCat process converts non-food biomass into renewable fuels and chemicals using a thermo-catalytic process in a fluid bed reactor containing HZSM-5 catalyst. Continuous catalyst circulation between reactor and regenerator is used to address short-term, temporary catalyst deactivation due to coke deposits and to utilize the energy released by coke combustion in the regenerator to drive the biomass conversion reactions occurring in the reactor. Besides coking, there are other catalyst deactivation mechanisms that can result in permanent deactivation of zeolites and much is known about them from similar use of zeolites in the petroleum fluid catalytic cracking process (FCC), which has been practiced since the 1940s. This presentation will describe Bio-TCat catalyst activity management strategies, special concerns of biomass processing with respect to catalyst deactivation, Anellotech's preferred method of mitigating deactivation, and pilot-scale demonstration of the technology.

Bio: Chuck Sorensen has been with Anellotech since 2013 and currently serves as the company's Chief Technology Officer where he oversees development of the Bio-TCat process jointly with Anellotech, IFPEN, Axens, and Johnson Matthey. He has extensive experience in oil refining and chemical process development having worked at Mobil Oil for 15 years in a variety of capacities. In 2000, he switched careers to work for Corning Inc. and led groups that commercialized new vehicle exhaust aftertreatment technologies including catalytic converter substrates and filters for gasoline direct injected engines and diesel particulate filters used for automobile, heavy duty truck, and off-road engine applications. Later he led an advanced glass technology group to develop chemically strengthened glass applications for automobile, appliance, and architectural uses. Chuck has a BS in chemistry from Michigan State and a PhD in chemical engineering from the University of Delaware and is a licensed professional engineer.

Addison Killean Stark

Fellow and Program Director, Advanced Research Projects Agency–Energy

Towards a Multi-scale Modeling Framework for Fluidized Bed Reactor Simulation

Addison K. Stark[1], Christos Altantzis[2,3], and Ahmed F. Ghoniem[3]

[1]Advanced Research Projects Agency–Energy, Washington, DC, USA
[2]National Energy Technology Laboratory, Morgantown, WV, USA
[3]Massachusetts Institute of Technology, Cambridge, MA, USA

Abstract: Fluidized bed biomass gasification and biomass pyrolysis are promising technologies to enable the thermochemical conversion of biomass to drop-in fuels. Fluidized bed reactors are utilized for solid to gas conversion processes due to their ability to provide a high degree of gas-solid contact, fast solid-solid mixing, and fast gas mixing within the bed-zone due to solids-induced flow. These characteristics, though beneficial to the conversion itself, pose serious challenges to modeling the conversion at industrially relevant time and length scales with high fidelity. It is in the interplay of multi-phase hydrodynamics, heat transfer, and chemical kinetics where the challenges—and opportunities—for modeling lies.

In previous modeling efforts of fluidized bed gasifiers and pyrolyzers, researchers have assumed that the bed zone can be modeled as a continuously stirred tank reactor. Recent work has shown the limitations of this model and a path forward has been developed in which reactive CFD simulation is used in parallel to reactor network model development in order to more effectively capture the coupling of reactor-scale transport and chemical kinetic phenomena.

At the particle scale, the coupling of devolatilization models with both CFD and reactor network models is discussed. The influence of particle diameter on both the conversion efficiency and tar product distribution leaving the reactor is discussed. This coupling, via the interplay of internal heat transfer and pyrolysis kinetics, manifests itself in both the biomass particle conversion time and the product gas distribution leaving the reactor and has been shown to play an important role in the gas-phase conversion of the devolatilization products via a direct correlation between particle diameter and polycyclic aromatic hydrocarbon production in a pyrolysis reactor.

This talk will highlight challenges that the thermochemical biomass modeling community has recently overcome and is currently tackling through multi-scale modeling efforts. Additionally, this talk will offer insights into the challenges and opportunities that await.

Bio: Dr. Stark currently serves as an ARPA-E Fellow and Program Director focusing on advanced thermochemical conversion to fuels and chemicals, energy innovation in agricultural systems, and intensification of energy conversion reactor designs. Dr. Stark also serves as program director for the $32 million Advanced Research In Dry-cooling (ARID) portfolio, which consists of 14 projects focusing on the development of advanced technologies to reduce the water consumption of power production. Dr. Stark completed his PhD in mechanical engineering from MIT, where he was a member of the Reacting Gas Dynamics Laboratory and elucidated the role of transport phenomena on the thermochemical conversion of biomass in fluidized bed reactors (gasification and pyrolysis). Dr. Stark also holds SM degrees in mechanical engineering and technology and public policy from MIT. He received a BS and a BA in mathematics and chemistry, respectively, from the University of Iowa.

Michael Talmadge

Senior Process Engineer, National Renewable Energy Laboratory

Finished Fuel Blending Models for Assessing Integration of Biomass-Derived Products with Petroleum Refinery Products

Michael Talmadge, Asad H. Sahir, and Mary Biddy

Biorefinery Analysis and Exploratory Research, National Bioenergy Center, National Renewable Energy Laboratory, Golden, CO, USA

Abstract: As the bioenergy industry focuses on the near-term development of conversion pathways from biomass feedstocks to infrastructure-compatible fuel blendstocks, analysis capabilities and models are essential for assessing the values of biomass-derived blendstocks based on them fuel properties and the constraining parameters for blending them with petroleum-derived products. Funding from DOE's Bioenergy Technologies Office (BETO) has enabled the analysis team to develop both linear programming models (Aspen PIMS) and process models (Aspen Plus and HYSYS) to meet the new analysis needs. In addition to developing these analysis tools, the team has also utilized published experimental blending data to validate the results of the models and to improve blend property predictions. These models are already playing a vital role at NREL in understanding the potential to integrate fuel products from biomass conversion pathways under BETO's research and development portfolio.

This presentation will focus on (1) an overview of the analysis approaches and process models developed under this effort, (2) the benefits for utilizing the tools for assessing biomass-derived blendstocks, (3) examples of blending analysis results, (4) comparison of results from blending models relative to experimental data, and (5) future work for this effort in assessing blending of oxygenated compounds.

