Biomass Densification Workshop Summary Report
“Transforming Biomass to Feedstocks”

Workshop – August 23–24, 2011
Idaho Falls, Idaho
Webinar – August 30, 2011

U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy
BIOMASS PROGRAM

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Summary Report

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Idaho Falls, Idaho

Post-Workshop Webinar – August 30, 2011

Sponsored by the U.S. Department of Energy–Biomass Program, in collaboration with the Office of Science and the Advanced Research Projects Agency–Energy (ARPA–E)

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FOREWORD

Why raw biomass needs help becoming feedstock

Whether producing biofuels, biopower, or other bioproducts, all bioenergy industries depend on supply systems that ensure high-volume, reliable, and on-spec availability of biomass feedstocks. The United States has a diverse and abundant potential of biomass resources[a] *that can be used as bioenergy feedstocks; however, biomass in its raw, "as-harvested," form is not necessarily good feedstock.*

Biomass cannot be inserted into conversion infeed systems until it undergoes some level of size reduction and other preparation, depending on the type of conversion for which it is intended.

In its "as-harvested" form, herbaceous biomass lacks both the bulk density and energy density necessary for cost-efficient bioenergy production. It also lacks flowability characteristics that allow it to be moved from location to location in existing transportation and handling infrastructures. Biomass must also be managed for chemical stability in aerobic storage environments so that the product can be stockpiled to enable a reliable year-round supply to biorefineries.

Other than a few niche resources, the U.S. biomass supply lacks spatial density across the landscape, with diverse supplies available in scattered locations and in varying quantities and qualities.This greatly restricts the development of national-scale biomass markets that can stabilize feedstock supply and demand and reduce risk for both feedstock producers and biorefineries.

Finally, the inherent diversity of the resource itself, with variability in

- *Material properties among species (e.g., wood vs. herbaceous material)*
- *Genetic differences between varieties within each species*
- *Environmental differences (e.g., soil type, weather patterns)*
- *Management practices (e.g., plow vs. no-till, fertilizer and chemical applications)*

can be a significant supply system barrier depending on the sensitivities of the targeted end-use biorefining technology.

The viability of bioenergy industries is tightly coupled to successfully addressing these biomass densification and diversity challenges.

At a biomass workshop held at Idaho National Laboratory, August 23–24, 2011, experts from industry, U.S. Department of Energy (DOE) offices and DOE-funded laboratories, and academia met to explore approaches to addressing the densification challenge and providing high-volume on-spec feedstocks to enable cost-effective feedstock supply systems for biomass conversion technologies.

Workshop participants were selected from experts in diverse segments of industry, national laboratories, and academia, with a large contingent from DOE-funded Integrated Biorefinery projects.

The workshop was sponsored by the U.S. DOE–Biomass Program, in collaboration with the DOE–Office of Science and the Advanced Research Projects Agency–Energy (ARPA-E).

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[a] *U.S. DOE (2011) U.S. Billion-Ton Update: Biomass Supply for a Bioenergy and Bioproducts Industry. RD Perlack and BJ Stokes (Leads) ORNL/TM-2011/224. Oak Ridge National Laboratory, Oak Ridge TN.*

EXECUTIVE SUMMARY

Transforming Raw Biomass into Feedstocks

Densification Challenge

Biomass, with its energy-rich stores of fixed carbon and volatiles, is estimated to have a worldwide bioenergy potential ranging from nearly 10% to more than 60% of primary energy consumption[b]. U.S. energy policy has set an aggressive goal for moving biofuels into the marketplace by increasing the supply of renewable transportation fuels to 36 billion gallons by 2022[c]. Realizing the potential of biomass at a meaningful scale will require broad industry scale up, including reliable, sustainable, and economical lignocellulosic feedstock supply systems.

Secretary of Energy Steven Chu named "densification of biomass" one of the key research challenges facing biofuels[d]. The IEA *Bioenergy Status and Prospects Report* cites "development of advanced densification and other pre-treatment technologies" as crucial to future deployment of biorefineries and bioenergy trade[e].

Densification Workshop

On August 23–24, 2011, experts from industry, government, and academia gathered for a biomass workshop held at Idaho National Laboratory to discuss potential solutions to address the densification challenge and accelerate bioenergy industry expansion. Sponsored by the U.S. Department of Energy–Biomass Program, the workshop gave participants the opportunity to explore the theme "Transforming Raw Biomass to Feedstock" through presentations, demonstrations, and a tour of the Feedstock Process Demonstration Unit (PDU).

Densification is generally associated with those processes that increase bulk density(mass per unit volume) of bulk solid materials including pelletization, briquetting, and granulation. For this workshop, densification concepts were expanded to include (1) liquefaction processes, such as pyrolysis that produces a bio-oil of increased bulk and energy density compared to the biomass feedstock from which it is produced, as well as (2) biomass yield improvements that, in effect, increase both mass and energy density on a per-unit-area of production (e.g., ton/ac). These concepts of densification to transform raw biomass to feedstock provide many benefits to the biofuels production chain, including improvements to logistics systems through improved stability, handling, and transportability (including higher payloads and reduced supply areas), as well as improvements to conversion systems through improved feeding, more consistent and uniform feedstocks, and, in some cases, improved conversion performance. Based on these wide-ranging benefits, the concept of densification was used as a springboard to introduce and discuss other advanced preprocessing concepts—referred to as "preconversion" and "formulation"—that also offer potential improvements to biomass logistics and conversion systems. The term "preconversion" refers to those biomass preprocessing operations that occur prior to primary conversion to improve and/or stabilize biomass to achieve biorefinery quality specifications.

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[b] Richard TL (2010) Challenges in scaling up biofuels infrastructure. *Science*, 13: 793:796.

[c] Energy Independence and Security Act of 2007, 42 USC § 17001 (2007).

[d] Chu S (2011) Keynote Address. *Biomass 2011: Replace the Whole Barrel, Supply the Whole Market, July 26-27, 2011, National Harbor MD.*

[e] IEA Bioenergy (2009) *Bioenergy: A Sustainable and Reliable Energy Source.* ExCo: 2009:06.

Workshop Conclusions

Common Themes

The recurring message received from workshop participants was that technologies exist and can be optimized to address the densification challenge. Participant input indicated strong support of the vision and mission areas presented, with 85% agreeing that "increasing performance and reducing variability by converting raw biomass into feedstocks will be important for developing a national-scale bioenergy industry." They also expressed caution about making feedstock commodity supply system economics viable for a self-sustaining bioenergy industry.

Biotechnology/Genetics

Several presentations discussed current research and trends in biotechnology to genetically modify biomass crops for improved yield and conversion performance. Over 60% of participants believed that plant breeding and biotechnology would have a beneficial impact on supply system and conversion performance. Because of the ability of biotechnology to target specific biomass traits, it was regarded by workshop participants to be most impactful to biochemical conversion pathways that involve more intricate deconstruction processes compared to thermochemical conversion. Participants were evenly split regarding the time frame in which plant breeding will have a significant impact on the bioenergy industry; half considered this to occur within 10 years, and half considered it to be beyond a 10-year horizon. In both cases, the long time frame is driven by socioeconomic constraints associated with the adoption and regulation of genetically modified crops.

Mechanical Preprocessing

Two presentations were given related to the mechanical preprocessing approaches to producing feedstocks with consistent particle size and handling characteristics (i.e., flowability). Workshop participants generally agreed that many mechanical preprocessing treatments related to size reduction and impurity removal, such as grinding and bark removal, are already in place today. These operations were generally regarded as standard preprocessing operations and not transformational technologies that will have a significant impact on future biofuels production.

Thermal Preconversion

This topic area included thermal treatments over the full spectrum of temperatures, with and without oxygen, which were defined as non-reactive, reactive, and destructive drying regimes (i.e., torrefaction) to produce thermally treated solid feedstocks, as well as pyrolysis to produce a liquid intermediate bio-oil. Workshop participants noted the benefits of thermal treatments to improve biomass stability in storage. However, participants also agreed that thermally treated biomass has advantages for use in thermochemical conversions such as pyrolysis, gasification, or combustion; however, participants also expressed concern that the destructive nature of aggressive treatments such as torrefaction could adversely affect biochemical conversion processes.

Chemical Preconversion

Two specific technologies were presented to demonstrate chemical preconversion concepts. Chemical leaching was presented as an example of non-destructive treatment for removing ash-related contaminants common in raw, "as harvested" biomass. Ammonia Fiber Expansion (AFEX®[f]) was presented as an

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[f] Registered trademark of Michigan Biotechnology Institute.

example of a destructive treatment for imparting structural changes to biomass to improve subsequent preprocessing and biochemical conversion performance. Participants believed chemical preconversion has the potential to improve feedstock value for biochemical, thermochemical, and biopower conversion processes, as well as improve feedstock stability. Participants were divided as to where chemical preprocessing would be best located, with suggestions for both decentralized depots and proximate to the conversion refinery. Waste water treatment was the biggest concern for locating chemical preconversion at a depot.

Formulation

Research results on pretreatment of blended feedstocks (a mixture of corn stover, switchgrass, eucalyptus, and pine) were presented as a specific example of formulation. The production of this blended feedstock was also demonstrated on the Feedstock PDU. Some participants saw formulation as an important aspect of reducing feedstock variability and as a key requirement for achieving uniform feedstocks. Many participants recognized that formulation is already practiced in biopower operations and discussed its potential benefits to biofuels production by reducing feedstock variability and mitigating the effects of undesirable components such as chlorine. In view of the blended feedstock presentation, some participants thought formulation may be limited by geographic co-location of biomass resources. Overall, participants thought that more information was necessary in order to fully understand the value of formulation.

Densification

Pelleting was discussed with an emphasis on optimizing process parameters to affect physical characteristics (density, durability), solid fuel properties, and biochemical conversion performance. Preliminary research results on the pretreatability of pelletized corn stover were presented, and process development technologies using a laboratory-scale pellet mill were demonstrated. For the most part, densification was seen as a way to facilitate logistical improvements, primarily in transportation, storage, and handling. Despite the presentation reporting laboratory results that indicated no negative pretreatment impact, the potential for densification to be a detriment to feedstock performance was a recurring theme. Finally, participants questioned how energy-intensive pelletization processes could be economical for the development of high-volume biomass feedstock supply systems.

Points of Emphasis

Many of the advanced preprocessing technologies presented were considered by participants to be better suited for either biochemical or thermochemical conversion pathways; however, in most cases, research is lacking to support these conclusions. Participant feedback consistently raised questions and concerns regarding the cost-to-value relationship of the advanced preprocessing technologies and concepts presented, with a need to balance increased cost and energy requirements with gains and improvements to logistics and conversion processes. A common theme among all workshop sessions was that additional research, process data, and economic analysis is needed to better understand the potential of preconversion, formulation, and densification technologies and their value for both the feedstock supply system and conversion performance.

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Acronyms

AFEX	ammonia fiber expansion
ANOVA	analysis of variance
BAC	bacterial artificial chromosome
BC	biochemical
CAD	cinnamyl alcohol dehydrogenase
DEC	dedicated energy crops
DNA	deoxyribonucleic acid
DOE	Department of Energy
EU	European Union
GMO	genetically modified organism
GT	glycosyltransferase
HPLC	high-performance liquid chromatograph
HSD	honestly significant difference
INL	Idaho National Laboratory
JBEI	Joint Bioenergy Institute
JGI	Joint Genome Institute
PDU	Process Demonstration Unit
PNNL	Pacific Northwest National Laboratory
RI	refractive index
RWA	reduced wall acetylation
SA	salicylic acid
SSF	simultaneous saccharification and fermentation
SSR	simple sequence repeat
TC	thermochemical
TEY	theoretical ethanol yield
USDA–APHIS	United States Department of Agriculture–Animal and Plant Health Inspection Service

WORKSHOP OVERVIEW

The Densification Challenge

Biomass, with its energy-rich stores of fixed carbon and volatiles, is estimated to have a worldwide bioenergy potential ranging from nearly 10% to more than 60% of primary energy consumption[g]. U.S. energy policy has set an aggressive goal for moving biofuels into the marketplace by increasing the supply of renewable transportation fuels to 36 billion gallons by 2022[h]. Realizing the potential of biomass at a meaningful scale will require broad industry scale up, including reliable, sustainable, and economical lignocellulosic feedstock supply systems[i].

As an energy source, biomass has benefits of renewability, abundant domestic production capacity in a variety of environments, versatility of end product use, and carbon sequestration potential. There are also challenges to establishing an industrial-scale biomass feedstock supply system that is capable of offsetting conventional fossil energy consumption:

- Biomass is low in energy density and bulk density and has great variability of physical attributes, which can reduce the feedstock's energy value and make all supply system logistics more complex and expensive; biomass densification and feedstock format become critical industry enablers.
- Being an organic material, biomass is subject to degradation, which can result in material loss, reduced energy value, environmental concerns, and reduced logistics efficiencies; thus, cost-effective methods of minimizing degradation are imperative.
- Different types and sources of biomass can have significant variability in chemical composition and moisture content, and different supplies of field-run biomass may require different preprocessing or upgrading treatments to meet the quality and format requirements of the end-use biorefinery.
- The resource supply is fragmented, and whether the feedstock will be converted locally or enter more distant markets, an optimized and well-coordinated supply system infrastructure will be required to maximize the energy value of the biomass and ensure sufficient resource availability.

All of these considerations are essentially risk factors for the biorefinery and the feedstock producer. Industrial-scale biorefineries require large volumes of feedstock (hundreds of thousands of dry tons per year) that meet their particular specifications. Currently, these biorefineries are generally restricted to single-species niche resources that are produced close by and undergo some level of preprocessing to achieve the required quality standard. Expanding bioenergy industries beyond these niche resource pools introduces additional logistics challenges, including cost, biomass degradation during storage, and unstable supply and demand balance.

Together, industry, government laboratories, and academia have made good progress in addressing these challenges through optimizing supply system logistics and defining feedstock attributes that are compatible with existing solids-handling infrastructures. Biomass densification has become an increasingly important focus of feedstock supply system development for its potential impact on managing moisture content, reducing transportation costs, and improving the physical properties of the feedstock, among other benefits.

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[g] Richard TL (2010) Challenges in scaling up biofuels infrastructure. *Science*, 13:793–796.

[h] Energy Independence and Security Act of 2007, 42 USC § 17001 (2007).

[i] U.S. DOE (2011) *U.S. Billion-Ton Update: Biomass Supply for a Bioenergy and Bioproducts Industry*. RD Perlack and BJ Stokes (Leads) ORNL/TM-2011/224. Oak Ridge National Laboratory, Oak Ridge TN.

Secretary of Energy Steven Chu named “densification of biomass” one of the key research challenges facing biofuels[j]. The IEA *Bioenergy Status and Prospects Report* cites “development of advanced densification and other pretreatment technologies” as crucial to future deployment of biorefineries and bioenergy trade[k].

On August 23–24, 2011, experts from government, academia, and industry gathered for a biomass workshop held at Idaho National Laboratory (INL) to discuss potential solutions to address the densification challenge and accelerate bioenergy industry expansion. Sponsored by the Department of Energy (DOE)–Biomass Program, in collaboration with the DOE–Office of Science and the Advanced Research Projects Agency-Energy (ARPA-E), the workshop gave participants the opportunity to explore the theme “Transforming Raw Biomass to Feedstock” through presentations, demonstrations, and a tour of the Feedstock Process Demonstration Unit (PDU).

Workshop Purpose and Structure

The Densification Workshop began with an opening session in which DOE–Biomass Program officials and INL managment welcomed attendees. John Ferrell, DOE–Biomass Program Supervisor over Feedstocks, presented the R&D focus areas and objectives for the workshop:

Focus Areas

- Increasing the bulk and energy density of biomass resources for improved logistics
- Upgrading biomass through preconversion and formulation for improved performance in bioenergy applications.

Objectives

- Generate a Biomass Densification Workshop report for Secretary Chu that includes bioenergy industry feedback
- Integrate plant genetics that improve biomass productivity/energy density and ease of conversion
- Broaden the view of biomass densification solutions to include preprocessing approaches, with introduction of preconversion and formulation concepts
- Solicit industry opinions on the impact of preconversion, formulation, and densification
- Demonstrate the Feedstock PDU and encourage partnership opportunities for its use.

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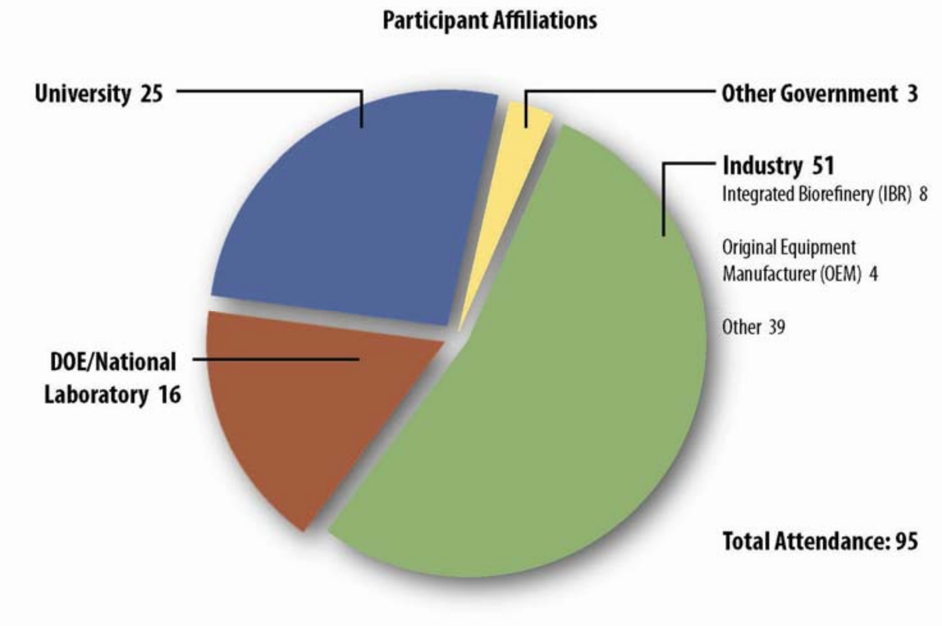
[j] Chu S (2011) Keynote Address. *Biomass 2011: Replace the Whole Barrel, Supply the Whole Market, July 26-27, 2011, National Harbor MD.*

[k] IEA Bioenergy (2009) *Bioenergy: A Sustainable and Reliable Energy Source.* ExCo: 2009:06.

Participant Affiliations

The workshop was designed to gather input from a variety of interests in bioenergy development, with particular emphasis on industry, which was well represented during the proceedings (Figure WO–1).

Figure WO–1. Breakdown of workshop participant affiliations, with more than half of participants representing industry, including Integrated Biorefinery Partners.



Integrated Biorefinery Partnerships

Biofuels are produced in integrated biorefineries that efficiently convert a broad range of biomass feedstocks into affordable biofuels, bioproducts, and heat and power. The DOE–Biomass Program focuses its efforts on key supply chain challenges. These include developing replicable feedstock supply systems and innovative conversion technologies, both of which result in lower production costs.

The success of the U.S. bioenergy industry depends in part on the quantity and quality of biomass available, as well as the industry's ability to collect, store, and cost-effectively transport it. In cooperation with several partners, the program is identifying sustainable biomass feedstock resources, developing economically viable and environmentally sound production methods, and designing feedstock logistics systems to ensure resource readiness.

R&D Vision to Address the Challenge: Feedstock Commodities

Ferrell introduced a sustainable feedstock supply vision that included development of advanced uniform-format supply system designs and improved capacity and efficiency of each feedstock logistics operation as important enablers of bioenergy industry expansion. The mature state of this vision provides the infrastructure necessary to access resources that are currently stranded due to poor economics and/or lack of market accessibility. It also provides flexibility for market integration as practical to help balance demand/supply disruptions and participate in regional, national, and international trade. Figure WO–2 shows how an advanced uniform-format supply system with distributed preprocessing ("depot") can increase the resource draw areas using the highly efficient, high-volume handling and transport systems that currently exist.

Ferrell also described the Biomass Program activity areas of focus to address the major R&D challenges associated with developing production and logistics systems capable of supplying biorefineries with high-density, aerobically stable, and high-quality biomass feedstocks (Table WO–1).

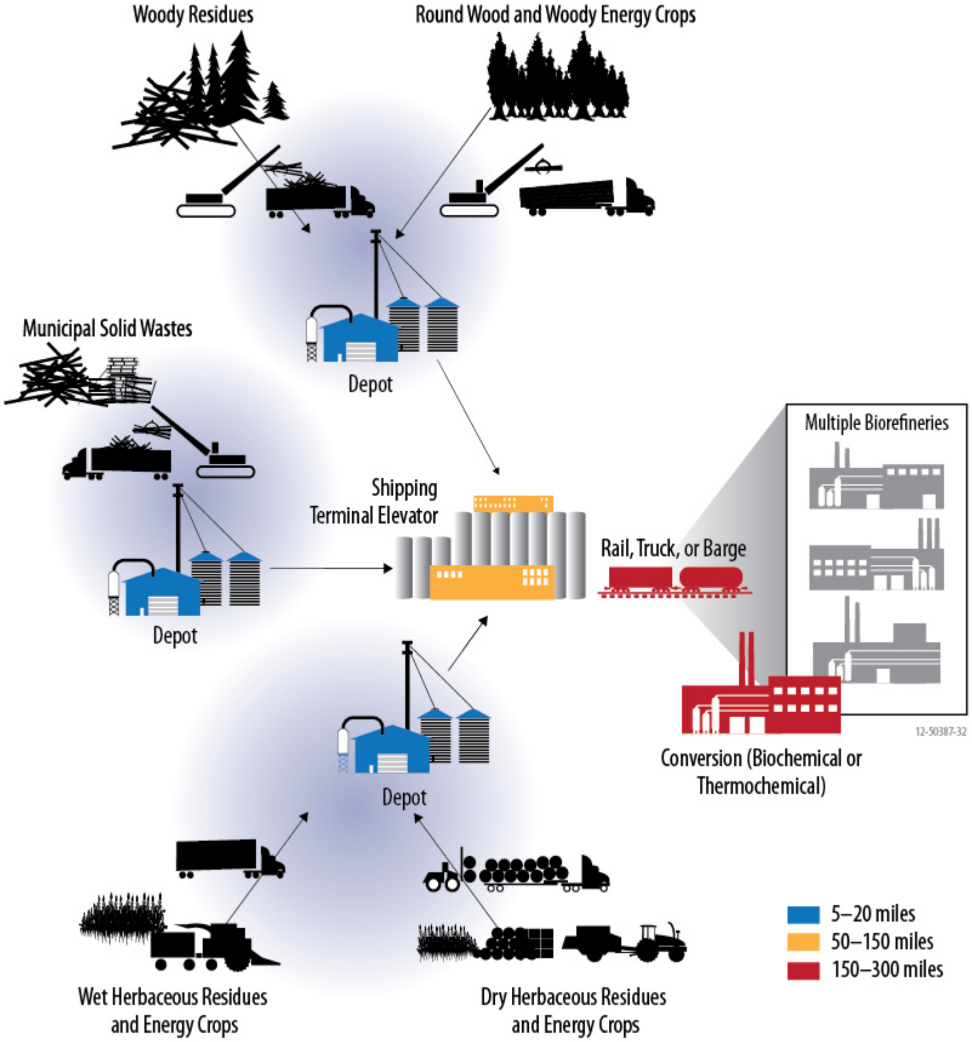


Figure WO–2. Conceptual advanced uniform-format feedstock supply system design that incorporates regionally distributed biomass preprocessing depots near biomass production locations to support flexible feedstock commodity trade.

Table WO–1. The DOE–Biomass Program Feedstock Supply and Logistics Platform addresses supply system R&D in an incremental approach that supports supply chain stages of development.

Platform Focus/Term	Resource Base	Moisture	Resource Variety
Existing supply systems (near term–through 2012)	Access to a niche or limited resource	Based on dry supply system (i.e. field-dried)	Designed for specific feedstock (i.e. corn stover)
Depot supply systems (longer term–2012+)	Access to a broader resource	Accepts higher-moisture feedstocks into system	Design addresses multiple feedstock types

Sam Tagore, Biomass Program Technology Manager in Feedstocks Logistics, discussed the role of feedstock density and quality in meeting biorefiners' feedstock specifications and introduced various preconversion, formulation, and densification approaches of interest to the Biomass Program (Figure WO–3).

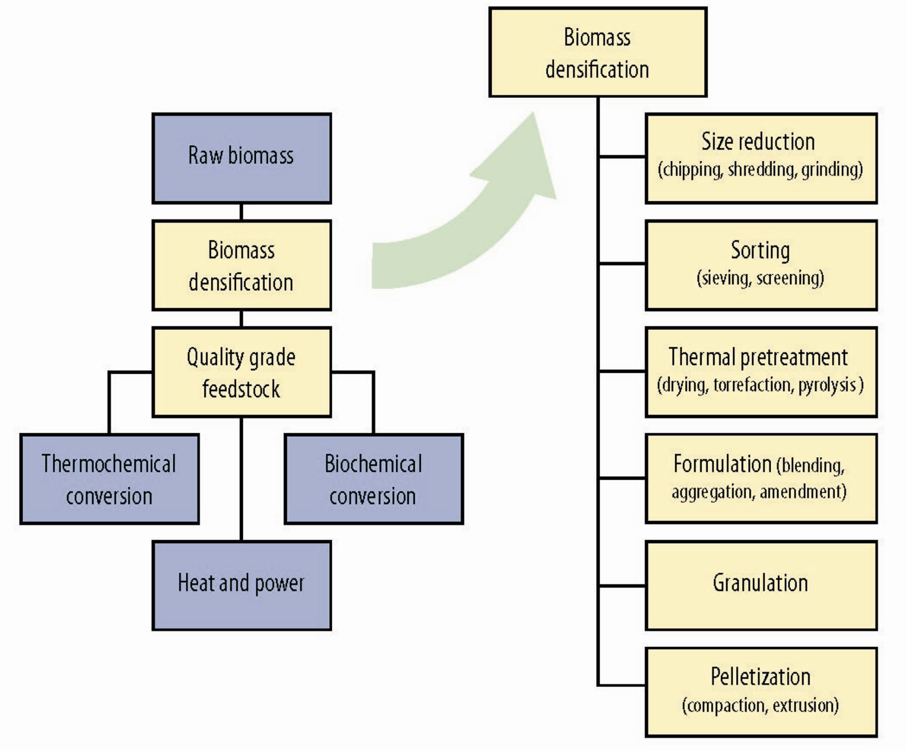


Figure WO–3. The densification challenge can be addressed through a variety of technologies, depending on the end-user's specifications.

Melissa Klembara, Biomass Program Technology Manager in Integrated Biorefineries (IBR), presented IBR project sensitivity analyses that indicate feedstock cost and quality are the highest risk areas for biorefiners. This directly impacts their ability to get financing. The risks of feedstock cost, quality, and quantity need to be addressed, and biorefiners need to be able to demonstrate the existence of a reliable and secure feedstock supply. Klembara suggested that the ideal feedstock would be dense, good quality, and aerobically stable, so that it can be managed with existing infrastructure. From her IBR technical perspective, consistent physical and compositional attributes are also important to allow biorefineries to run on "autopilot" and still achieve consistent yields.

Mission Areas

J. Richard Hess, Biofuels and Renewable Energy Technologies Department Manager at INL, presented three mission areas that would help address the biomass densification and quality challenges and enable industry expansion:

- Improve biomass density, stability, and infrastructure compatibility
- Improve biomass quality and end-use performance
- Increase accessible biomass quantities/diversity, and supply stability.

Hess oriented these mission areas within the context of program accomplishments and proposed future directions. The DOE–Biomass Program has shaped the vision of a national-scale bioenergy industry and supporting feedstock supply system that manages diversity and density early in the system to improve overall logistics costs.[l] He emphasized that much progress has been made in developing and reaching this vision through optimizing biomass logistics and defining product attributes compatible with existing high-volume, solids-handling infrastructure.

Now, this vision is expanding to include processes that ensure relieable, sustainable, and affordable supplies of feedstocks that not only meet biorefiners' specification requirements but are also optimized for supply system and conversion performance (Uniform Commodity Feedstocks). Constraints the vision must be accomplished within were presented: cost, energy balance, and greenhouse gas and sustainability requirements.

The concept of regionally distributed biomass preprocessing was presented as part of a feedstock commodity infrastructure network to help achieve the vision within the vision constraints and support the mission areas. "Feedstock Preprocessing Depots" manage resource diversity and optimize logistics by decoupling preprocessing from centrally located conversion facilities and performing some of these functions at regionally distributed centers that are proximate to the biomass production sites[l,m]. The objective of this approach is to achieve the feedstock quality and performance specifications required by biorefiners as near as practical to the site of production to benefit downstream logistics costs and overcome constraints.

The vision and mission areas were presented as hypotheses for addressing feedstock supply system challenges of today while enabling technologies, products, and markets of the future.

Research Elements to Accomplish Mission Areas

Among industry developers, terminology is inconsistent for describing the processes available to produce densified, on-spec feedstocks from raw, "as-harvested" biomass. To avoid confusion over frequently overlapping terms such as "logistics," "densification," "pretreatment," "preprocessing," and "upgrading," and to clearly distinguish supply system processes from conversion processes, the densification workshop was organized into six research elements, included in this report as chapters, that work together to transform biomass into easier-to-handle, denser, more homogenous feedstocks:

Biotechnology/ Genetics	Mechanical Preprocessing	Thermal Preconversion	Chemical Preconversion	Formulation	Densification

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[l] Hess JR et al. (2009) *Uniform-Format Solid Feedstock Supply System: Commodity-Scale Production of an Infrastructure-Compatible Bulk Solid from Herbaceous Lignocellulosic Biomass*, Report INL/EXT-09-15423, Idaho National Laboratory, Idaho Falls, ID.

[m] Pragnya et al. (2010) Advanced regional biomass processing depots: A key to the Logistical challenges of the cellulosic industry. *Biofuels, Bioprod, Bioref*, 5: 621–630.

Desired R&D Outcomes

The research elements explored during workshop presentations provide a framework to achieve critical industry-enabling production, supply, and logistics outcomes. Advancements in the research elements individually or collectively roll up to these outcomes, as shown in Table WO–2.

Table WO–2. Desired R&D outcomes to help establish sustainable, economically viable feedstock supply systems that meet biorefiner's specifications and enable industry expansion.

PRODUCTION	SUPPLY	LOGISTICS
Maximize gross & functional yield	*Improve conversion performance*	*Develop infrastructure-compatible logistics systems*
Increase biomass yield	Reduce/manage variability	Extend biomass stability
Ensure sustainable production systems	Maintain/recover biomass purity	Improve logistics efficiency
	Preserve/improve reactivity	Increase mass density
		Increase energy density

Workshop sessions discussed R&D currently underway that focuses on achieving these outcomes by (1) Biotechnology – Improving biomass yield and quality through crop development and science-based best management practices, and (2) Preprocessing – Managing resource diversity/upgrading biomass to achieve feedstock specifications, via R&D in mechanical preprocessing, thermal and chemical preconversion, formulation, and densification technologies.

During the course of workshop presentations, participants considered feedstock cost, handling format, and chemical composition specifications required by biorefineries and innovative applications of science and engineering that might be used to address the biomass densification challenge and produce consistent, economical, high-energy-value feedstocks from raw, "as-harvested" biomass.

Workshop Conclusions

Densification is generally associated with those processes that increase bulk density (mass per unit volume) of bulk solid materials including pelletization, briquetting, and granulation. For this workshop, densification concepts were expanded to include (1) liquefaction processes, such as pyrolysis, which produces a bio-oil of increased bulk and energy density compared to the biomass feedstock from which it is produced, as well as (2) biomass yield improvements that, in effect, increase both mass and energy density on a per-unit-area of production (e.g., ton/ac).

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Research results on pretreatment of blended feedstocks (a mixture of corn stover, switchgrass, eucalyptus, and pine) were presented as a specific example of formulation. The production of this blended feedstock was also demonstrated on the Feedstock PDU. Some participants saw formulation as an important aspect of reducing feedstock variability and as a key requirement for achieving uniform feedstocks. Many participants recognized that formulation is already practiced in biopower operations and recognized the potential benefits to biofuels production by reducing feedstock variability and mitigating the effects of undesirable components such as chlorine. In view of the specific blended feedstock presentation, some participants thought formulation may be limited by geographic co-location of biomass resources. Overall, participants thought that more information was necessary in order to fully understand the value of formulation.

Densification

Pelleting was discussed with an emphasis on optimizing process parmeters to affect physical characteristics (density, durability), solid fuel properties, and biochemical conversion performance. Preliminary research results on the pretreatability of pelletized corn stover were presented, and process development using a laboratory-scale pellet mill was demonstrated. For the most part, densification was seen as a way to facilitate logistical improvements, primarily transportation, storage, and handling. Despite the presentation of laboratory results that indicated no negative pretreatment impact, the potential for densification to be a detriment to feedstock performance was a recurring theme. Finally, participants questioned how energy-intensive pelletization processes could be economical for the development of high-volume biomass feedstock supply systems.

Points of Emphasis

Many of the advanced preprocessing technologies presented were considered by participants to be better suited for either biochemical or thermochemical conversion pathways; however, in most cases, research is lacking to support these conclusions. Participant feedback consistently raised questions regarding the cost-to-value relationship of the advanced preprocessing technologies and concepts presented, with a need to balance increased cost and energy requirements with gains and improvements to logistics and conversion processes. A common theme among all workshop sessions was that additional research, process data, and economic analysis is needed to better understand the potential of preconversion, formulation, and densfication technologies and their value for both the feedstock supply system and conversion performance.

Feedstock R&D Tools

Feedstock PDU

One of the highlights of the workshop was demonstration of the DOE–Biomass Program's Feedstock Process Demonstration Unit (PDU), which is managed and operated by INL's Bioenergy Program (Figure WO–4). Transforming raw, "as-harvested" biomass into uniform-format commodity feedstocks is the focus of the Bioenergy program at INL, and the Feedstock PDU provides a venue for bioenergy developers to work with the DOE–Biomass Program and INL to test preprocessing technologies and advance feedstock engineering into the development phase.

The scale of the Feedstock PDU (nominally 5 ton/hr) allows larger volumes to be produced in a reasonable time and provides processing data and information about scale-up issues from laboratory- and bench-scale systems.

For the Densification Workshop, the Feedstock PDU was demonstrated using a formulation of four types of biomass (corn stover, switchgrass, pine, and eucalyptus), which were combined in a 1-1-1-1 ratio and then densified into a pelletized product (Figure WO–5). The same formula was demonstrated using laboratory-scale equipment on the previous day, which helped to identify initial operating conditions for the larger system. This particular formulation was developed by a customer who determined this mixture provided beneficial results in their conversion process.

Figure WO–4. The Feedstock PDU is a flexible research system developed to test feedstock preprocessing, formulation, and densification processes, collect process data, and produce large quantities of advanced feedstocks for conversion testing.

Figure WO–5. Feedstock formulation was demonstrated using four types of biomass (corn stover, switchgrass, pine, and eucalyptus) processed in a 1-1-1-1 ratio and densified into a pelletized product.

Biomass Resource Library

Feedstock characteristics have a significant impact on conversion performance, and understanding performance-based relationships between specific feedstock specifications and conversion performance is crucial to the success of the bioenergy development. A significant effort within the DOE–Biomass Program's Feedstock Supply and Logistics Platform is understanding and capitalizing on the relationships between feedstocks and conversion performance to develop sustainable feedstock supply systems that are capable of providing reliable, commodity-scale supplies of consistent and economical feedstocks to biorefineries.

A cornerstone of this effort is the DOE–Biomass Resource Library and associated biomass characterization capabilities, which were presented at the workshop (Figure WO–6). The Biomass Resource Library is comprised of more than 14,000 physical feedstock samples, robust characterization capabilities, and a sophisticated data and sample management system. The feedstock sample data includes agronomic, harvest, storage, preprocessing, and physiochemical data that researchers can use to understand the variability of feedstock materials.

The Biomass Resource Library includes specification-performance data for a variety of feedstocks and processed intermediates to enable better understanding of how specific supply-chain operations (process-to-intermediate-to-specifications) influence the downstream conversion processes. Figure WO–7 shows examples of biomass variability relative to a biochemical and thermochemical specification.

Figure WO–6. The Biomass Resource Library provides bioenergy conversion developers with valuable understanding of the differing chemical and material characteristics between "as harvested" biomass materials and the pristine biomass feedstocks that conversion technologies have been designed around.

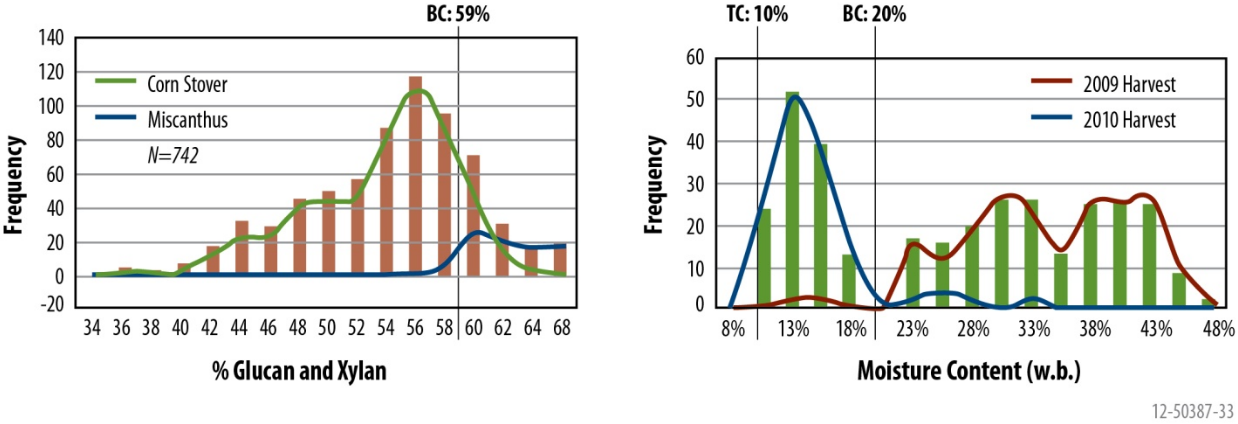


Figure WO–7. Feedstock variability in composition (a) and moisture (b) can have significant impact on . biochemical (BC) and thermochemical (TC)biorefinery operations.

Exploring Research Elements

Mini-Reviews and Bioenergy Industry Feedback

This Densification Workshop Summary Report provides a discussion of each of the research elements explored at the workshop. Research element chapters also include a mini-review of the topic and an overview of the workshop presentations, demonstrations, discussions, and participant feedback. The research element chapters are organized in two sections: “Biotechnology” and “Preprocessing.”

