IEA Bioenergy

Task 34 - Pyrolysis

Country Update - USA

PNNL (Pacific Northwest National Laboratory)
Upgrading by hydroprocessing remains a key component of the research into effects of operating parameters and catalyst composition to prevent fouling and extend the lifetime of the catalyst bed. Alan Zacher: alan.zacher@pnnl.gov

In cooperation with Battelle's catalytic pyrolysis process development, a new potentially regenerable upgrading catalyst was developed on non-carbon support. We are currently working out improvements to the catalyst and regeneration methods prior to 1000 hr run scheduled later in 2014. Huamin Wang: huamin.wang@pnnl.gov

PNNL is developing steam-reforming and catalytic upgrading technologies to utilize the organic compounds in the aqueous phases produced at various points in the biomass-to-fuel value chain. Conversion of the organic compounds into hydrogen, chemicals and/or fuel-range hydrocarbons will reduce external H2 demand or improve the overall utilization of biogenic carbon while improving the aggregate economics of bio-refineries. Karl Albrecht: karl.albrecht@pnnl.gov

PNNL with NREL and INL (Idaho National Laboratory) have revised the 2009 Pyrolysis and Upgrading Design Report (published in 2013) for the DOE Bioenergy Technologies Office (BETO). The report draws upon PNNL research to date as well as current pyrolysis and upgrading publications by other entities. An external review was received from industry, universities and research organizations. The report is available here: http://www.pnnl.gov/main/publications/external/technical_reports/PNNL-23053.pdf

NREL (lead) with PNNL and INL are developing a catalytic pyrolysis design case for BETO. External review was received and the final report will be published by the end of 2014. Sue Jones: sue.jones@pnnl.gov

PNNL is also deeply involved in hydrothermal process development for conversion of biomass to liquid fuels. Hydrothermal Liquefaction (HTL) is performed at two scales of operation at PNNL in continuous-flow systems processing water slurries of lignocellulosic biomass, algae and wet waste biomass. Research partners include Algenol, Reliance Industries Ltd., the Water Environmental Research Foundation (WERF), ConAgra Foods and Ste Michelle Wineries. Andy Schmidt: andrew.schmidt@pnnl.gov

NREL (National Renewable Energy Laboratory)
NREL seeks to develop novel catalysts and processes for the upgrading of biomass pyrolysis vapours, specifically leveraging advanced synthetic techniques and model compound studies coupled with theoretical modelling. Joshua Schaidle: Joshua.Schaidle@nrel.gov

Continued on next page...

Country Update - USA …continued

NREL continues to focus on the catalytic conversion of biomass vapours from fast pyrolysis. Vapour phase upgrading will be conducted with a Davison circulating riser (DCR) system coupled with a biomass fast pyrolysis system that will provide vapours to the DCR along with condensed oil. Vapour composition will be assessed pre and post hot gas filter with an online molecular beam mass spectrometer and product composition with 2D GCTOFS, NMR, and carbon analyses. Work during 2015 will assess how much vapour can be co-processed with vacuum gas oil using equilibrium ZSM5 catalyst. Kim Magrini: kim.magrini@nrel.gov

NREL is conducting laboratory and bench scale experiments of the upgrading of biomass pyrolysis vapours in order to improve catalyst performance. Novel catalysts are being prepared by Johnson Matthey, NREL, Colorado School of Mines and Massachusetts Institute of Technology and are being tested with real pyrolysis vapours and model compounds. Experimental work is being supported by computational modelling. Mark R. Nimlos: mark.nimlos@nrel.gov

Assessing the viability of producing hydrogen and fungible carbon fuel intermediates from aqueous bio-oil fractions via catalytic upgrading continues with a techno-economic analysis of both processes conducted in 2015. Kim Magrini: kim.magrini@nrel.gov

NREL (with INL and PNNL) is working to identify and quantify the key biomass characteristics that impact thermochemical conversion performance with the goals of reducing feedstock costs while satisfying process requirements. Recent work has focused on assessing the performance of several feedstocks in a fast pyrolysis process, followed by hydrotreating of the bio-oils to a hydrocarbon fuel blendstock, to obtain modelled conversion costs and carbon efficiencies as a function of feedstock. Daniel Carpenter: daniel.carpenter@nrel.gov