Techno-economic and Sustainability Analysis for Co-processing Fast Pyrolysis Oil with Vacuum Gas Oil in an FCC for Second Generation Fuel Production

Michael Talmadge[1], Yimin Zhang[1], Christopher Kinchin[1], Andrea de Rezende Pinho[2], Mary Biddy[1], Helena L. Chum[1], Earl Christensen[1], Marlon B. o B. de Almeida[2], and Luiz Carlos Casavechia[3]

[1]National Renewable Energy Laboratory, Golden, CO, USA
[2]PETROBRAS, Centro de Pesquisas e Desenvolvimento Leopoldo A. Miguez de Mello (CENPES), Ilha do Fundão, Rio de Janeiro, Brazil
[3]PETROBRAS-SIX, São Mateus do Sul, Brazil

Abstract: Over the past several years, NREL has worked closely with Petrobras to develop modeling tools and analysis approaches to assess the feasibility of pyrolysis oil co-processing on the basis of economics and sustainability. As the Petrobras team conducted many co-processing experiments with fast pyrolysis oil from woody biomass and standard Brazilian gasoil on their 200 kg.h-1, demonstration-scale fluid catalytic cracking (FCC) unit, the NREL analysis team evaluated the FCC yield data and developed novel modeling approaches to simulate and optimize the co-processing scenarios. The Petrobras experiments clearly prove that co-processing raw bio-oil in the FCC is technically feasible. The purpose of this analysis is to prove that co-processing can also be economically and sustainably feasible.

The authors have developed two unique techno-economic analysis (TEA) tools for the purpose of assessing the pyrolysis oil co-processing with vacuum gas oil in FCC and product finishing units (gasoline/diesel hydrotreaters and alkylation). The first analysis tool is an empirical correlation-based FCC yield model developed directly from the experimental data produced by Petrobras in the demonstration-scale FCC unit using JMP statistical software. The second analysis tool is an Aspen HYSYS FCC model tuned to the experimental data and utilized to predict commercial FCC yields and product qualities. Both analysis tools are integrated with Excel-based product finishing models for FCC cracked naphtha hydrotreating to finished gasoline blendstock, FCC light cycle oil hydrotreating to finished ultra-low sulfur diesel blendstock, and conversion of FCC C_4 olefins and iso-butane to gasoline blendstock via alkylation.

The authors have developed complete TEA and sensitivity analysis scenarios using the modeling tools and have assessed the economic feasibility of many co-processing cases. TEA results show high potential for pyrolysis oil co-processing scenarios to be economically attractive for petroleum refiners depending on benchmark crude oil (WTI) prices and refining margins. This presentation will summarize the applied assessment approaches and results from TEA and other aspects of analysis including uncertainty, sensitivity, life-cycle, and market impact analyses.

Bio: Mr. Talmadge has 15 years of experience in fuel production technologies with the first 10 years of his career spent in petroleum production and refining process development with ExxonMobil Research and Engineering Company and Valero Energy Corporation. Since joining NREL, Michael has supported the development of biomass-derived fuel technologies through process modeling and techno-economic analysis of biomass-to-fuels pathways. He has also contributed to the development of strategies to incorporate biomass-derived intermediates and finished fuel blendstocks into existing petroleum refining infrastructure through the National Advanced Biofuels Consortium and other subsequent collaborative projects.

Sylvain Verdier

Principal Research Engineer, Haldor Topsøe A/S

Characterization and Upgrading of Catalytic Flash Pyrolysis Oils from Pine Trees

Sylvain Verdier[1], Ofei Mante[2], Asger B. Hansen[1], Josephine Lübeck[3], Jan H. Christensen[3], Mette Kristensen[3], Kristoffer G. Poulsen[3], Giorgio Tomasi[3], Linus W. Malmquist[3], Peter Christensen[3], D. Duayne Whitehurst[1], Jostein Gabrielsen[1], and David Dayton[2]

[1]Haldor Topsøe A/S, Lyngby, Denmark
[2]Energy Technology Division, RTI International, Research Triangle Park, NC, USA
[3]Department of Plant and Environmental Sciences, University of Copenhagen, Denmark

Abstract: Production of biocrudes from wood using catalytic flash pyrolysis (CFP) was successfully investigated by RTI International over the last few years. Using a novel single-step process, biocrudes with low oxygen content were produced in a large-scale CFP unit.

In this study, five biocrudes were produced from loblolly pine at different CFP severities. Each of these feeds was subsequently hydrotreated in a once-through hydrotreating pilot plant unit. The various feeds and related products were thoroughly analyzed using the following methods:

- Standard ASTM analyses such as Sim. Dist., elemental analysis, viscosity, MCR, etc.
- GC×GC-FID and GC×GC-TOFMS
- Derivatization followed by GC×GC-TOFMS
- SFC-TOFMS

These different analytical tools allow us to compare the five feeds and identify key compounds influencing the hydroprocessing step. The characterization of the products enables the identification of the most refractory compounds and the understanding of the impact of catalyst deactivation on product composition and properties.

Bio: Sylvain has been working for 10 years in R&D Refinery at Haldor Topsøe A/S focusing on pilot plant testing, catalyst testing, kinetic modeling, analytical chemistry, heavy oil upgrading, hydrotreating, and hydrocracking. He holds an MSc in chemical engineering from the University of Pau (France) and a PhD in chemical engineering from the Technical University of Denmark (Denmark).

Kaige Wang

Research Chemical Engineer, Energy Technology Division, RTI International

Reactive Catalytic Fast Pyrolysis of Biomass into Hydrocarbon-Rich Bio-crude

Kaige Wang, David C. Dayton, Jonathan Peters, and Ofei Mante

RTI International, Research Triangle Park, NC, USA

Abstract: Fast pyrolysis has been explored for decades as a potential pathway to produce a liquid intermediate that can be further upgraded into transportation fuels. However, fast pyrolysis bio-oil is still incompatible with existing petroleum refineries due to its poor physical and chemical properties. To improve the physiochemical properties of bio-oils, a variety of catalytic pyrolysis technologies are currently being investigated for producing a high quality liquid intermediate that is suitable for integrating into a conventional refinery without significant pretreatment.