Section 1 – Biotechnology

Improving Biomass Yield and Quality

Chapter 1: “Biotechnology/Genetics” captures the concepts presented in the joint session on opportunities for biotechnology and genetics to increase resource availablity and address supply system and conversion performance issues.

Section 2 – Preprocessing

Managing Resource Diversity/Upgrading Biomass to Achieve Feedstock Specifications

Section 2 captures the workshop breakout session concepts and provides a more detailed exploration of the preprocessing research elements. These research elements are explored in Chapter 2: “Mechanical Preprocessing,” Chapter 3: “Thermal Preconversion,” Chapter 4: “Chemical Preconversion,” Chapter 5: “Formulation,” and Chapter 6: “Densification.” Each chapter provides a mini-review of the research element in terms of its application to development of advanced feedstocks that are energy-dense, on-spec, and affordable for biorefineries.

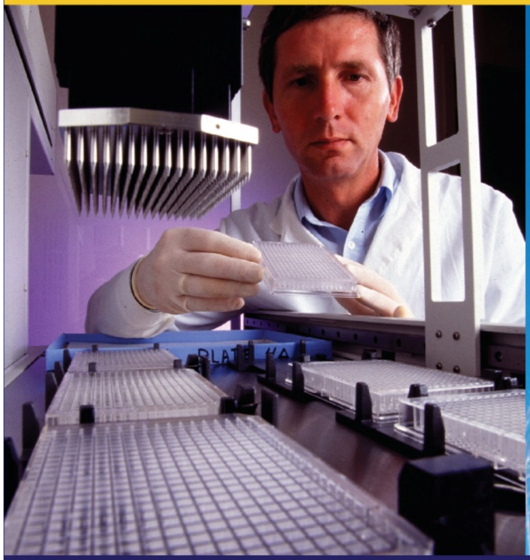
Appendixes

Participant comments are referenced with superscript numerals in the text and can be located verbatim as end notes in Appendix A.The workshop agenda, survey, and information about the Biomass Resource Library and Feedstock PDU demonstrations are also attached as appendixes.

Developing a sustainable bioenergy industry capable of meaningfully offsetting fossil fuel consumption presents a number of challenges for current production systems. While existing systems are effective at meeting present demands for food, feed, and fiber, the amount of biomass needed to support a bioenergy industry will require more efficient use of existing systems and development and implementation of new systems and practices to achieve significantly higher levels of biomass production than current baselines. The challenge requires several approaches, which include increasing crop yield and preserving feedstock quality.

Section 1 – Biotechnology

Improving Biomass Yield and Quality



Chapter 1 — Biotechnology/Genetics

Jeffrey A. Lacey (Idaho National Laboratory)

Henrik Scheller (Joint Bioenergy Institute)

David Agneta (Agrivida, Inc.)

Jisheng Li (Ceres, Inc.)

Deoxyribonucleic acid (DNA) sequence availability has increased the impact that biotechnology can potentially have on feedstock crop variety development through both marker assisted breeding and genetic engineering approaches. The ever-increasing volume of newly generated sequence information has necessitated the development of a variety of computer-assisted sequence and metabolic pathway analysis tools, as well as the technology to validate hypotheses *in planta*. All of these advanced biotechnological tools are being employed as researchers begin to identify and manipulate genes and metabolic pathways that affect both the yield and quality of biomass feedstocks (Figure 1–1).

Figure 1–1. The Biotechnology/Genetics joint session discussed current research and trends to genetically modify biomass crops for improved yield and conversion performance (Agneta 2012).

Biotechnology/Genetics Technologies

Recently available genome-scale sequencing efforts on higher plants (PlantGDB 2012) and the Biofuel Feedstock Genomics Resource (Childs et al. 2012) provide insights into a variety of potential energy crop species at the gene, transcript, protein, and genome scale. *Arabidopsis thaliana* was the first plant genome sequenced due to its small genome size and has been a valuable model plant species used to investigate many plant traits deemed valuable in bioenergy feedstocks. The complete genomes of rice (*Oryza sativa*), sorghum (*Sorghum bicolor*), and poplar (*Populus trichocarpa*) are now also available.

There is a considerable amount of interest in obtaining the genomic sequence for switchgrass, a dedicated bioenergy crop; however due to a large and complex genome, as well as multiple ploidy levels within the species, the sequencing and assembly of the complete switchgrass genome will take some time. There are major sequencing efforts underway and considerable progress has been made toward a completed switchgrass genome sequence. Great advances have been made in large-scale research tools, including genomics, transcriptomics, proteomics, and metabolic modeling. As examples of this recent progress, a switchgrass gene-expression microarray with over 100,000 probe sequences was recently developed (Fu et al. 2012) using newly obtained gene sequences, and a switchgrass bacterial artificial chromosome (BAC) library was created that gives approximately 10× coverage of the genome (Saski et al. 2011).

The availability of candidate genes with assigned putative functions has also stimulated the development of the technology required to validate gene-function hypotheses *in planta*. These methods include gene insertions, gene knock-outs, and gene silencing. Genetic transformation methods have been developed for all major crop plants, including switchgrass (Richards et al. 2001; Mann et al. 2011). Highly effective tissue-specific promoters are also being identified. To enhance gene expression of introduced genes in switchgrass, the promoters from two constitutively expressed switchgrass polyubiquitin genes (PvUbi1, PvUbi2) have been identified and cloned, and several transgenic plants have been generated using these promoters.

In addition to their use in switchgrass, these promoters have been shown to be effective in rice and tobacco (Mann et al. 2011). Methods are being developed for the introduction of genes into crops through engineered plastids. Researchers have been successful in using this system in tobacco and soybean, but nont in cereal or dedicated bioenergy crops. Advances in this area are expected as the plastid genomes of these crops are sequenced (Daniell 2002; Clarke & Daniell 2011). Plastid genetic engineering and its applications are discussed in a following section.

The ability to understand and influence key biomass traits will lead to the development of biomass crop varieties with superior characteristics, including higher density and yield, enhanced or customized composition, improved photosynthetic efficiency, reduced nutrient and water requirements, improved disease resistance and abiotic stress tolerance. Improvements in some or all of these traits will improve the value and utility of the feedstock while improving the sustainability of agricultural and silvicultural practices. The use of biotechnology to improve biomass crops does not come without risks. If strategies for improvement of biomass feedstock crops come to rely on genetic engineering, development costs will rise, and real and perceived risks will need to be addressed via trait containment strategies and the appropriate regulatory agencies.

Workshop Presentations

This section identifies and discusses research areas that represent some of the opportunities for biotechnology to benefit feedstock characteristics, including yield and quality. The rapid growth of available genomic sequence, combined with enhanced bioinformatic analyses and genetic transformation methods, has enabled considerable progress toward a better understanding the biochemistry of biomass synthesis, deconstruction, and the altering of enzymes and biochemical pathways that could lead to biomass with improved characteristics. While workshop participants generally viewed genetic enhancements as potentially beneficial to feedstock quality and quantity[1], there were some issues identified that deserve careful consideration as biotechnology is deployed in feedstock production[2]. While increases in yield seem to be the most universally beneficial and easily attainable feedstock enhancement, the successful deployment of biotechnology in feedstock will likely require enhancements in both quantity and quality traits[3,4].

Three workshop participants addressed some of these opportunities in their presentations and shared highlights of feedstock-related research being conducted at their institutions. The presented topics, as well as a few other key topics, are discussed in the following sections as a mini-review of the role and impact of biotechnology on feedstock improvement.

Development and Improvement of Dedicated Energy Crops

Dedicated energy crops with very high-density biomass and low input requirements will transform the bioenergy sector. They will enable reliable, full-scale feedstock supplies to displace oil and coal for biofuel and biopower production and be produced from less land, lower-quality land, and at lower cost than standard varieties. Reducing nitrogen fertilizer inputs will be further transformative because it will reduce N_2O, NOx, and other greenhouse-gas emissions, increase life-cycle energy ratios, reduce run-offs and water pollution, and drive production costs down even further. Workshop participants expressed mixed opinions on the subject of yield. While increased yield will improve the economics of feedstock utilization[5,6,7], some participants expressed concern that the cost of genetically modifying the crops would drive up the cost of the raw materials[8,9], while others felt that yield was only one of the traits that needed to be improved[10,11].

Scientists at Ceres, Inc. (Workshop presenter) have discovered several genes that increase plant biomass and reduce nitrogen-fertilizer requirements, and are applying them to carbon-negative dedicated energy crops (DECs). Ceres is evaluating four genes regulating the efficient use of nitrogen in switchgrass and miscanthus, and is applying the best of them to sorghum. A pipeline of cloning, transformation, lab evaluation, and field trials is well established. Switchgrass plants are growing under United States Department of Agriculture–Animal and Plant Health Inspection Service (USDA–APHIS) permits in Texas, Tennessee, Arizona and Georgia for determination of biomass increases, reductions in nitrogen requirements, and increases in carbon sequestration. Miscanthus trials are being planted, and sorghum evaluations are set for next year. Consecutive years of switchgrass data show promising outcomes. Results will be used to advance DEC towards commercialization and to model greenhouse-gas reductions and fossil fuel displacement deployed on a commercial scale. In another recent study, researchers have shown that the overexpression of a single miRNA that targets a family of transcription factors can increase biomass yields in switchgrass by 58–101% (Fu et al. 2012).

Traditional breeding programs have benefitted from advancements in biotechnology through marker assisted breeding. Researchers at Oklahoma State University have been involved in switchgrass breeding for 20 years, with a major focus on the development of new cultivars. One recent product of this switchgrass breeding program, Cimarron, produces significantly more biomass (5–15%) (Wu and Taliaferro 2008) than the highest-yielding commercial cultivar (Alamo). To better understand the association between phenotype and genotype, two mapping populations of switchgrass were created. Over 1,000 simple sequence repeat (SSR) markers have been identified and developed for use (Wang et al. 2011), as has a high-density SSR linkage map of switchgrass (Liu et al. 2012). These molecular tools will enable researchers to link chromosomal regions with biomass quality traits and provide the identity of gene and biochemical pathways to target for developing cultivars with higher yields and improved characteristics.

Enhanced Composition

One of the recurring topics in workshop participants' comments was related to the use of biotechnology to limit feedstock variability[12]. The reduction of variability in composition in feedstocks would enhance the efficiency and stability of the biochemical conversion processes[13,14]; however, this could be difficult due to the variety of feedstock sources currently being considered[15]. Feedstocks for biofuel production are composed mostly of the walls that surround plant cells. These cell walls are made of complex polymers (polysaccharides, glycoproteins, and lignin) that evolved to be highly resistant to the impact of the environment and to microbial degradation. It is therefore not surprising that their efficient conversion into biofuels is challenging.

The major obstacles to converting plant cell walls to fermentable sugars are significant:

1. Cell-wall polymers are difficult to depolymerize and convert into fermentable sugars; this requires pretreatment and high-cost enzymes for optimal conversion
2. Plant biomass contains compounds (e.g., acetate esters and aromatic compounds) that are inhibitory to biofuels fermentation (Manabe et al. 2011)
3. About half of the sugars in biomass are pentoses, which are much more difficult to ferment into fuels than hexoses (Pauly & Keegstra 2010; Scheller & Ulvskov 2010)

4. Lignin constitutes about 30% of plant biomass and is not only the major reason for the difficulty in degrading the cell walls, but also comprises a large fraction of biomass with little current value (Simmons et al. 2010).

Cost-efficient conversion of lignocellulosic biomass into energy will require the development of genetically improved bioenergy crops, such as switchgrass and poplar, that are optimized for biomass production, agronomically useful cell-wall characteristics, enhanced density and yield, and improved nutrient- and water-use efficiency.

There are significant gaps in the current understanding of cell-wall assembly that must be addressed before customized crops with enhanced composition can be developed: first, the mechanism of plant cell-wall assembly is very poorly understood, and second, the composition of plant cell walls and its relationship to recalcitrance needs to be determined. To address these gaps, the primary objective of the Feedstocks Division at the Joint Bioenergy Institute (JBEI, Workshop presenter), one of the DOE–Bioenergy Research Centers, is to generate basic knowledge about plant cell-wall biosynthesis and modification to facilitate the development of a new generation of feedstocks.

Enhanced Carbohydrate Content

JBEI has made breakthroughs in identifying and characterizing key enzymes involved in biosynthesis of cell-wall polysaccharides. JBEI researchers used an array of bioinformatic and proteomic tools to identify candidate genes, which were subsequently validated by studies of corresponding mutants of heterologously expressed proteins. Many of the bioinformatic tools were developed to allow an optimal selection of candidate genes (Heazlewood 2007; Durek et al. 2010; Jung et al. 2010; Oikawa et al. 2010; Joshi et al. 2011; Lee et al. 2011; Seo et al. 2011; Smith-Moritz et al. 2011), and JBEI has cloned all glycosyltransferases (GTs) (central enzymes in cell-wall biosynthesis) in Arabidopsis and many in rice, particularly those likely involved in biosynthesis of hemicellulose. JBEI has identified the GTs responsible for adding glucuronic acid and xylose side-chain residues to the xylan backbone (Oikawa et al. 2010), and their activity has been confirmed by biochemical characterization of the purified enzymes. The knowledge obtained with this approach has been used to modify plants and improve feedstock properties by manipulating characterized genes.

The modifications to hemicellulose and pectin are important, both in the plant and for biofuels production. However, none of the genes responsible for these modifications has been previously identified. JBEI identified four reduced wall acetylation (RWA) proteins in Arabidopsis with putative roles in cell-wall acetylation (Manabe et al. 2011). Loss-of-function mutants in the RWA proteins resulted in up to 30% less acetylation of polysaccharides in the leaf and stem cell walls, while maintaining normal growth and disease resistance (Manabe et al. 2011). This reduction in acetate led to a two to threefold increase in sugar yield after pretreatment and decreased inhibition of subsequent yeast fermentation to fuels.

Recently, it was confirmed that RWA proteins are not acetyltransferases by themselves, but function together with proteins belonging to the large DUF231 family (Oikawa et al. 2010; Manabe et al. 2011). As with acetate, reduction in ferulate relieves inhibition in biofuels fermentation (Harholt et al. 2010). A rice mutant that overexpresses one of the BAHD acyltransferase genes was shown to have reduced ferulic acid in leaves, with increased coumaric acid. Growth of the plants was indistinguishable from the wild type, and they showed a twofold improvement in saccharification. This gene was transferred to switchgrass, and transgenic switchgrass lines expressing the gene are being generated. The application of advanced techniques to improve switchgrass as a bioenergy crop relies on detailed genome information. In close collaboration with the Joint Genome Institute (JGI) and Clemson University, JBEI has made significant progress in sequencing the switchgrass genome.

Altered Lignin Content

The most basic approach for modifying lignin content is to have the plant produce less total lignin. When the amount of lignin in the plant is reduced, there is, by default, proportionally more cellulose and hemicelluloses in the plant that should be easier to access. Plants have been engineered to produce less total lignin; however, the resulting plants were low yielding. In a recent study, the yield deficiency in a low-lignin plant was overcome by also removing salicylic acid (SA), a plant stress hormone that affects plant growth and development. SA levels in plants are also inversely proportional to lignin, so when lignin levels are low, SA levels are high. By genetically removing SA from a low-lignin Arabidopsis mutant, researchers were able to restore normal plant-growth characteristics (Gallego-Giraldo et al. 2011).

The lignin synthesis pathway consists of many biochemical reactions, and all of these can be targeted as researchers work to reduce lignin levels. Several approaches have been used to both investigate lignin biosynthesis and alter this synthesis in a manner that would benefit saccharification efficiency. Lignin in switchgrass has been modified by reducing the function of the last gene in the lignin biosynthesis pathway, cinnamyl alcohol dehydrogenase (CAD). The resulting mutant plants released more glucose when subjected to an alkaline pretreatment than did control plants (Saathoff et al. 2011).

Reduction of the degree of polymerization of lignin polymers is one approach that has proved to be a highly successful strategy. In this approach, researchers at JBEI partially replaced native monolignols with novel monolignol derivatives that hinder further condensation of polymers or reduce branching. Plants were generated that accumulated the modified monolignols using a secondary wall promoter. The resulting transformants had lignin with a reduced degree of polymerization and altered composition. The plants have the same content of total lignin but highly improved saccharification properties.

Researchers at JBEI have also designed a strategy to reduce lignin or xylan content in fiber cells by complementing mutants using vessel-specific promoters. Unlike mutants in xylan or lignin biosynthesis, which are impaired in growth and development, the plants engineered at JBEI grow as well as wild-type plants in spite of the reduced xylan or lignin content. With this approach, JBEI researchers have generated healthy plants with reduced lignin or xylan content and have increased stem density by up to 20% compared with non-modified plants. The engineered plants also have highly improved deconstruction properties.

Discussion of Technology Impacts and Challenges

Plant-Expressed Enzymes

Plants have the ability to express lignocellulose-degrading enzymes that can be used in the conversion of biomass to fermentable sugars, and progress in this field of research was recently reviewed (Sainz 2009). One of the challenges of using engineered plants to produce their own lignocellulose-degrading enzymes is keeping the expressed enzymes from degrading the living plant. Enzyme inactivation strategies are needed for success in this endeavor, and some researchers are making progress. Agrivida (Workshop presenter) is an agricultural biotechnology company developing industrial crop feedstocks for biofuels and biochemicals. Agrivida’s crops have improved processing traits that enable efficient, low-cost conversion of cellulosic components into fermentable sugars.

Currently, pretreatment and enzymatic conversion of the major cell-wall components, cellulose and hemicellulose, into fermentable sugars is the most expensive processing step that limits the widespread adoption of biofuels technologies. To reduce production costs Agrivida is consolidating pretreatment and enzyme production within the crop (Figure 1–2). In this strategy, transgenic plants express engineered cell-wall-degrading enzymes in an inactive form that can be reactivated after harvest. Agrivida researchers have engineered protein elements that disrupt enzyme activity during normal plant growth.

Upon exposure to a specific processing condition, the engineered enzymes are converted into their active form. The technology significantly lowers pretreatment costs and enzyme loadings (>75% reduction) below those currently achieved in the industry.

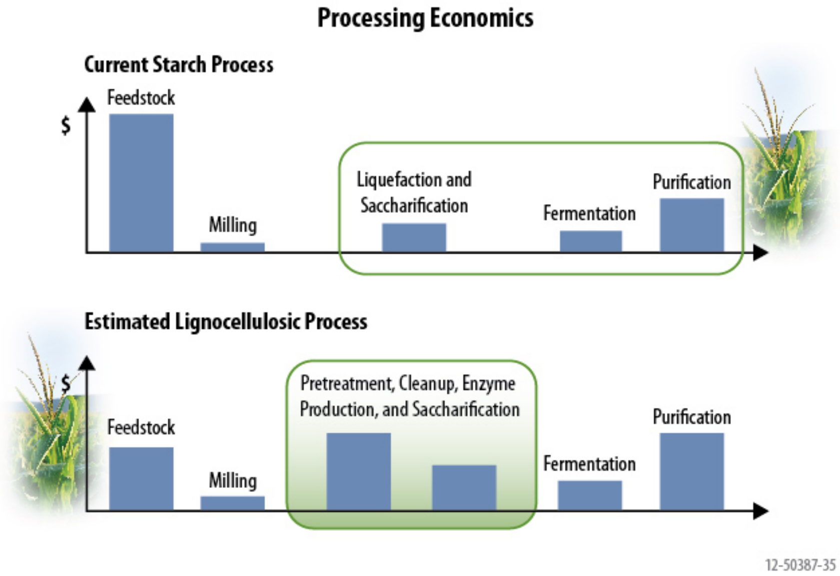


Figure 1–2. Biotechnology may help reduce pretreatment and enzymatic conversion costs by enabling consolidation of these processes within the crop by implementing plant-expressed enzymes (Agneta 2012).

Reduced Ash Content

While silica modification and ash reduction were not topics addressed by the workshop presenters, many attendees indicated that the use of biotechnology for the reduction of ash should be one of the top priorities, especially for thermochemical conversion processes[16,17,18,19,20,21,22,23,24]. Ash is a component of biomass that includes all mineral content. This would include, but is not limited to, Si, P, K, Na, Cl, and many other minor elements, such as Mo and Se. Ash content is the sum of that which is intrinsic to the plant (i.e. internal) and that which comes in as dirt (i.e. surface contamination). Ash is undesireable in all biomass conversion pathways, but it can be particularly problematic in biomass that is destined for thermal conversion. Silica, chlorine, and other ash constituents can melt together, creating a slag layer inside the furnace. This layer decreases the efficiency of the furnace and must be removed periodically.

While mechanical steps could be devised to reduce surface contaminant ash, the genetic control of intrinsic ash content is not well understood. Recent research has suggested that genetics do play a role in ash composition in wheat straw and that modifications and selections could be made to reduce the concentrations of some of the less-desirable minerals, such as silica, chlorine, and potassium (El-Nashaar et al. 2010). As the molecular pathways that uptake, transport, and deposit minerals into the plant tissues become known, researchers can begin to devise strategies to alter, reduce, or even customize the ash content in specific crops.

Silicon is the most plentiful mineral found in soil and biomass, especially the herbaceous species. Although not an essential mineral for growth, studies have shown that its presence in the plant tissue has many benefits, including enhanced yields, improved resistance to pests, and resistance to lodging. Silicon is actively transported in the plant in the form of silicic acid, and uptake and deposition can be affected through genetic modifications. Silicon-transporter genes were first discovered in rice *(Oryza sativa)* and since have been identified in other plants, including barley and maize. In rice, there are three known genes that contribute to silica content: low silicon rice 1 (Lsi1), Lsi2, and Lsi6. Lsi1 is a constitutively expressed silicon transporter in the roots (Ma et al. 2006) and is located on the distal side of the root cells. Suppression of this gene resulted in plants with reduced silica levels due to its role in silicon uptake from the soil (Ma et al. 2006; Yamaji and Ma 2007). Lsi2 is localized on the proximal side of the root cells and moves the silicon from the root cells to the stele (Ma et al. 2007a), where it can then be transported throughout the plant.

Increased plant-tissue silica levels are positively correlated with increased abundance of Lsi1 and Lsi2 in rice roots (Ma et al. 2007b; Ma & Yamaji 2008). Once inside the vascular system of the plant, Lsi6 is involved in the transfer of silicon throughout the plant and its deposition in specific tissues (Yamaji et al. 2008; Yamaji & Ma 2009). Lsi6 has also been found in the nodes, transporting silicon preferentially to the panicles (Yamaji & Ma 2009). Similar transporters have been identified in barley (*Hordeum vulgare*) (Chiba et al. 2009; Mitani et al. 2009) and maize (*Zea mays*) (Mitani et al. 2009); however, the pathways differ from that identified in rice (Mitani et al. 2009). Additionally, some of the silicon transporters have yet to be discovered in some plants (Zhang et al. 2011; Ma et al. 2011). Six chromosomal regions in wheat (*Triticum aestivum*) associated with silica deposition have been identified (Peleg et al. 2010). This study showed increased levels of silica in domesticated lines of wheat and suggests that this could be an indirect result of the selection of another trait. Efforts to identify additional silicon pathway genes are still ongoing (Zhang et al. 2011; Ma et al. 2011).

Transgene Containment

Although not a topic discussed by the workshop presenters, there was concern expressed by the workshop participants related to the real and perceived risks associated with the containment of transgenes from the genetically modified crops[25,26,27]. Biotechnology research is currently being done to develop technologies that will address these concerns, including the development of trait-containment technologies. Trait containment serves two main purposes: (1) it will keep the transgene in the plant through reproduction, and (2) it will keep the transgene from contaminating the genomes of neighboring crops, native plants, and weeds. During sexual recombination, the transgenes can be lost. There are several trait-containment strategies that are currently being investigated and/or developed. Two of these strategies that could benefit from biotechnological advances include plastid transformation and apomixis.

During typical plant sexual reproduction, chloroplasts are passed on to the progeny exclusively from the maternal plant. No plastids are passed on from the paternal plant as the egg only accepts the DNA from the pollen sperm cell. The chloroplast also has its own genome, and scientists have been successful in introducing genes into the chloroplast for expression in the plant. Because chloroplasts are not passed on to the next generation through pollen, chloroplast genetic engineering has been successfully developed as a trait-containment strategy in some plants (Day & Goldschmidt-Clermont 2011). However this technology has not been used in any bioenergy crops (Clarke & Daniell 2011). This technology will likely become widely applied to biomass crops as the chloroplast genomes of relevant biomass species become available.

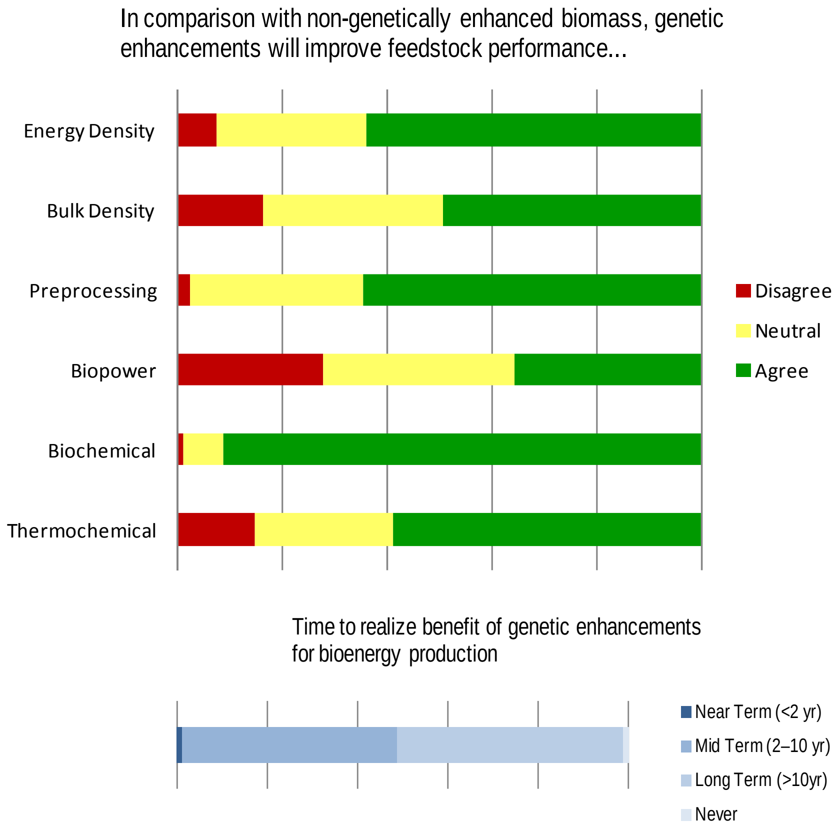
Apomixis represents another possible method for transgene containment. Apomixis is a form of asexual reproduction observed in many plants and results in seeds that are genetically identical to the maternal plant. Apomixis is not found in any food-crop species, and the genetic pathways inducing apomixis still need to be discovered. If combined with male sterility, apomixis would function to both eliminate the loss of transgenes during reproduction and keep the genetic modifications from escaping to neighboring fields and plants. If apomixis could be induced in high-yielding hybrid plants, the seed from the high-yielding hybrid crops could be used to plant the next year’s crop. While apomixis represents a promising technology, its mechanisms and pathways have proven difficult to identify and understand. Recent efforts to better understand its pathway in crop plants have included selective breeding of partially apomictic sorghum (Elkonin et al. 2012) and a gene-expression microarray study of partially apomictic sorghum (Carmen et al. 2007). Progress is being made toward an understanding of this reproductive phenomenon; however, more progress is needed if this is to become a viable trait-containment technology for use in the field.

Workshop Conclusions

Biotechnology can play a prominent role in feedstock improvement. Workshop participants expressed that biotechnology will have the greatest impact on biochemical conversion of feedstocks, and more than half expect that improvements also can be made in yield, preprocessing, and thermochemical conversion processes (Figure 1–3). While the potential for this improvement is promising, its use and successful deployment is not without challenges. (See Table 1–1 for a summary of common themes and points of emphasis from Biotechnology/Genetics presentations, discussions, and participant surveys.)

Particants identified a number of challenges that may be encountered as researchers use biotechnology approaches to improve feedstock yield and quality. Technology, especially biotechnology, can take years to develop from concept to field application. While researchers are certain that they can make the feedstock improvement discoveries and advancements that will be required to support the growing needs for fuels and chemicals[28], there is some concern as to whether this progress will occur rapidly enough[29] (Figure 1–3). Another concern is public acceptance of genetically modified crops[30,31,32,33]. The required regulation and monitoring of genetically modified crops will not prevent their deployment; however, these may make their use more cumbersome, ultimately affecting the cost of the feedstock[34,35,36,37]. In addition, patents and other intellectual property concerns may limit access to high-value cultivars[38,39], again affecting the cost of the feedstock.

While these concerns are not insurmountable, they should be points of consideration during all phases of research and development. The successful deployment of this technology will require the coordinated effort and cooperation of researchers, regulators, and educators.



In comparison with non-genetically enhanced biomass, genetic enhancements will improve feedstock performance...

Time to realize benefit of genetic enhancements for bioenergy production

Figure 1–3. There was interest in the benefits of plant breeding and biotechnology to bioenergy feedstock development, and these were considered to be mid- and long-term advancements.

Table 1–1. Summary of common themes and points of emphasis from Biotechnology/Genetics presentations, discussions, and participant surveys.

Desired R&D Outcomes	Potential Approaches	Barriers/Constraints
SUPPLY (Conversion Performance) • Variability – reduce through plant breeding • Purity – reduce undesirable constituents through (1) plant breeding and (2) optimized cropping systems • Reactivity – reduce recalcitrance through plant breeding **LOGISTICS** • Stability – improve moisture management **PRODUCTION** • Density – increase production density through increased biomass yields • Sustainability – develop dedicated energy crops	• Develop genetically modified organisms (GMOs) that address multiple desirable traits - Increase biomass yields - Reduce variability and increase stress resistance - Manage content of particular constituents that impact conversion processes (i.e. calcium, potassium, sodium, chlorine, nitrogen, ash, silica, organic sulfur compounds, oxygen) • Install plant-expressed enzymes that enhance supply system and conversion performance	• Time to commercialization • Developing feedstocks with same GMO traits (large variety of feedstocks and range of production conditions) • “Proprietary” limitations of researchers • Reduced disease/damage resistance, invasiveness, and other unintended consequences • Limited understanding of how developments will affect agricultural production and agronomic properties • Regulatory concerns common to GMOs • Carbon balance/footprint, cost of carbon emissions, land-use efficiency • Cost recovery on low-value feedstocks

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Technologies exist to meet densification objectives, and ultimately, provide dense, consistent, on-spec and affordable feedstocks to biorefineries. There is much to understand about the practicality of implementing these technologies and where the greatest opportunities for positive supply chain impact reside.

Section 2 – Preprocessing

Managing Resource Diversity/Upgrading Biomass to Meet Feedstock Specifications

Chapter 2 — Mechanical Preprocessing

Tyler Westover, Christopher T. Wright, Neal Yancey (Idaho National Laboratory)

James H. (Jim) Dooley (Forest Concepts, LLC)

Mechanical preprocessing is one of the primary operations in the feedstock supply system for a lignocellulosic biorefinery. It is the means by which raw biomass from the field or forest is mechanically transformed into an on-spec feedstock with characteristics better suited for the fuel-conversion process. Current understanding accepts that the characteristics of raw biomass are unable to meet the requirements of both logistic and fuel-conversion systems and must be upgraded prior to delivery at the biorefinery plant gate (Hamelinck et al. 2005).

Mechanical preprocessing is widely considered crucial to the success of a large-scale lignocellulosic fuel industry (Miao et al. 2010; Bitra 2009; Yancey et al. 2009), and its operations are often located early in the supply system to maximize system performance and preserve feedstock quality. Important features of mechanical pretreatment processes include low capital and operational costs and efficacy on a wide range of materials.

The objectives of mechanical preprocessing can be summarized as the production of feedstock materials with at least the following five characteristics:

1. High mass density for efficient storage and transportation
2. Flowability as a bulk granular solid or portability as a large bale
3. High aerobic stability to minimize mass and energy losses during storage
4. High conversion efficiencies (i.e. low recalcitrance)
5. Easy separability into components with different values/chemical compositions.

These characteristics are inter-related and are impacted in different ways by a wide array of preprocessing operations at all levels within the feedstock supply system. This chapter discusses these characteristics in relationship to common mechanical preprocessing technologies and the growing biofuels industry.

At the Densification Workshop, the Mechanical Preprocessing breakout session focused on two technology pathways for mechanical preprocessing:

- *Size reduction*, or “comminution,” to facilitate material handling, aerobic stability, and conversion efficiency (i.e. low recalcitrance)
- *Mechanical separation*, or “fractionation,” to separate target constituents from bulk material (DOE 2002).

Within mechanical preprocessing operations, size reduction is often the process by which the desired feedstock characteristics are achieved. For example, comminution to particle sizes of 1 to 2 mm, which is necessary for biochemical conversion (Walsum et al. 1996), fast pyrolysis (Mohan et al. 2006), or gasification (Kumar et al. 2009), not only generates new surface area for improved heat transfer and microorganism access (Dien et al. 2005), but it also releases dissolved organic components (Sun and Cheng 2002) and opens material structures that impede microbial and acid attack (Dien et al. 2005; Palmowski and Muller 1999). Size reduction has also been shown to decrease recalcitrance by reducing the degree of polymerization and cellulose crystallinity (Sun and Cheng 2002). Importantly, size-reduction technologies result in increased material density because smaller particles more easily fill void spaces and increase packing density. Small and relatively smoother particles that result from comminution typically also have improved material handling characteristics and, in some cases, can be handled very efficiently in equipment designed for bulk grains. Lastly, the comminution process can provide a means to mechanically separate, or fractionate, biomass materials so that high- or low-value constituents can be isolated for different end uses.

Mechanical Preprocessing Technologies

Size Reduction

The most common mechanical preprocessing technologies focus heavily on size reduction (comminution) and include hammer-and-knife milling/grinding, chipping, shredding, and ball roller milling. These technologies are briefly introduced in this chapter. It must be remembered, however, that although these technologies are the most widespread, they are not necessarily the most efficient and can consume more than 30% of the energy required to convert biomass to ethanol (USDA 1993; Aden et al. 2002). For certain materials, other approaches such as veneering and knife shearing have demonstrated far greater efficiencies, and these alternate technologies are also introduced in this chapter, along with techniques to achieve mechanical separation or fractionation of plant parts for use according to their greatest value or minimum negative impact.

Hammer Milling: Hammer mills use large rotating bars (i.e., hammers) that impact the material at high velocity to shatter and tear material particles. Hammer mills are recognized as the technology that is capable of finely grinding the greatest variety of materials (Bitra 2009; Igathinathane et al. 2008) and are noted for achieving high size-reduction ratios and yielding cubic-shaped particles (Nikolov 2004; Mani 2005). Fine or especially difficult-to-grind materials are often best comminuted using high-speed hammer mills with small diameter rotors (Bitra 2009). High tip speeds also result in material striking the outlet screen at steep angles while slower speeds result in material trajectories more perpendicular to the screen, allowing greater numbers of coarse particles to pass through (Bargen et al. 1981). Operating speed, moisture content, and initial particle size appear to be crucial in minimizing effective specific-energy requirements for biomass size reduction (Yancey et al. 2009).

Knife Shearing: Knife mills have worked successfully for shredding forages under various crop and machine conditions. The specific energy consumption of knife mills can be higher or lower than that of hammer mills, depending on the desired particle-size reduction and the material to be comminuted (Cadoche and López 1989). In general, the energy required to grind herbaceous materials is much less than what is required to grind woody materials (Zhu et al. 2011). Knife shearing may also promote starch gelatinization for improved pelletization and conversion performance (Kaliyan and Morey 2006).

Linear Knife Shearing: Linear knife-shearing tools typically consist of grid arrangements of sharp knife blades to slice biomass into small pieces. This technique has been reported to be an efficient first-stage size-reduction technique for high- and low-moisture switchgrass and corn stover (Igathinathane et al. 2008, 2009).

Industrial Veneering: Industrial veneering employs large lathes to convert roundwood logs into industrial-grade veneer that has the thickness desired in the end-product feedstock. Veneer making is followed by oriented shearing of the veneer sheets by a rotary bypass shear with cutter widths equal to the desired particle length along the fiber grain. The resulting wood breaks naturally along the grain with minimal energy input to form small uniform particles with highly uniform length and thickness (Lutz 1974).

Mechanical Separation

Mechanical separation, or fractionation, is the process of separating biomass into different anatomical fractions so that each may be used for different purposes. Fractionation techniques are well developed for many harvesting technologies. For example, wheat grain, corn kernels, peas, and other crops are routinely separated from the remaining plant material during harvest. However, for biomass materials, fractionation can be useful at locations far from the field to separate different tissue types that are better suited for divergent conversion pathways. Although research in chemical fractionation techniques is well developed, corresponding research in mechanical techniques to fractionate materials is still emerging.

Workshop Presentations

Mechanical preprocessing is generally recognized as an essential operation within the biomass feedstock supply chain to transform biomass from the raw harvested state (e.g. bales, chips, etc) to the format specification required by a biorefinery (e.g. ground bulk format). Mechanical preprocessing is one of the most expensive and energy-intensive operations within the feedstock supply chain. Two presentations were given at the workshop to highlight work being done to improve mechanical preprocessing operations. The first presentation focused on increasing the throughput and efficiency of a hammermill and then separating the comminuted material in order to create fractions with specific chemical properties. The second presentation exhibited rotary shearing results to demonstrate the substantial gains in efficiency that can be achieved by selectively comminuting materials along naturally weak boundaries. These presentations are included in this section as case studies. After the case studies are described, the technology impact of mechanical preprocessing will be discussed, including improvements in throughput, efficiency, and handling, and tighter control of resulting particle size and shape distributions.

Case Study: Optimization Opportunities in Mechanical Preprocessing to Create Cost-Effective, High-Quality Feedstocks

Tyler Westover, Christopher T. Wright, and Neal Yancey (Idaho National Laboratory)

Energy-intensive mechanical preprocessing operations such as comminution tend to be expensive relative to the low-value feedstock that they produce. This study investigates optimization opportunities to reduce capital and operating costs associated with biomass comminution. Three aspects of mechanical preprocessing are considered: (1) improved size reduction via optimization of hammer mill configuration, (2) improved size reduction via pneumatic-assisted hammer milling, and (3) improved control of particle size and particle-size distribution through proper selection of grinder process parameters. This case study also discusses the importance of flowability and provides an overview of flowability measurements.

