Challenges on the Road to Biofuels

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Lignocellulose-based ethanol offers a renewable, sustainable and expandable resource to meet the growing demand for transportation fuels. The main hurdles to be overcome include feedstock-supply logistics, conversion technology and workforce availability. Agronomists, agricultural engineers, and implement-manufacturing companies are addressing feedstock production, harvest, storage and transportation. Several universities, especially those in the Midwest, are developing new curricula and programs to bolster the workforce pipeline in bioprocessing. Therefore, the focus of this presentation will be on issues related to conversion technology.

The US ethanol industry is primarily based on processing of corn grain (*i.e.* starch) through either dry-grind or wet-milling processes. Development of the dry-grind industry began in the mid-1970s, and South Dakota State University (SDSU) was a leader in that effort. SDSU was the site of the nation's first on-campus ethanol production facility, and Figure 1 shows the distillation columns. Work at SDSU established initial costs (Dobbs *et al.*, 1984) and energy-balance data (Stampe, 1982) for farm-scale ethanol plants, as well as technology innovations such as thin-stillage recycling (Gibbons and Westby, 1982) that are still in use today.

Based on the pioneering work at SDSU, the fledgling industry expanded as multi-million gallon, farmer-owned plants sprung up across the Midwest. Figure 2 shows the basic process flow in modern ethanol plants, while Figure 3 shows the current status of US ethanol production. The current (mid-2007) US production capacity exceeds 6 billion gallons per year, with another 6 billion gallons of plant capacity under construction

Figure 1. Distillation column of the SDSU farm-scale ethanol plant.

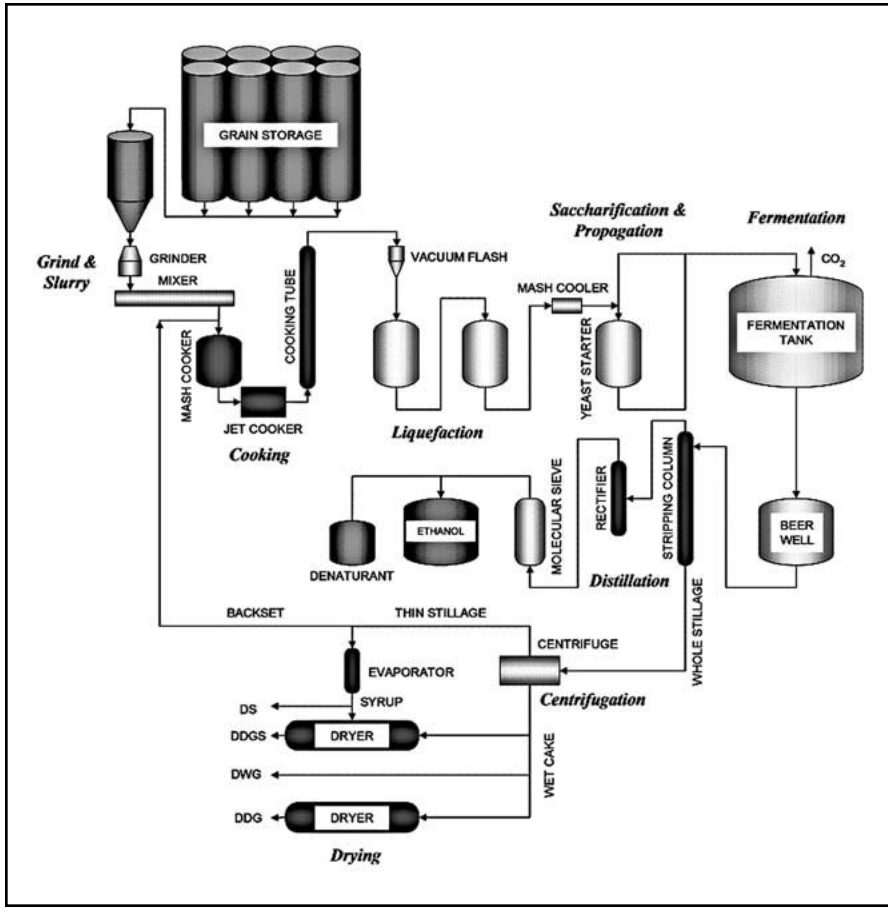

Figure 2. Corn dry-grind process (courtesy of Kurt Rosentrater[1]).

(http://www.ethanolrfa.org). However, based on projected corn-grain availability, there is a general consensus that the upper limit for corn ethanol will be in the 14–15 billion gallons per year range.