In this work, we propose reactive catalytic fast pyrolysis (RCFP), an atmospheric pressure catalytic pyrolysis process in hydrogen to improve bio-oil quality and control char and coke formation. We also investigate the influence of reaction conditions; temperature and hydrogen concentration; and materials, catalysts, and feedstock. The products from the RCFP process were characterized, and the hydrogen utilization during the RCFP process was investigated systematically. With selected catalysts, the atmosphere pressure RCFP process produced a high yield of bio-crude with comparable quality as that from the high pressure hydropyrolysis process. Though mild hydroprocessing is still needed to obtain hydrocarbon transportation fuels from RCFP biocrude, the H_2 demand downstream will be lower and overall conversion efficiency will be improved.

Bio: Dr. Wang, is a Research Chemical Engineer in the Energy Technology Division at RTI International. His current research focuses on novel process development for advanced biofuel production and related techno-economic analysis. Dr. Wang has many years of research experience in biomass thermochemical conversion. Prior to joining RTI, Dr. Wang received his PhD in mechanical engineering and with a co-major in biorenewable resource and technology from Iowa State University in 2014. Dr. Wang also holds an MS in thermal engineering from Zhejiang University in China.

Phil Westmoreland

Professor, Chemical and Biomolecular Engineering, North Carolina State University

Pyrolysis of Two- and Three-Carbon Monosaccharides to Understand Hemicellulose and Cellulose Pyrolysis

Phillip R. Westmoreland[1], Vikram Seshadri[2], and Patrick J. Fahey[3]

[1]North Carolina State University, Raleigh, NC, USA
[2]Eastman Chemical Company, Kingsport TN, USA
[3]U.S. Naval Academy, Annapolis MD, USA

Abstract: Pyrolysis chemistry of two- and three-carbon monosaccharides is examined using experiments and quantum-chemical calculations of pericyclic transition states, aiming to understanding key steps in the pyrolysis of hemicellulose and cellulose. Glycolaldehyde dimer, glyceraldehyde, and 1,3-dihydroxypropanone dimer were flash-pyrolyzed (Pyroprobe® Model 5200, CDS Analytical) and analyzed with GCxGC-TOF-MS (two-dimensional gas chromatography with detection by time-of-flight mass spectrometry, Pegasus 4D, Leco). Glyoxal and formaldehyde were the only two products detected from the pyrolysis of glycolaldehyde; calculation gave rate coefficients for unimolecular, water-assisted, and glycolaldehyde-assisted routes. At 200 °C, dehydration is observed in both glyceraldehyde and dihydroxyacetone pyrolysis, forming propanedial and methyl glyoxal. At 400 and 600 °C, glycolaldehyde and formaldehyde were observed in both glyceraldehyde and dihydroxyacetone pyrolyses, presumably from retro-aldol condensation of glyceraldehyde-forming formaldehyde and ethene-1,2-diol, which tautomerizes to glycolaldehyde. Methanol and ethanol are observed in glyceraldehyde pyrolysis while being absent in dihydroxyacetone pyrolysis. Concerted routes such as dehydration, retro-aldol condensation, aldehyde-alcohol, and dehydrogenation reaction can explain formation of many of the products, generally supported by transition-state calculations.

Bio: Dr. Westmoreland is a professor of chemical and biomolecular engineering at North Carolina State University and Interim Executive Director of the Southeast Regional Center for a new DOE Smart Manufacturing Institute. He worked previously at ORNL (1974–79), UMass Amherst (1986–2009), and NSF (2006–09). His degrees are in chemical engineering from N.C. State (BS ’73), LSU (MS ’74), and MIT (PhD ’86). His group uses pyrolysis and flame experiments, molecular-beam mass spectrometry, computational quantum chemistry, and reactive-flow modeling for research on clean energy from fossil and biofuels, chemical looping, and the international data cyberinfrastructure PrIMe. He is author or co-author of 111 peer-reviewed publications and five books. He was 2013 President of AIChE and is a trustee of the educational nonprofit CACHE Corporation, serving as its president in 2004–06. He is a past board member of the Combustion Institute (2002–14), Council for Chemical Research (2005–07), and AIChE (2009–11).

Tyler Westover

Research Engineer/Scientist, Biotechnologies Department, Idaho National Laboratory

Determination of Impact of Feedstock Composition on Fast Pyrolysis Oil Yield and Quality Using Multiple Linear Regression Modeling

Tyler Westover[1], Rachel Emerson[1], Sergio Hernandez[1], Daniel Carpenter[2], and Daniel T. Howe[3]

[1]Idaho National Laboratory, Idaho Falls, ID
[2]National Renewable Energy Laboratory, Golden, CO, USA
[3]Pacific Northwest National Laboratory, Richland, WA, USA

Abstract: Feedstock composition can affect final fuel yields and quality for the fast pyrolysis and hydrotreatment upgrading pathway. Recently, INL, NREL, and PNNL collaborated to study the impacts of feedstock composition on the yields and qualities of fast pyrolysis followed by catalytic hydrodeoxygenation (HDO) of various feedstocks and blends, including clean (debarked) pine, tulip poplar, hybrid poplar, forest residues, sorted construction and demolition waste, switchgrass, and corn stover, as well as blends of those materials. INL prepared the feedstocks, NREL performed the fast pyrolysis, and PNNL performed the catalytic HDO. Multiple linear regression models were used to correlate feedstock composition to bio-oil yields and qualities. Within experimental error, oil yields from fast pyrolysis and upgrading are shown to be linear functions of the blend components. The water content of fast pyrolysis oils was also observed to increase linearly with the summed content of potassium and sodium, ranging from 21% for clean pine to 37% for switchgrass. Pyrolysis oil yield on a dry basis (unit mass of dry oil per unit mass of dry feedstock) was observed to be affected primarily by three components (predictor variables) in the feedstock: volatile matter, total lignin, and the summed content of potassium and sodium. Importantly, the predictor variables are correlated, primarily because the herbaceous materials have high lignin and alkali metal contents and low volatile matter contents also exhibit lower fast pyrolysis oil yields than the woody materials. The best multivariate model to predict fast pyrolysis oil yield only requires volatile matter and total lignin contents as predictor variables and achieves a coefficient of determination (R^2) of 0.94 with root mean squared errors of calibration and cross-validation both less than 2%. Presumably, only two predictor variables are needed for the multivariate model because of correlation between the primary important feedstock components