1. *Improved size reduction via optimization of hammer-mill configuration (hammer design, tip speed, shear plate tolerance)*

Hammer-mill grinding tests were conducted using a small commercial grinder with a nominal power rating of 85 hp (63.4 kW) to evaluate the effects of grinder configuration and process parameters on grinder capacity and efficiency. The process parameters included hammer-tip speed and shear-plate tolerance. Capacity was measured in DM ton/hr, and efficiency was measured in DM ton treated/gal fuel consumed.

A baseline capacity and efficiency was determined using standard fixed cutters (see data labeled “Original Hammer” in Figure 2–1) and screen configurations (1.25-in. hexagonal screen) found on several models of nearly all major grinder manufacturers who offer machines capable of grinding large baled herbaceous biomass. Due to the proprietary nature of the specific hammer configurations, data are presented as Original Hammer, Hammer 1, and Hammer 2.

Grinder capacities for the three hammer configurations and three feedstock varieties (switchgrass, corn stover, and wheat straw) are shown in Figure 2–1. Although the results are mixed when comparing the Hammer 1 and Hammer 2 designs, the new hammer configurations showed significant improvements over the original hammers. Overall, Hammer 2 produced the best improvements in grinder capacity, with an average improvement of 200% and exceeding the baseline capacity by as much 425%. As such, Hammer 2 was used to evaluate two additional grinder modifications, namely an increase in tip speed and a combined increase in tip speed and tighter tolerance between hammers and shear plate. Increasing the tip speed improved grinder capacity for all feedstocks, but reducing the gap between the shear plate and the hammers decreased grinder capacities compared to tip speed alone. Combined uncertainty from run time and feedstock weight measurements is estimated to be less than 5% of the reported values and is represented as error bars in Figure 2–1 (due to cost constraints, additional test runs were not performed to further validate experimental uncertainties and explore additional combinations of hammers and feedstocks).

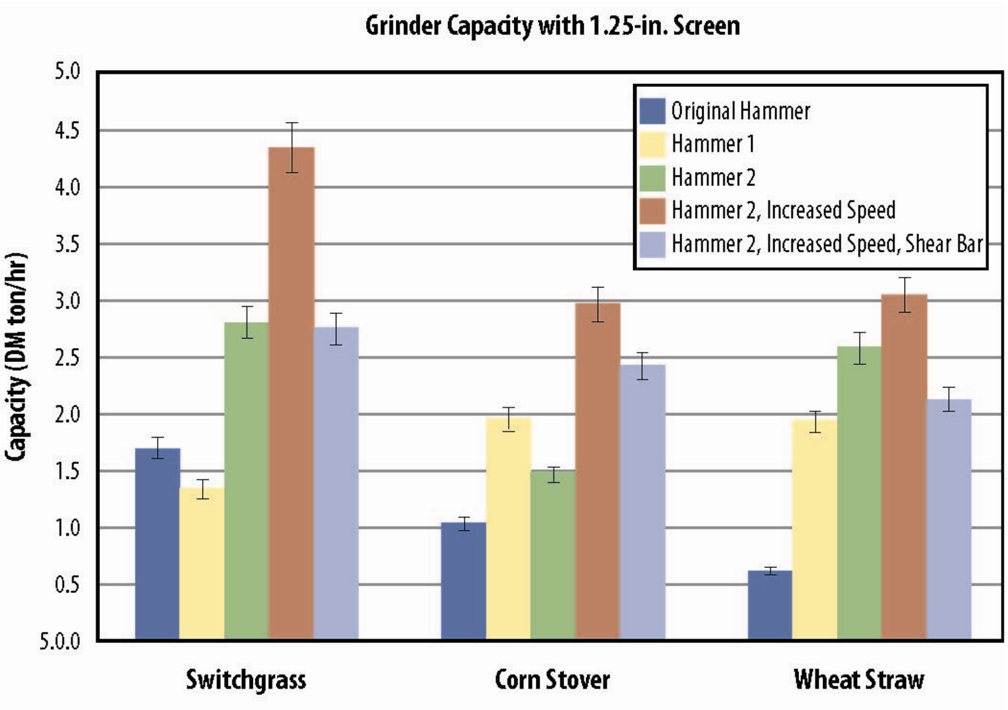

Figure 2–1. Grinder capacity for three feedstock varieties preprocessed using three hammer configurations, increased tip speed, and addition of a new shear bar. For all feedstock varieties, the Hammer 2 configuration operated at increased speed resulted in the greatest increase in grinder capacity.

The Hammer 2 configuration also demonstrated the greatest improvements in grinder efficiency (Figure 2–2). While tip speed clearly increased grinder capacity for all feedstocks tested (Figure 2–1), the effect of tip speed on efficiency is not as clear, with most of the results being well within the estimated uncertainty of the measurements. Decreasing the shear plate tolerance generally resulted in a reduction of both capacity and efficiency. Interestingly, the effect of tip speed appears to be much greater for corn stover than for switchgrass or wheat straw, while the effect of shear plate tolerance appears to be much greater for switchgrass and wheat straw than it is for corn stover. This may be attributed to the more aggressive grinding conditions being beneficial to break up the fibrous “birds-nest” formations typical of ground corn stover. Taking into account both grinder capacity and efficiency, the best overall performance was achieved with Hammer 2 at high tip speed. However, neither Hammer 1 nor Hammer 2 excelled over the other for all feedstocks tested, indicating that feedstock type must be considered during grinder optimization.

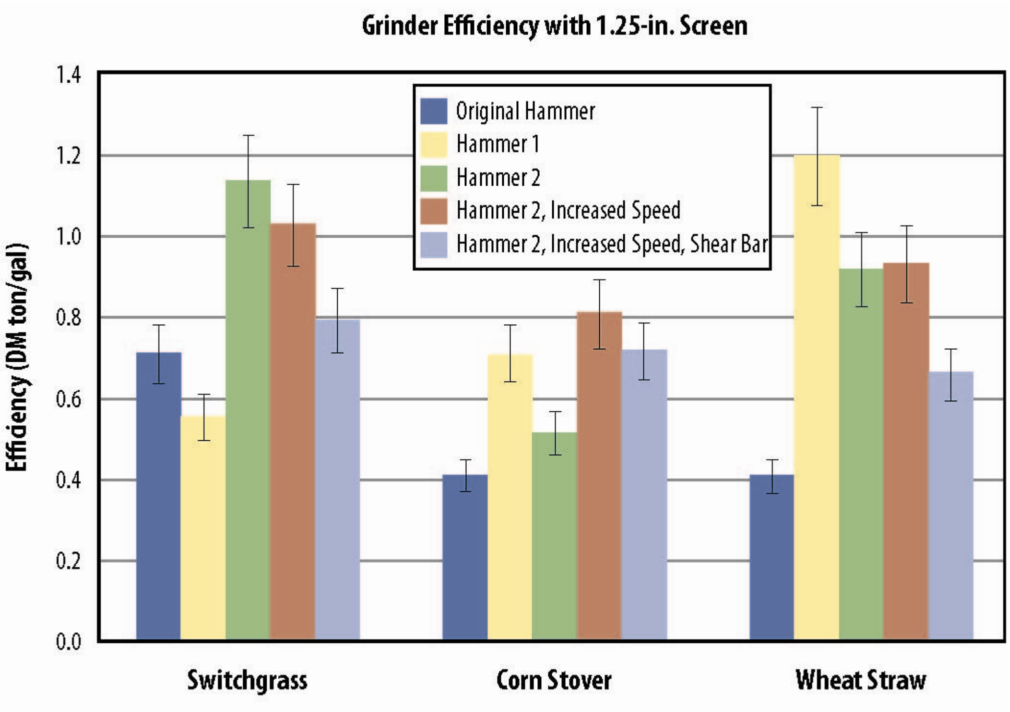

Figure 2–2. Grinder efficiency for three feedstock varieties preprocessed using three hammer configurations, increased tip speed, and addition of a new shear bar. Despite the increased capacity resulting from the Hammer 2 configuration operated at increased tip speed, efficiency was highly variable among all hammer configurations, depending on feedstock type.

2. *Improved size reduction via pneumatic assisted grinding.*

In a hammer mill, it is speculated that a significant portion of grinding energy is consumed by the hammers striking the same particles multiple times before the particles finally exit through the outlet screen. In addition to this potential waste of energy, impacting some particles multiple times can also result in excessive generation of finely powdered material. A separate set of experiments evaluated the effectiveness of pneumatic conveyance to quickly remove smaller particles from the grinding chamber to improve grinding efficiency, throughput, and product uniformity. A photograph of the hammer mill equipped with the pneumatic conveyance system is shown in Figure 2–3. Importantly, however, the benefit of pneumatic conveyance to more easily convey fine particles is also a limitation in that it is most effective for grinding configurations that involve small outlet screen sizes. Consequently, a 3/16-in. screen was employed in the grinder to evaluate the effectiveness of pneumatic conveyance to improve the grinding process (this is much smaller than the 1 1/4-in. screen used in the experiments described above). Grinder capacities (see Figure 2–4) were measured both with standard belt conveyance and experimental pneumatic conveyance for four different feedstocks and employing a fixed grinder configuration (Hammer 2, increased speed, and reduced shear-bar tolerance).

The data for sorghum stover were collected using the standard belt conveyance discharge, while the corn stover, switchgrass, and wheat straw data were collected using the pneumatic conveyance system. Previous tests showed that sorghum and corn stover perform similarly in this type of grinder, making it possible to use the sorghum grinder capacity as an approximate baseline to evaluate the effectiveness of pneumatic assist on the grinding performance of corn stover and, by extrapolation, switchgrass and wheat straw. Figure 2–4 compares grinding capacities of sorghum and corn stover and indicates an estimated 180% improvement in grinder capacity with pneumatic assist. Adding pneumatic assist did not appear to have a significant impact on grinder efficiency, as estimated by comparing the grinding efficiencies of sorghum with belt conveyance and corn stover with pneumatic assist in Figure 2–5.

Figure 2–3. Grinder setup to test pneumatic conveyance of the test feedstocks.

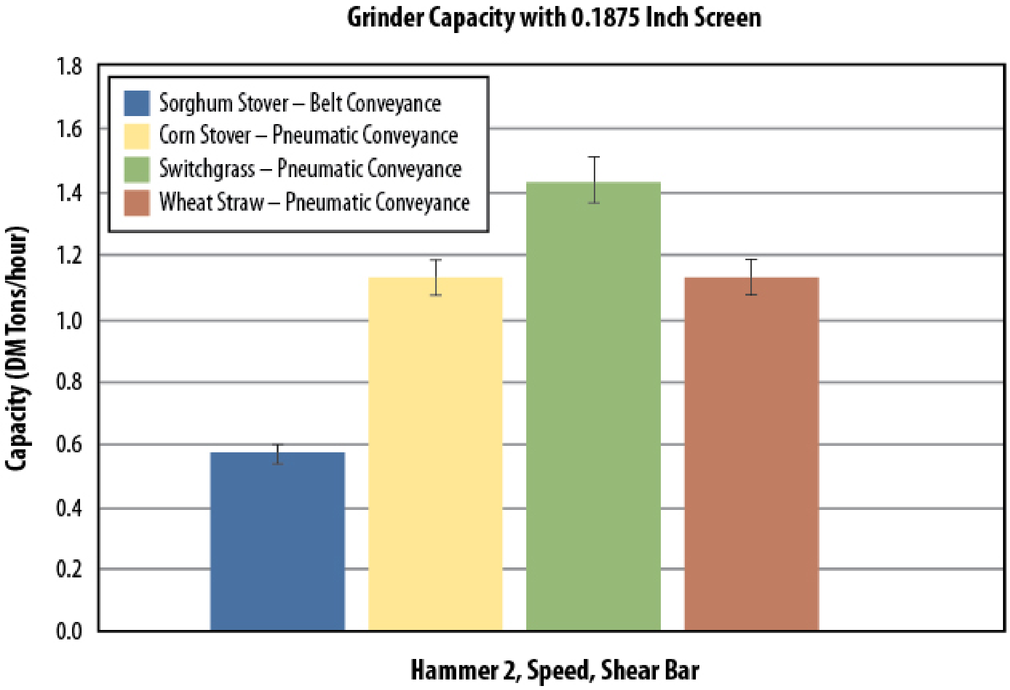

Figure 2–4. Comparison of grinding capacity for belt and pneumatic conveyance using Hammer 2, increased speed, and new shear-bar configuration. Pneumatic conveyance improved capacity for all biomass types tested.

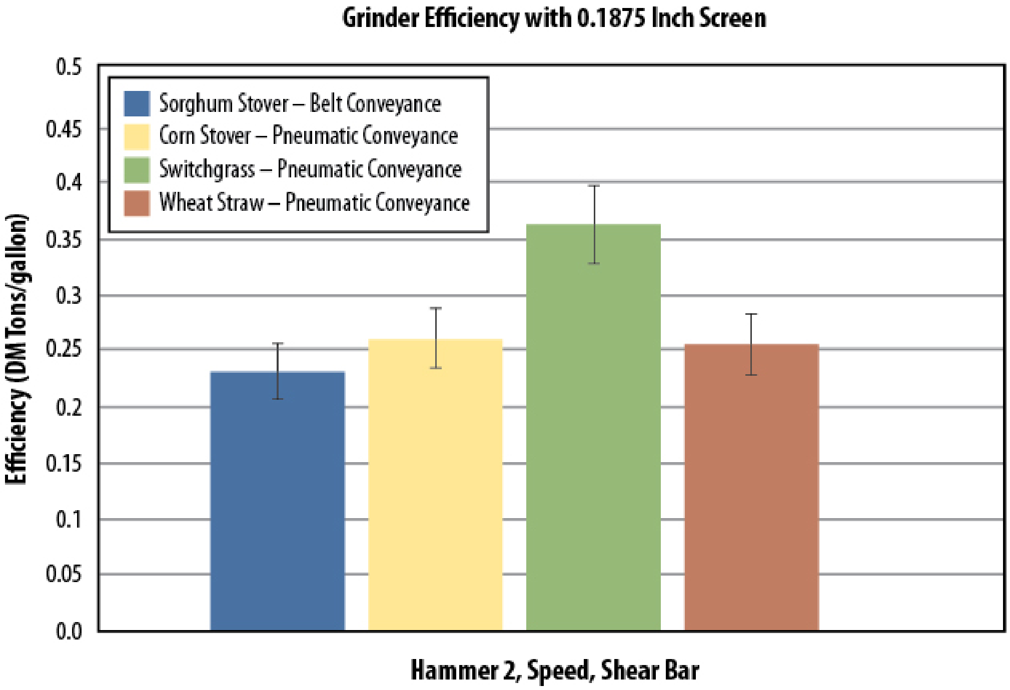

Figure 2–5. Comparison of grinding efficiency for belt and pneumatic conveyance using Hammer 2, increased speed, and reduced shear-bar tolerance. Pneumatic conveyance increased efficiency for all biomass types tested.

Notably, the improvements in grinder performance due to hammer configuration and tip speed are additive with improvements in grinding capacity due to pneumatic assist. An estimate of the total potential for grinder improvement can be made by combining the 300% improvement in capacity using Hammer 2 at high speed to grind corn stover (Figure 2–4) with the 180% improvement due to pneumatic assist (Figure 2–5) to achieve nearly a 500% improvement in grinder capacity. If these improvements are applied to commercial-scale grinding, the economic impacts of such improvements would correlate to a five-fold reduction in preprocessing cost.

3. *Fractionation during hammer-mill grinding using pneumatic assist*

In addition to the economics of size reduction, consideration must also be given to product characteristics. One key characteristic of ground biomass feedstocks is particle-size distribution, primarily related to the amount of fines. Excessive fines can cause problems ranging from fugitive dust issues during handling to problems with chemical penetration in excessively dense-packed bed reactors.

Research conducted at INL is focused on understanding the relationships between material properties (moisture content, physiological structure, etc.), grinder process parameters (screen size, hammer speed, etc.), and product particle-size distribution. In a study conducted at INL, biomass deconstruction in a hammer mill was studied to understand the relationship of grinding forces—both impact and shear—as well as residence time in the grinder on particle size distribution. A high-speed cameral was used to qualitatively evaluate the deconstruction process in a hammer-mill grinder (Figure 2–6). High-speed video analysis revealed that fines generation in hammer-mill grinding largely results from non-fibrous tissues that disintegrate into small particles when they are impacted with the rotating hammers and/or fixed shear plates. Fibrous tissues such as the outer rind, leaf, and husk from corn stover remain intact upon impact, and require shear forces to break them up before exiting the grinder. Given these deconstruction mechanisms, a noticeable quantity of fines are always generated regardless of the screen size at the grinder outlet. Smaller screen sizes were observed to result in more collisions per particle, which resulted in a reduction of the maximum particle size exiting the grinder and also an increase in the amount of fines.

Figure 2–6. High-speed video analysis revealed that fines generation in hammer-mill grinding largely results from non-fibrous tissues that disintegrate into small particles when they are impacted with the rotating hammers and/or fixed shear plates.

Evidence of this deconstruction behavior is clearly manifested by sieve analysis of material generated using different screen sizes in a horizontal grinder. In a field study conducted by INL near Pella, Iowa, in November 2007, miscanthus was ground through a commercial grinder configured with different screen sizes ranging from no-screen (7-in. rectangular opening) to a 1-in. round screen. The resulting materials were then separated using a series of sieves. In the first case, the grinder screen was removed so that the miscanthus pieces would experience only one or, at most, a few collisions before passing out of the grinder. This configuration resulted in many large particles with over 35% of the original mass associated with particles that would not pass through a 3/4-in. sieve (vertical bar labeled ‘A’ in Figure 2–7), while only 5% of the original mass was reduced to particles that passed through the smallest sieve (0.08-in. openings) (bar labeled ‘B’ in Figure 2–7). Inserting a 6-in. screen in the grinder dramatically reduced the quantity of material retained on the ¾-in. sieve (black bar under grouping ‘C’). The proportion of large particles continued to decrease with decreasing screen size, and an associated increase of smaller particles is evidenced in Figure 2–7 by the distributions labeled ‘D.’

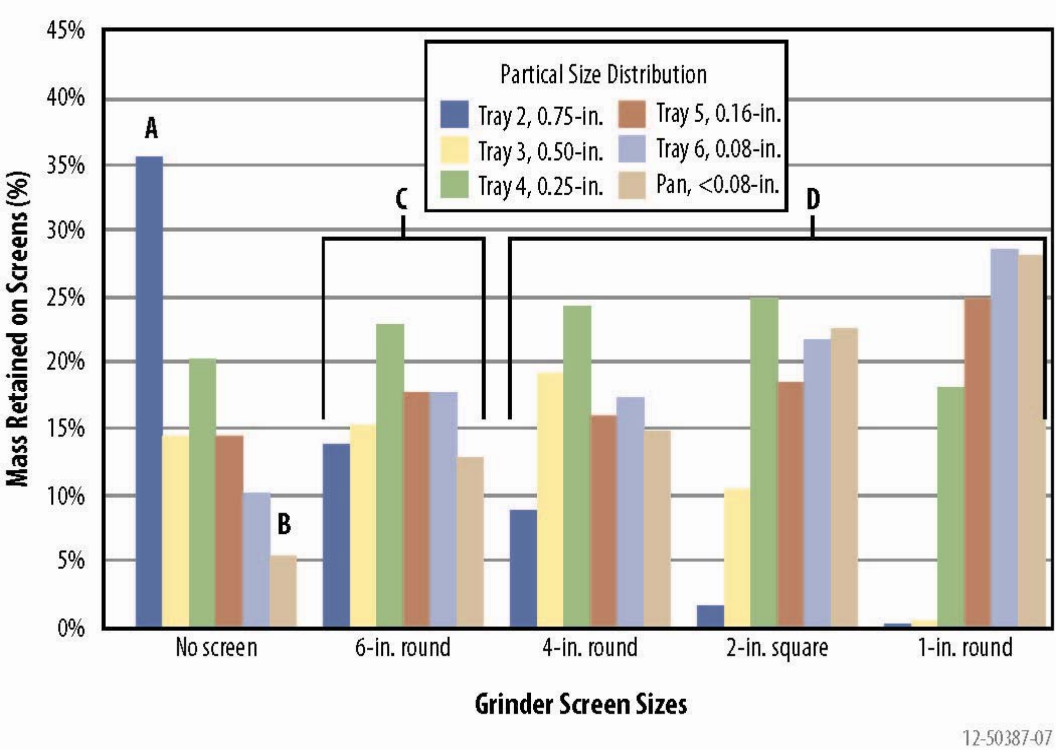

Figure 2–7. Miscanthus particle-size distributions after hammer-mill grinding operations with no screen in hammer mill and with screens of 6-, 4-, 2-, and 1-in. round openings.

An interesting result of this study is that the test conducted with no screen resulted in the deconstruction of pith and other tissues that compositional analysis revealed to have higher lignin content than the larger particles. These smaller, lignin-enriched fractions could be sieved out following grinding to produce separate fractions with high- and low-lignin content.

Another advantage of separating material based on particle size is the removal of unwanted fractions of biomass. Literature and preliminary work at INL indicate that fractions of fine particles often have higher ash content (Bakker and Elbersen 2005; Obernberger et al. 1997; Bridgeman et al. 2006). Because the fines typically represent only a small portion of the total biomass weight, it is possible to remove a substantial portion of the ash content while only losing a small amount of sample mass. A reduction in ash content is desirable for both thermochemical and biochemical conversion processes.

The occurrence of deconstructed fractions partitioning by composition is known as fractionation. Fractionation requires that the material first be deconstructed into components that have diverse physical properties (e.g. particle size, density, etc.) such that the products can be subsequently separated.

Case Study: Size Reduction with Selective Material Orientation

James H. (Jim) Dooley (Forest Concepts, LLC)

The Forest Concepts' proprietary rotary-shearing technology has been under development since 2002, with commercial use of their WoodStraw® enterprise since 2005. The U.S. Department of Energy became interested in this technology in 2007 as it became evident that comminution energy was much less than that consumed by hammer and other attrition mills to make small wood particles. Energy savings accrue from careful orientation of cutting operations to minimize cross-grain shear and maximize parallel-to-grain slicing. Further energy savings are achieved by cutting particles to a well-defined particle size that is optimized for each end use.

The rotary shearing process first converts roundwood logs into industrial grade veneer that has the thickness desired in the end-product feedstock. Veneer-making is followed by oriented shearing of the veneer sheets by a rotary bypass shear with cutter widths equal to the desired particle length along the fiber grain. The resulting strips of sheared biomass naturally break along the grain to form small uniform particles having controlled length and thickness.

The SBIR Phase I program of research and feasibility analysis demonstrated that primary breakdown of logs into veneer and subsequent shearing into uniform length (along the grain) particles produced high surface-area, uniform-sized, flowable, and low-comminution energy particles. The initial task for the Phase II project was to confirm comminution energy at larger sample sizes and across a range of veneer thicknesses.

Primary breakdown of logs into veneer produces sheet stock that can be stacked into banded units, as shown in Figure 2–8, for high-density storage, high-payload transportation, and efficient materials handling. Units of veneer can be transported by rail, truck, or other modes at a green density of more than 40 lb/ft^3 and more than 28 oven-dry lb/ft^3. In comparison with pelletization to achieve high transport density, veneering is lower in capital and operating costs.

Figure 2–8. Veneering raw wood (a), stacked veneer sheets (b), and final Crumbles® product (c).

A series of experiments was conducted using 4.8-mm-wide (3/16-in.) rotary shear cutters to process high-moisture-content veneer at 1-, 2-, 3-, and 4-mm thicknesses into cross-grain precision particles. Other samples of conventional 2.5-mm (1/10-in.) and 4.2-mm (1/6-in.) veneer were tested at wet and dry conditions. The results plotted in Figures 2–9 and 2–10 indicate that the comminution energy increases with veneer thickness, which is contrary to conventional wisdom and suggests that shearing energy is directly related only to shearing area and not the shear layer thickness (i.e., if the conventional hypothesis were true, then the curves in Figure 2–9 would be horizontal lines). The comminution energy for high-moisture veneer ranges from 25 to ~40 MJ/odt as the material thickness increases from 1 to 4 mm. As expected, dry veneer takes more energy to shear than high-moisture veneer. This is exactly opposite of the moisture-comminution energy relationships for hammer-milling, where the energy decreases with dryer biomass.

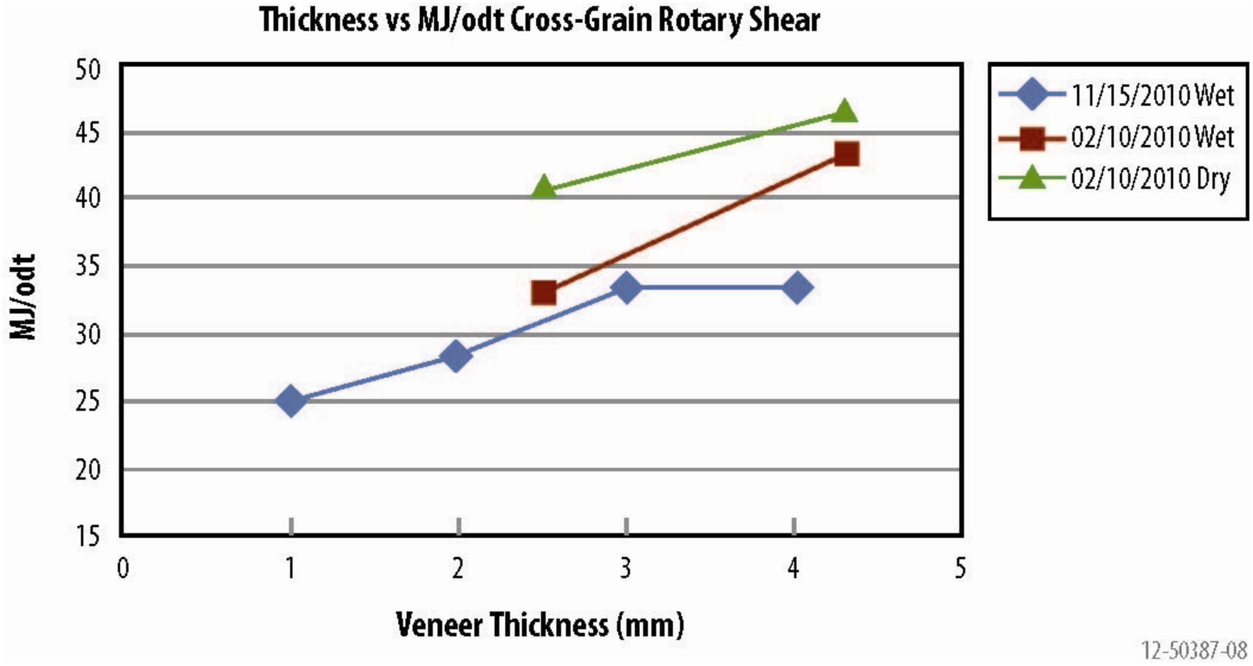

Figure 2–9. Results of experiments relating cross-grain comminution energy per unit mass with veneer thickness for high- and low-moisture Douglas fir veneer.

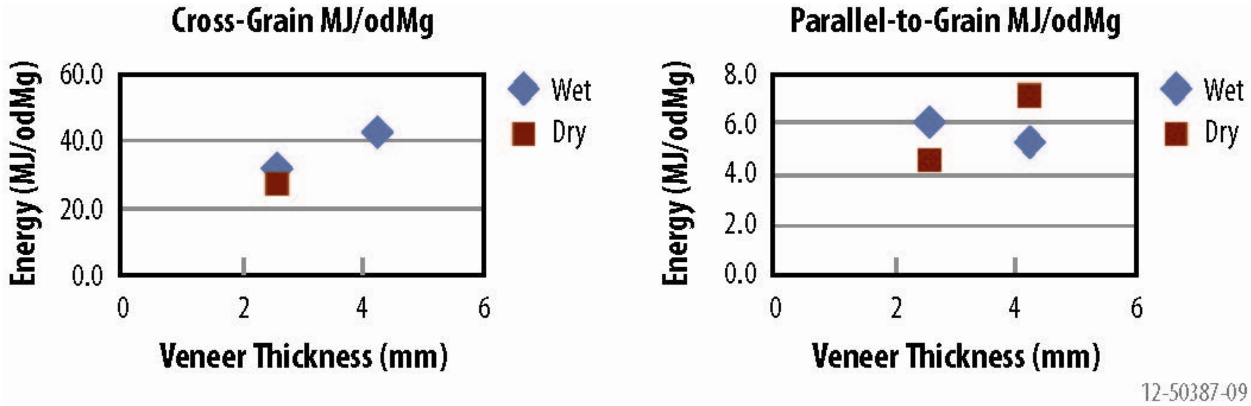

Figure 2–10. Comminution-specific energy per unit mass for shearing Douglas fir wood veneer with 4.8-mm wide cutters parallel to grain (a) and cross-grain (b). Note that the Y-axis scales are different.

Figure 2–10 shows that the amount of energy required to cut parallel to grain is approximately 1/6 of the energy required to cut cross-grain in this material. Therefore, it makes sense to produce feedstock particles that are rectangular rather than cubic if possible. There is some experimental evidence from Pacific Northwest National Laboratory (PNNL) and Washington State University that particle length is not limiting until the length-to-thickness ratio is larger than about 3:1. Thus, a minimum comminution particle with a 2-mm nominal thickness and width may have a length of 4 to 6 mm. In that case, the comminution energy consumed per unit feedstock produced is at a global minimum without compromising conversion yield.

Similar results have been demonstrated on other fibrous feedstocks using Forest Concepts' proprietary WoodMuncher™ machinery for comminution of corn stover, switchgrass, bamboo, and wood chip raw materials.

Discussion of Technology Impacts and Challenges

The primary role of mechanical preprocessing in the biofuels production pathway is to prepare the biomass feedstock for the conversion process by comminuting the materials to achieve the particle-size specification of the biorefinery. Comminution facilitates handling and feeding into the conversion process and also increases surface area making the biomass more reactive to biological, chemical, or thermal treatment (Walker and Wilson 1991; Mansfield et. al. 1999). A secondary role of mechanical preprocessing operations is to produce materials that are easily and efficiently handled and conveyed during storage and transportation operations. Reducing shipping and handling costs requires that feedstock materials have high mass and energy densities to minimize handling and storage footprints. As-harvested biomass generally has a loose bulk density well below 200 kg/m^3, depending on the particle size and material type (e.g. herbaceous or woody). Bulk density of raw material can be substantially increased by comminution to smaller particles. Vibration is another option to increase packing density in chopped or ground biomass and can enhance bulk density values by 25% or more. However, to increase density beyond 200 kg/m^3, biomass usually must be mechanically compacted into cubes or pellets (Sokhansanj et al. 1999). Densification via pelletization or briquetting is discussed in greater detail in Chapter 6 – Densification.

Minimizing the effective specific-energy requirements for mechanical preprocessing operations such as comminution is largely recognized as being crucial to reduce the high costs and energy consumption of mechanical preprocessing[40] (Yancey et al. 2009). Equipment throughput (material processed per hour) [41,42,43] and cost[44] are also important factors. The mechanical preprocessing case studies demonstrate two approaches to achieve these goals. Each of these approaches, though different in application, is based on an understanding of biomass material properties in order to exploit natural vulnerabilities in biomass deconstruction. The INL approach used knowledge of the differences of deconstruction vulnerabilities of fibrous and non-fibrous tissues to design new hammers and operating conditions to increase grinder throughput and efficiency. The Forest Concepts approach exploits material-property vulnerabilities by shearing parallel to the grain of woody biomass for efficient size reduction of roundwood biomass.

Mechanical preprocessing optimization strategies are often unique to each material as well as for each process. Workshop participants recognized that the ability to handle as wide a variety of materials as possible is important for the wide-spread adoption of specific mechanical preprocessing technologies[45,46,47,48], but that the large variability in physical characteristics of different biomass materials make the development of a single robust mechanical preprocessing system challenging[49]. The case studies demonstrated the difficulty of developing a single technology that can be applied with maximum efficiency and capacity for all biomass materials. The differences in material properties between herbaceous and woody biomass, and even among different varieties within each of these classes, require different size-reduction techniques.

The INL case study demonstrated the sensitivities of hammer-mill grinding to tissue types, requiring different mechanisms to deconstruct different tissue types. Non-fibrous, easily friable tissues respond well to impact forces, while fibrous tissues require shear forces to deconstruct. Optimization of grinder throughput and energy consumption required a different grinder configuration (i.e. hammer design and reduced shear plate tolerance) for corn stover, which tends to be highly fibrous, compared to less-fibrous switchgrass and wheat straw.

Biomass moisture content is also an important consideration in selection and optimization of size-reduction processes. As moisture content increases, hammer-mill grinding efficiency decreases dramatically[50,51]; however, for alternate deconstruction processes such as veneering, moisture content is not detrimental and may even be helpful[52,53]. Moisture content also plays a significant role in particle-size distribution, and the amount of fines generated during hammer milling typically increases as moisture content decreases.

The role of mechanical preprocessing within the biomass supply chain is often relegated to size reduction at the biorefinery to achieve a feedstock size specification prior to insertion into the conversion process. However, when mechanical preprocessing operations are designed within the context of the entire supply chain, additional synergistic benefits can be realized. These include lower logistical costs associated with transportation, handling, and storage[54,55,56,57,58,59,60], as well as improved pretreatment and conversion properties due to smaller particle sizes and increased surface area[61]. It has also been demonstrated that deconstructed material structures can have lower recalcitrance (Kaliyan and Morey 2006). A holistic design approach also recognizes that harvest and collection methods, because of their impact on material properties (particularly moisture content) and composition, directly affect mechanical preprocessing operations[62]. Thus, proper selection and optimization of mechanical preprocessing must consider all other aspects of the supply system to account for different biomass types, formats, and characteristics[63,64,65,66,67].

Mechanical preprocessing also encompasses more than just comminution. The INL case study introduced a value-added concept of fractional deconstruction. This concept involves preferentially deconstructing biomass by exploiting deconstruction vulnerabilities of different anatomical fractions or tissue types to produce fractions that differ in chemical and physical composition. Subsequent separation of these fractions, by sieving for example, can then produce multiple feedstock products targeted for different end uses. The case study, for example, demonstrated that fractions of high/low lignin or ash content may be produced in this manner. Some workshop participants pointed out the similarity of this concept to the bark removal and grinding operations that are already in place today[68,69]. Workshop participants recognized that fractional deconstruction has very promising possibilities for subsequent conversion[70] but also expressed reluctance to embrace the impacts of this concepts because the economics for industrial-scale fractional deconstruction have not yet been worked out[71].

Realizing the full impacts of mechanical preprocessing, including synergistic benefits on supply-chain logistics (e.g., transportation, handling, and storage), as well as the potential to produce value-added feedstocks through fractionation and separation, requires that mechanical preprocessing occur upstream of the biorefinery. Workshop participants generally agreed that operations to accomplish these goals should be performed as close to the harvest location as practical in order to reduce the number of times material is handled[72] and to reduce costs associated with subsequent shipping of the material[73,74,75,76,77,78].

Finally, both case studies demonstrated consideration for required characteristics of the final product (i.e., feedstock specifications), which determines the extent of mechanical preconversion that is needed. Shipping distance is a particularly strong driver in the choice of mechanical preprocessing options[79,80]. As-harvested biomass generally has a loose bulk density well below 200 kg/m^3, depending on the particle size and material type (e.g., herbaceous or woody). Bulk density of raw material can be substantially increased by comminution to smaller particles. Vibration is another option for chopped or ground biomass to increase packing density and can enhance bulk density values by 25% or more. However, to increase density beyond 200 kg/m^3, biomass must usually be mechanically compacted into cubes or pellets (Sokhansanj et al. 1999). Densification via pelletization or briquetting is discussed in greater detail in Chapter 6 – Densification.

The ability of feedstock material to flow freely is an important property for easy and efficient handling. Different materials must be processed into a uniform physical format (though not a uniform chemical format[81]), so that acceptable transport and handling characteristics are assured[82,83,84]. The material attributes that determine how easily a feedstock will flow include its bulk density, bulk compressibility and springback (elastic windup), unconfined yield (shear) strength, and wall friction. These attributes are impacted by the material’s particle size and shape distributions, moisture, temperature, and the pressure it has experienced as a function of time (pressure history). Comminution to uniform, low-aspect-ratio particles on the order of 1 mm greatly benefits material flowability (INL – manuscript in preparation).

A disadvantage of comminution is that it can open material structures to facilitate microbial attack (Dien et al. 2005; Palmowski and Muller 1999), and consequently, decrease aerobic stability. The effect of comminution on all of these material properties must be considered before any proposed mechanical preprocessing operation is implemented.

The cost of achieving the characteristics described is this chapter can be substantial and must be minimized or offset in order for lignocellulosic fuels to gain widespread use. The cost of implementing a viable biomass preprocessing operation in the feedstock assembly system is constrained by three basic performance parameters: machine capacity (throughput), operational efficiency, and material output quality. The first two parameters, capacity and efficiency, are primarily dependent on the physical configuration of the equipment and the physical characteristics of the biomass feedstock. Research at INL has shown that the interaction between machine hardware and the biomass structure can significantly impact the resulting capacity and efficiency of the operation (Yancey 2009). Different feedstock varieties—such as corn stover, switchgrass, pine, poplar, etc.—possess different preprocessing parameters that must be considered in the integral design to account for their impacts on machine performance. This high inherent variability in feedstock characteristics requires trade-offs in both equipment operating capacity and efficiency in cases where the same equipment must handle multiple types of materials. In such cases, it may be necessary to select different machine configurations in order to optimize capacity, efficiency, and effectiveness of the equipment for different materials.

Workshop Conclusions

Nearly 80% of workshop participants agreed that mechanical preprocessing treatments have an important positive impact on supply-system logistics and feedstock-conversion performance (Figure 2–11), while less than 5% felt that the opposite was true. A majority of participants also agreed that mechanical preprocessing would benefit from being located as close to the field or forest as possible, although over 40% of workshop participants were unsure or disagreed that the depot was an important benefit to mechanical preprocessing (Figure 2–11). Furthermore, a substantial portion of participants (38%) felt that the benefits of mechanical preprocessing operations are either already being realized or could be realized within 2 years, while approximately 10% of participants were concerned that realizing such benefits would require more than 10 years (Figure 2–11). Compared to other pretreatment operations discussed in subsequent sections of this report, these results indicate that workshop participants generally view mechanical preprocessing as an important immediate area of emphasis to improve supply-system logistics and feedstock-conversion performance. (See Table 2–1 for a summary of common themes and points of emphasis from Mechanical Preprocessing presentations, discussions, and participant surveys.)