NREL, with PNNL, are completing final revisions for the publication of a design report on catalytic *in situ* and *ex situ* fast pyrolysis vapour upgrading followed by hydroprocessing of the organic liquid product to fuel blendstock. This work was supported by the DOE Bioenergy Technologies Office. The report is expected to be published by the end of 2014. Abhijit Dutta: abhijit.dutta@nrel.gov

NREL and PNNL are working together on standardizing analytical techniques for bio-oil analysis. Over the past year, they have standardized GC/MS, carboxylic acid titrations (CAN/TAN), carbonyl titrations, and 31P NMR. In the next year, these methods will be validated in a Round Robin. Jack Ferrell:

Continued on next page...

Country Update - USA ...continued

jack.ferrell@nrel.gov

Hydrogenation of oils from catalytic pyrolysis is being studied using model compound mixtures and pyrolysis oils produced in a bench-scale fluidized bed reactor. Kristiina Iisa: kristiina.iisa@nrel.gov

As part of a multi-lab DOE computational consortium, NREL seeks to utilize advanced computational methods to model pyrolysis reactors and catalytic chemistry in order to inform, optimize, and direct biomass pyrolysis research. David Robichaud: david.robichaud@nrel.gov

ORNL (Oak Ridge National Laboratory)
Six different tasks are included in the materials degradation project. Task A consists of laboratory corrosion studies with bio-oils and aqueous samples provided by a wide variety of project participants. Task B involves evaluation of the samples exposed in the off-site facilities as well as examination of components that have been removed from such facilities after significant exposure time in the process streams. Chemical characterization and development of new analytical techniques are the topics of Task C.

Task D consists of corrosion studies of non-metallic materials, i.e., polymers, elastomers, plastics, etc. in biomass derived oils. Task E will involve a systematic study of the changes in corrosivity and oxygenate content as a function of the degree of hydrotreating to remove oxygen. Task F will involve participation in a round robin study led by PNNL to compare results of five different tests conducted at several different laboratories. ORNL's role in this project is to evaluate the corrosion resistance of potential structural materials under conditions that simulate the environment of refinery catalytic crackers processing a mix of biomass-derived oil and petroleum products. Jim Keiser: keiserjr@ornl.gov

A new class of robust inorganic membranes, called HiPAS (High Performance Architectured Surface Selective) membranes, are being tested for improved efficiency of bio-oil processing. Michael Hu: hum1@ornl.gov

ORNL is developing a novel class of catalysts based on transition metal carbides for bio-oil hydroprocessing. Enhanced catalyst economics are targeted by designing catalysts, which do not require precious metals or sulfiding agent addition, are intrinsically robust under the harsh bio-oil environments, and consume less hydrogen. Jae-Soon: Choi choijs@ornl.gov

USDA-ARS (US Department of Agriculture-Agricultural Research Service)

Continued on next page...

IEA Bioenergy

Task 34 - Pyrolysis

Country Update - USA ...continued

The Agricultural Research Service (ARS), the principal intramural research arm of the United States Department of Agriculture (USDA), has continued its work on producing stable partially deoxygenated pyrolysis liquids through both catalytic and non-catalytic processes. The researchers at the Eastern Regional Research Centre (ERRC, Philadelphia, PA) have improved these pyrolysis processes through continued use and modification of ERRC's 5 kg/h pyrolysis process development unit (PDU), "the Kwesinator." Research on utilization of pyrolysis oils including direct combustion and upgrading via hydrotreating and separations technologies is also advancing.

In addition, Dr. Boateng is the director of the USDA-NIFA funded "FarmBio3" project. Two years into the project, FarmBio3 has made significant progress on feedstock logistics, robust catalyst development for both pyrolysis and upgrading and life cycle analysis, all focused on farm scale systems. Fabrication of a two metric ton per day mobile pyrolysis unit has been completed as part of FarmBio3. The first partial on farm demonstration of this unit was done in September 2014, with more demonstration events to be held in the near future. Akwasi Boateng: akwasi.boateng@ars.usda.gov
Charles Mullen: charles.mullen@ars.usda.gov
Yaseen Elkasabi: yaseen.elkasabi@ars.usda.gov

GTI (Gas Technology Institute)