Bio: Dr. Westover is a research engineer/scientist for INL's Biotechnologies Department. He holds a doctorate in mechanical engineering from Purdue University and did postdoctoral research at Sandia National Laboratories. Since 2010, he has done work supporting the Department of Energy's Biomass Program. His work focuses on a range of feedstock concerns for biofuels conversion, including determining the impact of feedstock properties on conversion yields and processability, the feeding and handling of raw and preprocessed biomass, and the effects of mechanical and thermal pretreatments that convert plant material to uniform format feedstocks for conversion to biofuels. During his professional career, Dr. Westover has also employed micro- and nano-scale technologies as well as laser-based spectroscopies to characterize emerging materials. He has expertise in the areas of scanning electron, transmission electron, and atomic force microscopies, and also microphotoluminescence spectroscopy, Raman spectroscopy, laser-induced breakdown, and low-energy electron spectroscopies.

Gavin Wiggins

Research Scientist, Energy and Transportation Science Division, Oak Ridge National Laboratory

Modeling the Impact of Biomass Particle Size Distribution and Shape on Heating Behavior During Fast Pyrolysis

Gavin Wiggins[1], Stuart Daw[1], and Peter Ciesielski[2]

[1]Oak Ridge National Laboratory, Oak Ridge, TN, USA
[2]National Renewable Energy Laboratory, Golden, CO, USA

Abstract: Fast pyrolysis is currently a leading candidate for the thermochemical conversion of biomass into liquid fuels and high-value chemical products. Fluidized beds are one of the most prevalent types of fast pyrolysis reactors, operating either in the bubbling or circulating regimes. Numerous investigations have demonstrated that these reactors are capable of achieving the high biomass particle heating rates (hundreds to thousands of degrees K/s) needed to maximize liquid yields. But to achieve these high heating rates, the biomass feed particles must be relatively small (less than 5 mm) and sufficiently well contacted with the fluidized bed solids to reach the optimal temperature (about 500 °C) and conversion before they exit the reactor. From a practical standpoint, it becomes extremely challenging to optimize liquid yield when the highly variable particle shapes and broad size distributions of typical ground feedstocks are taken into account.

In this presentation, we report the results of an intensive review of the particle-scale heat up models currently available in the literature. We propose a process for reconciling the inconsistencies in the models and developing low-order approximations that can be used to estimate the impact of feedstock properties on particle heating rate in fast pyrolysis reactors. To illustrate our main points, we assume characteristic properties for a range of ground woody biomass and extra-particle heating conditions typical of bubbling bed reactors. With these assumptions, we demonstrate how to account for realistic particle geometry and anisotropic properties on intra-particle heat conduction using a low-order methodology that does not require substantial computational resources. We show how these methods can be used with realistic feed streams of ground biomass having broad particle size distributions and variable aspect ratios. Finally, we briefly discuss how we expect that heat conduction can be linked with chemical reactions, mass transfer, and drying using additional low-order approximations. This low-order approach should be able to rapidly achieve useful estimates of raw bio-oil yields for assisting process design and control development as well as techno-economic assessments of pyrolysis technology options.

Bio: Mr. Wiggins is currently developing computational models (written in Matlab and Python) at ORNL to simulate the fast pyrolysis of biomass particles in bubbling and circulating fluidized-bed reactors. His goal is to provide insight into the operation and design of these reactors to efficiently produce bio-oil that can be upgraded to transportation fuels.

This research is part of the Computational Pyrolysis Consortium, which is a collaboration among five U.S. Department of Energy national laboratories in support of the Bioenergy Technologies Office. Mr. Wiggins' educational background consists of two MS degrees from Clemson University in mechanical engineering and environmental engineering and earth science and a BS in mechanical engineering with a minor in mathematical sciences. He has previous research experience with Savannah River Site and Clemson University's Intelligent River Project.

Seunghyun Yoo

PhD Student, Department of Forest Biomaterials, North Carolina State University

Chemical Activation of Fast Pyrolysis Biochar for the Production of Electrically Conductive Carbon

Seunghyun Yoo[1], Junyeong Park[1], Nanfei He[2], Wei Gao[2], Steve Kelley[1], and Sunkyu Park[1]

[1]Department of Forest Biomaterials, North Carolina State University, Raleigh, NC, USA
[2]Department of Textile Engineering, Chemistry and Science, North Carolina State University, Raleigh, NC, USA

Abstract: Biochar is a major by-product of the fast pyrolysis process and is considered an inexpensive solid fuel used for heating pyrolysis reactors. Separately, recent work has revealed the potential high-end applications of biochar as electrodes for electrochemical energy storage systems and conductive materials for sensors and electronic devices. High-value applications for biochar and activated carbon can contribute to the expansion of biomaterial markets. Our objective in this work is to understand the complex reactions associated with development of biomass-derived carbon structures during fast pyrolysis of biomass and activation of biochar. In this study, the physical and the electronic structures of loblolly pine (*Pinus Taeda*)–derived biochar and activated carbon were systematically analyzed by interpreting electron energy loss spectra, BET surface areas, X-ray diffraction patterns, and electrical conductivities. SEM and STEM images were also collected to better understand the formation of biomass-derived carbon structures. Specifically, loblolly pine was carbonized at four different temperatures (300 °C, 350 °C, 500 °C, and 700 °C) using quartz tube furnace. Then, four biochar samples were impregnated with NaOH and heated to 800 °C to produce an 'activated' carbon. Carbon sp^2 content was quantitatively determined by electron energy loss spectroscopy. The sp^2 content of biochar produced at 300 °C is 58% and the sp^2 content gradually increases to 73% as the carbonization temperature is elevated to 700 °C. The sp^2 contents of activated carbon are 74%, 78%, 79%, and 85%, where precursor biochar carbonization temperatures are 300 °C, 350 °C, 500 °C, and 700 °C. Polyaromatic cluster size and graphitic stacking thickness were determined by analyzing the x-ray diffraction patterns. The average size of the polyaromatic clusters and the graphitic stacking thickness both increased as the carbonization temperature increased. BET surface areas of activated carbon are 959.9 cm^2/g, 872.8 cm^2/g, 435.4 cm^2/g, and 16.2 cm^2/g. Four stages of biomass-derived carbon physical structural development were determined. Carbon paste electrodes were produced by mixing biochar or activated carbon powders with a solution of polyvinylidene fluoride. Biochar electrodes behave more like an insulator with very low electrical conductivity. Activated carbon electrodes had good electrical conductivities with