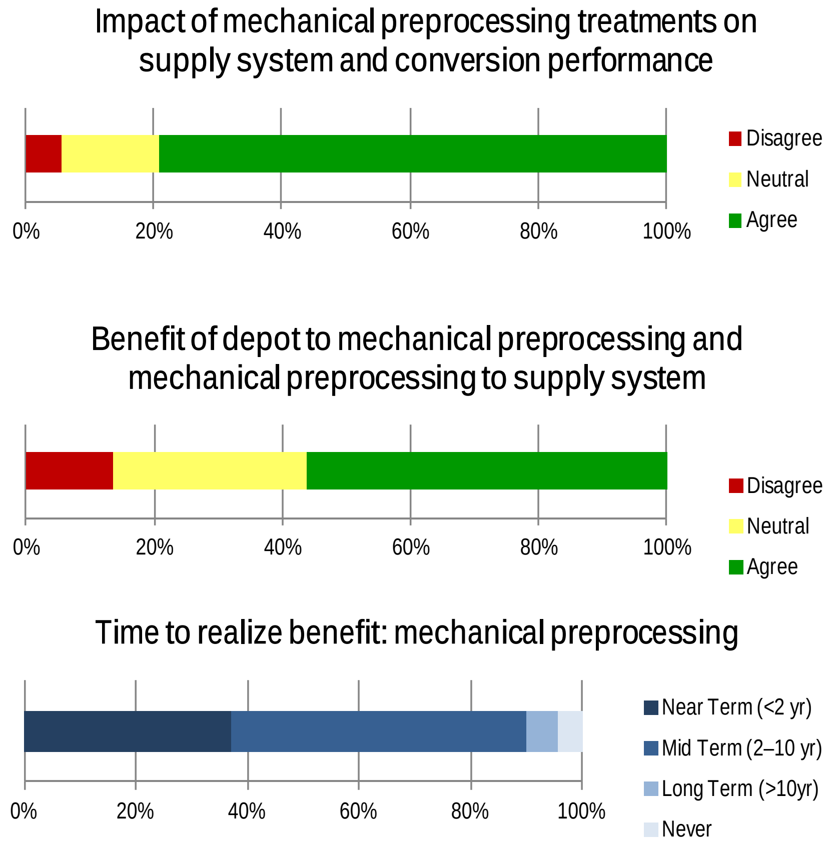

Figure 2–11. Participants believed that the benefits of mechanical preprocessing are already or will soon be realized. A substantial number believed that locating mechanical preprocessing at regional distributed preprocessing depots will add value.

Participant surveys showed that there is already acceptance of the benefits of mechanical preprocessing when process energy requirements and other economics are minimized. Many mechanical preprocessing techniques, such as bark removal and grinding, are already in place today[85,86], and many participants believed that such operations should be performed as close to harvest as possible to reduce costs associated with subsequent shipping of the material[87,88,89,90,91]. Conducting several mechanical preprocessing operations with a single, robust system that can handle a variety of materials was suggested to capture greater efficiencies in the supply system, depending on the requirements of the densified end product (i.e., shipping distance).

Mechanical preconversion processes and equipment are more valuable if they can handle a wide variety of materials[92,93,94,95]. Equipment throughput (material processed per hour)[96,97,98], cost[99], and energy consumption[100] are important factors for all operations. Moisture content is an important factor for typical grinding operations, and as moisture content increases, grinding efficiency decreases dramatically[101,102]. However, for alternate deconstruction processes, such as veneering, moisture content is not detrimental and may even be helpful[103,104]. Fractional deconstruction has very promising possibilities for subsequent conversion[105]; however, the economics for industrial-scale fractional deconstruction have not yet been determined[106]. Flowability of materials in industrial equipment is also a concern, and different materials must be processed into a uniform mechanical format (again, not a uniform chemical format[107]), so that acceptable transport and handling characteristics are assured[108,109,110]. Opinions were also expressed that mechanical preconversion has the greatest benefit for storage[111] and that research effort should focus on processes that can be done now[112].

It is well understood that the physical characteristics of different biomass materials will make the development of a single robust mechanical preconversion system challenging[113]. Simultaneously addressing equipment capacity, efficiency, cost, and energy consumption along with biomass physical and chemical quality is part of the research moving forward. Though mechanical preprocessing is centered on distributed preprocessing concepts, it includes other critical elements such as production, harvest and collection, storage, and transportation and handling as key influencing technologies. Thus, an integrated research, development, and demonstration program has been established to account for different biomass types, formats, characteristics, and supply system processes[114,115,116,117,118].

Table 2–1. Summary of common themes and points of emphasis from Mechanical Preprocessing presentations, discussions, and participant surveys.

Desired R&D Outcomes	Potential Approaches	Barriers/Constraints
SUPPLY (Conversion Performance) • Variability – reduce through (1) fractionation (isolating and separating plant fractions) to achieve more uniform compositional (2) better control of comminution processes to create narrow particle size distributions LOGISTICS • Efficiency – improve through (1) low-cost, efficient size reduction, fractionation, and separation; and (2) formatting to ensure efficient and trouble-free handling and conveyance • Density – increase energy density through comminution and fractionation	• Explore/optimize mechanical preprocessing technologies for feedstock production - Conventional – chipping, debarking, flailing, grinding, billeting - Unconventional – low-energy shearing, veneering, fractional deconstruction • Understand interdependence of mechanical and chemical properties and variabilities and their impacts on mechanical preprocessing operations • Identify qualities that will benefit other preprocessing and conversion processes (i.e., moisture management, binding, energy consumption)	• Energy costs • Must meet specs required by handling equipment and process being fed • Compatible with existing transportation and handling infrastructure • Demonstrate near-term benefits • Demonstrate positive investment-to-value ratio

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Chapter 3 — Thermal Preconversion

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Thermal preconversion technologies are important for transforming raw biomass into material that has structural homogeneity, as well as superior handling, milling, and co-firing properties. Untreated biomass has a wide range of moisture content (25 to 60%), large particle-size distribution (10 to 100 µm), low energy density (8 to 14 MJ/kg), and low bulk density (60 to 100 kg/m^3) coupled with fibrous interlocking particles that tend to resist flow. These biomass characteristics introduce challenges for conversion processes, particularly thermochemical conversion processes such as gasification, pyrolysis, and combustion. These conversion processes can be optimized when on-spec feedstock is used (Mani 2005; Sokhansanj et al. 2009).

Thermal Preconversion Technologies

Exposure of biomass to elevated temperatures results in thermal degradation of its structure, which is often accompanied by loss of mass. The degree of thermal degradation depends on the duration of the heating and temperature[21–23]. Thermal treatment process variables that can influence the structural and chemical compositional changes include biomass composition, particle size, processing temperature and time, heating rate, gas composition, pressure, and flow rate.[9]

Thermal preconversion technologies include heating treatments at various ranges of temperature severity, which are defined in this paper as non-reactive drying (50 to 150°C), reactive drying (150 to 200°C), and destructive thermal preconversion, or torrefaction (200 to 300°C). Figure 3–1 illustrates these ranges and describes the intensity of physical and chemical changes that occur within each range (Tumuluru et al. 2011). The description of biomass change during various thermal treatments, provided in the following paragraphs, is generalized for the purpose of illustration. In practical applications, different types of biomass behave somewhat differently depending on composition.

As shown in Figure 3–1, at drying temperatures of 50 to 150°C (A), biomass loses moisture and shrinks. This also results in reduced porosity in the biomass, but it may still have the ability to retain its structure if rewetted. This region is defined as “non-reactive” because most of the chemical constituents of the biomass remain intact. At the higher end of these temperatures (i.e. 120 to 150°C) (B), the lignin softens and makes the material more suitable for densification, as softened lignin acts as a binder. Temperature regime C (150 to 200°C) is defined as reactive because in this range initiates the breakage of hydrogen and carbon bonds and also results in the emission of lipophilic extractives and compounds due to thermal degradation of biomass solids. This temperature also results in structural deformity in which biomass loses its ability to regain its original structure if rewetted. Also, according to Bergman and Kiel, depolymerization of hemicellulose results in shortened, condensed polymers with solid structures.[31] Increasing the temperature further, into Regime D, is defined as “destructive” drying (200 to 300°C), and results in carbonization and devolatilization.

The destructive drying temperate range represents the torrefaction process limits, which result in the disruption of most inter- and intra-molecular hydrogen bonds and C-C and C-O bonds, and produce hydrophilic extractives, carboxylic acids, alcohols, aldehydes, ether, and gases like CO, CO_2, and CH_4. At these temperatures, cell structure is completely destroyed as the biomass loses its fibrous nature and becomes brittle. Bergman reports further that increasing the temperature to >300°C results in extensive devolatilization and carbonization of the polymers.[32]

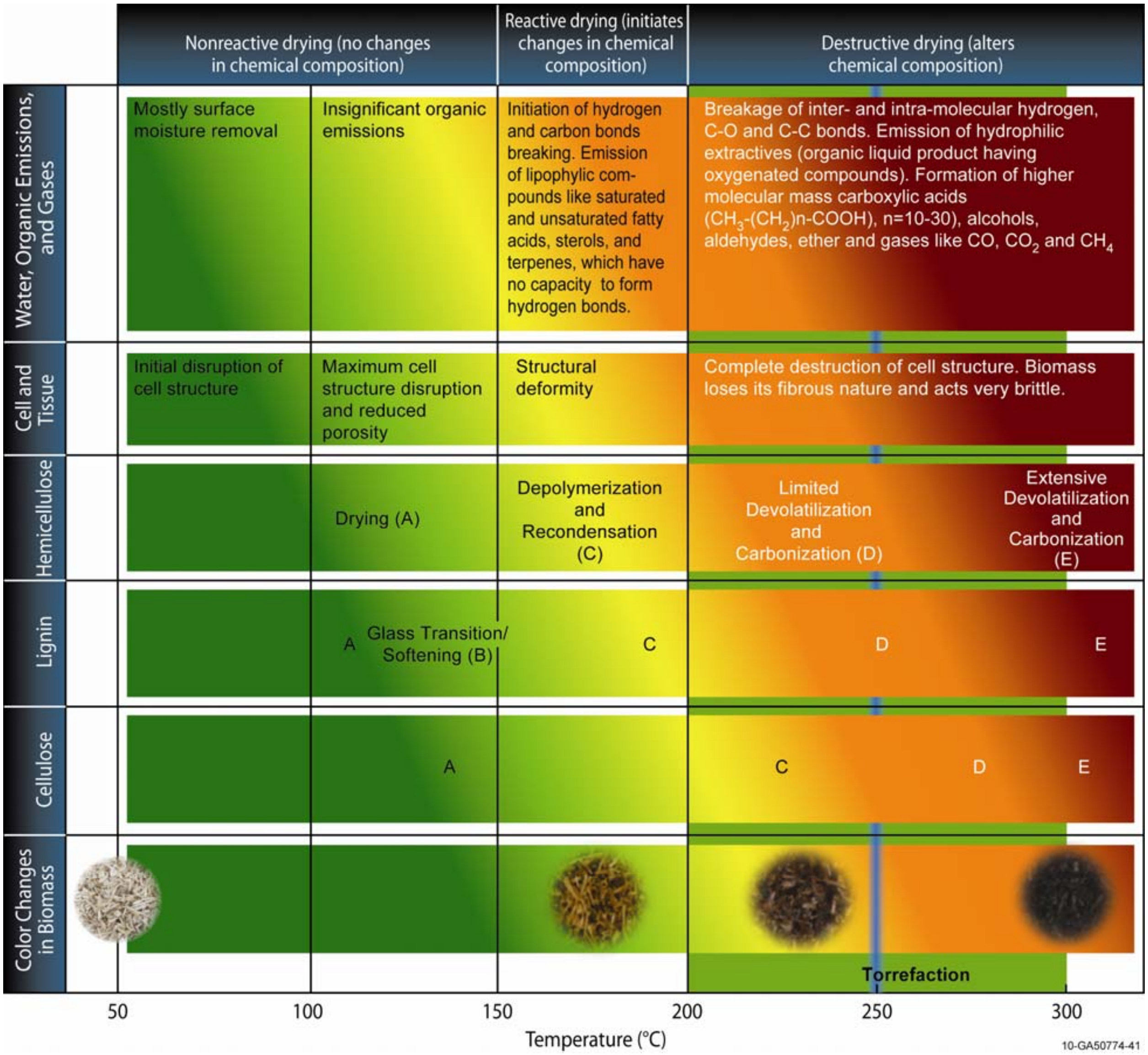


Figure 3–1. Impacts of thermal preconversion treatments on the primary components that are found in biomass. Approximate conditions for important changes in the various components are marked and include simple drying (A), glass transition/softening (B), depolymerization and recondensation (C), limited devolatilization and carbonization, (D) and extensive devolatilization and carbonization (E) (Tumuluru et al. 2011).

The blue line in Figure 3–1 shows a distinct point of biomass change. At torrefaction temperatures lower than 250°C, the mass loss is at a minimum, as biomass decomposition primarily comes from limited devolatilization and carbonization of the hemicellulose. At temperatures higher than 250°C, the hemicellulose decomposes extensively into volatiles and a char-like solid product. Lignin and cellulose show limited devolatilization and carbonization.

The biomass color changes that occur during thermal treatment can be useful indicators of the degree of torrefaction. During torrefaction, the biomass turns brown to black at 150 to 300°C, which can be largely attributed to chemical compositional changes. Lam et al. (year) quantified the severity of steam treatment based on color coordinates [33] and then developed multi-linear regression models to describe chemical compositional changes like carbon and hydrogen based on color changes in steam-exploded wood pellets.[33] Color measurement can also be a good indicator for identifying impurities like bark, ash, or any other foreign material present in the biomass, similar to the way color change is used in the coffee bean roasting process to define the changes in its chemical composition.[34]

Table 3–1 summarizes the typical mass and energy yields that occur within the different treatment regimes. Note that mass and energy losses are generally small for treatments below 200°C, even in reactive treatment ranges. As the treatment temperature increases above 200°C (torrefaction) mass losses become more pronounced, and energy (heat content) is also lost, although to a lesser degree.

Table 3–1. Thermal preconversion process variables for different process regimes and their impacts on bulk and energy densification (Shankar Tumuluru et al. 2011). All processes are conducted at ambient pressure and employ a heating rate less than 50°C/min.

Process Reaction	Non-Reactive Drying (50–150°C)	Reactive Drying (150–200°C)	Destructive Drying (200–300°C)
Time (min)	30–120	30–120	<30
Drying environment/ pressure	Air/atmospheric pressure	Air/atmospheric pressure	Inert atmosphere
Mass yield (%)	~90–95	~90	~70
Energy yield (%)	~100	Research Needed	~90

In addition to process variables presented in Table 3–1, the heating mode can be either direct or indirect (Bergman et al. 2005). In *direct* heating processes, the heat carrier is in direct contact with the biomass. Examples include convective dryers, rotary-drum dryers, fluidized-bed dryers, and the superheated-steam torrefier. In *indirect* heating processes, the biomass is not in direct contact with the heating medium and is separated by a wall. Examples of equipment used in this technology are indirectly heated screw reactors (Pechiney process), rotary kilns, steam-tube dryers, and most carbonization and slow pyrolysis reactors. For both direct and indirect heat modes, the required heat may be supplied by combustion of torrefaction gas to increase thermal and process efficiencies. The heating modes used for thermal preconversion have been developed and proven for other applications (drying, combustion, pyrolysis, and gasification) (Bergman et al. 2004; Bergman et al. 2005; Kleinschmidt & Bv; Persson, Olofsson & Nordin 2007; Reed 2002).

Destructive Drying – Torrefaction

Thermal preconversion carried out at temperatures between 200 and 300°C, under atmospheric pressure and in absence of oxygen, is termed torrefaction. Torrefaction is a combination of drying and incomplete pyrolysis and is characterized by low heating rate (<50°C/min) and a residence time of less than 30 min (Bergman et al. 2005; Persson et al. 2007). Residence time typically refers to the time period that the material is actually exposed to the target treatment temperature between the heating and cooling phases. Key torrefaction parameters include biomass composition and particle size, heating rate, gas-flow rate, target treatment temperature, and residence time.

Torrefaction can be used with many types of biomass to improve feedstock value (Zanzi et al. 2004), and much work has been performed on the impacts of thermal preconversion in the destructive drying, or torrefaction range. The benefits and challenges of torrefaction are widely discussed in literature, and balancing the costs of torrefaction with supply-chain and conversion improvements is the subject of ongoing research. Table 3–2 summarizes some of the advantageous properties of torrefied biomass and the associated mechanisms and benefits.

Torrefaction also has been shown to benefit supply system processes and increase energy density of the feedstock (Couhert et al. 2009; Pach et al. 2002; Sadaka and Negi 2009). A study by Yvan (1985) showed that after torrefaction, cellulose and lignin were still intact, while hemicellulose, which had the lowest thermal stability component, was completely decomposed, giving off highly reactive volatile compounds (Yvan 1985). As a result, the solid state of torrefied products is much reserved and is a dry, hydrophobic, dark brown, and brittle solid material with reduced O/C and H/C ratios. The degree of structural and chemical change in torrefied products depends primarily on the treatment temperature. Figure 3–2 shows non-torrefied biomass alongside four torrefied products treated at progressively higher temperatures.

Table 3–2. Properties, mechanisms, and benefits associated with torrefaction of biomass in feedstock production.

Improved Property	Mechanism	Benefits
Size reduction and feeding characteristics	Decomposition of hemicellulose results in destruction of fiber network and loss of fiber coherence. Torrefied biomass has less tenacity and is friable, reducing energy cost associated with size reduction and meeting particle size specifications. Torrefied biomass occupies less isotropic in its fiber resulting in shorter grain when pulverized. This enhanced property is beneficial for feeding and fluidizing for burners.	Lower energy input required in pulverization Longer life time use for milling equipment More efficient in co-feed and co-firing biomass with coal
High energy content	Losing O, non-combustible element constituent, and H in dehydration and release of oxygen-rich products increases C/O, and C/H, and therefore calorific value of solid biofuel.	Higher efficiency in thermochemical conversion processes Lower cost of storage and transportation
Low moisture content and hygroscopicity	Reduction of OH groups to form hydrogen bonds with acidic hydrogen atoms of water molecules and the formation of O-acetyl groups resulted in subsequent cross-link formation between the biomass fiber are clamed to contribute to hydrophobicity of heat treated biomass (Kocaefe et al. 2008).	Lower cost of storage and transportation Lower mass loss Lower risk of self- ignition Lower risk of biological degradation Larger market channel biomass can be traded
Reduced emission	Torrefied biomass contained substantially less moisture content and volatile compounds due to the dehydration and devolatization during torrefaction (Arcate 2000; Felfli et al. 2005; Pach et al. 2002; Pentananunt et al. 1990).	Combustion is more efficient as loss in smoke, caused by unburned fuel gas, is avoided. Acid corrosion in any gasification or combustion of torrefied material is also minimized as biomass acid is the main liberated volatiles.

Raw Biomass 225°C 250°C 275°C 300°C

Figure 3–2. Resultant product torrefied in the range of torrefaction (200 to 300°C) (Phanphanich & Mani 2010).

Currently, torrefaction is going through the commercial demonstration phase. The market potential of this material includes large-scale power production, industrial heating, and residential/district heating, where cost-effective and secure supplies of biomass are needed (Kleinschmidt 2011). There are challenges that need to be resolved before the benefits of torrefaction can be fully realized in a bioenergy industry, and densification of torrefied biomass is one of the most significant.

Workshop Presentations

Two presentations were given at the workshop to highlight research being performed in thermal treatments. The first presentation focused on increasing the throughput and efficiency of a hammermill and then separating the comminuted material in order to create fractions with specific chemical properties. The second presentation discussed pyrolysis studies to produce a densified pyrolysis oil, or "bio-oil." For this report, pyrolysis is included in Chapter 6—Densification, as the result is a densified, flowable, and saleable feedstock.

Case Study: Thermal Treatments T ≤180°C—Effects on Xylose Yields in Dilute-Acid Pretreatment and Enzymatic Digestibility

Manunya Phanphanich and Allison E. Ray (Idaho National Laboatory)

Torrefaction has been the topic of much research, with results showing torrefaction to enhance biomass quality for thermochemical conversion. In comparison, little is known of the benefits of thermal treatments in the reactive drying range. Non-destructive thermal treatments (T <200°C) are relatively inexpensive and simple compared to destructive treatments (T >200°C) and can still produce desirable feedstock attributes. The preliminary study being performed at INL attempts to capture some of the benefits of torrefaction with less severe and costly non-reactive and reactive drying regimes. This case study explores less understood non-reactive and reactive drying treatments (referred to in this case study as "deep drying") with a particular focus on evaluation of deep drying as a preconditioning treatment prior to grinding and as a preconversion treatment prior to biochemical conversion. The deep-drying experiment used air as a heating medium and subjected biomass to a range of temperatures (120, 140, 160, and 180°C) for various residence times (30, 90, and 150 min). The results are presented in this case study.

Deep Drying as Preconditioning Prior to Grinding

In all cases of drying temperatures and residence times, dry-matter loss of corn stover was less than 1%. The dried samples were tested in an instrumented laboratory knife mill, and grinding energy was recorded. Results (Figure 3–3) showed that grindability was significantly improved by drying over the entire temperature range compared to the raw sample. The reduction in grinding energy ranged from 58 to 65% with little variation over the range of thermal treatment process parameters. Notably, grindability was mostly unaffected by drying time, with only incremental improvements at the highest temperature (180°C).

The milled materials were also analyzed with a dynamic image analyzer (Camsizer) to evaluate the effects of thermal treatment on particle size. Mean particle size decreased for all thermal treatments compared to the untreated materials (see Figure 3–4). Smaller particle sizes resulted in higher specific surface area, which increased with both temperature and residence time. In general, specific surface area indicates accessibility of fuel in heat and mass-transfer aspects.

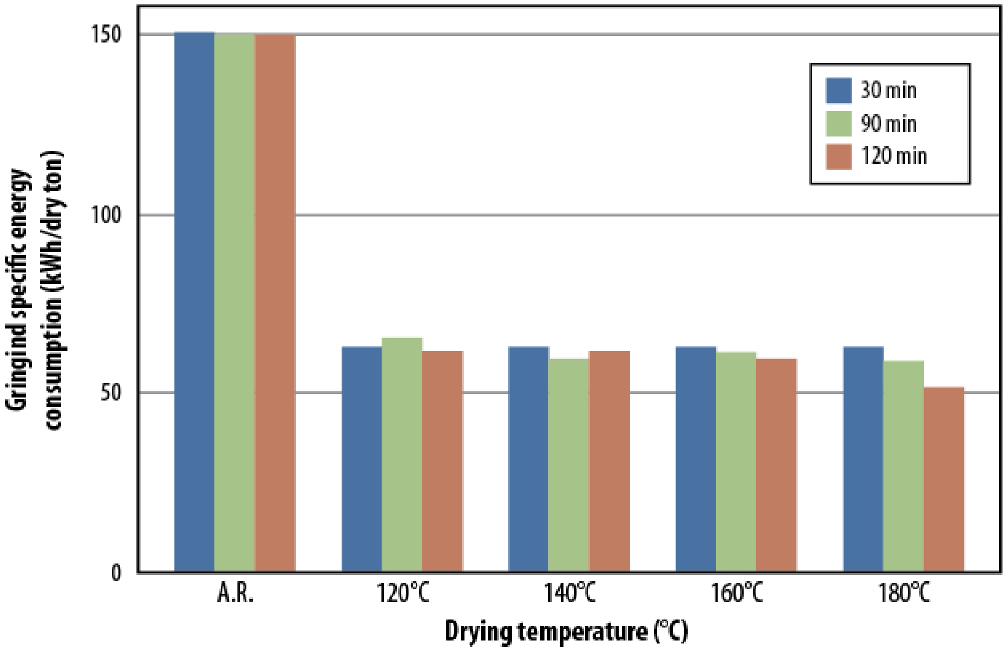


Figure 3–3. The reduction in specific energy required in grinding of deep-dried corn stover. AR indicates the corn stover with moisture content as received (10.7 % wb) (INL research data, August 2011).

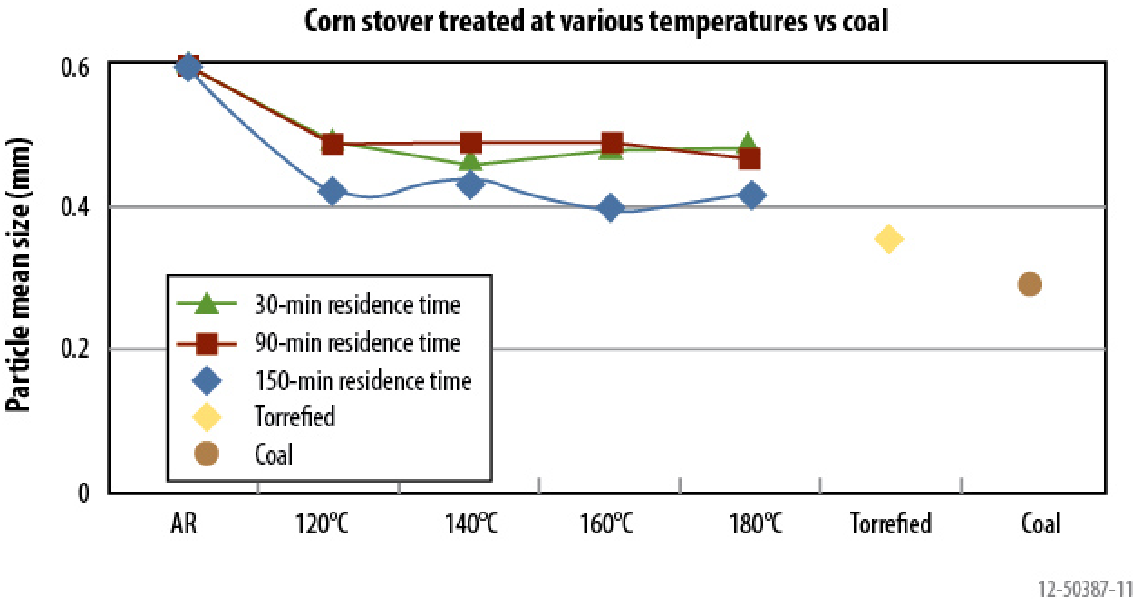


Figure 3–4. Mean particle sizes of deep-dried corn stover grinds as determined by Camsizer™ Digital Image Processing System. AR is the corn stover with moisture content as received (10.7 % wb) (INL research data, August 2011).

Deep Drying as a Preconversion Treatment – Effects on Biochemical Conversion Performance

While much has been discovered about the benefits of thermal preconversion treatments for thermochemical conversions, little is known about its effects on biochemical conversion performance. The deep-drying study assessed the effects of non-reactive and reactive drying regimes on conversion performance of corn stover to ethanol. Corn stover composition and pretreatment efficacy is compared over the range of temperatures (120, 140, 160, and 180°C) and residence times (30 and 90 min) discussed above. Results are also compared to air-dried corn stover control samples.

The glucan, xylan, and lignin content of deep-dried corn stover ranged from 25.4 to 36.6%, 20.3 to 27.2%, and 13.8 to 17.8%, respectively (Table 3–3). Since all of the deep-dried treatment samples were generated with the same source material, it was assumed that measured differences in structural sugar content were a result of time-temperature combinations of thermal treatments; however, there were no obvious trends in composition relative to thermal treatments in the samples examined. Structural sugar contents of 90-min thermal treatments were least variable and highest in glucan and xylan contents after the air-dried control; compositional analyses yielded whole-mass closures around 95% for all samples. For all of the 30-min treatments, whole-mass closures of the compositional analysis ranged from 86 to 93%, which likely contributed to the notable differences in glucan, xylan, galactan, and lignin contents relative to the air-dried and 90-min treated samples. For this reason, interpretation of results for pretreatment efficacy and ethanol yields are only included for the 90-min thermal treatments.

Table 3–3. Structural sugar content of deep-dried corn stover. Sample descriptions indicate biomass type (CS=corn stover), drying method (AR=air dried or DD=deep dried), drying temperature (120, 140, 160, or 180°C), and drying time (30 or 90 min).

Sample Description	% Glucan	% Xylan	% Galactan	% Arabinan	% Lignin
CS-AR-0-0	36.6	27.2	2.0	3.7	14.3
CS-DD-120-30	33.5	20.7	0.0	3.6	17.2
CS-DD-140-30	33.0	21.5	0.0	3.5	17.0
CS-DD-160-30	25.4	25.5	6.3	2.7	16.7
CS-DD-180-30	32.9	20.3	0.0	3.6	17.8
CS-DD-120-90	36.1	26.9	2.2	3.9	14.0
CS-DD-140-90	35.9	26.0	2.2	4.1	13.8
CS-DD-160-90	35.3	26.6	2.1	3.9	14.2
CS-DD-180-90	35.8	26.1	2.1	3.8	14.0

Deep-dried corn stover and air-dried control samples were pretreated with dilute sulfuric acid (0.8% w/w H_2SO_4) using an autoclave at 121°C for 30 min. Pretreatment was performed as previously described (Duguid et al. 2007).

Soluble components of the pretreatment liquors (monomeric and oligomeric sugars) were measured as previously described (Sluiter et al. 2008). After hydrolysis, samples of pretreatment liquor were neutralized and filtered prior to sugar analysis using a high-performance liquid chromatograph (HPLC) with a refractive index (RI) detector (Waters, Milford, MA), an effluent flow rate of 0.6 mL/min, column temperature of 85°C, and a 50-µL injection.

Simultaneous saccharification and fermentation (SSF) was performed as described previously by Duguid et al. (2007) with some modifications. In this study, *Saccharomyces cerevisiae* D_5A was used as the fermenting organism, and Accellerase 1500 (Genencor, Madison, WI) was used as the cellulase enzyme complex and loaded at 15 FPU/g pretreated biomass (dry matter basis).

Monomeric xylose yields are an important performance indicator used to measure the efficacy of dilute-acid pretreatment. Pretreatment results for the deep-dried corn stover at 120 to 180°C for a 90-min interval are presented in a box and whisker plot (Figure 3–5). In this plot, the bottom, middle, and top of the box represent the 25th, 50th (median), and 75th percentiles, respectively; the lower and upper "whiskers" represent the minimum and maximum observed values, respectively. Deep-dried samples at 120°C (treatment T190) had the highest average monomeric xylose yields (67.5% ± 0.5%), and the lowest average yields occurred at 160°C (treatment T390, 62.1% ± 5.3%). However, there were no significant differences in monomeric xylose yields among 90-min thermal treatments or the air-dried control. These results suggest that for the conditions tested, deep drying had neither a positive nor a negative effect on pretreatment reactivity.

Results from laboratory-scale SSF experiments demonstrated that, in general, there was no difference in theoretical ethanol yield (%TEY) achieved by Day 7 among 90-min deep-dried treatments or the air-dried control (Figure 3–6). One-way analysis of variance (ANOVA) detected differences at a level of $p<0.1$; Tukey's honestly significant difference (HSD) test of multiple-comparisons revealed that the 180°C (T490) sample had a higher %TEY relative to the air-dried and 140°C (T290) treatments ($p<0.1$). The 180°C sample had the highest average %TEY, 83.2% ± 2.3%, while the 140°C treatment had the lowest average %TEY at 78.1% ± 2.0%.

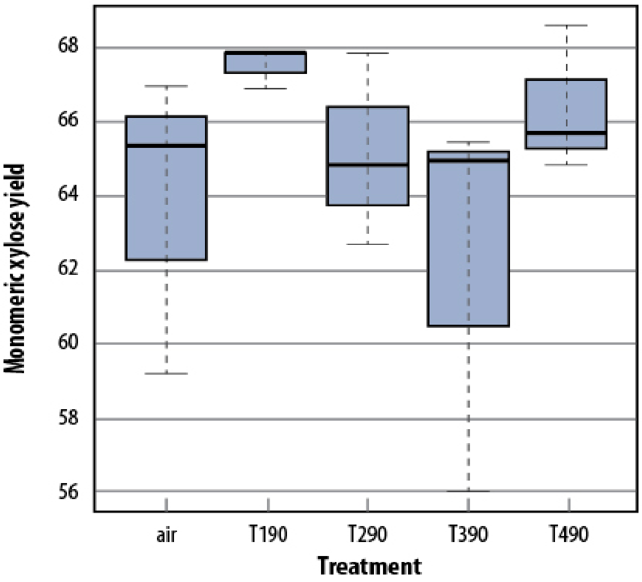
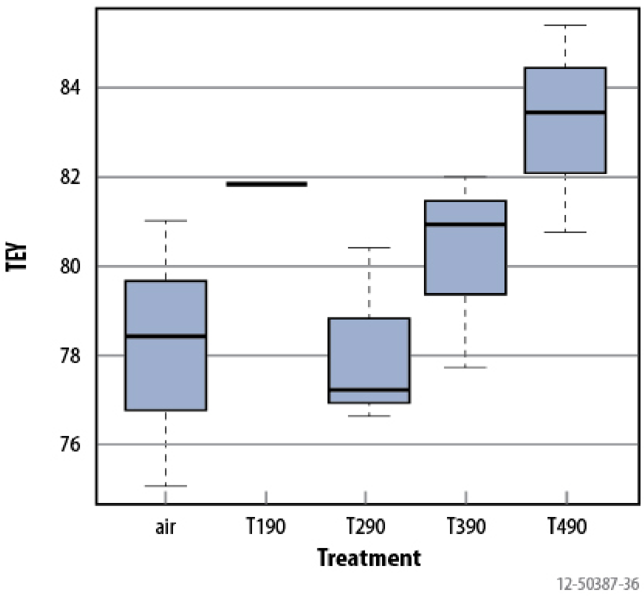


Figure 3–5. Box and whisker plots of monomeric xylose yields (%) for 90-min thermal treatments, where T1–T4 denote 120, 140, 160, and 180°C, respectively. No significant differences in monomeric xylose yields were detected with one-way ANOVA.

Figure 3–6. Box and whisker plots of the %TEY from conversion of C6 sugars on Day 7 of the experiment. One-way ANOVA detected significant differences at p<0.1. Using Tukey's HSD test, 180°C samples had higher % TEY when compared to air-dried and 140°C treatments at a level of p<0.1.



These results demonstrate that corn stover dried at temperatures ranging 120 to 180°C for 90 min performed similarly to an air-dried control in terms of pretreatment reactivity and ethanol yields. Dry matter losses were minimal (<1% in all cases) in corn stover samples dried at 120 to 180°C for 90 min.

Discussion of Technology Impacts and Challenges

The two main metrics by which thermal treatments are generally evaluated include mass and energy yields. Table 3–1 summarizes the typical mass and energy yields that occur within different treatment regimes. Mass and energy losses are generally small for treatments below 200°C, even in reactive air environments. In these ranges, researchers (Govin et al. 2009; Obataya & Tomita 2002) found that thermal decomposition was unlikely, and there was negligible mass loss in the solid portion of dried wood. As the treatment temperature increases above 200°C (torrefaction) mass losses become more pronounced, and energy (heat content) is also lost, although to a lesser degree. Of course, the above statements are generalizations, and each biomass type behaves somewhat differently depending upon its specific composition.

The mass loss that occurs during thermal treatment may be offset by other benefits. Several studies have found that torrefaction increases mass energy density by as much as 40%, which allows for more efficient supply-chain logistics (Phanphanich and Mani 2010; Prins et al. 2006; Pimchuai et al. 2010). As much as 30% of the initial energy content, which is stored in volatile compounds, can be lost during torrefaction. This energy can be recovered by capturing the effluent gases/chemicals and using them for specific purposes, such as heating the reactor or for drying (Figure 3–7). Torrefaction has been reported to have high process efficiency, as high as 94%, compared to pelletization and pyrolysis, which have been estimated to have process efficiencies of 84% and 64%, respectively (Uslu et al. 2008).

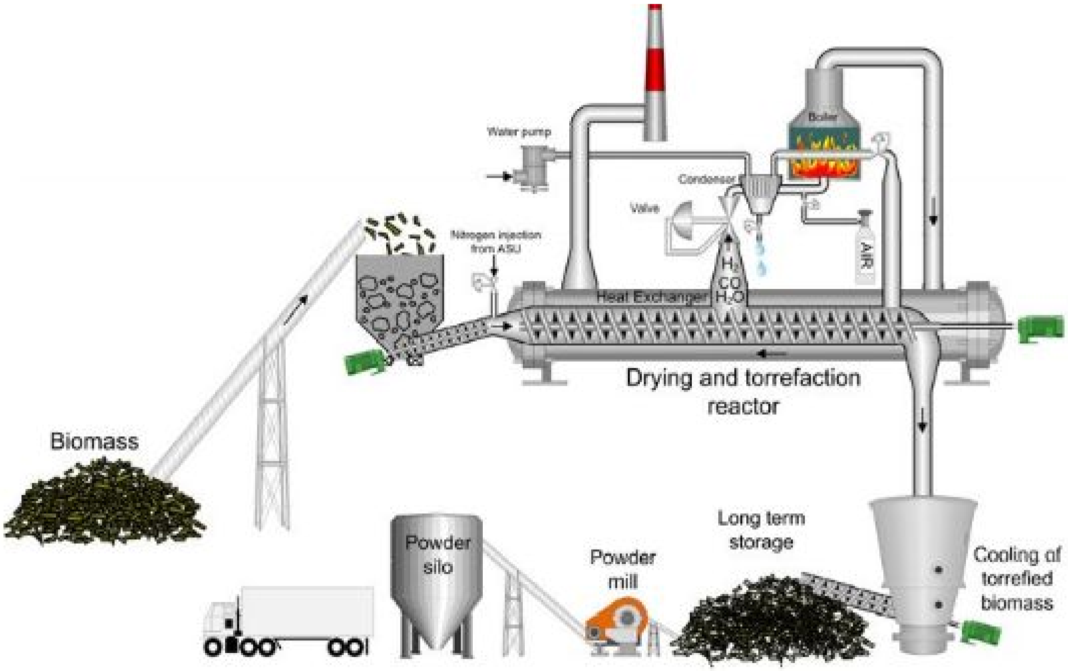


Figure 3–7. A direct/indirect torrefaction concept that captures energy that would otherwise be lost as hemicellulose breaks down and volatiles are released. In this concept, gaseous and liquid torrefaction products are combusted to provide process heat to help fuel the torrefaction process (Persson et al. 2007).

Thermal treatment of biomass has been studied primarily for its benefits to thermochemical conversion (see Table 3–5), which include increased energy densities and conversion efficiencies, higher quality fuel products (e.g., syngas and pyrolysis oil), and improved feedstock preprocessing. In comparative studies of the conversion performance of raw and torrefied woody feedstocks, collaborators at INL and PNNL found that pyrolytic oil produced from torrefied woody feedstocks had a lower water content and higher pH, desirable properties for increasing energy density and reducing corrosivity of bio-oil and finished fuels. After pyrolysis, char percentage of torrefied biomass was higher than that of the original raw biomass. The benefits of torrefaction in addressing thermochemical conversion challenges are widely cited, and Table 3–4 summarizes some of the more well understood impacts for specific thermochemical conversion pathways.