GTI has completed more than 3500 h of testing in their 50 kg/day continuous IH2® pilot plant using integrated hydropyrolysis and hydroconversion to directly convert biomass to drop in gasoline and diesel fuels. The patented IH2® process operates at moderate temperature (425-440° C) and pressure (23-34 bar) under a hydrogen atmosphere in a fluidized bed using a specialty catalyst from CRI Catalyst Company which deoxygenates and hydrogenates the devolatilized biomass vapours. The products from the IH2® process are high quality fuels with no measurable oxygen, and no measurable TAN (total acid number). The hydrocarbon fuels produced will be used in gasoline and diesel fuel qualification tests. This technology is commercially licensed by CRI Catalyst Company, a division of Shell. http://www.cricatalyst.com/catalysts/renewables/videos.html

- US patent 8,492,600 Hydropyrolysis of Biomass for Producing High Quality Liquid Fuel
- US 8,816,144 Direct production of fractionated and upgraded hydrocarbon fuels from biomass
- US 8,841,495 Bubbling bed catalytic hydropyrolysis utilizing large catalyst particles and small biomass particles featuring an anti-slugging reactor

Continued on next page...

Country Update - USA …continued

RTI International
RTI International has designed and installed a 1 TPD catalytic biomass pyrolysis pilot plant that has been in operation since August 2013. Several design modifications have greatly improved the system operability and biocrude product collection efficiency. In July 2014, over 1000 lbs. of pine sawdust was fed in 15 hours, with 10 hours of steady-state operation. The team has produced 25 gallons of biocrude for upgrading into gasoline and diesel by our partners at HaldorTopsoe in Denmark. By the end of 2014, a new hydrotreating reactor system will be installed at RTI to demonstrate an integrated biorefinery process for converting biomass into gasoline and diesel based on our novel catalytic biomass pyrolysis technology.

Battelle Memorial Institute
Battelle has developed a process to convert biomass to bio-oil via fast pyrolysis, and then convert the bio-oil to a high-value chemical. The pyrolysis process uses mechanical circulation of a heat carrier between a reactor and a char combustor. Use of mechanical devices for the circulation of the heat carrier eliminates the need for fluidization gas, which greatly reduces equipment size and capital cost. Good mixing between the heat carrier and the biomass results in high yield of bio-oil, comparable to that achieved by conventional fluidized-bed technologies. Battelle has scaled up this technology to a ¾ t/d pilot, which is being tested for continuous operation. The technology is presently being scaled up for a commercial demonstration project to convert 20 t/d of biomass to a high value chemical. Zia Abdullah: abdullahz@battelle.org

Iowa State University (ISU)
Iowa State University's (ISU) Bioeconomy Institute is investigating novel methods to hydrogenate bio-oil, easing the path from biomass to fuels and chemicals. Called low-temperature, low-pressure (LTLP) hydrogenation, the process begins by recovering bio-oil as stage fractions using a fractionating bio-oil recovery system in conjunction with a fast pyrolysis reactor. The heavy ends of the fractionated bio-oil are a mixture of sugars and phenolic oligomers. Washing these heavy ends separates the water-soluble sugars from water-insoluble phenolic oligomers.
Ryan G. Smith: rgsmith@iastate.edu

The phenolics are then hydrogenated under conditions as mild as ambient temperature and atmospheric pressure, converting carbonyl bonds to alcohols and saturating carbon-carbon double bonds to aliphatics. Mass yields of LTLP hydrogenated bio-oil are in the range of 85 to 99.8%. The viscosity of the heavy-end phenolics is reduced by as much as 47-99%. Accelerated aging studies show dramatically improved stability as well.

Continued on next page...

Country Update - USA ...continued

Moreover, hydrogen/carbon and oxygen/carbon ratios are within the Pyrolysis Liquid Biofuel Fuel Oil Standard Specifications (ASTM D7544-12). Whole bio-oil can be also be hydrogenated utilizing the same LTLP approach. Robert C. Brown: rcbrown3@iastate.edu

At the combustion research group of ISU, researchers are investigating the vaporization characteristics of novel fuels, including bio-oil and its upgraded transportation fuels. Understanding the vaporization characteristics of liquid fuels is critical to the design of fuel injection systems and the operation of combustion systems. Song-Charng Kong: kong@iastate.edu