values between 1.14 S/cm and 1.58 S/cm. The details of biomass-derived carbon electrical property development during the fast pyrolysis and the activation will be further discussed.

Bio: Mr. Seunghyun received a BS in environmental materials science at Seoul National University, South Korea. As an undergraduate, he was a research assistant at a paper engineering lab where he did characterizations of nano-fibrillated cellulose. Before starting his PhD program, Mr. Seunghyun joined Dr. Sunkyu Park's group at NCSU as a visiting researcher to study biomass enzymatic hydrolysis kinetics. Now Mr. Seunghyun's major research interests are characterizations and applications of biomass-derived carbon materials. By utilizing several analytical techniques, he has characterized chemical, physical, and electronic structures of disordered biomass carbon. The target of Mr. Seunghyun's research is the production of superior porous carbon for supercapacitor electrodes.

Posters

Topic	Title	Presenter	Affiliation
Gasification			
G1	**Tar Formation during Gasification of Lignin Model Dimers**	Sushil Adhikari	*Auburn University*
G2s	**Investigation of Nickel Supported Catalysts in Steam Reforming of Tar Using Simulated Toluene as a Model Compound in Hot-Gas Clean-Up of Syngas**	Talal K. Ahmed	*North Carolina A&T State University*
G3s	**Influence of Biochar Supported Metal Catalysts on the Reaction Kinetics of Biomass CO_2 Gasification**	John K. Eshun	*North Carolina A&T State University*
G4	**Hybrid Lagrangian-Eulerian Simulation of a Bubbling Fluidized Bed Gasifier**	Abolhasan Hashemisohi	*North Carolina A&T State University*
G5s	**Parametric Investigation of the Solids Circulation Rate in the CFD Modeling of Dual Fluidized-Bed System**	Hui Liu	*University of California San Diego*
G6	**Indirect Liquefaction of Biomass to Transportation Fuels via Mixed Oxygenated Intermediates**	Michael Talmadge	*National Renewable Energy Laboratory*
Hydrothermal			
H1	**Effect of Biochemical Composition on the Bio-oil Yield from Hydrothermal Liquefaction of Algae and Subsequent Upgrading of the Produced Bio-oil**	Sushil Adhikari	*Auburn University*
H2s	**Optimized Hydrothermal Liquefaction for High- and Low-Lipid Algae**	Feng Cheng	*New Mexico State University*
H3s	**Investigation into the Effect of Feedstock Moisture on Solvent Liquefaction of Lignocellulosic Biomass in Non-aqueous Solvents**	Martin R. Haverly	*Iowa State University - Bioeconomy Institute*
H4	**An Innovative Method for Efficiently Liquefying Biomass Using Raney Nickel and NaOH as the Combined Catalysts**	Yunquan Liu	*Xiamen University*
H5	**Characterization of Aqueous Byproducts Obtained from Hydrothermal Liquefaction ofIndustrial and Municipal Waste Streams**	Balakrishna Maddi	*Pacific Northwest National Laboratory*

Topic	Title	Presenter	Affiliation
Pyrolysis			
P1s	**Catalytic Co-pyrolysis of Microalgae and Low Density Polyethylene Waste to Aromatic Hydrocarbons Using Activated Carbon**	Emmanuel Ansah	*North Carolina A&T State University*
P2s	**Low Pressure Catalytic (Hydro) Pyrolysis of Different Milled Lignins and Lignin Model Compounds Using Bifunctional Catalysts**	Xianglan Bai	*Iowa State University*
P3	**Pyrolysis of Solid Waste on Spacecraft for Water Recovery and Biochar**	Catherine Brewer	*New Mexico State University*
P4	**Development of a Low Volume Corrosive Tendency Screening Test**	Raynella M. Connatser	*Oak Ridge National Laboratory*
P5s	**Effects of Recycling Regenerated Heat Carrier on the Performance of an Auger Pyrolysis Reactor**	Tannon J. Daugaard	*Iowa State University*
P6	**Liquid-Liquid Equilibrium (LLE) Measurements and Modeling for Biomass Catalytic Fast Pyrolysis Products**	Abhijit Dutta	*National Renewable Energy Laboratory*
P7	**Biorenewable Calcined Coke from Pyrolysis Bio-oil**	Yaseen Elkasabi	*USDA-ARS ERRC*
P8	**Corrosion Studies with Model Bio-oils**	Matthew G. Frith	*Oak Ridge National Laboratory*
P9	**Impact of Feedstock, Temperature, and Residence Time on Pyrolysis Products Produced at Pilot-Scale**	Katherine Gaston	*National Renewable Energy Laboratory*
P10	**Pilot-Scale Pyrolysis: Investigating and Solving Operational Problems from Running a New Feedstock**	Katherine Gaston	*National Renewable Energy Laboratory*
P11s	**Reaction Network for Partial Oxidation of Pyrolysis Reactants and Products Under Simulated Autothermal Pyrolysis Conditions**	Patrick Hall	*Iowa State University - Bioeconomy Institute*
P12	**Metal-Modified Zeolites in the Upgrading of Pyrolysis Vapors**	Richard J. French	*National Renewable Energy Laboratory*
P13s	**Methylation of Technical Lignin to Produce High Value Chemicals**	Patrick A. Johnston	*Iowa State University - Bioeconomy Institute*