Workshop participants regarded thermal treatments in general—including both deep drying and torrefaction—as adding value by increasing feedstock performance in thermochemical conversion processes such as pyrolysis, gasification, or combustion. However, some participants expressed significant doubt regarding the value to biochemical conversion[119,120,121,122]. The mass loss alone associated with volatilization of hemicellulose has significant implications on biochemical conversion yields. Further, damage to cells also has implications on increasing recalcitrance.

Recognizing the tradeoff between the benefits of torrefaction and the mass loss associated with torrefaction, the deep-drying case study was conducted to evaluate whether benefits may be achieved with reduced-severity thermal treatments (i.e., deep drying) that also minimize mass losses. In particular, the case study focused on the implication of deep drying on biochemical conversion processes—a conversion pathway generally regarded as off-limits to torrefaction[123,124,125,126].

Table 3–4. Benefits of torrefaction on specific challenges associated raw biomass for various processes in thermochemical conversion pathways (Mani 2009).

Conversion Pathway	Challenges Associated with Raw Biomass	Impact of Torrefaction
Combustion	Difficulties cofiring with coal Low energy density High energy required for grinding	Improves carbon conversion (on-going research) Reduces thermodynamic losses, smoke and water vapor Improves combustion efficiency
Gasification	Tar formation Low C/H ratio for liquid fuel production	Improves pulverization characteristics Improves flowability of biomass powders Improves quality and quantity of syngas (Couhert et al. 2009)
Pyrolysis	Bio-oil instability Coke formation	Improves catalytic upgrading of bio-oil to fuels and reduces coke forming precursor

The deep-drying case study showed negligible mass loss for corn stover treated at temperatures ranging from 120 to 180°C and residence times of 30, 90, and 150 minutes. Treatment temperatures included both non-reactive and reactive thermal treatment regimes. Although chemical changes are known to occur within the reactive temperature range, there were no deterministic differences in the chemical composition among the thermal treated samples. Further, testing of pretreatment efficacy and potential ethanol yield also showed no difference between treated and non-treated corn stover samples. Some workshop participants expressed concern that the drying alone would be a detriment as biochemical conversion processes typically rewet low-moisture feedstocks for pretreatment[127,128,129]. However, the deep-drying case study suggests that drying, as well as any associated structural changes that may have occurred, were not sufficient to increase feedstock recalcitrance. Arguably, rewetting dried feedstocks may be a legitimate issue with respect to water-usage requirements of the conversion facility.

While more research needs to be conducted to fully understand the effects of compositional and structural changes on both biochemical and thermochemical conversion performance, changes to biomass mechanical and physical properties offer additional benefits to biomass supply-chain performance including reduction in grinding energy and improved stability in storage.

Thermal treatment has been shown to embrittle biomass tissues and thereby provide value as a preconditioning process to reduce energy requirements during grinding. Phanphanich and Mani (2010) used microscopy to observe biomass cell-wall structure changes in cut wood as a result of increasing torrefaction temperature. Figure 3–8 shows that untreated samples experienced the most difficulty in grinding, as evidenced by the apparent fibrous and tenacious structure. This was explained by the fact that the untreated sample only loses water during physical drying; therefore, cell wall components still remains undamaged (Lipinsky 2002).

Torrefaction was also shown to decrease the tendency of woody materials to splinter, with higher treatment temperatures resulting in less splintery materials. At the observed maximum torrefaction temperature (300ºC), torrefied wood clearly showed no fibrous structure, and the gap within a cell wall was solid. Additionally, damage to the cell structure also manifests itself in reduced particle size, more uniform particle-size distribution, increased specific surface area, and improved flowability.

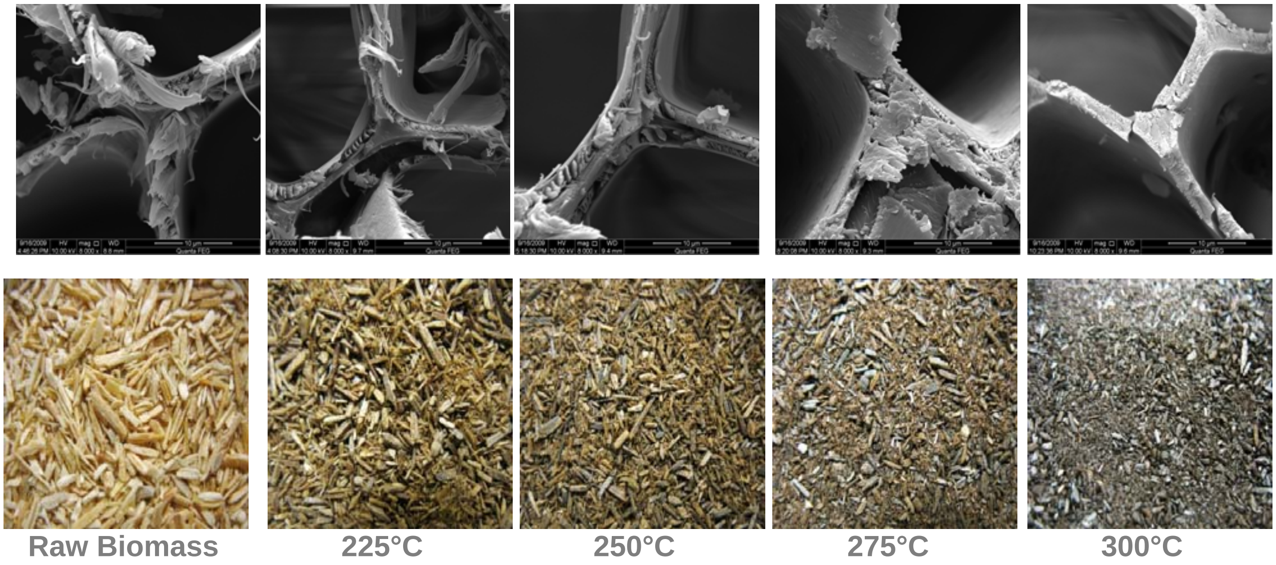


Figure 3–8. SEM images of destructive structure of wood cell wall at various torrefaction temperatures after size reduction procedure (top); photographic images of torrefied wood grinds (bottom).

Cell and tissue changes vary with treatment temperature. Cell-wall shrinkage and reduction of pore volume occurs at drying temperatures of 50 to 150°C (Tumuluru 2011). Research has suggested that the release of internal pressure built up and surface tension that occurred during the drying may induce fiber defect (Govin et al. 2009; Obataya and Tomita 2002; Turner 1998). Changes in glass transition and softening of lignin (representing change in the material stiffness) may also contribute to the ease in grindability (Turner et al. 1998). Similar material properties are thought to contribute to the brittle breakage character of coal (Mishra and Klimpel 1987). The deep drying case study confirms that benefits from the treating temperature range investigated (120 to 180°C) can be gained as a reduction (approximately 60%) in grinding energy compared to non-treated material. Notably, increasing treatment temperature had minimal effect on grinding energy, and only at the highest temperature (180°C) were additional improvements achieve by increasing drying time from 30 to 150 min.

In addition to the advantage in size reduction discussed above, thermal treatment alters biomass physical properties, most notably moisture content as the treatment can effectively reduce biomass moisture content to between 1 and 3%. Reduction of moisture content has several direct benefits including (1) reduced transportation costs due to increased dry-mass payloads, (2) increased biomass stability in storage due to reduced biological activity, and (3) improved conversion efficiencies in thermochemical conversion due to higher energy densities. Workshop participants generally regarded deep drying within the reactive temperature range as comparable to non-reactive drying, with moisture reduction effects benefiting stability in storage.

Depending on the distance to the biorefinery, biomass that is thermally treated prior to arriving at the biorefinery may need to be densified to increase volumetric energy density, improve transportability, and reduce the risk of combustion in transport. Studies have shown that pellets of torrefied biomass have consistent bulk densities of 750 to 859 kg/m^3 (Bergman 2005), which is greater than that of conventional wood pellets (500 to 650 kg/m^3) (Uslu et al. 2008). Furthermore, pellets from a wide variety of biomass materials (e.g., sawdust, willow, larch, verge grass, demolition wood, and straw) have been shown to have similar physical properties, which is not true for conventional biopellets, which can have bulk densities as low as 230 kg/m^3 (Uslu et al. 2008). The energy density of bulk pellets of torrefied biomass has been reported as 17.7 GJ/m^3, which is approximately 20% higher than commercial wood pellets (Bergman

2005).The cost of the combined technologies was reported to be lower than the sum of each individual process alone (Ciolkosz and Wallace 2011; Uslu et al. 2008).

Workshop participants noted that densification of thermally treated biomass is best done at distributed preprocessing depots if the feedstock is to be transported long distances or for coal replacement applications (see Figure 3–9). Integrating thermal treatment and densification technologies to densify thermally treated biomass while still hot and before the lignin hardens would potentially reduce pelleting energy and increase pellet density and durability. More work is needed to understand the fundamentals of producing thermally treated, densified feedstocks.

There are additional technical challenges (Kleinschmidt 2011) that need to be addressed for thermal preconversion to be broadly implemented in feedstock supply chains:

- *Resource types* – Initial stage of the technology is limited to woody biomass, as agricultural biomass tends to nest and plug in processing equipment. Herbaceous materials are also more inclined to ignite or carbonize during the treatment. Resource variables, such as moisture content, bulk density, and particle size distribution of the feed steam, need be precisely controlled to achieve desired product qualities and efficient process. Operational experience with the initial commercial demonstration plants is crucial to find the technical and economical optimum of the various types of biomass.

- *Emissions* – Liberated gases, including water, acid-based compounds, and tars can be problematic to the environment and the system itself. Appropriate technology is needed for separation, use, and elimination of the waste compounds.

- *Up-scaling* – While throughput and feed issues observed in smaller-scale tests may be minimized by scaling up, other factors, such as uniformity of product treatment, can be challenging and may require process and design modifications in order to meet expectations.

- *Process validation* – Temperature, residence time, and feed particle size are codependent parameters that are crucial to thermal treatment performance. Optimum operating conditions can vary for different biomass types and need to be empirically determined.

- *Product validation* – For each conversion pathway, feedstock quality specifications need to be determined and a reliable supply of high-volume, thermally treated feedstocks that are consistent, densified, and on-spec needs to be demonstrated.

Workshop Conclusions

Cost is the primary consideration expressed by participants, and additional experimental work is needed to explore the relationship of thermal treatment cost and feedstock value[130,143]. There were also environmental concerns about the emission of volatiles during the thermal treatment process, particularly in comparison with other energy production processes such as coal combustion[144,145,146]. (See Table 3–5 for a summary of common themes and points of emphasis from Thermochemical Preconversion presentations, discussions, and participant surveys.)

Participant surveys showed strong support that thermal preconversion treatments could be developed to have a beneficial impact, particularly for thermochemical conversion applications and increasing biomass stability and enabling storage, if concerns were adequately addressed (Figure 3–9). Locating thermal preconversion at distributed preprocessing depots was thought to be valuable if the feedstock were to be transported long distances or for coal replacement needs (Figure 3–10). Combining thermal treatment and densification technologies would have a number of beneficial impacts on the supply system, and work is needed to understand the fundamentals of producing thermally treated, densified feedstocks. Deep drying was thought to have greater near-term benefit and torrefaction would require more research and development to provide a positive cost-to-value return (Figure 3–11).

Figure 3–9 In the near term, thermal preconversion has the most value for thermochemical applications and has strong potential to benefit feedstock storage.

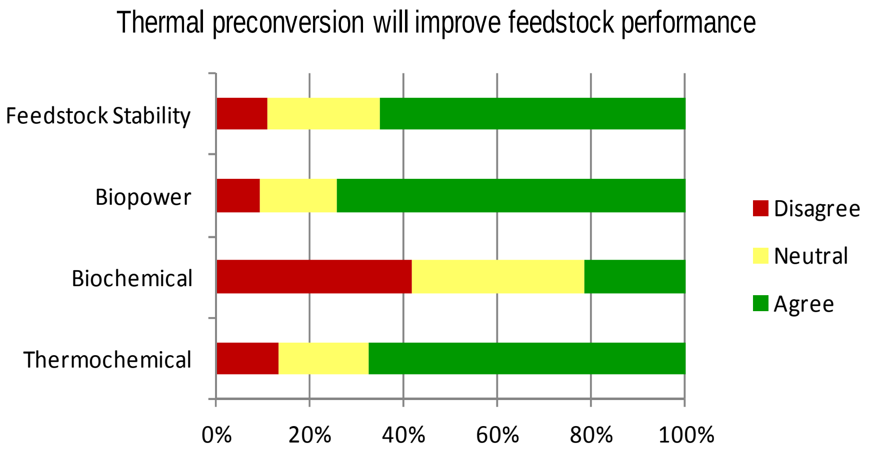


Figure 3–10 Thermal preconversion will realize its greatest value when located at distributed preprocessing depots.

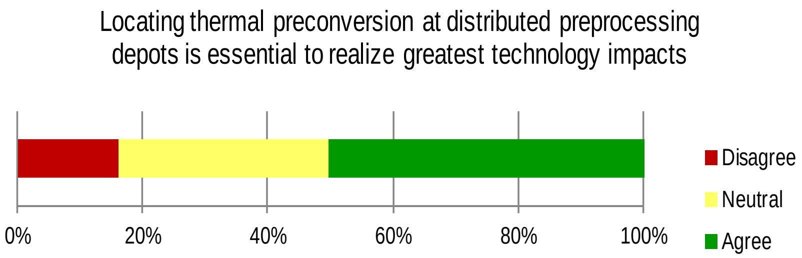
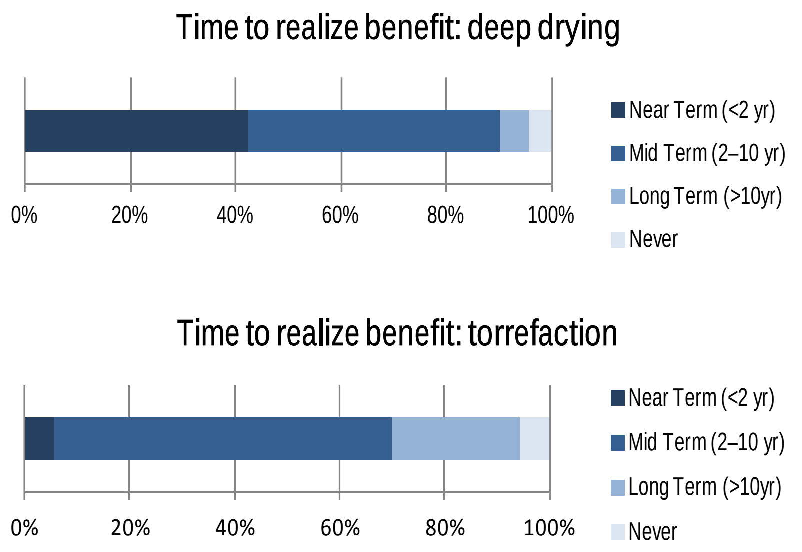


Figure 3–11 Deep drying can achieve the greatest near-term benefit (top) and torrefaction is of interest but likely will require more market development to realize benefits (bottom).



In the near term, thermal preconversion has the most value for combustion, gasification, and pyrolysis applications (thermochemical conversions). The market for thermally treated materials is anticipated to expand to other areas such as biochemical conversion. While thermally treated biomass exhibits many properties that are superior to untreated biomass, in order to economically enter biomass-to-energy chains, positive cost-to-value relationships will need to be clearly established and justified. Future research opportunities exist in improving the density and durability of densified forms of torrefied biomass, such as pellets (due to the low cohesive nature of torrefied biomass), characterization of chemical pathways of the torrefaction reaction, equipment design and related influence on the process, and clarification of supply-chain impact (Ciolkosz and Wallace 2011).

Table 3–6. Summary of common themes and points of emphasis from Thermal Preconversion presentations, discussions, and participant surveys.

Desired R&D Outcomes	Potential Approaches	Barriers/Constraints
SUPPLY (Conversion Performance) • Purity – reduce undesirable constituents (e.g., ash, volatiles) • Reactivity – improve reactivity for thermochemical conversion processes LOGISTICS • Density – Increase energy density • Efficiency – preconditioning for subsequent preprocessing operations • Stability – increase shelf life (moisture management, hydrophobicity)	• Explore existing non-reactive and reactive thermal treatment technologies and optimize for bioenergy feedstock production - Unconventional – residence drying, torrefaction, wet torrefaction • Understand interdependence of equipment/process variables and material properties and their impacts on cellular structure, chemical bonds, energy density, flowability, storability, densification, and conversion • Understand energy losses, off-gassing of volatiles, greenhouse-gas emissions • Capture values of byproducts (i.e., off-gasses and other emissions)	• Impact on biological conversion activity including enzyme activation and fermentation • Energy losses, greenhouse-gas impacts • Economics vary depending on cost of crude • Currently limited domestic benefit – near-term suitability is long-distance transport, such as the European Union (EU) market • Must meet specs required by handling equipment and process being fed • Compatibility with existing transportation and handling infrastructure • Demonstration of near-term benefits • Demonstration of positive investment-to-value ratio

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Chapter 4 — Chemical Preconversion

David Thompson (Idaho National Laboratory)

It has been shown that raw biomass is not particularly well suited for large-scale use to produce biofuels, biochemicals, or biopower, due to heterogeneity, introduced soil, and endogenous contaminants that are detrimental to downstream processing (Bakker and Jenkins 2003; Zheng et al. 2009). Chemical preconversion is defined as the use of chemicals within the feedstock supply chain to effect changes in the composition and/or structure of the biomass in such a way that its formatting, handling, and storage characteristics are improved over those of raw biomass. Targets for improvements include reducing the energy required to grind or densify the feedstock, improving flowability, improving the storage stability, and removing contaminants detrimental to downstream biorefinery processes. Chemical preconversion may be done with or without added heat, but its defining characteristic is that it accomplishes these effects without increasing the recalcitrance of the biomass at the biorefinery or reducing yields of product. However, depending on the chemical preconversion method employed, benefits such as reduced pretreatment severity may be realized by the end user.

The complex structure of lignocellulose, which protects the polysaccharides from degradation, makes it necessary to employ various chemical pretreatments at the biorefinery to obtain high yields of fermentable sugars. In biopower applications, contaminants such as silica and alkali metals form a low temperature eutectic mixture that causes slagging and corrosion in the combustors (Saddawi et al. 2011). Thermochemical processes such as gasification convert contaminating ash and heteroatoms originating from protein and DNA in the cell walls of the biomass to compounds that foul and/or inactivate catalysts (Sutton et al. 2001). Insofar as these contaminants are liabilities at the biorefinery, their removal within the feedstock supply chain while at the same time improving feedstock supply characteristics can provide multiple benefits.

Chemical Preconversion Technologies

Chemical preconversion of biomass can be used to improve a feedstock product both from the aspect of its ability to be densified as well as its ability to meet specifications, both of which affect cost and value. The primary goals of chemical preconversion within the feedstock supply chain are to improve feedstock characteristics for supply chain logistics, improve the cost-to-value proposition for the feedstock, and improve feedstock characteristics (composition and consistency) for the end user. Feedstock characteristics for supply chain logistics can be improved through reductions in grinding energy and pelleting energy, improvements in flowability, decreases in wettability, and reductions in nonreactive or deleterious components such as ash and unwanted extractable organic compounds. Grinding and pelleting energy can be affected by disrupting cell wall structure and by partially depolymerizing cell wall biopolymers. Chemical preconversion can improve the ability to densify the biomass, which will improve flowability. Chemical modification of lignin or lignin redistribution can decrease wettability. Leaching or releasing physiological ash from within cell walls can reduce contaminants. The contaminants and/or structural modifications of interest will vary with the end use desired. In some cases, structural or chemical modifications achieved during chemical preconversion can improve the performance and yield for the end use.

Chemical conditioning and treatment of lignocellulose have been well studied for applications outside the feedstock supply chain. Examples include pre-steaming of wood for reduced pulping energy costs (Malkov et al. 2003) and for "value prior to pulping" (Marinova et al. 2010; Horhammer et al. 2011) in the forest products sector and, ammonia treatment of hay and agricultural residues (Dean et al. 2008) to improve the nitrogen content for use as feed in the agricultural sector. In the bioenergy sector, similar methods are commonly employed under mild to severe conditions to dissolve ash components (Jenkins et al. 1998; Thompson et al. 2003), and/or to swell the matrix or to remove hemicellulose and/or lignin to increase cellulose surface area available to cellulase enzyme systems (Zheng et al. 2009). Acidic and alkaline catalysts, solvents and other reactive molecules are utilized to achieve these results. In addition, enzymatic (Smith et al. 2009) and/or biological treatments (Houghton et al. 2004; Taniguchi et al. 2010) can also be applied. While leaching treatments are typically done at lower temperatures, chemical treatments are performed at high temperature and pressure and very high or very low pH. For feedstocks destined for biochemical conversion, chemical preconversion would be properly characterized as low severity, incomplete pretreatment of the biomass. As such, chemical preconversion focuses on implementing these pretreatment chemistries at considerably lowered severity, which necessarily avoids the formation of soluble saccharides (preventing yield losses and formation of inhibitors). For feedstocks destined for biopower, thermochemical and hybrid systems that are sensitive to contaminants such as ash components, chemical preconversion would be properly characterized as chemical leaching and dissolution of these contaminants from the feedstock.

The simplest chemical preconversion is leaching of nonreactive or deleterious components from biomass. Leaching of biomass typically consists of low temperature chemical treatments with solvent or catalyst washes utilizing water, dilute acid, dilute alkali, organic solvents, or supercritical fluids(Thompson et al. 2003; Bakker and Jenkins 2003; Davidsson et al. 2001; Nutalapati, et al. 2007; Kuo et al. 2011; Lu et al. 2006). These methods are capable of removing soluble salts, organics, polyphenols and silica. (Table 4–1 summarizes the various low temperature leaching methods and the classes of compounds leached from the feedstock.)

Table 4–1. Effects caused by low-temperature chemical washes (Bakker and Jenkins 2003; Davidsson et al. 2001; Nutalapati et al. 2007; Kuo et al. 2011; Lu et al. 2006).

Wash Component		Removed from Feedstock
Water		salts and low molecular weight soluble organics
Dilute acid		salts, acid-soluble organics and acid-soluble lignin fragments
Dilute alkali		salts, silica, alkali-soluble organics, alkali-soluble lignin fragments
Organic solvent		nonpolar organics and polyphenols
Supercritical fluid	Polar	polar organics
	Nonpolar	nonpolar organics and polyphenols

A second category of chemical preconversion methods involves reduced-severity chemical pretreatments that result in structural changes to the feedstock but avoids production of soluble saccharides that would result in reduced yields at the biorefinery. Table 4–2 summarizes these types of pretreatments and their effects on feedstocks.

A third class of preconversion techniques utilizes reduced severity gas phase pretreatments of feedstocks which have the advantage of potentially cheaper recovery of treatment chemicals, as well as reduced waste from the process. Table 4–3 summarizes various methods and their effects on feedstocks.

The deciding factor in whether a chemical preconversion can be applied within the feedstock supply chain will invariably be its cost:value proposition, which extends across the feedstock supply and bioenergy conversion boundaries. Chemical preconversion has the potential to enable the supply of chemically and compositionally consistent commodity feedstocks to the growing bioenergy industry.

However, adding steps to the feedstock supply chain will invariably add cost to the feedstock. In some cases, there may be unfavorable trade-offs within the feedstock supply chain among preconversion, formatting, densification, handling, storage , and transportation costs. Hence, chemical preconversions that improve the performance of the commodity feedstock on the conversion side will be equally important to the cost:value proposition, for example, reducing silica and alkali metals for biopower or reducing the required pretreatment severity for biochemical conversion.

Table 4–2. Reduced-severity liquid phase pretreatments and their effects on feedstocks (Zheng et al. 2009; Brodeur et al. 2011).

Chemical	Expected Maximum Temperature (°C)	Effect
Water	<150	Partially depolymerize hemicellulose
Dilute acid	<130	Partially depolymerize hemicellulose and lignin
Dilute alkali	<60	Partially solubilize hemicellulose and lignin
Anhydrous liquid ammonia	<90	Partially depolymerize and redistribute lignin; partially depolymerize hemicellulose
Organic solvent	solvent-dependent	Partially solubilize lignin and some hemicellulose
Supercritical solvent	solvent-dependent	Solvent-dependent; potentially any of the above

Table 4–3. Reduced-severity gas phase pretreatments and their effects on feedstocks (Bazzana, et al. 2011; Kumar et al. 2009; Gupta et al. 2011; Taherzadeh and Karimi 2008).

Chemical	Effect
Ammonia	Partially depolymerize hemicellulose and lignin
Ozone	Partially depolymerize lignin and hemicellulose; oxidize lignin
Chlorine dioxide	Partially depolymerize hemicellulose and some lignin
Nitrogen dioxide	Partially depolymerize hemicellulose and some lignin
Sulfur dioxide	Partially depolymerize hemicellulose and some lignin

Workshop Presentations

Two specific technologies were presented to demonstrate chemical preconversion concepts. Hydrothermal treatment was presented as an example of a treatment for removing physiological ash-related contaminants common in raw biomass. Ammonia Fiber Expansion (AFEX®) was presented as an example of a destructive treatment for imparting structural changes to biomass to improve subsequent preprocessing and biochemical conversion performance. Participants believed chemical preconversion has the potential to improve feedstock value for biochemical, thermochemical, and biopower conversion processes, as well as improving feedstock stability. Participants were divided as to where chemical preprocessing would be best located with suggestions for both decentralized depot locations and proximate to the conversion refinery. Waste water treatment was the biggest concern for locating chemical preconversion at a depot.

Technologies to Enable Regional Biomass Processing for the Production of Fuels, Chemicals and Animal Feed

Tim Campbell, MBI, Lansing, Michigan

Large centralized biorefineries (50 to 100 million gallons/yr) face a significant challenge in feedstock supply logistics; specifically, the high cost of transporting the vast amounts of lignocellulosic biomass (2,000 to 5,000 ton/day) required for the production of fuels and chemicals at this scale. The logistical, contracting and storage issues connected with supplying these large bioconversion plants with consistent feedstock material are formidable. These facilities are also tied irrevocably to whatever biomass exists in its immediate collection area since it is prohibitively expensive to ship low bulk density biomass more than a few dozen miles. The resulting feedstock supply uncertainties add to the risk and expense of cellulosic biofuels.

One of the leading concepts for addressing the feedstock logistics challenge is the relocation of preprocessing and pretreatment operations closer to biomass feedstock harvest locations through a system of Regional Biomass Processing Depots (RBPDs). In this decentralized concept a series of small, geographically dispersed RBPDs would preprocess, pretreat, and densify locally available biomass prior to transport to a central biorefinery for final conversion into advanced biofuels/chemicals.

In this presentation we will discuss a novel batch process for Ammonia Fiber Expansion (AFEX®) treatment as a potential prechemical conversion technique for biomass. This process has specifically been designed for operation in dispersed RBPDs and offers lower capital costs, simple operation and scalability not available in previous continuous AFEX® designs. In addition, this design is applicable to many herbaceous crops and residues (Figure 4–1), does not degrade hemicellulose, has no wash or waste streams, offers low chemical usage due to ammonia recycle, prepares biomass for enzymatic hydrolysis and fermentation and finally improves digestibility of biomass for use as an animal feed.

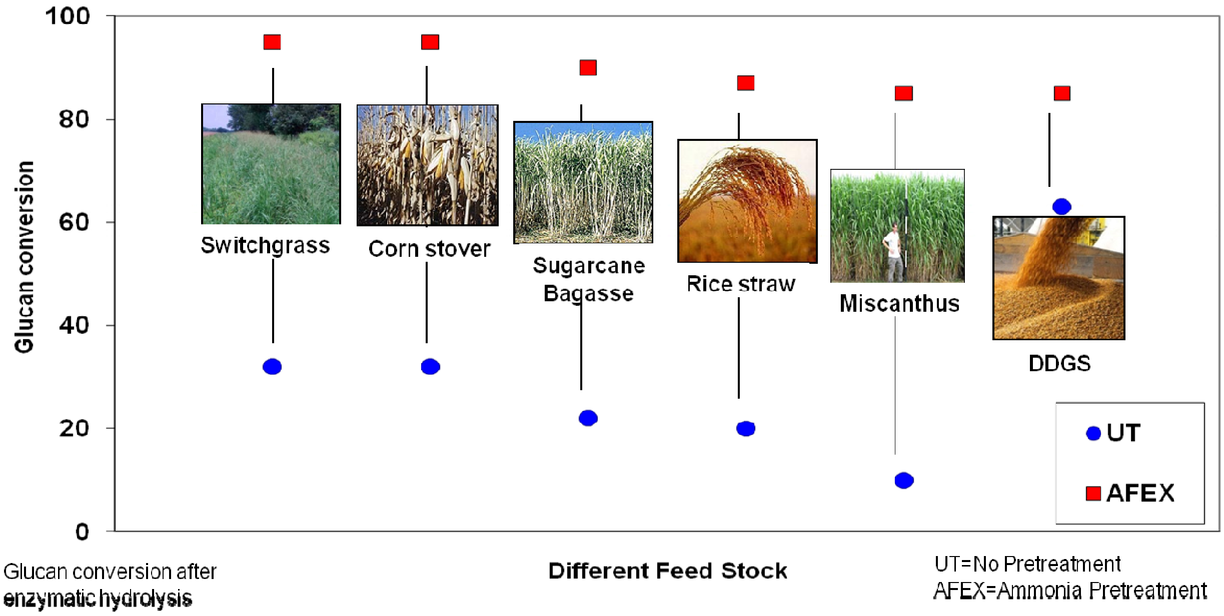

Figure 4–1. Biomass conversion for different feedstocks before and after AFEX® treatment

In this novel AFEX® treatment moist biomass is contacted with ammonia and the temperature and pressure are increased. This material soaks for a specified at temperature and ammonia load. The pressure is then released and the ammonia is recovered and reused. Figure 4–2 shows typical ammonia loading and bed pressure diagrams as a function of time.

Another advantage of AFEX® treatment in RBPDs is that AFEX® treated biomass is easily densified into briquettes (Figure 4–3) with bulk density increases from 6 to 50 lb/ft^3, comparable to the density of coal.

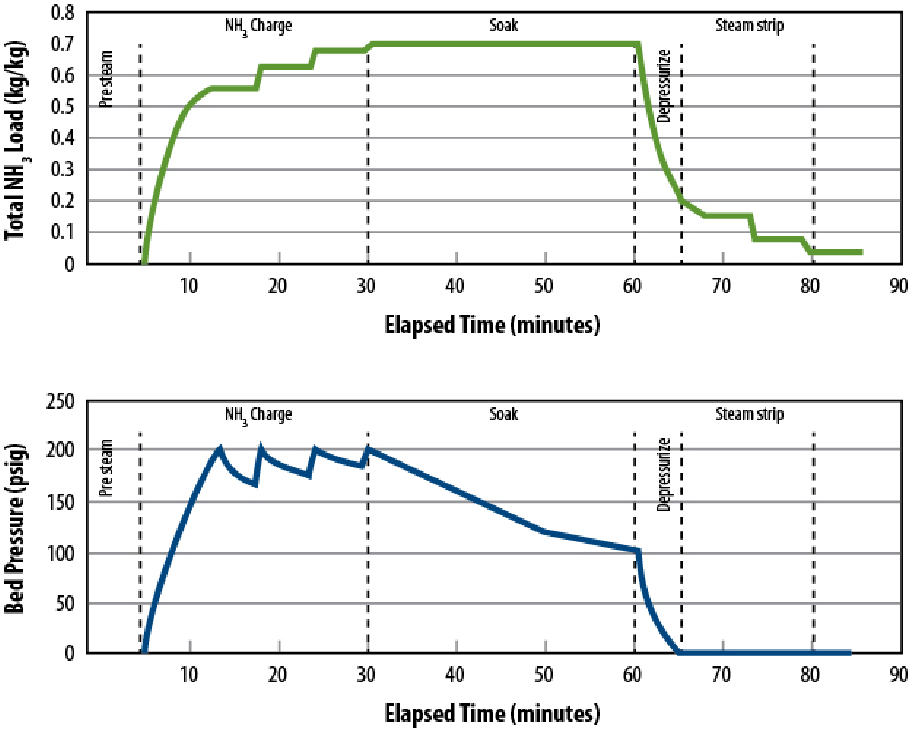

Figure 4–2. Ammonia loading and bed pressure during AFEX® treatment as a function of time.

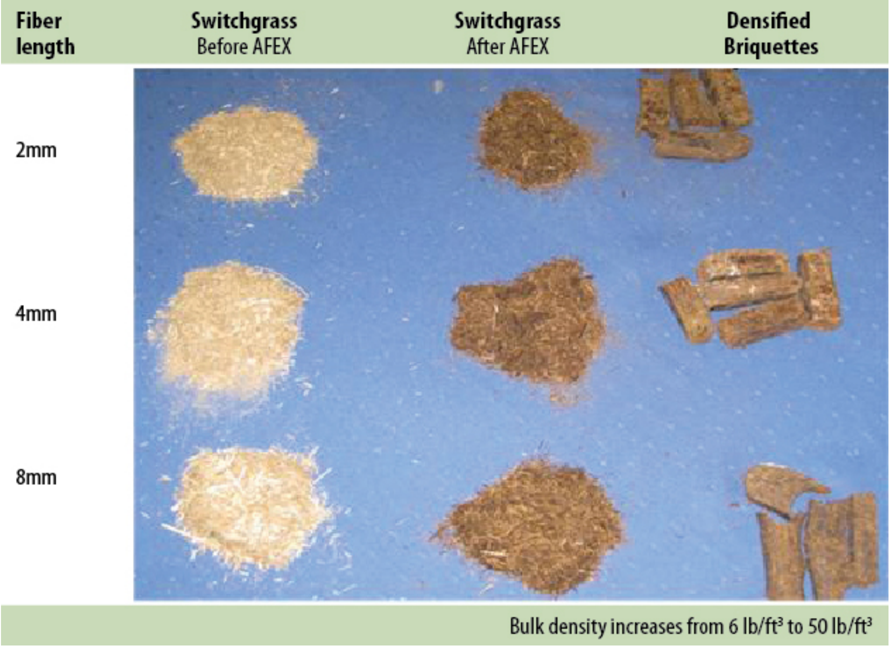

Figure 4–3. *Switchgrass before AFEX® treatment, after AFEX® treatment, and after densification.*

AFEX® treatment technology shows potential for a 50% reduction in the capital cost of biomass pretreatment at commercial scale (100 ton/day) RBPDs. The process is expected to produce a stable, highly densified biomass (up to 50 lb/ft^3), as a consistent commodity available to a centralized biorefinery enabling a 30% reduction in production cost of the advanced biofuel. In addition to use as feedstock to integrated biorefineries for production of biofuels and bio-based chemicals, the densified stable commodity may also have significant value as an animal feed, which could reduce or eliminate “food vs. fuel” controversies associated with biofuels.

The RBPD approach has the potential to significantly accelerate the commercialization of cellulosic biofuels and chemicals through improved feedstock logistics systems and the establishment of a consistent feedstock commodity for use by integrated biorefineries. The positive impact that this system could have on rural development is substantial by creating regional jobs and establishing a flexible commodity product that will have multiple uses in several markets and thereby tempering the effects of volatility in a single market. However, there are significant challenges to making this concept an economically viable option. This presentation will address both the benefits and challenges facing the deployment of technologies in a regionally distributed biomass processing scenario and progress in development of technologies to enable the RBPD concept.

Issues Associated with Trace Contaminants in Biomass Co-firing Feedstock Upgrading Leaching Solution

Luis Cerezo (Electric Power Research Institute)

It is estimated that 1.5 billion tons of sustainable biomass (U.S. DOE 2011) will be available annually by 2030 for bioenergy uses such as biopower and biofuels. This biomass consists of agricultural products such as harvesting residues, processing residues and animal wastes; forestry products such as harvesting residues and primary and secondary processing wastes; municipal wastes such as domestic/industrial wastes and urban green wastes; and woody and herbaceous energy crops. The current challenge to use biomass in biopower applications such as direct combustion or combined gasification and combustion, is the high ash content of biomass (Figure 4–4) which can cause corrosion, slagging and fouling of equipment (Jenkins et al. 1998).

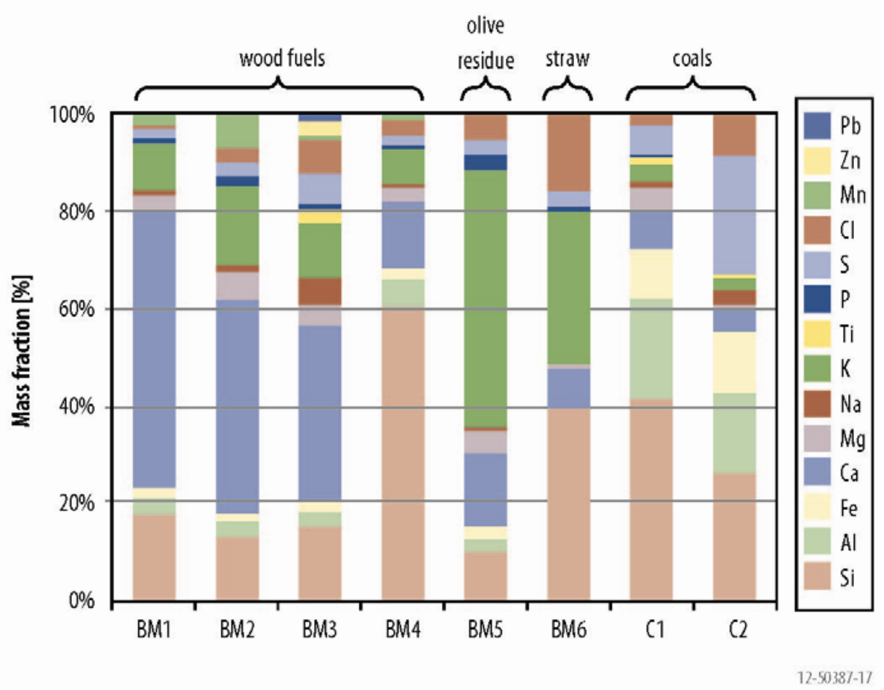

Figure 4–4. Ash elements in biomass versus coal.