University of Maine

The University of Maine is actively participating in research efforts to understand fundamental pyrolysis mechanisms, as well as the effect of reactor design and process conditions on the overall quality of pyrolysis oil. Other research is focused on various pretreatment technologies to produce a stable pyrolysis oil with low oxygen content. In addition to a bench-scale fluidized bed pyrolysis reactor, UMaine has a 50 L semi-batch reactor for slow pyrolysis, an "in-flight" pyrolysis reactor, a micropyrolyzer-GC/MS system, several continuous and batch reactors for hydrotreating and a well-equipped analytical lab for product characterization. Bill DeSisto: wdesisto@umche.maine.edu

Washington State University/ Pullman

The programme focuses on the following areas: (1) Fundamentals of cellulose and lignin pyrolysis, (2) Testing additives to enhance the production of fuel and chemicals precursors (fermentable anhydrosugars and lignin monomers) and develop more selective pyrolysis reactors, (3) Evaluation of the potential of auger pyrolysis reactors and fractional condensation systems to obtain high yields of a good quality bio-oil, (4) Development of new analytical methods to characterize the chemical composition of bio-oil and the physical and chemical properties of bio-chars, (5) Evaluation of new concepts to refine bio-oils focusing on the fermentation of anhydrosugars and C1-C4 oxygenated compounds derived from cellulose and hemicelluloses and on the hydrotreatment of pyrolysis oils, (6) Production and testing of engineered bio-chars for the removal of environmental pollutants, and (7) Testing the properties of pyrolysis-derived fuels.

There are several pyrolysis reactors (Py-GC/MS, TG-FTIR, spoon reactor, atmospheric and vacuum wire mesh reactors, 1 kg/h auger pyrolysis reactor), a hydrotreatment unit, reactors for bio-char activation and a well-equipped analytical lab for products analysis. Manuel Garcia-Perez: mgarcia-perez@wsu.edu

Continued on next page...

Country Update - USA …continued

Washington State University/ Tri-Cities
Catalytic microwave pyrolysis and torrefaction are operated in the Bioproducts, Sciences, and Engineering Laboratory. A patent pending technology was developed to convert pyrolysis bio-oils to phenols by catalytic upgrading, and gasoline and jet fuel range aromatics and hydrocarbons by catalysis. Dr. Hanwu Lei: hlei@wsu.edu

University of Minnesota (UMN)
The research programme focuses on fast microwave-assisted pyrolysis of various biomass materials, using both small lab scale and large demonstration scale systems. Wood sawdust, corn stover and microalgae are considered as good materials for bio-oil production using microwave-assisted pyrolysis. In addition, some catalysts including HZSM-5, H-Y, and H-Beta have been investigated. R. Roger Ruan: ruanx001@umn.edu

In the newly established Dauenhauer Laboratory at UMN, experimental research addresses fundamental aspects of pyrolysis including melt-phase reaction pathway analysis, kinetics and reaction mechanisms. Macroscopic studies evaluate cellulose melt behaviour including aerosol generation, jetting, and surface wetting. Integration of fundamental reaction and transport phenomena within microstructured lignocellulosic biomass particles provides a complete, multi-scale understanding of pyrolysis. Paul J. Dauenhauer: hauer@umn.edu

University of Washington
The Biofuels and Bioproducts Laboratory at the University of Washington is carrying out catalytic fast pyrolysis and hydropyrolysis experiments to convert biomass into drop-in fuels and high-value chemicals. We have recently finished the construction of an ablative reactor for fast pyrolysis, and we will pyrolyze wood chips in this system to determine the upper particle size limit to be used in ablative systems. This information will be useful in mobile pyrolysis units that will be carrying out pyrolysis of woody material in the forest. This project is funded by the USDA NIFA and the main feedstock of interest is beetle-killed lodge pole pine.

We have also concluded the construction of a high-pressure fluidized-bed system (70 bar) for hydropyrolysis of biomass. This unit will be using bi-functional catalysts for the production of cycloalkanes and other molecules with importance for jet fuels.

Purdue University
Purdue University has developed the H2Bioil process that uses fast-hydropyrolysis to convert biomass to partially oxygenated vapours which are then immediately converted, prior to cool down to room temperature, by catalytic hydrodeoxygenation to

Continued on next page...