Topic	Title	Presenter	Affiliation
P14	**Compatibility of Fast Pyrolysis Bio-oil with Infrastructure Elastomers**	Mike Kass	*Oak Ridge National Laboratory*
P15	**Red Mud as an In Situ Pyrolysis Catalyst: Its Ability and its Concurrent Remediation**	Andrew W. Lepore	*University of Tennessee / ORNL*
P16s	**Time Resolved Measurements of Condensed Phase and Vapor Phase Products during Fast Pyrolysis of Cellulose**	Jake K. Lindstrom	*Iowa State University*
P17s	**Vapor Phase Decomposition of Levoglucosan**	Jake K. Lindstrom	*Iowa State University*
P18s	**Thermal Deconstruction of Cellulose with Subsequent Hydrolysis to Fermentable Sugars**	Jake K. Lindstrom	*Iowa State University*
P19s	**The Tug and Pull of Lignin Fast Pyrolysis**	Ross D. Mazur	*Iowa State University - Bioeconomy Institute*
P20	**The Effect of Nitrogen and Sulfur Containing Molecules on Standard Methods for Accurate Determination of Oxygenates in Bio-oils**	Asanga B. Padmaperuma	*Pacific Northwest National Laboratory*
P21	**Catalytic Deoxygenation Reaction Pathways of Bio-Oil Model Compounds**	Jonathan E. Peters	*RTI International*
P22	**Method for Hot Real-Time Sampling of Pyrolysis Vapors at Pilot Scale**	Marc Pomeroy	*National Renewable Energy Laboratory*
P23s	**Modeling the Early Stages of Cellulose Pyrolysis**	Juan S. Proano-Aviles	*Iowa State University*
P24s	**Simulation of Cellulose Deconstruction under Variable Temperature Profiles in a Free Fall Pyrolyzer**	Juan S. Proano-Aviles	*Iowa State University*
P25s	**Identification of the Species Responsible for Morphology Conservation in Lignocellulosic Pyrolysis: Visualization Studies of Sugarcane Bagasse and its Pseudo-components**	Filip Stankovikj	*Washington State University*
P26	**Effects of Hot-Water Extraction on the Thermochemical Conversion of Shrub Willow via Fast Pyrolysis**	Paul C. Tarves	*USDA-ARS ERRC*
P27	**Catalytic Co-pyrolysis of Biomass and Waste Plastic on Py–GC/MS**	Changsen Zhang	*Zhengzhou University*

Topic	Title	Presenter	Affiliation
Upgrading			
U1	**Non-oxidative Direct Conversion of Methane for Higher Hydrocarbons**	Sushil Adhikari	*Auburn University*
U2	**Understanding the Effect of Catalytic Pyrolysis Bio-Oil Produced using CaO during Hydrotreatment**	Sushil Adhikari	*Auburn University*
U3	**Techno-economic and Lifecycle Analysis for Renewable Acrylonitrile Precursor for Production of Carbon Fibers**	Lindsey Chatterton	*Southern Research*
U4	**Effect of Inorganic Elements on Vapor Phase Upgrading of Biomass Pyrolysis Products**	Singfoong Cheah	*National Renewable Energy Laboratory*
U5	**Integrated Process for the Conversion of C2+ Oxygenates to Middle Distillates via $Zn_xZr_yO_z$ Mixed Oxide Catalysts**	Robert Dagle	*Pacific Northwest National Laboratory*
U6s	**Renewable Transportation Fuels via Fast Pyrolysis and Electrocatalytic Hydrogenation**	Sabyasachi Das	*Michigan State University*
U7	**Catalytic Hydroprocessing of Fast Pyrolysis Oils: Impact of Feedstock**	Steve P. Deutch	*National Renewable Energy Laboratory*
U8	**Hydrodeoxygenation of Model and Real Vapor-Phase-Upgraded Pyrolysis Oils**	Richard J. French	*National Renewable Energy Laboratory*
U9	**Distillate Generation via Guerbet Alcohol Coupling from Biomass**	Michel J. Gray	*Pacific Northwest National Laboratory*
U10	**Reaction Mechanism Studies of Ethanol Coupling over Mixed Oxide Catalyst**	Heather M. Job	*Pacific Northwest National Laboratory*
U11	**Catalytic Upgrading of Propionic Acid, a Bio-oil Model Compound, to Alcohol and Olefin Using Metal Doped Mo_2C**	Andrew W. Lepore	*University of Tennessee / ORNL*
U12	**Hydrodeoxygenation of Biomass Derived Oxygenates Using Molybdenum Carbides**	Zhenglong Li	*Oak Ridge National Laboratory*
U13s	**Upgrading of Bio-oil by Catalytic Hydrodeoxygenation over Pd-Ni_2P Catalyst**	Yonggang Liu	*Zhengzhou University*
U14s	**Catalytic Sulfur Tar Reformer Characterization through Upstream and Downstream Organic Sulfur Species Identification**	Michael Long	*University of California Davis*