The presence of silica, sulfur and alkali metals such as potassium and sodium are of particular concern since they form alkali silicates or alkali sulfates which melt or soften at temperatures as low as 700°C (Saddawi et al. 2012) and are problematic in current technology high temperature combustors. High silica and potassium levels and low levels of calcium are commonly found in agricultural residues and result in ash with low fusion temperatures. Animal wastes such as manures and poultry litters have high levels of chlorine, calcium and phosphorus which also result in low fusion temperature ashes. Ash in biomass fuels generates particles that stick to heat transfer surfaces and lower the rate of heat transfer and are potentially corrosive (Figure 4–5).

A potential solution to these issues is leaching of biomass to remove/eliminate troublesome constituents such as alkali metals, chlorine, sulfur, and phosphorus. This technology presents the opportunity to solve many of the problems faced by firing and/or co-firing low cost and low grade agricultural biomass and waste materials for the production of energy and fuels. EPRI has recently taken interest in accelerating the development of this technology. As part of this endeavor EPRI sponsored through its Technology Innovation (IT) program, the performance of an extensive set of bench scale tests using a number of low cost biomass and waste materials, to optimize and assess the potential of innovative leaching pre-treatment technology. The main target of this project was to verify the leaching technology capability to remove/eliminate the troublesome constituents from the ash of different biomass sources and waste materials in an efficient and economical way, to produce clean biomass that could be used for firing/co-firing with coal applications to produce energy and fuels.

In total ten different biomass and waste materials were treated during the bench-scale testing of the leaching technology. All these materials have great potential to be used as low cost feedstock for the production of energy and fuels, if the ash-related problems associated with their combustion/gasification could be satisfactory resolved. These materials included rice straw, rice hulls, sugarcare trash, empty fruit bunches, city wood waste, olive residue, wheat straw, DDGS, and switchgrass. Leaching technology parameters, selection of the most promising solvents for each biomass/waste material, study of the process economics and initial Aspen Plus modeling of the leaching process were conducted during this project. Laboratory analyses of the initial biomass and waste materials, the resulted leached materials as well as of the liquids from the leaching process were performed to determine the liquid, biomass and ash compositions and assist with the evaluation of the effectiveness of the technology.

Figure 4–5 Secondary super heater fouling: potassium sulfate (left); potassium chloride (right).

The tested leaching technology was proven to work efficiently in all cases with all the different biomass and waste materials. Different solvents were specifically formulated to maximize the effect of the leaching on specific biomass feedstock. The amounts of alkali metals were reduced by more than 90% in all cases, while chlorine by more than 99% and sulfur and phosphorus from 30 to 80%. Ash melting points increased around 400 to 800°C depending on the solvents used and the specific biomass material (Figures 4–6 and 4–7).

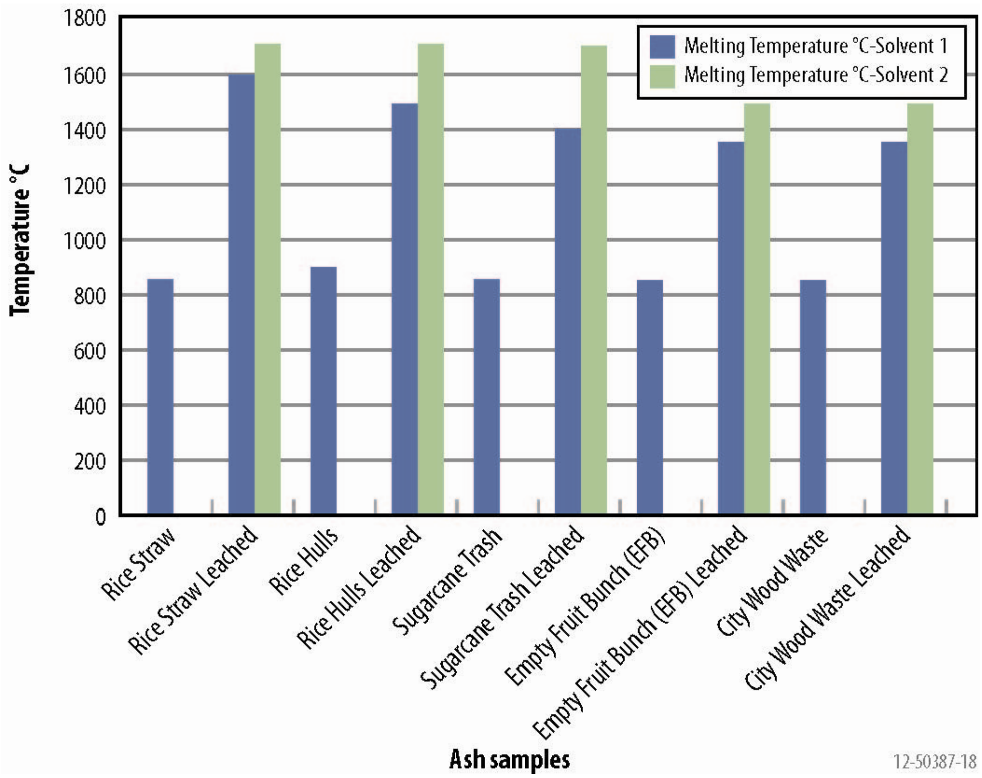

Figure 4–6. Leaching impact on biomass ash melting temperatures

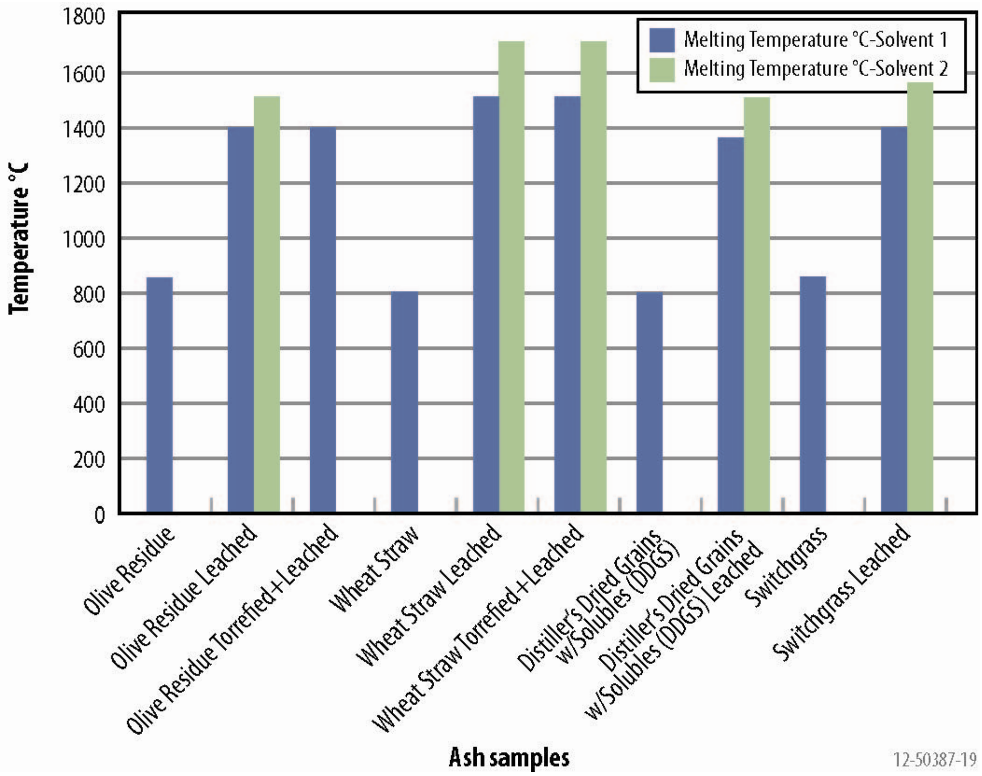

Figure 4–7. Leaching impact on biomass ash melting temperatures.

This study demonstrated at biomass washing-leaching with specially engineered solvents showed high potential to eliminate many of the barriers to use low grade feedstock in high efficiency energy conversion processes such as co-firing with coal, supercritical boilers, oxy-combustion, gasification and pyrolysis. Leaching could be combined/integrated with torrefaction and pelleting to produce clean bio-coals from low grade biomass. Leaching may also contribute to expanded use of short rotation sustainable biomass to energy processes including high ratios in co-firing with coal. Pilot and pre-commercial demo projects are currently being scheduled to validate performance and optimize production costs.

Discussion of Technology Impacts and Challenges

Based on the totality of workshop participant input, it was generally expected that chemical preconversion techniques could have impacts for both the feedstock supply for the end user and in improved feedstock logistics. A number of potential approaches were discussed, as well as real and potential barriers and constraints to their application in the feedstock supply chain. (See Table 4–4 for a summary of common themes and points of emphasis from Thermochemical Preconversion presentations, discussions, and participant surveys.)

For feedstock supply, the impacts were expected to be related to conversion performance, and were focused on feedstock purity and reactivity. For biopower and thermochemical conversions, removal of deleterious ash components was seen as the largest benefit.[36,46,47] For biochemical conversions, improved reactivity was seen to be a potential impact,[45,57] which would be dependent on the subsequent pretreatment and conversion method employed by the end user. An example of such a benefit would include removal of toxic or inhibitory soluble organics or compounds that are converted to toxic or inhibitory compounds during pretreatment. In addition, modification of the cell wall structure of the feedstock biomass to eliminate the need for a pretreatment at the biorefinery or enable reduced severity pretreatments and physiological ash removal could be potentially high impact for the end user.

For feedstock logistics, the impacts were expected to be in the areas of feedstock preprocessing and transportation efficiency.[41,42] Improvement in storage stability was discussed as a potential impact,[48] although it was noted that no data currently exists to support this potential.[30,49] Modification of cell wall structure to effect physiological ash removal and reductions in energy consumption in grinding and pelleting operations, as well as achieving reductions in transportation costs via less costly densification would be examples of potential impacts of chemical preconversion. The potential for impacts in storage stability would likely be chemical preconversion method-specific, focusing on chemical preconversion methods that could affect decreases in wettability of the feedstock and reduction in the biological load in the biomass before it is placed into storage.

The potential for application of chemical preconversion in the feedstock supply chain was generally seen as depending on the application of these methods at a smaller, less capital-intensive scale than would be envisioned for the conversion facility.[41,42,43,44] It was generally believed that this would require further work to understand to capital and operating costs.[33,34,51,52,53,58] Ultimately, these costs must be balanced with improvements to the feedstock in terms of material and conversion properties. Relevant focus areas to achieve impacts include improving biomass consistency, managing undesirable constituents, reducing biological degradation, preconditioning biomass for densification, and reducing pretreatment severity. Depending on the desired end use, further data is needed on feedstock properties including impacts of chemical preconversions on cellular structure, chemical changes, energy density, storability, densification, and conversion performance.

Several barriers and constraints were identified that should be considered for the application of chemical preconversion in the feedstock supply chain. It was noted that the chemical preconversion should not have negative impacts on downstream biological conversion processes,[39,58] which would include cellulolytic digestibility, activation of heterologous plant-expressed enzymes, and fermentation. Another example includes maintaining the ability to meet physical properties required by existing handling equipment and transportation infrastructure, while at the same time maintaining the compositional and conversion specifications required for biological conversion processes. The potential environmental impacts of chemical use and waste in a feedstock depot were also considered to be a constraint.[51,58] Finally, it was generally felt that at the current stage, the lack of information on potential near-term benefits and the potential for a positive investment-to-value ratio (i.e. the relative values of the cost:value trade-offs) was a barrier to application of chemical preconversions in the feedstock supply chain.[33,34,51,52,53,58]

Table 4–4. Summary of common themes and points of emphasis from Chemical Preconversion presentations, discussions, and participant surveys.

Desired R&D Outcomes	Potential Approaches	Barriers/Constraints
SUPPLY (Conversion Performance) • Purity – reduce undesirable constituents • Reactivity – structural changes that reduce pretreatment severity LOGISTICS • Efficiency – preconditioning for subsequent preprocessing operations	• Explore addition of chemical or enzymatic catalysts to biomass to effect structural or compositional changes that - Improve biomass consistency - Manage undesirable constituents - Reduce biological degradation - Precondition biomass for densification	• Should not have negative impact on biological conversion including enzymatic digestibility, activation of heterologous plant-expressed enzymes, and fermentation • Environmental impacts of chemical use • Must meet specs required by handling equipment and process being fed • Compatible with existing

• Stability – reduce biological degradation and improve shelf life	- Reduce pretreatment severity • Understand interdependence of chemical process and material properties variables and their impacts on cellular structure, chemical bonds, energy density, storability, densification, conversion performance	transportation and handling infrastructure • Demonstrate near-term benefits • Demonstrate positive investment-to-value ratio

Workshop Conclusions

Following the workshop presentations summarized above, discussions were conducted among the workshop participants to assess the potential for the application of chemical preconversion in the feedstock supply chain as well as the barriers and constraints. A common theme among workshop discussions was that additional research, process data, and economic analyses are needed to better understand the potential of chemical preconversion and its value for both the supply system and conversion performance. Participants specifically identified the need for more information in the areas of storability,[147] applicability to feedstock growing conditions and types,[148,149] economics,[150,151] and feedstock performance.[152,153,154,155] Participants were divided as to where chemical preprocessing would be best located with suggestions for both decentralized depot locations[156,157,158] or being placed at or near the conversion refinery.[159,160,161] Chemical preconversion was believed to have the potential to improve feedstock value for biochemical,[162] thermochemical,[16,163] and biopower[164] conversion processes, as well as improving feedstock stability.[165,166] It was noted that the economics of chemical preprocessing[4,5,13,167,168,169,170] and waste issues[22] were concerns and that further study would be necessary.

Several important considerations specific to the potential application of the chemical preconversion methods presented at the workshop were also discussed among workshop participants. As industry and conversion platform developers work to scale up their processes, they are gaining a better understanding of the limitations of raw biomass resources—primarily the diversity and variability of raw biomass resources standing in the field—and the effects that this has on feedstock availability at large scale and on processability. A general theme was that this demonstrates a need for advanced preprocessing techniques to provide on-spec commodity-scale feedstock materials. For example, even though the AFEX® technique has been extensively investigated,[171] there was a general concern about the lack of information on chemical preconversion and the use of chemical treatments as a preconversion method, and more work would be needed before they can be applied at industrial scale.[172] The value or applicability of chemical preconversion was believed to have the greatest impact on biological conversion platforms[173,174,175] although the leaching efforts presented were specifically directed at biopower.

One key consideration noted was that incorporation of advanced chemical preconversion techniques into a depot setting would be relatively novel as compared to more conventional preconversion techniques, such as grinding, densification, and stabilization. The techniques themselves (AFEX®, solvent leaching, steam explosion, hydrothermal treatment, steam explosion, dilute-acid, alkaline treatment, etc.) are fairly well established, but are typically viewed as pretreatment options aimed at improving conversion performance without regard to the feedstock supply chain.

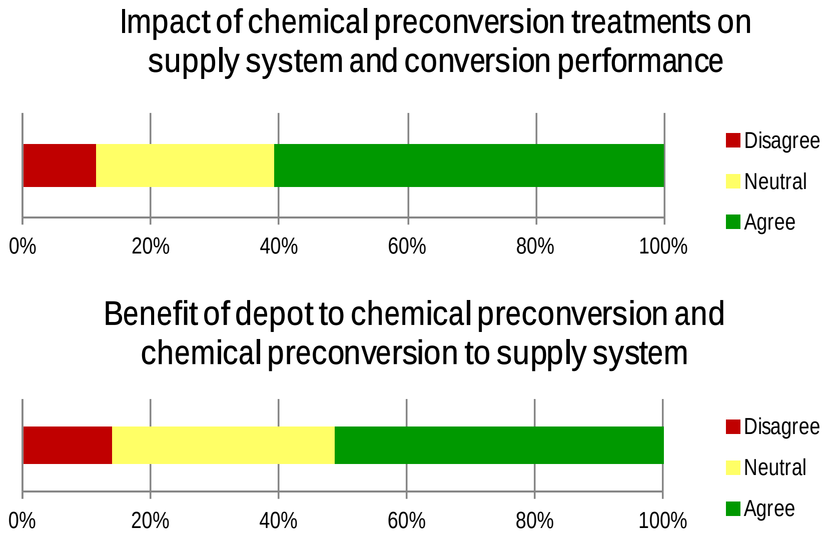

Figure 4–8. Participants were divided about the benefit of chemical preconversion both at distributed preprocessing depots and at or near biorefineries, with half or more expressing it can have a positive impact.

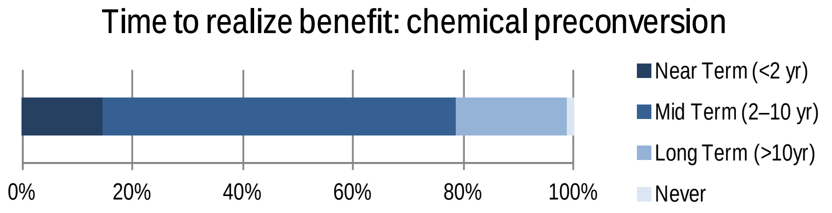

Figure 4–9. Participant input indicates that there are near-term benefits to be realized through chemical preconversion, but the more substantive benefits will take longer to achieve.

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Chapter 5 — Formulation

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In order to accomplish large-scale utilization of biomass feedstocks to produce biofuels, biochemicals, or biopower, a consistent and stable supply of feedstock accessed from a variety of sources will be critical. Formulation combines various preprocessed biomass resources and/or additives to produce an on-spec feedstock that is capable of being traded and used as a commodity. Formulation can also be used to mitigate the effects of undesirable components in raw biomass resources. The resulting feedstock will provide consistency and lower costs to bioenergy industries because they can design their processes around a single feedstock.

To meet the Department of Energy's goal of replacing 30% of current U.S. petroleum consumption, it is estimated that approximately 1 billion tons of biomass must be available annually. A joint UDSA-DOE report that explored the feasibility of supplying this biomass found that it would be necessary to consider biomass residues from both forestland and agricultural land as well as convert a portion of idle and pasture cropland to perennial bioenergy crops (Perlack et al. 2005). A consequence of this diversity of feedstocks is that a typical biorefinery may receive a range of feedstocks ranging from switchgrass to corn stover to miscanthus to eucalyptus. These feedstocks vary widely in composition and recalcitrance, and would require biorefineries to re-optimize (and possibly re-engineer) their processes for each different type of biomass, thus increasing costs.

Complicating this further is that feedstock diversity varies markedly from region to region (Figure 5–1) and each feedstock within a region varies from year to year based on weather conditions, handling, storage, and crop variety. This will result in different types of biorefineries needed in every region which will further increase costs for construction and operation since there will be no "standard" biorefinery.

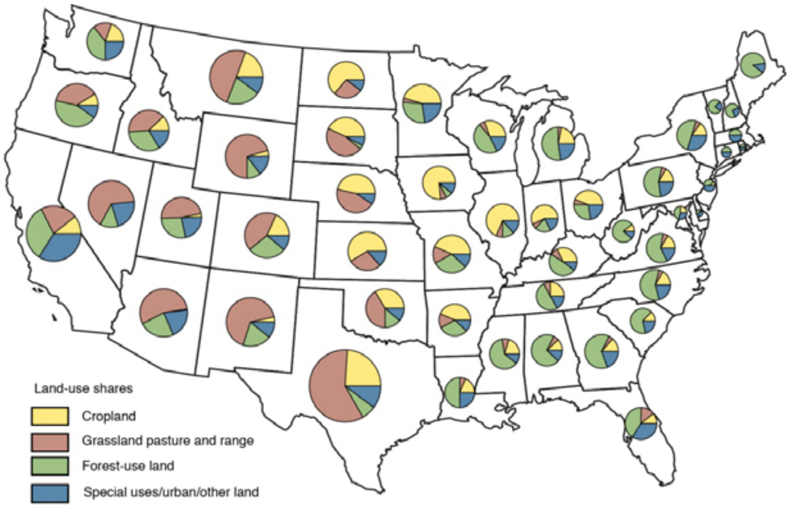


Figure 5–1. Major land-use-types by state (Lubowski et al. 2005).

While this will necessarily be the case in regions that have only limited feedstock availability, meeting the 2030 goals for renewable fuels will require much more versatile feedstocks. Formulation, in conjunction with mechanical preprocessing and preconversion technologies explored in this report, offers a potential solution to these issues by combining feedstocks to acquire desired feedstock specifications, reduce undesirable properties, and to simplify downstream processing.

Formulation Strategies

The overarching goal of biomass formulation is to facilitate the use of consistent feedstocks comprised of different and variable sources of biomass. In addition, potential benefits may exist beyond the feedstock supply chain. In order to accomplish this goal, potential synergies among feedstock factors and conversion factors that may exist in the formulation of aggregated feedstocks will need to be identified, along with the mechanisms responsible for achieving these synergies.

Feedstock formulation is not a new concept in many market sectors. For example, different grades of coal are blended to reduce sulfur and nitrogen contents for power generation (Boavida et al. 2004; Shih and Frey 1995), grain is blended at elevators to adjust moisture content (Hill 1990), animal feeds are blended to balance nutrient content (Reddy and Krishna 2009), forage crops are amended with propionic acid to improve storage stability (Coblent and Bertram 2012) or amended with lactic acid bacteria in silage piles to improve digestibility and improve aerobic stability (Danner et al. 2003; Thompson et al. 2005; Ando et al. 2006), and high ash biomass sources are mixed with low ash coal to allow their use in biopower (Sami et al. 2001).

There are three basic strategies for formulating a consistent, on-spec biomass feedstock, including blending, aggregation, and amendment. While the third strategy could logically include amendment with catalysts such as acid, alkali or enzymes, such amendments would be aimed at pre-impregnating the feedstock with catalysts required for stability of the feedstock or for pretreatment beyond the biorefinery gate. The three formulation strategies, and some examples of each, are described below.

Blending refers to the combination of multiple sources of the same biomass resource to average out compositional and moisture variations. Examples include blending corn stover from multiple landowners that was sourced from different varieties having different compositions, or blending switchgrass that was stored and handled in differing ways that cause to variations in composition and aerobic stability. This strategy will average out differences for a single biomass resource caused by differing weather, fertilization, cultivation and harvesting techniques, cultivars, and post harvest storage and produce a consistent feedstock.

Aggregation refers to the combination of different raw or preprocessed biomass resources to produce a single, consistent feedstock with desirable properties. Examples include mixing blended corn stover with blended switchgrass; mixing blended wheat straw with blended softwood residuals; and mixing blended miscanthus with blended rice hulls. This strategy will allow desirable characteristics of many types of feedstocks to be combined to achieve a better feedstock than any of the feedstocks alone.

Amendment refers to the combination of raw or preprocessed biomass resources with non-biomass additives to produce a consistent, on-spec feedstock. Examples include pre-impregnating the feedstock with dilute acid to improve the storage stability, and pre-impregnating the feedstock with catalysts important to biorefinery processes. In this strategy, additives will preserve the feedstock and allow longer storage times, or may result in lower pretreatment severity and less enzyme required in biorefineries, or in some cases, improved conversion properties after pretreatment (see case study below). A challenge in this strategy is ensuring that the additives do not cause downstream processing issues.

Workshop Presentation

Formulation strategies are widely used in many industries to solve the problems associated with variable sources of raw feedstock materials. It is likely that formulation strategies will similarly benefit biomass feedstocks by providing the end user with a more consistent feedstock that meets their specifications. A presentation was given in the workshop describing a four blend mixture of hardwood, softwood, grass and agricultural residues and determining the effects of mixtures on the bioconversion to ethanol. In addition to demonstrating no negative effects with this mixture, they also presented data showing synergy within the mixture and increased ethanol yields versus each material by itself.

Case Study: Efficient Conversion of Mixed Feedstocks using Ionic Liquids

Rohit Arora, Chenlin Li, Ian Matthews, Kevin George, Taek Soon Lee, Blake Simmons, and Seema Singh (Joint BioEnergy Institute)

Efficient and cost-effective biomass pretreatment remains one of the most significant hurdles towards the realization of biofuels that can displace fossil fuels. Pretreatment represents one of the most significant costs from an operational perspective, and as such JBEI is developing novel biomass pretreatments to help drive the overall costs of the biorefinery down. One cause of this expense, and limited deployment thus far, for the more common biomass pretreatments (e.g. dilute acids, autohydrolysis, dilute bases, organic solvents, steam explosion, lime) is that they are typically only effective on a narrow range of the available lignocellulosic feedstocks. For instance, while dilute acid and ammonia fiber expansion may be relatively effective in pretreating grasses and corn stovers, they are not that effective in pretreating soft woods and hard woods. And no pretreatment exists today that is known to efficiently pretreat and liberate sugars from mixed feedstock streams (e.g. hardwoods, softwoods, grasses, and agricultural residues fed simultaneously).

Ionic liquids are a relatively new class of solvents developed as an environmentally friendly alternative to organic based solvents. An ionic liquid is a salt composed of anions and cations that are poorly coordinated, with melting points typically under 100°C (Simmons et al. 2010). Swatloski et al. 2002, reported 1-butyl-3-methylimidazolium cations and Cl^-, Br^- or SCN^- anions could dissolve microcrystalline at concentrations up to 25% using 3 to 5 seconds full power pulses in a microwave. We have previously demonstrated that certain ionic liquids (e.g. 1-ethyl-3-methylimidazolium acetate) were also very effective in pretreating switchgrass by disrupting and solubilizing the plant cell wall (Singh et al. 2009) within 2.5 to 3 hours at 120°C. Figure 5–2 shows a time course of pretreated switchgrass samples using confocal fluorescence imaging. It can be seen within ten minutes of treatment that the cell walls are visibly swelled and within three hours they have been completely solublized. The solubilized cellulose could be regenerated (dark fibers in the recovery image of Figure 5–2) from the pretreated sample by addition of anti-solvent (water) and it appears that lignin did not co-precipitate with the cellulose.

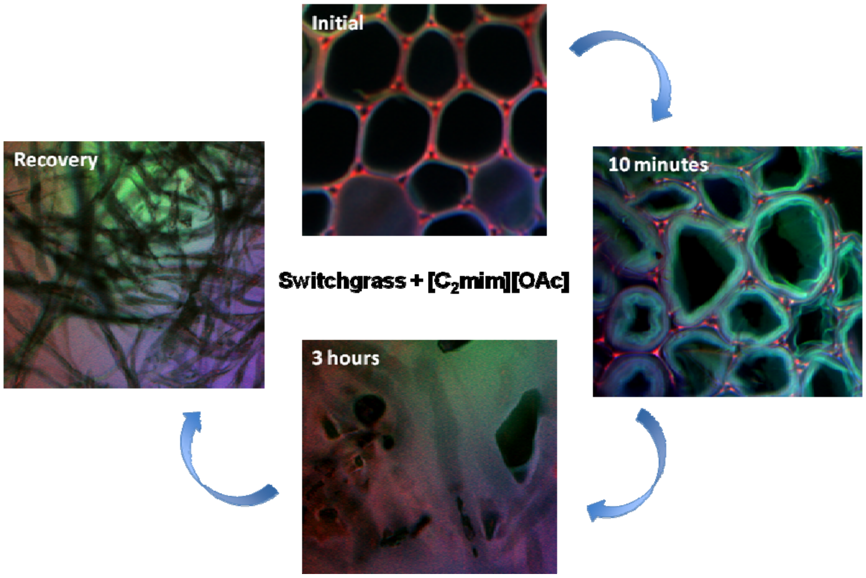


Figure 5–2. Confocal fluorescence imaging of ionic liquid pretreated switchgrass.

We have also demonstrated that ionic liquids can effectively pretreat a wide range of feedstocks, but have yet to demonstrate that this pretreatment technology can efficiently process mixed feedstocks. The focus of this study is to examine and quantify the use of ionic liquids on mixed feedstocks.

Five feedstocks (eucalyptus, pine, switchgrass and corn stover and a 1:1:1:1 mixture) were pretreated with 1-ethyl-3-methyl imidazolium acetate at 15% solids loading and 120°C for 3 hr. The sugars released for each feedstock are shown in Figure 5–3. The amount of glucose released for the mixed feedstock was very similar to the glucose released for eucalyptus and switchgrass and higher than the glucose released for pine and corn stover pretreated by themselves. A similar trend was observed for xylose release. The mixed feedstock appeared to release more glucose than the average of the four feedstocks pretreated separately. We also examined whether ionic liquid pretreatment of mixed feedstock would liberate inhibitors for the subsequent fermentation step. These data are shown in Figure 5–4. There is no apparent inhibition for either the M9 or EZ-Rich strains regardless of sugar concentrations from either feedstock versus the control. It also appears that for the M9 strain, the highest sugar concentration from both the mixed feedstock and the eucalyptus feedstock appeared to enhance growth over the control case.

In this study, for the first time we have developed and demonstrated that ionic liquids can process a mixed feedstock (eucalyptus, pine, corn stover, and switchgrass) input. Furthermore, we have demonstrated that the hydrolysates generated from this mixed feedstock are suitable for the production of advanced biofuels and/or biofuel precursors through microbial fermentation.

Figure 5–3. Sugars released after ionic liquid pretreatment of several different feedstocks.

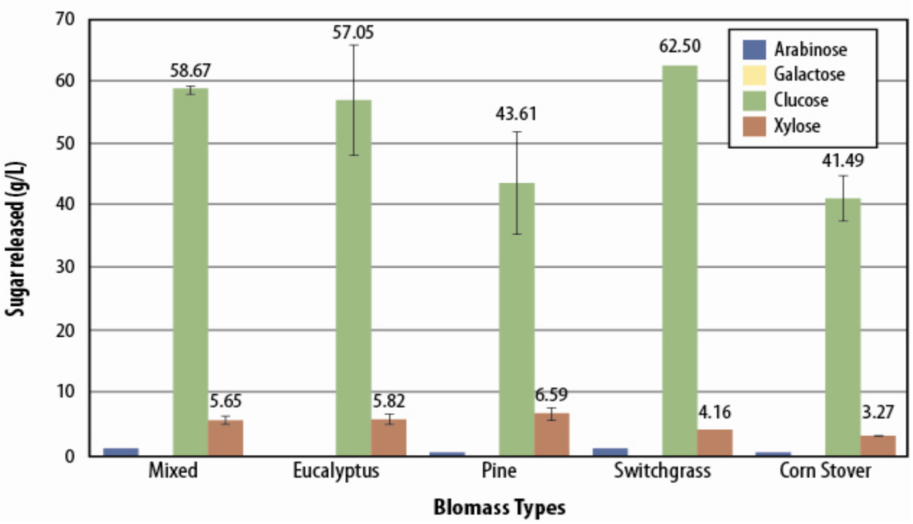
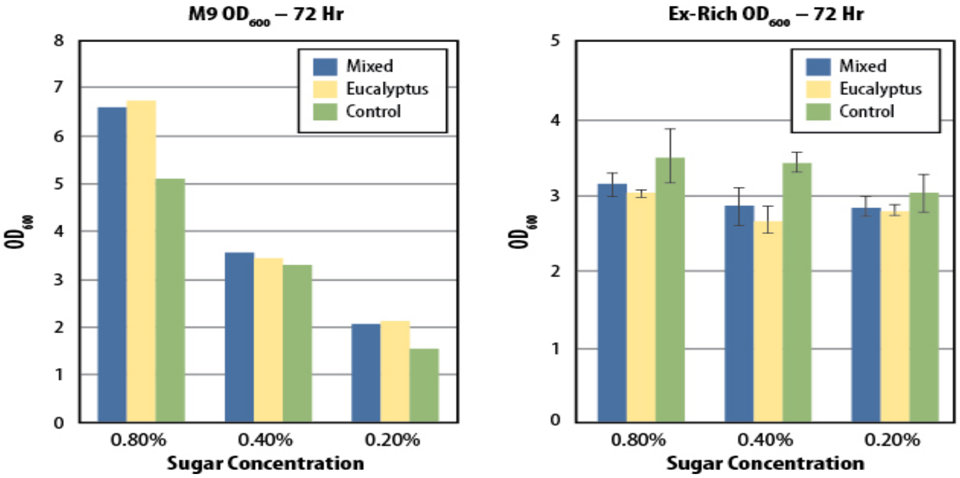


Figure 5–4. Growth of two E. coli strains on ionic liquid pretreated mixed feedstock, eucalyptus feedstock compared to controls.



Discussion of Technology Impacts and Challenges

Based on the workshop participant input, it was generally expected that feedstock formulation could have high impacts for both the feedstock supply for the end user and in improved feedstock logistics. A number of potential approaches were discussed, as well as real and potential barriers and constraints to their application in the feedstock supply chain. (See Table 4–4 for a summary of common themes and points of emphasis from Formulation presentations, discussions, and participant surveys.)

Overall the participants felt that formulation could have high impact for the supply of feedstocks by reducing compositional variability[81] and mitigating the effects of variable reactivities of different feedstocks. Participant consensus was that compositional variability would be most likely improved through blending of different qualities of similar biomass, or by aggregating different feedstocks to provide the benefit to the end user of a more consistent feedstock over the course of a year. Based on the work presented for ionic liquids, they felt that feedstock reactivity could potentially be improved by identifying synergistic affects resulting from aggregating different feedstock types. The use of amendents that affect downstream conversion performance was also considered to be high impact.

For feedstock logistics, the overall consensus was that logistics could be affected through improved stability of feedstocks for storage[101]. It was felt that feedstock stability would be improved by blending high and low quality feedstocks (e.g. wet and dry biomass) to achieve a more stable product, and/or by the addition of amendments that reduce biological degradation and thereby improve feedstock shelf life.

A number of potential approaches were discussed to achieve these high-impact solutions. In one approach, blending, aggregation, and/or amendment could be used to produce feedstocks having consistent composition and convertibility. It was noted that the appropriate mix of techniques would necessarily be region specific[99,100,101]. In areas where a single feedstock predominates such as the Midwest Corn Belt, blending was expected to be the predominant strategy to average out feedstock variations caused by weather, growing conditions, harvest methods, and storage conditions. Aggregation could be implemented as a method to reduce undesirable traits such as high ash content or high moisture content. Amendment could be employed to stabilize these feedstocks in storage. In regions where a great deal of feedstock diversity exists, aggregation would likely be the predominant strategy, with some blending, as well as amendment for storage stability. An example of this situation exists in the state of California, where biomass availability is roughly split evenly among agricultural, forestry and municipal wastes (Jenkins et al. 2005). The diversity expands further in California within each of these categories. Agricultural residues in California include 350 different crops that consist of both herbaceous and woody feedstocks as well as animal manures and food processing wastes. Forestry residues consist of logging slash, forest thinning, mill residues and chaparral, while municipal wastes include solid wastes, waste water and sewage and biosolids.

Another approach discussed was to utilize formulation to mitigate the effects of undesirable constituents in biomass feedstocks[84,102]. Aggregation was discussed as a method to reduce undesirable traits such as high ash content or high moisture content[91.92,93,94]. For this approach, formulation techniques would depend upon the end use for the feedstocks. In biopower applications, blending or aggregration would be utilized to reduce overall ash content and help limit slagging problems[90]. For biofuel applications[81], blending could be utilized to average out physical parameters such as moisture content, while aggregation could be utilized to provide a consistent feedstock by averaging out compositional differences and differences in recalcitrance. Similar techniques to those described above could also be employed here.

Finally the participants suggested that formulation techniques should not be developed in isolation since synergies were likely to exist between formulation and other preconversion techniques discussed in this report including mechanical, thermal, chemical methods. Synergies could also exist with current research efforts to improve biomass quantity and yield through biotechnology and genetic methods. The participants suggested that existing research and development pathways that are in development should be leveraged.

Barriers and constraints to formulation were also addressed by the participants of the workshop. One theme was that formulation strategies should not have any negative impact for downstream processing of feedstocks. One constraint was that chemical amendments should not produce any structural or compositional changes to the feedstocks. Another specific concern was that formulation should not introduce more recalcitrance to feedstocks that would hinder downstream conversions. Resource proximity was also a theme discussed as a challenge for formulation strategies; and, as discussed above, these strategies will have to be developed regionally[83,99,100,101]. Participants felt that formulated feedstocks must meet the specifications for available handling equipment and for currently developed downstream processes. Along these lines, they also felt that formulated feedstocks must also be compatible with existing transportation and handling infrastructure. Finally, participants felt that formulation needed to demonstrate near term benefits in bioenergy applications and had to show a positive cost to value ratio.

Table 5–1. Summary of common themes and points of emphasis from Formulation presentations, discussions, and participant surveys.

Desired R&D Outcomes	Potential Approaches	Barriers/Constraints
SUPPLY (Conversion Performance) - Variability – reduce through aggregation of biomass of different quality - Reactivity – improve through (1) aggregation to achieve synergistic effects and (2) use of amendments to improve conversion performance LOGISTICS - Stability – improve through (1) blending wet and dry biomass to acceptable level and (2) addition of preservatives to reduce biological degradation and improve shelf life	Blend, aggregate, and/or amend biomass resources to produce consistent, (composition, convertibility) on-spec feedstocks Mitigate effects of undesirable constituents Leverage synergies between R&D pathways to produce feedstocks that are optimized for specific end-uses Formulate feedstocks that enable end-use conversion processes	Chemical amendments do not produce structural or compositional changes Should not have negative impact on recalcitrance in conversion Resource types available in proximity Must meet specs required by handling equipment and process being fed Compatible with existing transportation and handling infrastructure Demonstrate near-term benefits Demonstrate positive investment-to-value ratio

Workshop Conclusions

Some participants saw formulation as an important aspect of reducing feedstock variability for biochemical conversion platforms[176] and as a key requirement for achieving a uniform format feedstock.[177] (Figures 5–5 and 5–6) Formulated feedstocks were also viewed as a potential strategy for risk reduction to the supply chain[178] and mitigating the effects of undesirable components, like chlorine.[179] Specific interest was expressed regarding the details of the ionic-liquid pretreatment process, in terms of characterizing the resultant saccharide[180,181] and lignin[182] streams, process temperatures,[183] and fate of the ash[184] in this process. The benefits of formulation that have been realized for biopower operations[185] could prove beneficial to biochemical and/or thermochemical pathways for biofuel production.[186,187,188,189] Overall, participants felt that more information was necessary in order to fully understand the value of formulation.