Lignocellulosic Ethanol

Due to the large demand for transportation fuels and the fact that corn-based ethanol can, at most, account for 10–15% of this need, there is widespread interest in producing ethanol from lignocellulosic biomass. However, for this next step to be taken, several significant processing challenges must be overcome. As shown in Figure 4, the National

[1]Contributor to this volume, pages 105–125.

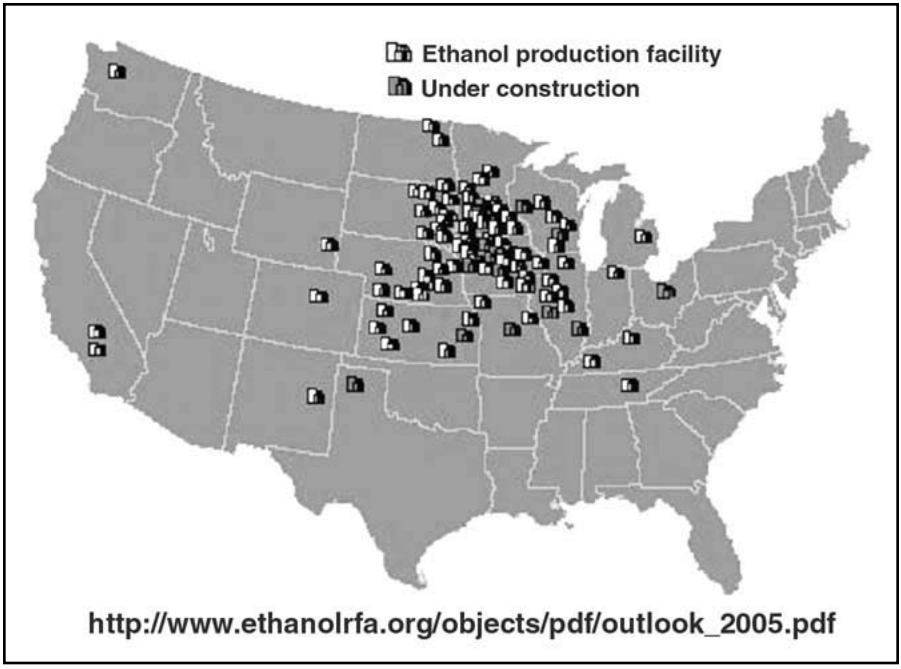

Figure 3. Current and planned ethanol biorefineries
(courtesy Renewable Fuels Association).

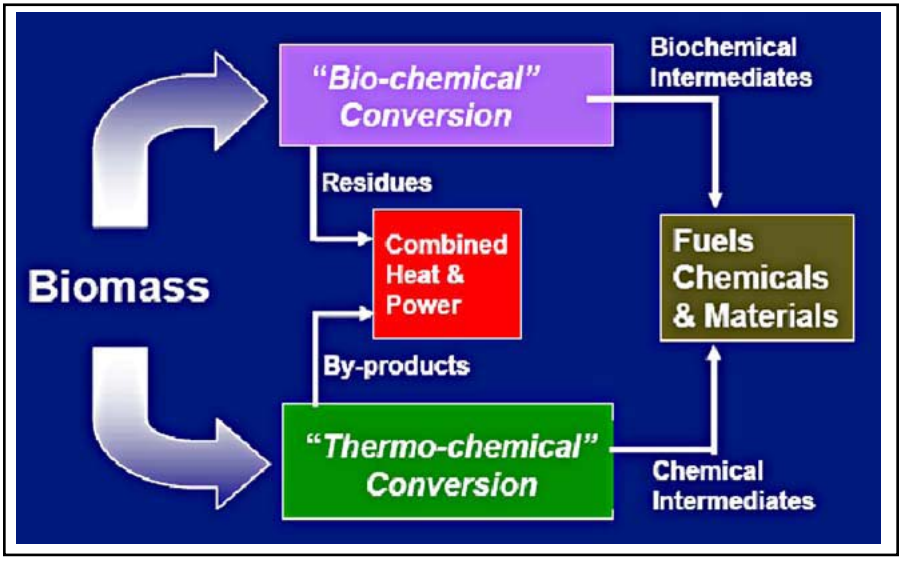

Figure 4. NREL biomass conversion platforms
(courtesy National Renewable Energy Laboratory).