Topic	Title	Presenter	Affiliation
U15	**Field-to-Fuel Performance Testing of Lignocellulosic Feedstocks for Fast Pyrolysis and Upgrading: Techno-economic Analysis and Greenhouse Gas Life Cycle Analysis**	Pimphan Aye Meyer	*Pacific Northwest National Laboratory*
U16s	**Mixed Alcohol Synthesis from Producer Gas from a Dual Fluidized Bed Gasifier**	Ulrich Niemann	*University of California, San Diego*
U17	**Recent Development on Upgrading of In-Situ Catalytic Pyrolysis Bio-oil to Liquid Hydrocarbon Fuels**	Daniel M. Santosa	*Pacific Northwest National Laboratory*
U18	**Upgrading of HTL Bio Crude Oil Using Nano Pd/Bio-C Catalyst**	Brajendra K. Sharma	*University of Illinois, Urbana-Champaign*
U19s	**Thermo-Catalytic Upgrading of Biomass Derived Lipids to Fuels and Chemicals**	Yaser Shirazi	*The University of Toledo*
U20s	**The Faith of Functional Groups during Pyrolysis Oil Stabilization over Ru/C Catalyst**	Filip Stankovikj	*Washington State University*
U21	**Valorization of Biorefinery Waste: Catalytic Upgrading of Catalytic Fast Pyrolysis Aqueous Phase to Chemical Intermediates**	Anne K. Starace	*National Renewable Energy Laboratory*
U22	**Toward Understanding of Condensation Reactions and Hydrogenation Reactions of Bio-oil during its Catalytic Stabilization**	Huamin Wang	*Pacific Northwest National Laboratory*
U23	**Phenols from Catalytic Fast Pyrolysis**	Nolan A. Wilson	*National Renewable Energy Laboratory*
U24s	**Deactivation Over Multilamellar MFI Nanosheet Zeolite during Upgrading Biomass Pyrolysis Vapors**	Mengze Xu	*Colorado School of Mines*
Other			
O1	**Softwood (Douglus Fir) Derived Bio-Char from Fast Pyrolysis for the Production of Energy Storage Material**	Sushil Adhikari	*Auburn University*
O2	**Improved Biofuel Feedstock through Plant Systems Biology**	Yuelong Guo	*RTI International*
O3	**Membrane Separations for Thermochemical Conversion of Biofuels**	Michael Z. Hu	*Oak Ridge National Laboratory*
O4	**Compatibility of Structural Materials with Biomass-Derived Oils**	James R. Keiser	*Oak Ridge National Laboratory*

Topic	Title	Presenter	Affiliation
O5s	**Syngas Production by Dry Reforming of Biogas over Biochar Supported Molybdenum Carbides**	Rui Li	*North Carolina A&T State University*
O6	**Influence of SiO_2 on the Transport Behavior of O_2, N_2, CO_2 and CH_4 through Polydimethylsiloxane Nanocomposite Membrane**	Emmanuel Ogbole	*North Carolina A&T State University*
O7	**Conversion of Sugar Stream to Hydrocarbon Fuels over Mixed Oxide Catalysts**	Asanga B. Padmaperuma	*Pacific Northwest National Laboratory*
O8	**Spark Ignition Fuel Properties of Bio-derived Materials and their Applicability as Gasoline Blendstocks**	Ellen A. Panisko	*Pacific Northwest National Laboratory*
O9	**Glycerol Steam Reforming for Hydrogen Production over MCM-41 and SBA-15 Supported Co and Ni Catalysts**	Taimoor Pasha	*North Carolina A&T State University*
O10s	**Bulk Gas to Atomized Liquid Syngas Fermentation Reactor**	Ashik Sathish	*Iowa State University: Agricultural and Biosystems Engineering*
O11	**Applications of Linear Programming Models for the Bioenergy Industry**	Michael Talmadge	*National Renewable Energy Laboratory*
O12	**Synthesis of Pt/mOMC Catalysts for Proton Exchange Membrane Fuel Cell Application**	Dereje Worku	*North Carolina A&T State University*
O13s	**Optimization of Acid Pretreatment for Increased Sugar Yields from Pyrolysis of Biomass**	Kayla E. Johnson	*Iowa State University*
O14	**Sulphur Sensitivity and Regeneration of a Ni-Fe-CaO Catalyst for Application to Biomass Gasification**	Reinhard Seiser	*University of California San Diego*
O15	**Determining Design Parameters for Adsorbent Based Separation of Pyrolytic Sugars and Phenolic Species**	John Stanford	*Iowa State University*

Notes

Technical Committee

Sushil Adhikari, PhD, PE
Associate Professor
Department of Biosystems Engineering
Auburn University

Catherine Brewer, PhD
Assistant Professor
Department of Chemical & Materials Engineering
New Mexico State University

Marion Carrier, PhD
MSCA Research Fellow
European Biomass Research Institute, Aston University

Daren E. Daugaard, PhD, PE
Head of Operations, Director of Research and Development
Cool Planet Energy Systems

Corinne Drennan, PhD
Laboratory Relationship Manager
Pacific Northwest National Laboratory

Yaseen Elkasabi, PhD
Research Chemical Engineer
Sustainable Biofuels and Coproducts

Thomas D. Foust, PhD, PE
Director, National Bioenergy Center
National Renewable Energy Laboratory

Amit Goyal, PhD
Program Manager, Sustainable Chemistry and Catalysis
Energy & Environment, Southern Research

Morten Boberg Larsen, PhD, MSc
Process Development Engineer, New Business Division
Haldor Topsøe A/S

Kim Magrini, PhD
Principal Scientist, Catalysis and Thermochemical Sciences Group Manager
National Renewable Energy Laboratory

Ofei Mante, PhD
Research Engineer
RTI International

Terry Marker, PhD
Bioenergy Initiatives Manager
Gas Technology Institute

Liz Moore
Technology Manager and Technical Project Officer
Bioenergy Technologies Office
U.S. Department of Energy

Calvin Mukarakate, PhD
Senior Scientist
National Renewable Energy Laboratory

Charles A. Mullen, PhD
Research Chemist
Sustainable Biofuels and Co-Products

Pedro Ortiz-Toral, PhD
Manager, R&D
Gas Technology Institute

Sunkyu Park, PhD
Associate Professor & University Faculty Scholar
Department of Forest Biomaterials
North Carolina State University

Tim Schulzke, Dipl.-Ing.
Group Manager Thermochemical Processes and Hydrocarbons
Department Biorefinery & Biofuels
Fraunhofer Institute for Environmental, Safety and Energy Technology UMSICHT

Trevor Smith
Senior Project Engineer, Bioenergy Technologies Office, U.S. Department of Energy
Allegheny Science and Technology (contractor to the U.S. Department of Energy)

Scott Q. Turn, PhD
Researcher
Hawaii Natural Energy Institute, University of Hawaii