Several important considerations specific to the potential application of formulation as presented at the workshop were also discussed among workshop participants. Some participants expressed concern about the use of formulation due to the difficulties associated with optimization of product conditions for feedstock aggregates[190] and the additional cost and energy inputs associated with its implementation.[191] Participants also expressed concern over the impact and utility of formulation without subsequent densification.[192,193] The geographical availability of biomass was identified as a major constraint for aggregated feedstocks,[194,195,196] and it was suggested that biomass that is both economically available and geographically co-located is likely best-suited for use in formulated feedstock blends.[197]

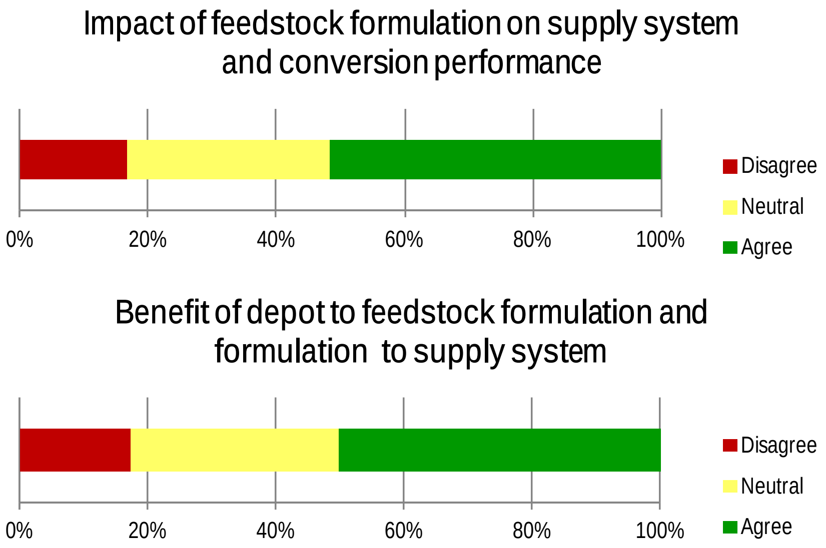


Figure 5–5. Participant response to the concept of feedstock formulation suggests it is a promising idea that needs fundamental work to understand it potential in a commodity feedstock supply system.

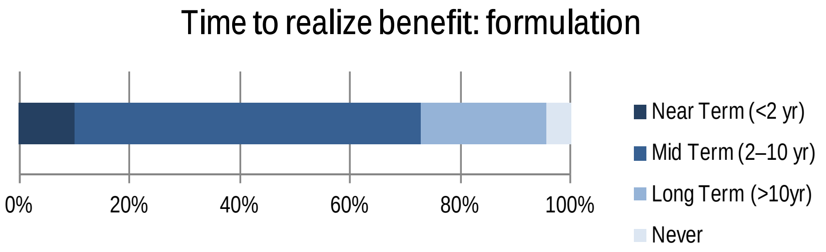


Figure 5–6. The majority of participants believed formulation benefits could be realized in a mid-term time frame.

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Chapter 6 — Densification

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Although biomass has received a good deal of interest for energy generation, its use at an industrial level has attracted less attention due to limitations such as low bulk density, high feedstock cost per energy extracted, and high moisture content. One way to overcome these limitations is to densify the biomass before it is finally used. Densification of biomass can include both solid and liquid format. Densification technologies have been used industrially for a long time. William Smith was the first to be issued a United States patent (1880) for biomass densification. Using a steam hammer at 66°C (150°F), Smith compacted waste from sawmills. Most of the densification technologies available today have been developed for other enterprises and are not optiized for a biomass-to-energy industry's supply system logistics or conversion facility's feedstock specification requirements. Solid densified products include pellets, briquettes and extruded logs, etc and liquid product is pyrolysis oil or bio-oil.

Densification of biomass can provide some valuable benefits for both supply system and biorefinery, such as:

- More homogeneous composition in the feedstock product, resulting in better control during thermochemical and biochemical conversion
- Solid and liquid densified biomass products have mass densities in the range of 600 to 700 kg m^3 and 1.2 to 1.3 g/mL, resulting in lower tranposrtion costs, reduced storage volume, and easier handling.
- Lower moisture content (humidity <10%), favoring longer storage with less loss during the storage period.
- Soild and liquid products have densities in the range of 18 to 19 MJ/kg and 19 GJ/m^3, which are typically higher by 5 to 7 times compared to raw biomass. The increase in the energy densities makes this material more suitable for energy applications.
- The existing grain handling structures for solid format and pipeline systems for liquid format can be used for transportation and storage purposes.

Biomass Densification Technologies

Densification systems are different for solid- and liquid-format feedstocks. Solid-format systems rely on extrusion, forging, and/or agglomeration processes to densify biomass and help improve the handling characteristics of the materials for transport, storage, etc.. Pelleting and briquetting are solid-format systems that have been applied for many years in several countries. Tumuluru et al. (2011) in their studies on densification systems for developing uniform feedstock commodity has explored various systems and the quality of the product produced using them. A liquid-format system of interest is fast pyrolysis for production of bio-oil.

Solid-Format Systems

Pellet mill

A pellet mill consists of a perforated hard steel die, with one or two rollers. By rotating the die or the rollers, the feedstock is forced through the perforations to form densified pellets (Figure 6–1a). In pelletization process the incoming biomass flows into the conditioner for the controlled addition of steam to soften and gelatinize the starch in the biomass. The conditioned biomass is further discharged over a permanent magnet and into a feed spout leading to the pelleting die. Inter-elevator and the feed distributor flights cover biomass evenly on the two rolls and the friction-driven rolls extrude the feed through holes in the die as the die revolves. Cut-off knives mounted on the swing cover cut the pellets as they are extruded from the die (Tumuluru et al. 2011).

Briquette press

Briquetting is usually performed using hydraulic, mechanical, roller or table press. Figure 6–1b shows cut-away diagrams of hydraulic and mechanical briquette presses. The output of hydraulic is lower compared to mechanical presses because the movement of the cylinder is slower. The required pressure in the hydraulic press is produced by a specially designed hydraulic cylinder that releases the compressed briquette once the required pressure is reached. The pressure is adjusted using a regulator to maintain consistency. The mechanical briquetting press develops a compression force of approximately 2000 kg/cm^2 to obtain high quality briquettes with high unit densities (> 1000 kg/m^3) and without the addition of binders. Mechanical piston presses are typically used for large-scale production, of >2.5 ton/hr. Energy loss in the machine is limited, and the output in relation to power consumption is optimal. The operating life of a mechanical press is considerably longer than hydraulic press and they have a better return on investment (Tumuluru et al. 2011).

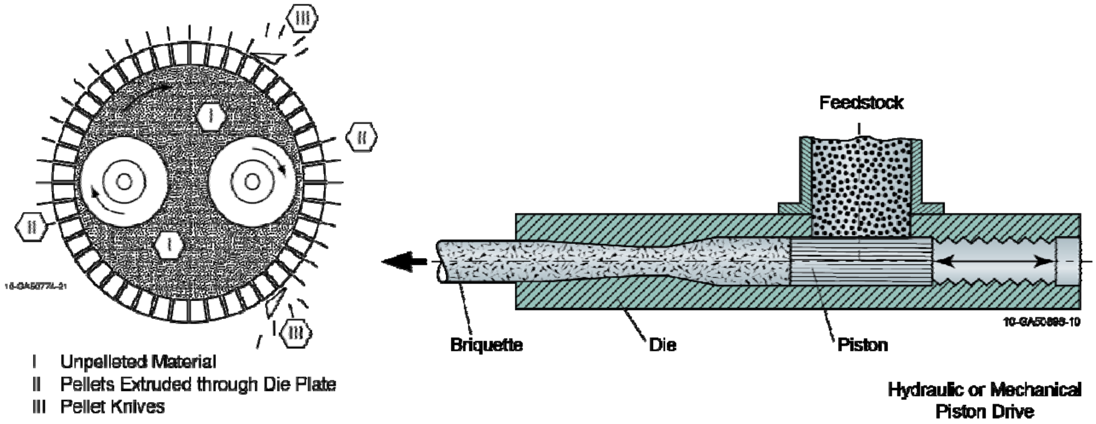


Figure 6–1. (a) Working process of pellet die and (b) mechanical or a hydraulic briquette press.

Roller press

Densification of biomass using roller presses works on the principle of pressure, where pressure is applied between two counter-rotating rolls (Tumuluru et al. 2011).. The typical working principle of a roller press is shown in Figure 6–2a. The biomass material when forced through the gap between the two rolls rotates with the rolls and densifies at the smallest gap (Yehia 2007). Design parameters that play a major role on the quality of the biomass are the diameter of the rolls, minimum gap, roll force, and shape of the die (Yehia 2007).

Tablet press

In a tablet press, a hydraulic motor and ram tightly presses the biomass in a 4 to 6-in. diameter cylindrical mold, reducing the material from about 10 to 2-in. (see Figure 6–2b). The application pressure typically is about 20,000 psi in the mold, which makes the biomass to stick together without addition of binders. In general coarse cut feedstocks are desirable as they bind together by interlocking. The densities of the tablets produced are between 50 and 55 lb/ft^3 compared to bale at 10 lb/ft^3 and pellets at 45 lb/ft^3. However, this process requires higher energy compared to other forms of densification. The literature data on application of tablet press for variety of biomass feedstocks is not available (Tumuluru et al. 2011).

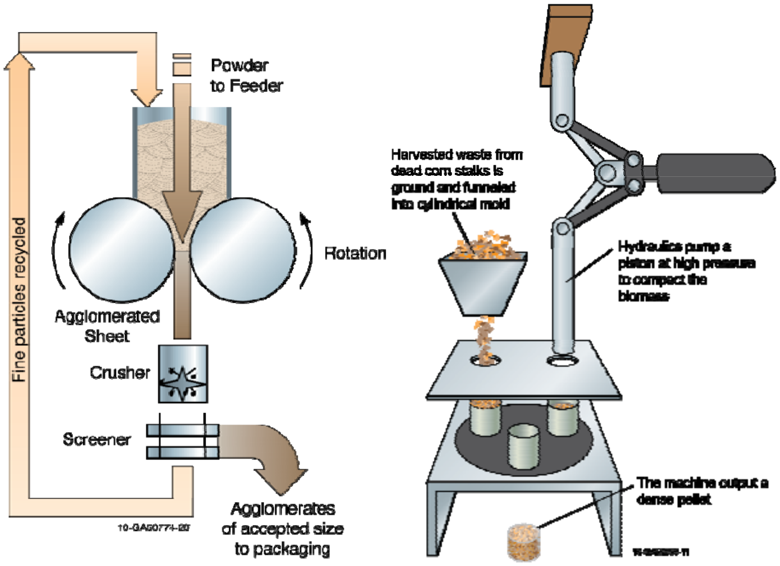


Figure 6–2 (a) Roller press and (b) tablet press.

Cuber

The cuber die ring and roller press (wheel) are similar to the die ring of a pelleter, where the chopped biomass is moved uniformly with an augur toward the openings of the die ring (Figure 6–3a)

As the material leaves the auger flight, the heavy press wheel forces the feed through the die openings in the ring. The typical pressures in a cuber range from 24 to 34 MPa. The binding of biomass in a cuber is due to natural binders in chopped biomass, high pressure of the press wheel, and heat generated bond the cubes as they are forced out of the die. An adjustable deflector outside of the die ring breaks the cubes in lengths of 50 to 75 mm (Tumuluru et al. 2011).

Screw press

In a screw extruder, the biomass moves from the feed port, with a rotating screw, through the barrel and against a die, which will result in significant pressure gradient and shearing of biomass due to friction. The combined effects of wall friction at the barrel, internal friction in the material, and high rotational speed (~600 rpm) of the screw, increase the temperature of the biomass. The heated biomass is further forced through the extrusion die to form briquettes or pellets. External heat using band or tape heaters is provided if the heat generated within the system is not sufficient to reach a pseudo plastic state for smooth extrusion. Figure 6–3b shows the typical screw extruder, with different zones for processing of biomass (Tumuluru et al. 2011).

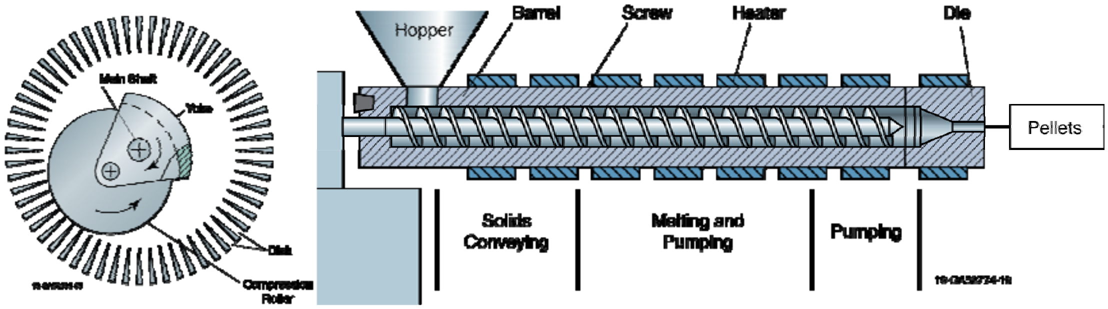


Figure 6–3 (a) Cuber and (b) Screw extruder .

Agglomorator

Agglomeration is a method of increasing particle size by gluing powder particles together. This system is used with a variety of powders such as hydrated lime, pulverized coal, iron ores, fly ash, cement, and others. The application of agglomeration for biomass is limited. The most commonly used method is tumbling agglomeration, which consists of a rotating chamber filled with balls of varying sizes and fed with powder and often a binder. The rotation of the agglomerator results in centrifugal, gravitational, inertial, and frictional forces. These forces press the smooth rolling balls against the powder, helping them to stick together and the particle sizes to grow. Different types of agglomerators are drum, pan, conical, and plate shaped (Tumuluru et al. 2011).

Liquid-Format System

Fast Pyrolysis to Produce Bio-Oil

Of the numerous biomass liquefaction technologies, fast pyrolysis currently is one of the most researched pathways for conversion of biomass to an intermediate bio-oil prior to upgrading to fuels and chemicals. As such, these technologies can play a role in a biorefinery model to expand the suite of product options available from biomass. Fast pyrolysis is thermal decomposition of biomass occurring in the absence of oxygen, and in this specific instance, in the absence of a catalyst or an additional gaseous reductant (Figure 6–4). Temperature and residence time affect the ratio of solid, gaseous, and liquid end product of pyrolysis, and moderate temperature (450 to 500 °C) and short reactor residence time (<2 s) are optimum for producing liquids (bio-oils). Fast pyrolysis for liquids production is currently of particular interest, as bio-oils have the potential for extended storability and can be transported using existing high-volume handling systems (IEA Bioenergy-Task-34 2010).

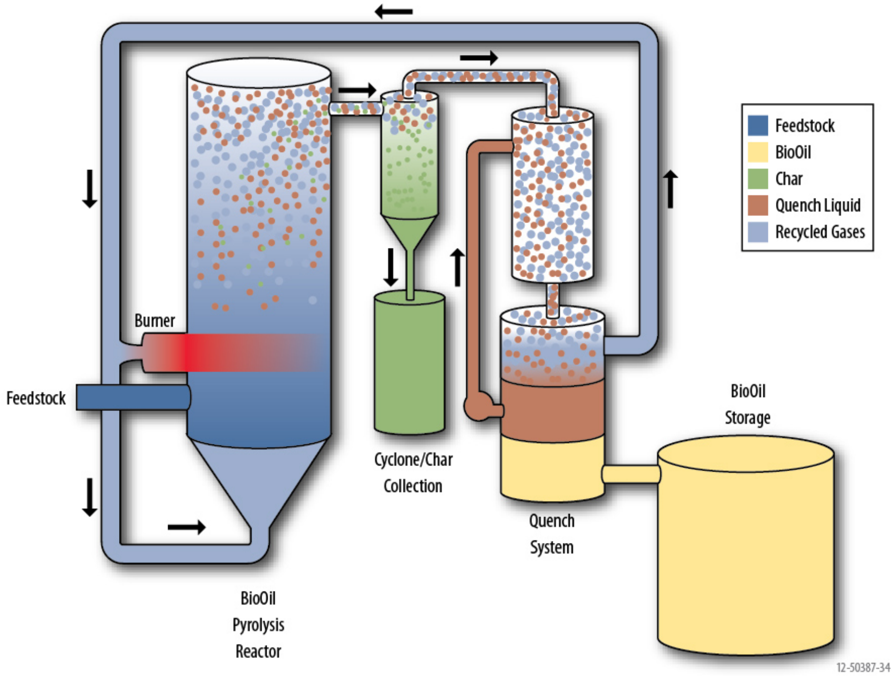
There are technical barriers to address before bio-oil can be a broadly marketable product. Bio-oil typically contains 35 to 40 wt% oxygen atoms, 15 to 25% water (weight basis), and has a high acidity (pH = 2.5, TAN > 100 mg KOH/g oil), which leads to instability factors such as phase separation and increased viscosity over time (Energy & Fuels 18: 590–598 2004) and corrosivity, all of which are the subject of ongoing research.

A number of pyrolysis reactor designs have been explored that are capable of achieving a uniform heat transfer during liquefaction, including:

- Fluidized beds, both bubbling and circulating
- Ablative (biomass particle moves across hot surface like butter on a hot skillet)
- Vacuum
- Transported beds without a carrier gas.

Among these designs, fluidized and transported beds have gained acceptance as the designs of choice for reliable thermal reaction devices capable of producing high bio-oil yields.

Figure 6–4. Process flow example of fast pyrolysis to produce bio-oil (Courtesy of/adapted from Dynamotive 2012)



Workshop Presentations

Development of a uniformly formatted, densified feedstock from lignocellulosic biomass is of interest to achieve a consistent supply of feedstock with enhanced physical properties for bioenergy production. Improvements in bulk density and durability that are achieved through mechanical densification provide logistical benefits for transportation, handling, and long-term storage; however, little is known about the impact of mechanical densification, in particular pelletization, on pretreatment performance and conversion to ethanol. Here, we sought to evaluate the implications of densified biomass on performance in biochemical conversion.

Case Study (Solid Densification): Pretreatment and Biochemical Conversion Performance of Densified Biomass

Allison E. Ray and William A. Smith (Idaho National Laboratory)

Introduction

Global demands for energy, diminishing petroleum reserves, and growing concerns about climate change have prompted considerable interest in lignocellulosic biomass as a sustainable and renewable energy source. Development of a uniform-formatted, densified feedstock from lignocellulosic biomass is of interest to achieve a consistent supply of feedstock with enhanced physical properties for bioenergy production. Improvements in bulk density and durability that are achieved through mechanical densification provide logistical benefits for transportation, handling, and long-term storage; however, little is known about the impact of mechanical densification, in particular pelletization, on pretreatment performance and conversion to ethanol. Here, we sought to evaluate the implications of densified biomass on performance in biochemical conversion.

Materials and Methods

Materials

Corn stover was harvested and baled in Palo Alto County, Iowa, between September and November of 2010. Stover was baled and stored field-side for approximately 9 months. Bales were shipped to INL in Idaho Falls, Idaho, during June 2011. The average moisture content of the bales as received was 13% (w.b.). Six bales were fed through a two-stage grinding process, and corn stover pellets were generated using the Feedstock PDU on June 29, 2011. Steam injection was used to preheat the biomass to 150°F/65.6°C, and on the day the stover was pelleted, the die temperature was recorded at 98°C using an infrared thermometer.

Compositional analysis

The chemical composition of corn stover samples was measured according to the NREL Laboratory Analytical Procedures (NREL 2011).

Pretreatment and Simultaneous Saccharification and Fermentation

Corn stover samples were pretreated with dilute sulfuric acid (0.8% w/w H_2SO_4) using an autoclave at 121°C for 30 minutes, and dilute acid pretreatment was conducted as previously described (duguid et al. 2007).

Soluble components of the pretreatment liquors (monomeric and oligomeric sugars) were measured as previously described (sluiter et al. 2008). After hydrolysis, samples of pretreatment liquor were neutralized and filtered prior to sugar analysis using an HPLC with an RI detector (Waters, Milford, MA), an eluent flow rate of 0.6 mL/min, column temperature of 85°C, and a 50 µL injection.

Simultaneous Saccharification and Fermentation

Simultaneous saccharification and fermentation (SSF) was performed as described previously by Duguid and colleagues (2007) with some modifications. In this study, *Saccharomyces cerevisiae* D_5A was used as the fermenting organism, and Accellerase 1500 (Genencor, Madison, WI) was used as the cellulase enzyme complex and loaded at 15 FPU/g biomass (dry matter basis).

Durability and Calorific Value

The durability of corn stover pellets was measured according to standard ASAE S269.4. Calorific value was measured using a LECO AC600 bomb calorimeter.

Statistical Analysis

Each set of experiments was carried out in quadruplicate, except for calorific value in which three replicates were measured. Statistical analyses were performed in the open-source language R (Team 2011); one-way analysis of variance (ANOVA) was used to test for significant differences, followed by Tukey's Honest Significant Difference (HSD) test for multiple-level comparisons.

Table 6–1. Physical properties of corn stover pellets produced with the Feedstock PDU.

Pellet properties	Measured Value
Moisture Content	11.3%
Durability	98.1%
Bulk Density	600 kg/m^3
HHV	16.55 MJ/kg

Results

The general physical and chemical properties of the corn stover pellets produced with the Feedstock PDU were measured and are presented in Table 6–1. The moisture content of the pellets was 11.3%; pellet integrity was acceptable, with a measured durability of 98.1%. The bulk and energy densites of the corn stover pellets was 600 kg/m^3 and 16.55 MJ/kg. There were small differences in the chemical composition of the pellets relative to conventional grinds of the source material (Table 6–2), most notably glucan and xylan contents of pellets were slightly lower than the other formats examined.

Table 6–2. Chemical composition of corn stover pellets produced with the Feedstock PDU.

Format	Lignin (%)	Glucan (%)	Xylan (%)	Galactan (%)	Arabinan (%)	Mannan (%)
Pellets	15.67	31.31	20.82	2.14	3.50	5.26
¼-in. minus	14.92	33.20	25.12	2.26	3.96	5.15
2 mm	13.82	32.07	21.52	2.63	4.63	5.62

Monomeric xylose yields are an important performance parameter used to measure the efficacy of dilute-acid pretreatment. Figure 6–5 gives box and whisker plots for the corn stover formats examined here. Yields were highest for pellets ($p<0.01$) under the low-severity pretreatment conditions tested here, with an average monomeric xylose yield of 59.3% ± 3.4%. Average monomeric xylose yields for both ¼-in. minus and 2-mm formats were ~37%.

Results from laboratory-scale SSF demonstrated that the pellets achieved the highest average ethanol yields of the formats examined and reached nearly 84% of theoretical ethanol yield from C6 sugars by the end of the experiment (Figure 6–6).

The conventional grind formats, ¼-in. minus and 2-mm grinds, had similar percent theoretical ethanol yield (%TEY) profiles achieving nearly 68% of TEY by Day 7. Actual ethanol yields on Day 5 of the fermentation were also compared for each format; one-way ANOVA identified differences in ethanol yields among formats at a level of $p<0.001$ (Figure 6–7).

Post-hoc multi-level comparisons identified that difference to be significantly higher yields for pellets over the other formats tested at the level of $p<0.001$. No differences were seen in ethanol yield between ¼-in.-minus and 2-mm stover formats. It is important to note that, although pellet composition was slightly reduced in C6 sugars relative to the other formats tested, densifed corn stover still achieved significantly higher actual ethanol yields (which also translated into higher %TEY).

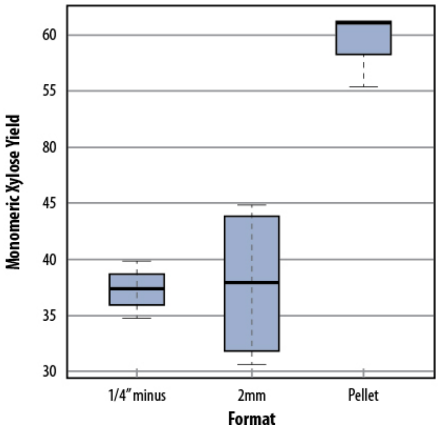


Figure 6–5. Monomeric xylose yields (%). Using Tukey's HSD test, pellets were found to have significantly higher monomeric xylose yields after pretreatment when compared to other formats tested p<0.01.

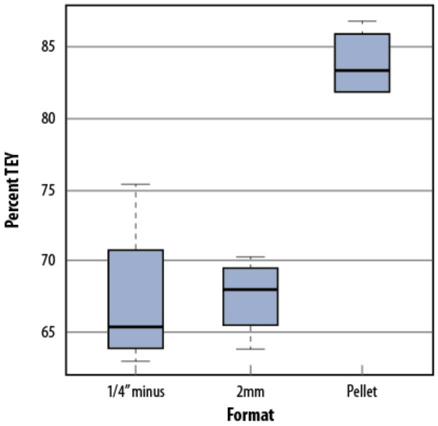


Figure 6–6. Theoretical ethanol yield (% TEY) from C6 sugars on Day 7 of the experiment. Using Tukey's HSD test, pellets had significantly higher % TEY when compared to other formats tested (p<0.001).

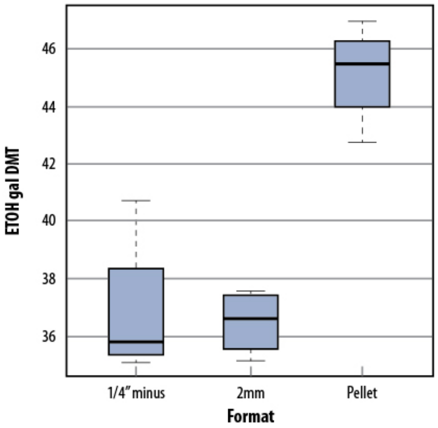


Figure 6–7. Actual ethanol yield (presented in gal/DMT) from C6 sugars on Day 5 of the experiment. Using Tukey's HSD test, pellets achieved the highest ethanol yields (p<0.001), despite having the lowest C6 content of all the formats tested.

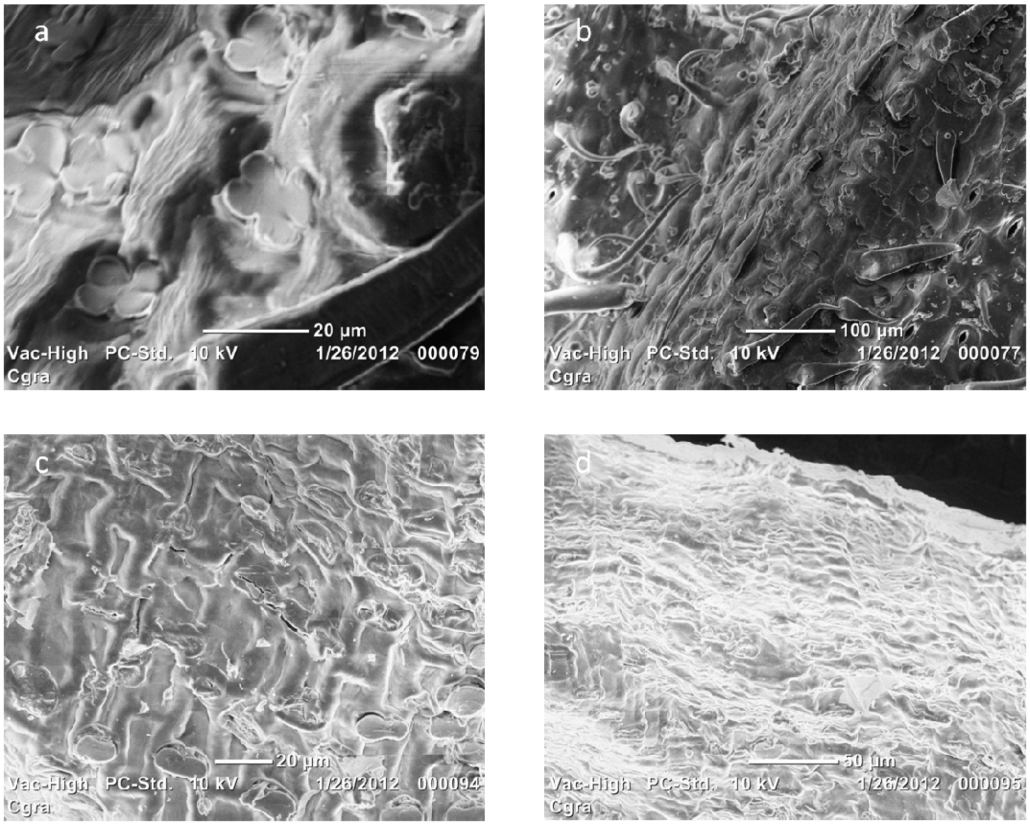


Figure 6–8. SEM images of (a) and (b) raw biomass, 3-in. minus corn stover; (c) and (d) pelleted corn stover.

Although we do not understand the potential mechanisms involved in the improved monomeric xylose yields upon pretreatment or %TEY that were measured here, densification appears to alter raw biomass physically (Figure 6–8) (i.e. potential tissue shearing that increases surface area for enzymatic accessibility, structural collapse, changes in porosity, tissue softening, etc.). Initial observations of the SEM indicated that there is a possibility that structural changes brought by densification can a good reason for their better conversion performance. Future work will explore the mechanisms responsible for the performance differences that are noted for densified and raw biomass.

Preliminary results suggest that pellets perform as well, if not better, than non-densified formats, in terms of pretreatment reactivity and enzymatic digestibility. In the present study, monomeric xylose yields and %TEY were highest for the pelleted corn stover using a low-severity, dilute-acid pretreatment followed by SSF. These results suggest that pretreatment methods may be tailored to densified formats in order to optimize biochemical conversion performance at reduced pretreatment severities. Future work includes harnessing the capabilities of the INL/NREL biochemical interface to explore the impacts of densification on downstream conversion and enhance our understanding of the feedstock characteristics required for meeting performance targets.

Presentation: Fast Pyrolysis and the Effects of Liquid Densification on the Properties of Bio-Oil

Jonathan Male (PNNL)

Liquefaction of biomass by pyrolysis has been identified as a possible route for stabilizing and densifying biomass so it can be conveniently and cost-effectively stored, pumped, transported, and converted to high value transportation fuels, chemicals, or combustor fuel. Pyrolysis is thermal decomposition occurring in the absence of oxygen and is the first step in combustion and gasification processes, where it is followed by total or partial oxidation of the primary products.

The pyrolysis product format can be controlled by varying processing conditions such as temperature and residence time, with lower temperatures and longer residence times favoring production of charcoal and higher temperatures and longer residence times favoring production of gas. "Fast pyrolysis," which is performed using moderate temperatures and short residence times, favors production of liquids, and is of particular interest for producing a liquid-format densified feedstock product that is compatible with high-volume liquid handling systems (similar to crude petroleum) (Table 6–3).

Table 6–3. Typical product yields produced during thermal treatments of wood as temperature and residence time are varied (dry wood basis) (IEA Bioenergy–Task–34).

Mode	Conditions	Bio-char (wt %)	Syngas (wt %)	Bio-oil (wt %)
Torrefaction	~290°C, solids residence time ~30 min	82	18	–
Slow Pyrolysis (Carbonization)	~400°C, long vapor residence time ~hrs→days	35	35	30
Fast Pyrolysis (Liquefaction)	~500°C, short hot vapor residence time ~1 sec	12	13	75
Gasification	~800+°C, short residence time ~0.1 to 1.1 sec	10	85	5

Fast pyrolysis process occurs in a very short time (i.e. in few seconds or less). Chemical reaction kinetics, heat and mass transfer processes, as well as phase transition phenomena, play important roles in this high temperature short time process. This case study reviews the technology and feasibility of biomass pyrolysis and provides a discussion about R&D that is underway to develop practical, cost-effective methods for stabilizing and upgrading the pyrolysis oils. Select examples of bio-oil in the industrial sector will be highlighted and knowledge gaps and future directions will be reviewed.

Bio-oil production from fast pyrolysis of biomass

Fast pyrolysis of biomass is a thermal process that requires temperatures near 500°C, rapid heat transfer, and low residence times. Technologies for fast pyrolysis of biomass are progressing rapidly to make low bulk density woody and herbaceous biomass into high-energy-dense liquid bio-oil that can be used as a fuel or as a raw material for producing valuable chemicals (Dobele et al. 2007). This fuel is considered carbon neutral because the biomass used for this conversion is still a part of the chemical cycle. When burned, this oil releases a low amount of nitrogen and no sulfur. This product can be stored, pumped, and transported similar to petroleum products. The limitations of bio-oil, such as high corrosivity, high viscosity, and possible stratification can be overcome by upgrading the oil (Bridgewater 1999). The application of bio-oil includes burning directly in boilers, gas turbines, and diesel engines for heat and power (Bridgewater et al. 2001; Czernik and Bridgewater 2005). Bio-oil has higher heating capacity of about 20 to 25 MJ/kg. In general, biomass is predried to 8 to 10% before pyrolyzing (Oasmaa and Meier 2002). The water content of the pyrolysis oils averages 25%, which results from pyroligneous water that is formed due to dehydration of carbohydrates. This has a significant effect on the calorific value. One way to overcome this limitation is to predry or torrefy the biomass. However, higher temperature drying can lead to development of thermal-oxidative reactions that may lead to cross linking and may affect the oil yield (Dobele et al. 2007). This presentation discusses fast pyrolysis process derived oil quality, details about pyrolysis system at PNNL, stabilization and upgrading, and important areas to be researched to advance the science of biomass pyrolysis.

PNLL’s Fast Pyrolysis System

PNNL’s fast pyrolysis system is based on systems at Aston and VTT (Figure 6–9). The operating conditions allow a maximum temperature of 550°C, maximum pressure of 34 kPa, and at feeding rate of 1 kg/hr.

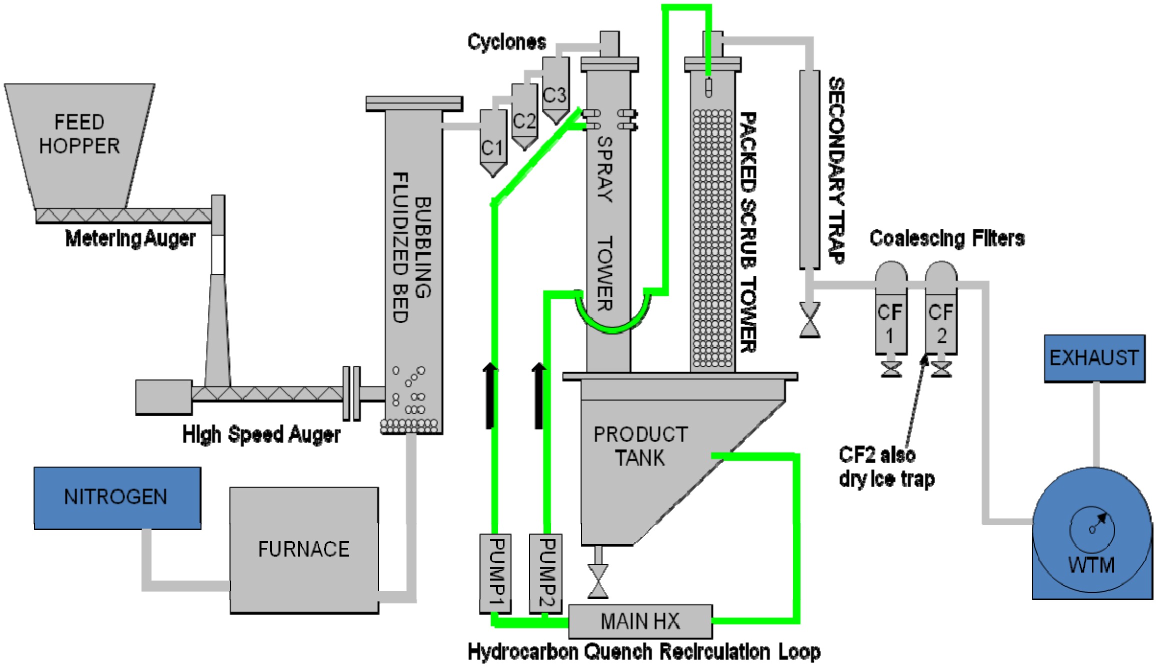


Figure 6–9. Process flow diagram of PNNL’s fast pyrolysis system.

Quality of the bio-oil produced based on wood

Table 6–4 shows some of the important physical and chemical composition of pyrolysis oil. In physical properties bio-oil has higher bulk densities compared to sawdust (0.21 to 0.30 g/mL), wood pellets (0.65 to 0.7 g/mL). Also the liquids are easier to transport and handle. When compared to heavy petroleum fuel bio-oils have higher moisture, higher insoluble solids and higher oxygen where as the carbon content is lower making it inferior quality fuel. According to Czernik and Bridgwater (2004), fast pyrolysis-derived bio-oil has many undesirable properties; the main technical barrier is the removal of oxygen:

- High O content: 35 to 40%
- High water content: 15 to 25 wt%
- High acidity; pH = 2.5, TAN > 100 mg KOH/g oil
- Unstable (phase separation, reactions – viscosity increases with time)
- Low HHV: 16 to 19 MJ/kg
- Distillation residue: up to 50 wt %
- Not miscible with hydrocarbons
- Mainly water miscible and comprises of many oxygenated chemicals

The elemental analysis of various feedstocks and pyrolysis oil products is given in Table 6–5. The quality of the bio-oil produced depends upon the liquefaction technologies followed. To list few other liquefaction technologies are hydrothermal liquefaction, hydropyrolysis and catalytic pyrolysis.

Table 6–4: Comparison of wood-derived bio-oils and petroleum fuel.

Characteristic	Fast pyrolysis bio-oil		Heavy petroleum fuel
	Wet —————	Dry	
Water content, wt%	15–25		0.1
Insoluble solids, %	0.5–0.8		0.01%
Carbon, %	39.5	55.8	85.2
Hydrogen, %	7.5	6.1	11.1
Oxygen, %	52.6	37.9	1.0
Nitrogen, %	<0.1		0.3
Sulfur, %	<0.05		2.3
Ash	0.2–0.3		<0.1
HHV, MJ/kg	17		40
Density, g/ml	1.23		0.94
Viscosity, cp	10–150@50ºC		180@50ºC

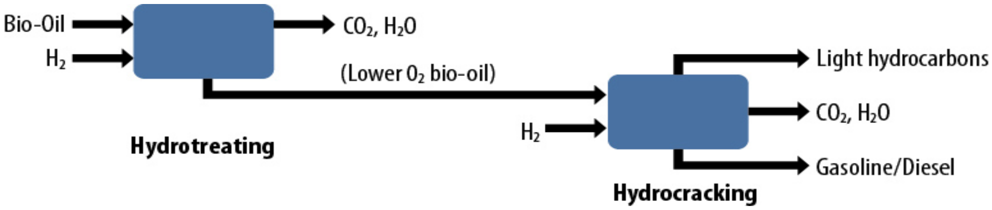
Table 6–5. Comparison of elemental composition of bio-oil produced from different feedstocks.