Country Update - USA ...continued

hydrocarbon fuels. To study the two steps of this process we have developed a number of specialized reactors including several dedicated pyrolysis reactors, two dedicated catalytic hydrodeoxygenation reactors, and two reactors that combine the both fast-hydropyrolysis and downstream catalytic hydrodeoxygenation.

Using the lab-scale fast-hydropyrolysis/ hydrodeoxygenation reactor, we recently demonstrated ~54% yield of C1-8+ hydrocarbons from intact biomass using a catalyst developed at Purdue (DOI: 10.1039/C4GC01746C). In addition to this work to apply knowledge gained in other reactors to produce hydrocarbons from biomass, we also study the chemical mechanisms of pyrolysis and catalytic hydrodeoxygenation of biomass model compounds.
Purdue Team: Rakesh Agrawal (agrawalr@purdue.edu); Fabio Ribeiro (fabio@purdue.edu); W. Nicholas Delgass (delgass@purdue.edu).

Ensyn Corp
Memorial Hospital, North Conway, and Valley Regional Hospital, Claremont, both in New Hampshire.

A recent ribbon-cutting ceremony at Memorial Hospital in North Conway, New Hampshire, celebrated the commissioning of Memorial's heating system conversion from traditional petroleum fuels to Ensyn's renewable liquid fuel known as Renewable Fuel Oil™ (RFO). Ensyn is supplying Memorial under a five-year, renewable contract that provides for the delivery of 300,000 gallons per year of Ensyn's RFO cellulosic biofuel. This contract allows Memorial to fully displace its petroleum heating fuels with Ensyn's renewable fuel, reducing Memorial's greenhouse gases from heating fuels by approximately 85%. In addition, adoption of Ensyn's RFO provides Memorial with substantial cost savings. Memorial's boiler has been operating successfully on 100 percent RFO since September 2014.

Following close on to the Memorial announcement was the subsequent announcement that Ensyn Fuels, a wholly-owned subsidiary of Ensyn Corporation, has signed a contract with Valley Regional Hospital in Claremont, New Hampshire, for the supply of RFO. Ensyn Fuels will provide the hospital with approximately 250,000 gallons/year of RFO for a renewable term of seven years, commencing deliveries by April 2015. This contract will allow Valley Regional to convert its entire heating requirements from petroleum fuels to Ensyn's renewable fuel, lowering the hospital's greenhouse gases from heating fuels by approximately 85% and reducing the hospital's operating cost.

Continued on next page...

Country Update - USA ...continued

Memorial is using its existing boiler for RFO combustion operations. In addition, Ensyn installed on-site tankage and an RFO delivery system, including an innovative new burner that provides Memorial with the flexibility to switch back and forth, at will, between petroleum fuels and RFO.

The burner was supplied and installed by Cleaver-Brooks. Ensyn is producing RFO at its 3 million gallons per year facility in Ontario, Canada. In the future, the production for these New Hampshire hospitals may be replaced by Ensyn projects currently in development closer to the hospitals. Ensyn's Ontario facility has recently been qualified by the U.S. EPA under the U.S. renewable fuel standards (RFS) program. Ensyn expects that renewable identification numbers (RINs) generated at Memorial under the RFS2 program will enhance contract economics. The RFO is produced from non-food solid biomass including forest and mill residues.

Renewable Oil International
The small-scale auger reactors were sold to a small group of investors in Maryland and Delaware last year. Unfortunately, they have had financial difficulties lately and the future path is unclear. A new 0.5 tpd PDU is under construction to test a new reactor design, and there are plans for a 10 tpd and a 50 tpd unit. Phil Badger: pbadger@renewableoil.com

Genifuel Corporation
Genifuel is currently in the process of commissioning a pilot-scale hydrothermal system to process 1 metric ton per day of wet biomass at 20% solids content. The system was designed in close cooperation with PNNL, and is being supplied to Reliance Industries Ltd. in India. The feedstock for this system is algae. The pilot system will be capable of producing biocrude in the liquefaction mode (HTL), as well as a 60/40 mix of methane and carbon dioxide in the gasification mode (CHG). The most common use of this combination of HTL and CHG processes is to first produce oil, then gasify the effluent water to extract remaining energy and clean the water. Jim Oyler: jim@genifuel.com.