Kaige Wang, PhD
Research Engineer
RTI International

Mark Wright, PhD
Assistant Professor
Iowa State University

Phillip R. "Phil" Westmoreland, PhD
Professor, Department of Chemical and Biomolecular Engineering
North Carolina State University

RTI Support

Maria Ashbaugh
Caroline Ball
Sharon Barrell
Scott Boggs
Alisa Clifford
Linda Cooper
Mikayla Eason
Loraine Monroe
Vikram Rao
John Theilgard

To visit the conference website:
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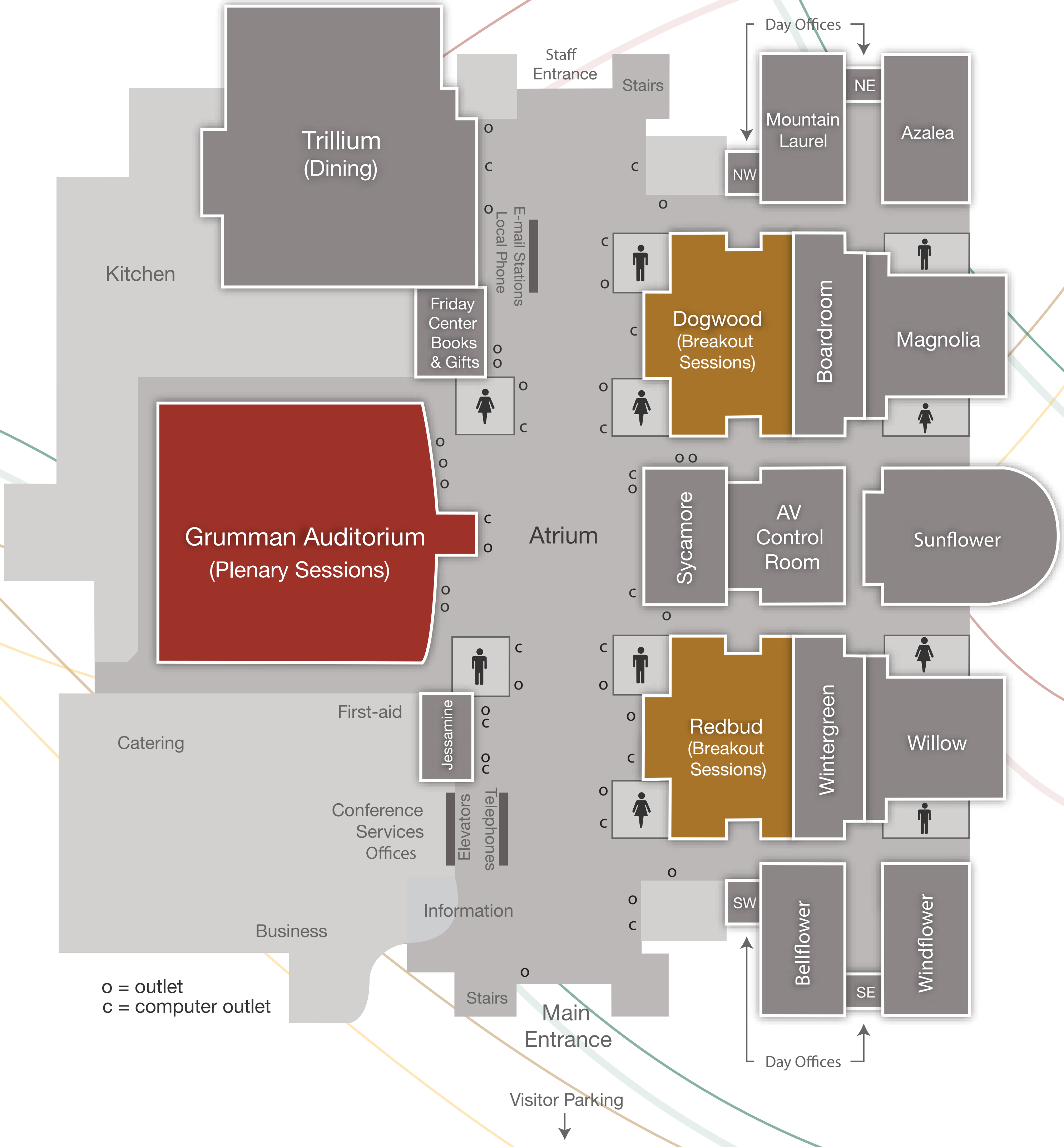
Friday Center Floorplan



o = outlet
c = computer outlet

At-A-Glance Agenda

	TUESDAY, NOVEMBER 1—DAY 1	WEDNESDAY, NOVEMBER 2—DAY 2	THURSDAY, NOVEMBER 3—DAY 3
TIME	SESSION	SESSION	SESSION
7:00 am		Continental Breakfast	Continental Breakfast
8:00 am	Continental Breakfast Registration/ Poster Setup	Plenary Session 2 Keynote: A. Boateng	Plenary Session 3 Keynote: G. Huber
9:00 am			
10:00 am	Welcome and Opening Remarks	Session 2.1: Technology Development Session 2.2: Pyrolysis (Analytical)	Session 3.1: Pyrolysis Fundamentals Session 3.2: Upgrading
11:00 am	Plenary Session 1 Keynote: J. Male		
12:00 pm	Lunch	Lunch	Lunch
1:00 pm	Session 1.1: Techno-economic Analysis (TEA) Session 1.2: Pyrolysis 1	Session 2.3: Gasification Session 2.4: Reactor Modeling	Presentation and Poster Awards Session 3.3: Hydrothermal Session 3.4: Upgrading and Products
2:00 pm			
3:00 pm	Break Session 1.3: Thermochemistry Session 1.4: Pyrolysis 2	Interactive Poster Session	
4:00 pm			Conference Wrap-Up
5:00 pm	Break	Break	FRIDAY, NOVEMBER 4
6:00 pm	Opening Reception and Poster Session	Conference Dinner	**Optional Facility Tour** RTI Headquarters 9:00 am to 12:00 pm
7:00 pm			
8:00 pm			


CAUTION
HARD HAT AND SAFETY GLASSES REQUIRED IN THIS AREA