Feed	Temp (°C)	Raw Feed (wt%)					Product Oil (wt%)				
		C	H	O	H_2O	Ash	C	H	O	H_2O	Acid#
Pine	480	48	5.5	38	7.4	0.4	48	5.5	27	16	84
	550						47	5.4	30	13	82
Maple	550	47	5.5	40	6.1	0.4	54	5.6	23	19	103
Switchgrass	504	47	4.4	32	8.9	6.5	40	4.9	22	28	65
Corn Stover	486	–	–	–	–	–	38	4.4	17	33	60

Stabilization and upgrading

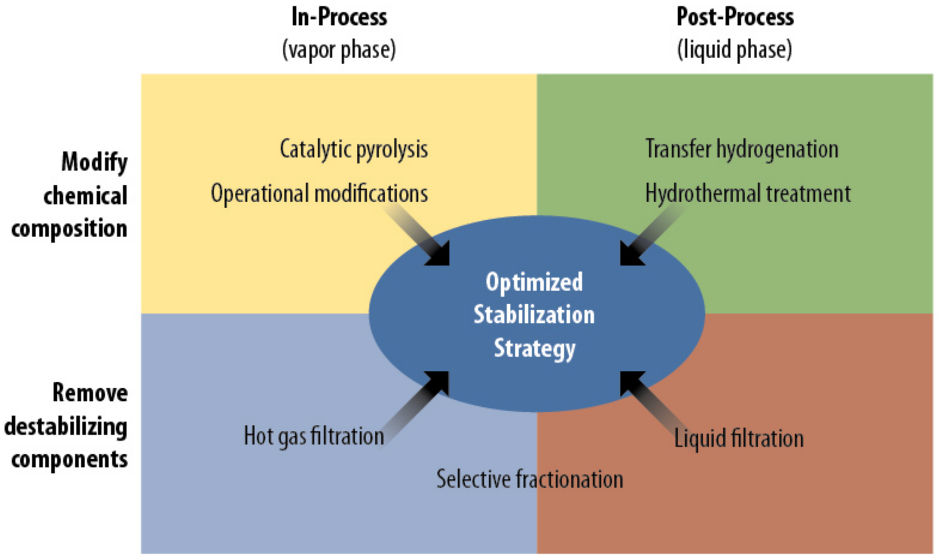
Two of the stabilization and upgrading methods currently receiving much attention are catalytic hydrotreatment and catalytic cracking (Figure 6–10). Catalytic Hydrotreatment has a 49% theoretical yield and requires (a) high pressure, (b) requires H2, (c) coking of catalyst may be a problem, and (d) produces aliphatic and aromatic hydrocarbons. Catalytic cracking has a 26% theoretical yield and (a) requires atmospheric pressure, (b) does not require H_2, and (c) produces mostly aromatic hydrocarbons (Elliott 2007).

Figure 6–10. Bio-oil stabilization and upgrading



Currently, PNNL is working to develop practical, cost effective methods for stabilizing biomass-derived bio-oil for a minimum of 6 months under ambient storage conditions. Additional research priorities include reducing char/ash content and developing and demonstrating long-term stability of catalysts for upgrading of bio-oil to bio-fuels or refinery-acceptable blend stocks. Figure 6–10 illustrates this integrated approach to advances in bio-oil stabilization.

Figure 6–10. Integrated R&D approach for achieving bio-oil stabilization objectives to enabling bioenergy industry expansion.



Discussion of Technology Impacts and Challenges

Low densities of biomass feedstocks and the associated handling, transportation, and storage costs are major impediments to the utilization of biomass for biofuel production. For the most part, the need for densification using pelletization process was seen by workshop participants as a way to facilitate logistical improvements, primarily storage[198,] transportation, and handling.

Biomass in its original form has low density of about 30 kg/m^3 (~2 lb/ft^3) and moisture content in the range of 10 to 70%. Densification increases the density of biomass by about 7 to 10 times and also reduces moisture content, reducing transportation costs and making it more suitable for use in existing grain storage and handling devices (Fasina and Sokhansanj 1996; Tumuluru et al. 2011). Transport costs are largely a function of the distance travelled and the energy and bulk density of the biomass type and transport form (chip or baled). Increasing biomass density increases transport payload, reduces transportation costs, and improves the economicss of cellulosic ethanol production, as the cost of feedstock is about 40% of the final cost of produced ethanol.

Another advantage of biomass densification is improved bulk flow properties (e.g., bulk density, particle density, and angle of repose), making it similar to other fuels and commodity products such as grain that can be loaded and unloaded in storage silos and transported by rail and trucks (White and Jaya, 2001). Producing bio-oil from biomass can capture similar benefits using the existing high-volume liquid transporting systems to transport high-energy-dense liquid interim products and blendstocks. Bio-oil energy density is six and seven times greater than the energy density of green whole tree chips at 45 and 56% moisture content, respectively (Badger & Fransham 2006; Czernik & Bridgwater 2004). Bio-oil can also be gasified and syngas can be utilized for ethanol production.

Densification also improves biomas stability in storage. Previous studies have demonstrated that biomass bales can experience high levels of dry mater loss and reduced glucan content during long-term storage (Montross and Crofcheck 2004; Shinners et al. 2007). On the other hand, densification of biomass produces a more stable product where losses during storage and transportation are minimal. Studies were performed at INL to examine the behavior of wood and corn stover pellets stored under high humidity (70% RH) and high temperature conditions (50°C and 70°C). After 300 hr of storage, pellet durability was virtually unchanged (98 to 99% in all cases). The moisture content of wood pellets increased from 6.9% to approximately 8.5%, while corn stover pellets at 11.3% moisture dried to 8.9% moisture at 70% RH/70°C. Dry matter losses were essentially zero for both corn stover

Workshop participants generally considered densification to be a cost of transport issue[199,200,201,202], and some participants noted that the savings offered by transporting and handling densified formats might be enough to offset densification costs and facilitate other value-add opportunities[203,204], but participants also expressed concern that it can also induce recalcitrance in the material for conversion applications. Therefore, the potential for densification to be a detriment to feedstock performance was a recurring theme[205,206,207], and participants expressed interest in gaining an understanding of the effect of process conditions on pellet quality and performance, both for biochemical and thermochemical conversion.

Preliminary results of an INL study to evaluate the conversion performance of pelletized corn stover were presented at the workshop, and also presented in the densification case study above. These results of pretreatment screening tests indicated that pellets perform better than the conventionally-ground formats; monomeric xylose yields after pretreatment and ethanol yields following enzymatic hydrolysis increased significantly for pelleted corn stover when compared to ¼-in. minus and 2-mm grinds. In response to this presentation, some participants suggested that there may be more effective ways of altering biomass structure to realize the similar performance gains. In addition to the issue of recalcitrance, some workshop participants also felt that crushing pelletized feedstocks prior to biochemical and thermochemical conversion is considered a drawback that limits or reduces the potential benefits of the densified product.

The INL study on biochemical conversion performance of corn stover pellets has indicated that crushing is not necessary because the pellets disintegrate when immersed in water.

Similar biochemical conversion results were reported by Rijal et al. (2012) for pelleted switchgrass. Pellet glucose and xylose yields were increased by 37% and 42%, respectively, relative to switchgrass milled through an 8-mm screen following an aqueous ammonia (SAA) pretreatment. Yield improvements measured for pelleted switchgrass were attributed reduced particle size, shear development, and thermal softening during the pelletization process. These findings suggest that potential transportation, storage, and handling benefits of pelleted biomass may be achieved without negatively affecting the downstream conversion process.

Theerarattananooon et al. (2012) conducted similar studies to investigate the effect of pelleting conditions on chemical composition and sugar yields of corn stover, big bluestem, wheat straw, and sorghum stalk pellets. Enzymatic conversion of cellulose was higher in all cases for pelleted feedstocks when compared to raw biomass; in particular, wheat straw pellets achievedthe highest sugar yields, at 94.5% of maximum enzymatic conversion. In addition, pelletization conditions were shown to affect the sugar yields. The glucan content of the biomass was positively affected by die thickness and negatively affected by mill screen size, while the opposite trend was observed for xylan content. Given preliminary findings and recent reports in the literature, it may be postulated that the process of densification causes shearing of biomass tissue that translates into increased surface area and improved accessibility for enzymatic hydrolysis.

There is much to be gained from efforts to more thoroughly understand the effect of pelletization conditions and the mechanisms responsible for these performance enhancements in order to optimize the densification process conditions for maximum sugar yield with least energy inputs. For example, it has been demonstrated that pretreatment or preconditioning of biomass prior to densification is also effective in improving conversion performance. Sokhansanj et al. (2011) found that steam conditioned pellets perform better for biochemical conversion performance compared to regular or untreated pellets.

Workshop Conclusions

For the most part, the need for densification was seen as a way to facilitate logistical improvements, primarily storage[208], transportation, and handling[209,210,211,212] (Figure 6–11). Densification was considered a cost of transport issue[213,214,215,216] and some participants suggested that there may be more effective ways of altering biomass structure to realize the similar performance gains. However, it was noted that the savings offered by transporting and handling densified formats might be enough to offset densification costs and facilitate other value-add opportunities.[217,218] The potential for densification to be a detriment to feedstock performance was a recurring theme[219,220,221], and participants expressed interest in gaining an understanding of the effect of process conditions on pellet quality and performance, both for biochemical and thermochemical conversion. See Table 6–6 for a summary of common themes and points of emphasis from Densification presentations, discussions, and participant surveys.

Important Considerations

There is value in looking at “rapid densification” to create a stable shell for storage, and biomass needs to be processed as close as possible to the harvest location[222,223] to realize the greatest benefits. The need to crush or break apart the densified product (i.e., create a pellet meal) prior to biochemical/thermochemical conversion is seen as a drawback that limits/reduces the potential benefits of a densified product[224,225,226,227]. There was also concern about the effect of mechanical densification on plant-expressed enzymes that are developed as part of energy cropping systems, which could negate savings created earlier in the supply chain[228]. However, the feasibility of densification depends on cost/energy constraints[229]; if these are low, it might provide value[230,231].

There is further research is need regarding the concern on the effect of mechanical densification on plant-expressed enzymes that are developed as part of energy cropping systems, which could negate savings created earlier in the supply chain. The workshop participants identified the following areas as potentials for further investigation to realize the complete benefits of densification of biomass:

- The energy penalty of pelletization relative to potential performance gains that can be realized with pellets[232,233,234]
- The effect of variable moisture environments and temperature cycling on storage, handling, and preprocessing of biomass (raw and pellets)[235,236]
- The effect of process conditions on pellet quality and performance, both for biochemical and thermochemical conversion[237,238,239]
- The cumulative effect of pretreatment processes, such as like steam explosion or ammonia fiber explosion (AFEX®) followed by densification, on biochemical conversion and energy consumption
- The effect of densification system process variables and feedstock variables on the biochemical conversion need to be thoroughly explored.

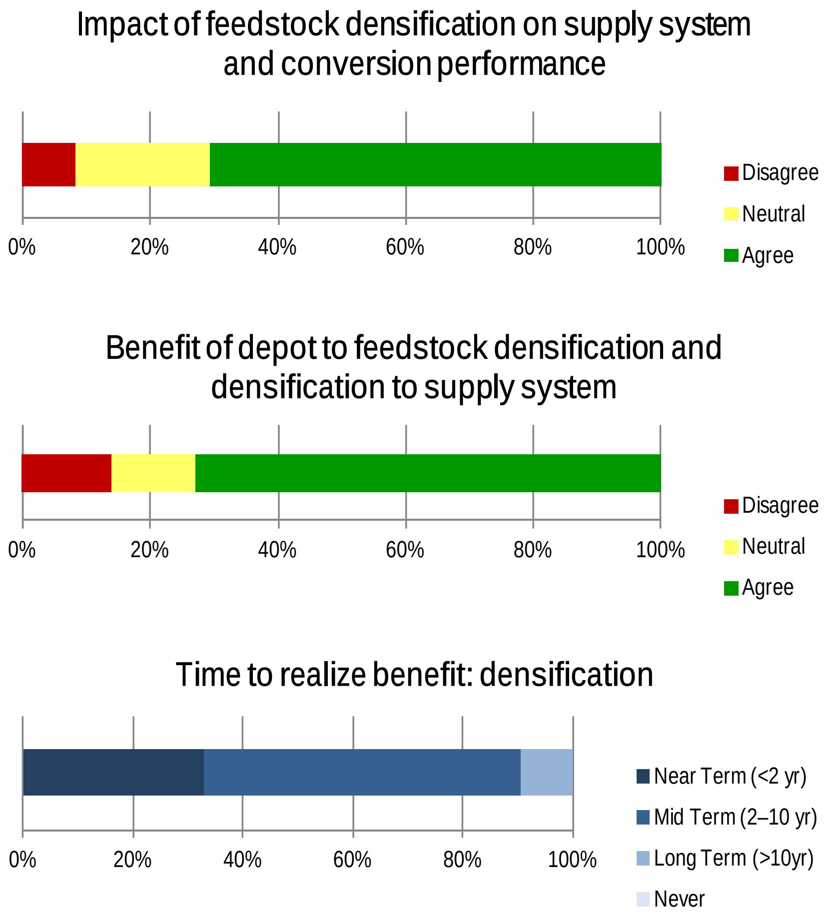


Figure 6–11. Participant response suggests that densification advancements have a good potential benefit and that those benefits can be realized both near and midterm. These projections are closely linked to distributed preprocessing.

Table 6–6. Summary of common themes and points of emphasis from Densification presentations, discussions, and participant surveys.

Desired R&D Outcomes	Potential Approaches	Barriers/Constraints
SUPPLY (Conversion Performance) Reactivity – reduce recalcitrance through lignin modification LOGISTICS Density – increase mass and energy density Efficiency – produce a highly compacted feedstock in a flowable, sturdy format as close as practical to production site Stability – improve carbohydrate preservation relative to raw biomass	Explore cellular structural changes that occur during extrusion, forging, and agglomeration for impacts on costs, quality, and conversion performance Explore impacts of densification pressure, temperature, flow condition on feedstock performance in various types of conversion Explore energy cost offset by energy required in preprocessing for decontamination (plot energy penalties against performance gains) Explore handling and transport cost reduction to justify densification costs	Should not have negative impact on biological conversion including enzymatic digestibility, activation of heterologous plant-expressed enzymes, and fermentation Must meet specs required by handling equipment and process being fed Compatible with existing transportation and handling infrastructure Demonstrate near-term benefits Demonstrate positive investment-to-value ratio

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APPENDIX A

PARTICIPANT INPUT

1 I took genetic enhancements to mean through conventional breeding and through biotechnology. I think there are a number of improvements we can make through conventional breeding as well.

2 Constraints for Biotechnology/Genetics: Regulatory concerns - Genetically Modified Organisms, Disease Resistance, Invasiveness, Invasiveness concern, Public discomfort with the technology, Carbon balance / footprint, Land use efficiency, Regulatory, Cost of carbon emissions, Plant agronomic properties

3 It seems that most of the approaches related to genetically modifying biomass target a specific trait but for a biorefinery to be viable, it needs to produce fuels, chemicals and products, so it is important to look at biomass as a feedstock for these 3 outputs.

4 The value of genetically modified plants will have to address multiple desirable traits.

5 Major issue is how genetics affect agronomic production practices and yield.

6 Need yield in energy crops for good economics.

7 I believe costs of these requirements will be fine and technology will be employed.

8 Based on electric generation from direct combustion, for other than increased yield, the other advantages of genetic engineering will not improve direct combustion biopower, probably increase cost of raw material.

9 Cost recovery on low value feedstocks may be challenging.

10 Genetics can be useful for yield, but may not be able to reduce variability of composition needed for stable conversion processes

11 The value of genetically modified plants will have to address multiple desirable traits.

12 Our experience with woody biomass and other bioenergy crops shows a lot of variability. Some of the variability is due to unit operations used in handling biomass. However the inherent variability play major role and I believe genetics will play a major role in reducing overall variability in feedstock quality and properties.

13 Biggest gain is in biochemical platform.

14 Genetics can be useful for yield, but may not be able to reduce variability of composition needed for stable conversion processes.

15 In order to be a benefit, a majority of the feedstock must be the same GMO traits, which is highly unlikely given the variety of feedstocks that will be in use and the geographic spread of conversion facilities and growth sites.

16 Appears most, if not all genetic enhancements are directed to biochemical conversions. Genetics should be considered for thermochemical platform too.

17 Reduction of Ca, K, Na, Cl, N, S in biomass would be greatly appreciated for thermal chemical conversion.

18 Biomass composition (CHOS and Ash) as constraint.

19 I am very unclear what kind of genetic enhancements would be useful or practical for improved performance of thermochemical conversion processes.

20 I think most underestimate effects of ash in the process.

21 I think DOE should fund improvements that are amenable to a broad suite of conversions. The "first gen" plant work often tends to be "overly” geared for "classic" biochemical conversion. Decreased or easily removed nitrogen (for feed) or ash (leave it in the field?) would help both biochemical and thermochemical conversion.

22 Remove silica

23 The presentations dealt with improving processability of biomass in biochemical routes. For thermochemical, carbon content, hydrogen are important and O, N, S, should be low. Also, ash should be low.

24 Presentations did not address genetic improvements for thermo chemical conversion, I believe similar advances are possible.

25 Constraints - unknown unintended consequences Commercial propagation as constraint.

26 Technological advances in genetic modification seem well posted to improve the objective performance. However, the strong potential concerns in proliferation of uncontrollable genetically modified organisms, at least from public perception, may more than negate the positive technological impacts.

27 Public Safety added as constraint.

28 Q: What the enhancements are/the value they bring. A: Some are likely within reach short/medium term; others long-term.

29 Can they be developed within the available window to launch biofuels industry.

30 Public acceptance of GMO is an issue.

31 Public acceptance of perennial GMOs may be slow.

32 Genetic modified plants may face strong public opposition if not carefully handled.

33 Public acceptance of genetically modified organisms could be major constraint.

34 Constraints for Biotechnology/Genetics: Regulatory concerns - Genetically Modified Organisms, Disease Resistance, Invasiveness, Invasiveness concern, Public discomfort with the technology, Carbon balance / footprint, Land use efficiency, Regulatory, Cost of carbon emissions, Plant agronomic properties

35 Permitting / environmental control issues will be biggest road blocks.

36 Long term adoption, regulations, etc.

37 Crop deregulation is important factor in the roll-out of energy crops.

38 Concern on "proprietary" limitations of the researchers and "monopoly" of the new plants

39 How do biotech patents affect the uniformity of supply line through licensing?

40 Q: How much energy is used in the process? A:10-30 Mega joules for a 2mm sample. On a 12" log we get about 95% yield.

41 Q: What is the throughput look like? What is dollar per ton? A: The product can be anything you want in any way that you would like, it just requires a different configuration. We have looked at some ways where it was around $20-$30 a ton for top grade veneer, not industrial veneer. Industrial Veneer would be much cheaper

42 Q: The throughput seems slower than a grinder. A: It can be faster, the lathe speed is the same so it can probably be used at the same speed as other processes. The Muncher can be connected to the lathe speeding up the process.

43 Q: In terms of total processing time, if you had a ton of material and put it through your process compared to a grinder, what is the time difference? A: If I had their horsepower I could out do them 4 to 1. It takes us about 5 seconds.

44 Still lab scale, economics not worked out.

45 Fuel suitability is very dependent on process being fed and specific handling equipment.

46 Q: Can you use this on residues or other non-veneer materials? A: It is more and more difficult when there are small branches and other things like that. We would have to make it into billets then process the material.

47 Q: What percentage of the woody biomass materials would go through your process well? A: This is particularly for dedicated energy crops that don’t do well in grinders. The smaller the diameter the more difficult it is to do this process.

48 Q: How would you run switchgrass through this? A: This approach doesn't work on those kinds of materials.

49 Q: Corn stover fibers bind better. Why are you using this grass?A: Corn stover is more cohesive meaning that it will interlock better. Understanding the tissue arrangement in plant physiology will make it fracture differently. The flow ability will change depending on the ratios and the physiology of the plant.

50 Q: Did you compare different times during the day to see moisture content and other environmental conditions? A: I believe you are referring to air moisture and we don’t have much air moisture here. We usually test during the afternoon just because it takes a while to get the machines set up.

51 Q: What is the impact of moisture content in this process? A:Moisture makes it more cohesive and more difficult to grind.

52 Q: What is the impact of moisture on low energy shearing? A: Wetter is better with this process. It is the opposite of what you typically think in other processes. The breaking that is done here is a different break than what other processes use, meaning that you don't have to dry materials to use in this process.

53 Q: Does the veneer Crumbles® material flow better? A: The moisture makes it more condensed, it will shear easier, but I don't think that it is necessarily easier. The fiber structure will change.

54 I would look for mechanical conversion processes that can be done now.

55 On Assumption 16: These can be on-site in individual machines.

56 Mechanical preconversion is often best accomplished during the harvesting of energy crops, i.e. a forage chopper that sizes the crop to a uniform 8 to 9mm for processing.

57 Key limited knowledge: location and distance of the processes decrease the transport cost.

58 place as close to harvest or during harvest as possible to reduce costs of transportation

59 Extent of mechanical preconversion dependent on end densified product.

60 Q: How far down can you go on pellet size? A: We can get it down to 2mm pellets fiber length that is still economically viable.

61 Pellets need more process energy to pulverize raw material.

62 Q: In terms of total processing time, if you had a ton of material and put it through your process compared to a grinder, what is the time difference? A: If I had their horsepower I could out do them 4 to 1. It takes us about 5 seconds.

63 Q: How was air flow measured? A: It was measured but first it was optimized, we were allowing more air or choking air flow to see where the optimal flow was.

64 Q: What was the harvesting process for the materials used?A: Everything has been baled. I don’t have information on harvesting but what we do know is that in the process of harvesting, if it is refined during harvesting, then it reduces energy consumption.

65 Q: What materials did you use for billets? A: We are trying to try everything to try to harvest many different types of materials.

66 Q: Are you recommending miscanthus for transport more than 50 miles? A: If you cut it into billets you can achieve longer transport distance. Other crops are outside of our scope so we haven't studied all materials.

67 Q: How do things like corn function in this technology?A: We move towards a sugar cane model by making them into billets. You feed the pieces through lengthwise instead of crosscutting and it works well. You can run wood pellets and other materials as well although they don't come out as uniform as veneer or billets.

68 I was under the impression that mechanical preconversion in some form was commonplace already today.

69 Already demonstrated with bark removal?

70 Love the possibilities of fractional deconstruction that might enable subsequent conversion.

71 Still lab scale, economics not worked out.

72 Conduct several processes together to reduce number of times material is handled.

73 On Assumption 16: These can be on-site in individual machines.

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76 Place as close to harvest or during harvest as possible to reduce costs of transportation

77 Conduct several processes together to reduce number of times material is handled.

78 Q: How probable is getting this process closer to the forest? A: The whole issue is making veneer in the forest. There have been several projects like this so that the veneering process is shipped out of the forest. Our goal is to put these into a depot or PDU. You would want to combine or separate processes depending on how you could keep the moisture in the wood the best.

79 Key limited knowledge: location and distance of the processes decrease the transport cost.

80 Extent of mechanical preconversion dependent on end densified product.

81 Based upon algae model: Homogeneity (chemical) in all feedstocks, regardless of conversion phase, should be a thematic criteria separate and apart from "uniform" (mechanically).

82 Fuel suitability is very dependent on process being fed and specific handling equipment.

83 Q: Does shape have some problems? Can you control that with your grinding equipment? A: Shapes are not uniform, which makes it difficult to keep the flowability. They are 3 dimensional particles that interlock and are difficult to move. You can't really control them.

84 Q: Do materials that are sticking get out of control very often? A: If you have the same moisture, size, etc. you would not have a problem, but that is not the case. The change in all of those factors create the variation that can cause these problems. When materials is more complex geometrically it makes it more difficult for flow ability.

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111 Mechanical preconversion has greatest benefit for storage (high material density) (Assumption 10-12 and 15: For storage issues alone.

112 I would look for mechanical conversion processes that can be done now.

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119 Assumption 19 - SD on chemical; agree on thermal (marked SD on votes).

120 Assumption 31 - depends on whether going to chemical or thermal process (midterm if Thermal; Never if Chemical). Stability of bio oils will be a factor and fit w/ infrastructure. Deep drying of biomass that is later put into a chemical (liquid-based) process can cause inefficiencies in that chemical processes. In those cases it is often better to use non-dried biomass. The only value is if the dried biomass is going into purely thermal processes where the biomass will be dried in-process anyway - pyrolsis, gasification, or combustion.This feels more like a sales pitch for INL/DOE technology than a request for input from industry. Thermal preconversion is really only beneficial when there is a longer ship distance from biomass to conversion side or where there are export/import process use (coal replacement) needs. Cost and yield loss are major hurdles to torrefaction and cost is barrier to deep drying.

121 Assumption 19 - If it does an good, it will be better for T.C. that for B.C.

122 Assumption 20 - Drying and/or torrefaction seems less desirable for biochem conversion since will add H2O for biochem system.

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128 Assumption 19 - If it does an good, it will be better for T.C. that for B.C.

129 Assumption 20 - Drying and/or torrefaction seems less desirable for biochem conversion since will add H2O for biochem system.

130 Q: Benefits of torrefacation were discussed. What are the negatives? A: Possibly some on the cost. Cost is on the order of 20-30 / ton in transportation.

131 Q: What is dry matter loss off gassing vs. particle what are the losses in torrefaction? A 10-30% depending on severity of temperature.

132 Q: Have you put it in a bio slurry does it take on moisture? A: It repels water.

133 Q: What is being lost w/ torrefication cellulose etc.?A: Loss of ½ mass.

134 Assumption 21 - added processing steps of questionable added quality.

135 Assumption 25 - believe thermal pre conversion is challenged from an economic side, so answers depend on $/bbl crude. Jury still out but promising.

136 Assumption 21 - agree cost is the issue.

137 Assumption 31 - depends on whether going to chemical or thermal process (midterm if Thermal; Never if Chemical). Stability of bio oils will be a factor and fit w/ infrastructure. Deep drying of biomass that is later put into a chemical (liquid-based) process can cause inefficiencies in that chemical processes. In those cases it is often better to use non-dried biomass. The only value is if the dried biomass is going into purely thermal processes where the biomass will be dried in-process anyway - pyrolsis, gasification, or combustion. This feels more like a sales pitch for INL/DOE technology than a request for input from industry. Thermal preconversion is really only beneficial when there is a longer ship distance from biomass to conversion side or where there are export/import process use (coal replacement) needs. Cost and yield loss are major hurdles to torrefaction and cost is barrier to deep drying.

138 Assumption 19 - yield loss (SD).

139 Assumption 29 - if cost barrier is resolved (NT). Q: At what cost? there steps all require energy/ money/ time, whether it makes sense depends on the cost/value of each step. My company gasifies non-treated biomass, we might want deep dried or torrefied feedstock, but it depends on what each cost and what each gets us.

140 Assumption 30 - Depends on end use. Very important to understand energy losses, GHG impacts of thermal preconversion. I have concerns on cost. The European heat and power market is the first market.

141 Assumption 28 - Need to capture the loss and gases. Troy Runge's talk on wet torrefaction belongs in this session. I'd like to see development of hydrothermal liquefaction. I'd like to see development of hydrothermal carbonization (i.e. wet torrefaction).

142 Assumption 26 - SA if stabilized hard to store. 20%-30% mass loss is substantial during torrefaction.Pyrolysis - any thoughts on increasing stability.

143 Assumption 24 - The value of "cost" has yet to be determined. Critical experiments need to be done to validate the cost of torrefaction and pelletization can be recouped in downstream processes. The amount of volatiles lost/ or used as heat are critical to the value proposition. Dilution of volatiles from torrefaction is important to enable it can be used for heat.

144 Q: Greenhouse gas testing .. more co2 or coal? A: Has more h2 than greenhouse gas emission than coal.

145 Q: What is the exposure to workers? A: It smells like BBQ... it is acidic, don't what to get it on you. PH is pretty low.

146 Assumption 30 - Depends on end use. Very important to understand energy losses, GHG impacts of thermal preconversion. I have concerns on cost. The European heat and power market is the first market.

147 Will need to see good data to actually agree with >/= 1 year; in response to assumption chemical preconversion can increase stability of raw biomass and enable feedstock storage greater than 1 year.

148 (excerpt of text) I would like to understand how much the metal and ash contents are affected by soil where crop is grown and how harvested.

149 In think the depot concept is not viable for the woody biomass industry. INL has tried to shoehorn a concept

150 Economic analysis not presented, so not included in my response.

151 Required pilot and pre-commercial plants to verify the process and evaluate capital costs and operational costs.

152 Chemical processing may or may not increase biochem performance; in response to assumption in comparison with raw biomass, chemical preconversion will increase performance of the feedstock in biochemical conversion processes.

153 Looks promising; in response to assumption In comparison with raw biomass, chemical preconversion will increase performance of the feedstock in thermochemical conversion processes.

154 Needs to be investigated; in response to assumption in comparison with raw biomass, chemical preconversion will increase performance of the feedstock in biochemical conversion processes.

155 No evidence for this; in response to assumption chemical preconversion can increase stability of raw biomass and enable feedstock storage greater than 1 year.

156 Preconversion, centrally or at depot scale, must be targeted for: a) biomass feedstock (forest, municipal solid waste, agriculture residue, energy crops); downstream processing.

157 Limit market to one or two bases.

158 Probably would agree if thinking about transportation; in response to assumption locating chemical preconversion systems at distributed biomass preprocessing depots is essential for these technologies to have their greatest impact.

159 I don't think it is essential but a good idea; in response to assumption locating chemical preconversion systems at distributed biomass preprocessing depots is essential for these technologies to have their greatest impact.

160 May be more economical to perform at the integrated biorefinery; in response to assumption locating chemical preconversion systems at distributed biomass preprocessing depots is essential for these technologies to have their greatest impact.

161 Need to be co-located with refinery; in response to assumption locating chemical preconversion systems at distributed biomass preprocessing depots is essential for these technologies to have their greatest impact.

162 This is possible for some, such as AFEX, ; is response to assumption in comparison with raw biomass, chemical preconversion will increase performance of the feedstock in biochemical conversion processes.

163 Removal of contaminants xuch as sulfur might be much more economic for thermoconversion than removing from syngas. The removal of contaminants prior to gasification not captured in the questions.

164 Pretreatmentto remove ash or nitrogen is particularly valuable to biopower and thermochemical

165 I think some chemical conversion processes can increase the stability of biomass for storage.

166 Only if feedstock is fully protected from moisture, making this an unreasonable consideration; in response to assumption chemical preconversion can increase stability of raw biomass and enable feedstock storage greater than 1 year.

167 Unless leaching is done alongside pretreatment for another purpose (i.e. acid hydrolysis) it is doubtful it will be economical on its own – unless going into a wet process (chemical, biological). Do not think it will pay for bio-power or thermochem like pyrolysis or gasification

168 Cost is worrisome so is the issue of waste. NH3 is expensive? What is the consumption of NH# per dry matter ton biomass?

169 All about the delta between cost and capital intensity.

170 Overall concern is the economics of these treatment processes.

171 I've read good things about AFEX in the literature.

172 Don't think the technology for AFEX is ready today; in response to assumption locating chemical preconversion systems at distributed biomass preprocessing depots is essential for these technologies to have their greatest impact.

173 Mostly focused on biochemical in terms of questions.

174 Chemical preconversion seems to be key primarily for biological conversion.

175All these things are needed at the biorefinery. Only works on-site. Need to integrate energy or drying costs will be prohibitive. Also need to integrate water and other energy. Some of the leached material is good for biological systems.

176 Extremely important to decrease viability of feedstock for B.C. important, but less for themochemical.

177 Uniform format feedstock requires formulation as a key.

178 New constraints. Loss of components (i.e. sugar). Geographical availability. Risk reduction

179 Could formulation be used to mitigate effects of components such as Cl?

180 Has time been spent characterizing saccharides. Yes, deconstruction people are evaluating separations of the streams.

181 New constraints. Loss of components (i.e. sugar). Geographical availability. Risk reduction

182 How does the process impact the lignin stream? It's being broken, but no details today

183 Temperature @ which the process dissolves? 120-180 degrees

184 What happens to ash--unknown.

185 Formulation has already been shown in biopower operations.

186 Assumptions 40, 41 & 44 - Potential looks positive, but more work needs to be done to prove that potential.

187 Assumption 40 - Too early to tell, but promising

188 I feel totally unqualified to respond to this technology. It would seem to hold promise, but this is the first I have heard about it.

189 Assumption 41 - I'd say this might be possible, too little is known about this right now.

190 Not sold on blending feedstocks. There are better ways to remove variability at the process for conversion. Difficult to optimize product conditions for different blend of feedstock.

191 Only in special cases should the addition of cost and energy be applied through formulation.

192 Is formulation possible/useful without densification?

193 Can formulation have impacts by itself that do not require a subsequent densification process?

194 New constraints: Loss of components (i.e. sugar), Geographical availability, Risk reduction

195 I think formulation could be great... if all the feedstocks are available economically in the geography.

196 The distance between processes will decide the distribution costs as well as have a significant impact on storage. The increase of density decreases the transportation cost.

197 Could formulation be used to mitigate effects of components such as Cl?

198 Looking at rapid densification to sear the outside of pellets and form a skin for storage.

199 Other than cellular structural changes densification is a cost of transport issue rather than improvement of process--since the pellets will need to be reground before being utilized in the process (usually). If cellular changes is pelletizing the most cost effective way of inducing those changes?

200 Assumption 52 - Reduces cost of transportation.

201 Participants expressed significant interest in the energy requirements & cost of commercial-scale densification and the cost/value trade-offs of densification and feedstock conversion performance. There was also concern regarding the need to crush/break/re-grind pellets (in a roller mill, etc.) prior to biochemical conversion (energy/cost vs. enhanced performance). Does the gain in performance override the increased cost of densification? A better understanding of total process costs and energy consumption per unit mass were seen as key issues that need to be quantified with rigor.

202 Participants were similarly interested in transportation costs and expressed skepticism about transporting feedstock 100’s of miles to a refinery when the final product is not very valuable.

203 Energy for densification could be offset by energy required for decontamination in preprocessing.

204 All depends on the cost, energy - constraints if these are low than might create value. Cost of handling and transportation a savings that might pay for pelletizing.

205 Material ash content was identified as a potential issue/concern for having detrimental effects on pretreatment and fermentation.

206 Understanding the mechanism(s) responsible for potential enhancements in the performance (in terms of ethanol production, improving reactivity/susceptibility of material to enzymatic digestiblity) of corn stover pellets relative to conventional grinds was viewed as a key issue. Answering the questions: “How does densification have the potential to improve performance? Do you understand the reason for the difference in performance between pellets & conventional grinds?”

207 Mechanical densification would denature plant-expressed enzymes that are part of “purpose-grown crop systems,” negating a potential savings of $0.80/gallon of ethanol207.

208 Looking at rapid densification to sear the outside of pellets and form a skin for storage.

209 Assumption 9: May or may not perform better; seems like point is to allow better logistics and handling is the main point. Caveat: Pressure, temperature, flow condition impacts may make some pellets better for T.C. vs. B.C. conversion.

210 Densification biggest benefits will be in transportation and storage

211 All depends on the cost, energy - constraints if these are low than might create value. Cost of handling and transportation a savings that might pay for pelletizing.

212 I'm not clear if there are benefits to densification other than streamlined handling and somewhat reduced transportation requirements.

213 Other than cellular structural changes densification is a cost of transport issue rather than improvement of process--since the pellets will need to be reground before being utilized in the process (usually). If cellular changes is pelletizing the most cost effective way of inducing those changes?

214 Assumption 52 - Reduces cost of transportation.

215 Participants expressed significant interest in the energy requirements & cost of commercial-scale densification and the cost/value trade-offs of densification and feedstock conversion performance. There was also concern regarding the need to crush/break/re-grind pellets (in a roller mill, etc.) prior to biochemical conversion (energy/cost vs. enhanced performance). Does the gain in performance override the increased cost of densification? A better understanding of total process costs and energy consumption per unit mass were seen as key issues that need to be quantified with rigor.

216 Participants were similarly interested in transportation costs and expressed skepticism about transporting feedstock 100’s of miles to a refinery when the final product is not very valuable.

217 Energy for densification could be offset by energy required for decontamination in preprocessing.

218 All depends on the cost, energy - constraints if these are low than might create value. Cost of handling and transportation a savings that might pay for pelletizing.

219 Material ash content was identified as a potential issue/concern for having detrimental effects on pretreatment and fermentation.

220 Understanding the mechanism(s) responsible for potential enhancements in the performance (in terms of ethanol production, improving reactivity/susceptibility of material to enzymatic digestiblity) of corn stover pellets relative to conventional grinds was viewed as a key issue. Answering the questions: “How does densification have the potential to improve performance? Do you understand the reason for the difference in performance between pellets & conventional grinds?”

221 Mechanical densification would denature plant-expressed enzymes that are part of “purpose-grown crop systems,” negating a potential savings of $0.80/gallon of ethanol221.

222 Mixed feedstock for pelletizing appears to have a logistics problem. Raw material transport, bi..., etc.

223 Assumption 54 - Important to process biomass closest to harvesting location.

224 Densified feedstock has to be undensified before thermochemical or biopower processes, so I can't say densified materials perform better or as well.

225 Assumption 9: May or may not perform better; seems like point is to allow better logistics and handling is the main point. Caveat: Pressure, temperature, flow condition impacts may make some pellets better for T.C. vs. B.C. conversion.

226 Other than cellular structural changes densification is a cost of transport issue rather than improvement of process--since the pellets will need to be reground before being utilized in the process (usually). If cellular changes is pelletizing the most cost effective way of inducing those changes?

227 Assumption 49 - They are ground then again before processing in biochemical process not as pellets I assume

228 Mechanical densification would denature plant-expressed enzymes that are part of “purpose-grown crop systems,” negating a potential savings of $0.80/gallon of ethanol

229 Cost is a big factor here.

230 Energy for densification could be offset by energy required for decontamination in preprocessing.

231 All depends on the cost, energy - constraints if these are low than might create value. Cost of handling and transportation a savings that might pay for pelletizing.

232 Should be located with some other system to minimize energy input and maximize energy integration.

233 All depends on the cost, energy - constraints if these are low than might create value. Cost of handling and transportation a savings that might pay for pelletizing.

234 Cost. Pelletizied process seems like a considerable energy penalty, but with a considerable performance gains. Have the two been plotted against one another?

235 What effect does variable moisture environments (T gradien sysles) have on chemical process efficiencies, and over time (storage, handling, pre-processing, etc.)?

236 Assumption 51 - Depends on where and how it is stored, absorbs moisture.

237 Densification could help or improve conversion depending on surface/volume requirements and integrations.

238 Pretreatment conditions can be optimized for both pelleted and nonpelleted materials.

239 Assumption 49 - Data looked good, but preliminary