Renewable Energy Laboratory (NREL) has categorized the various processing options into two categories. Biochemical conversion processes use pretreatment processes and enzymatic hydrolysis to break down biomass into fermentable sugars that are subsequently fermented to ethanol by microbes (typically yeast). Alternatively, thermochemical conversion processes use gasification or liquefaction to degrade biomass into one- and two-carbon molecules that are catalytically converted into more complex products. Our focus at SDSU and the Center for Bioprocessing Research and Development (CBRD) has been on the biochemical conversion route, with work in the areas of pretreatment, hydrolysis and fermentation.

Pretreatment and Hydrolysis

The goals of pretreatment and hydrolysis are to open the biomass structure and release the sugars in high yield and concentration, while producing minimal amounts of inhibitory byproducts such as furfurals. Most current chemical and physical pretreatment processes are limited by either not being intensive enough to release sugars in high yield, or are overly intensive, resulting in degradation of sugars (*e.g.* to furfural). A further disadvantage of most traditional processes is that the resulting hydrolysate streams contain a mixture of 5- and 6-carbon sugars. Commercial yeast strains cannot ferment 5-carbon sugars, and for microbes that can, the mixed sugars result in a diauxic fermentation in which 5-carbon sugars are metabolized only after the 6-carbon sugars are consumed. This two-stage process essentially doubles fermentation time, and, therefore, doubles required fermentation-tank capacity.

Our approach to overcoming these challenges is to develop a novel and economical reactor to fractionate and hydrolyze lignocellulose. The process is based on the clean-fractionation (CF) technology developed at the National Renewable Energy Laboratory (NREL) (Bozell *et al.*, 1997), which uses solvents (16% methyl isobutyl ketone, 34% ethanol, and 50% water) to fractionate the biomass. Lignin is dissolved in the solvent stream, hemicellulose in the aqueous stream, while cellulose is left behind in a moist pulp. One limitation is the cost of the solvents, and we are evaluating continuous high-shear extrusion to reduce solvent use. Clean fractionation extrusion should also improve efficiency and productivity of the process. Figure 5 shows our proposed process for incorporating clean fractionation extrusion into the lignocellulose conversion process.

Preliminary work on extrusion processing has evaluated both single- and twin-screw extruders. The single-screw extruder (Fig. 6) has a barrel length to diameter ratio of 20:1 and compression ratio of 3:1. We have investigated extrusion speeds of 80 and 120 RPM and temperatures of 120, 150, and 180°C. The twin-screw extruder (Fig. 7) has a barrel length to diameter ratio of 30:1 and compression ratio of 3:1. Conditions investigated included speeds of 200 and 400 rpm, temperatures of 25 and 100°C, and substrate-moisture levels of 15, 20, 25, 30, and 40%. Average results of extruding various warm-season grasses are shown in Table 1. In general, lower screw speeds (80 RPM) and higher temperatures (180°C) enhanced digestibility in the single-screw extruder, whereas in the twin-screw extruder the highest digestibility was found with 200 RPM, 25°C and 20% moisture content.

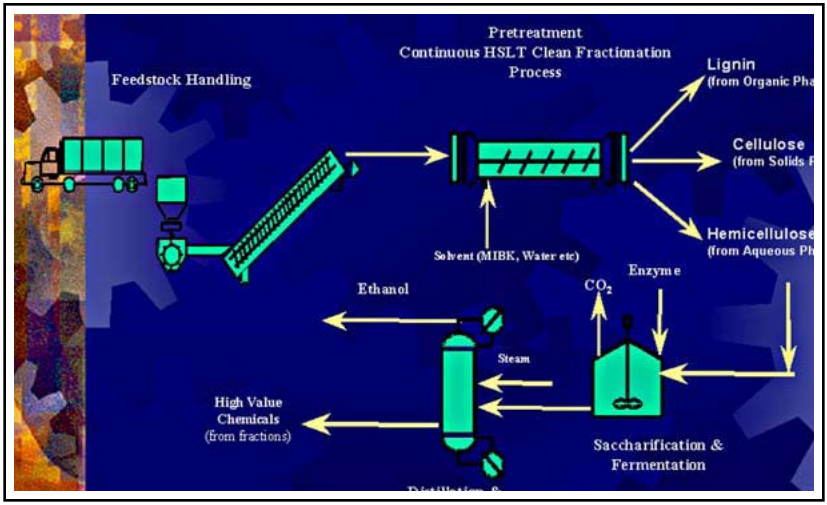

Figure 5. Clean fractionation extrusion processing system.

Figure 6. Single-screw extruder.

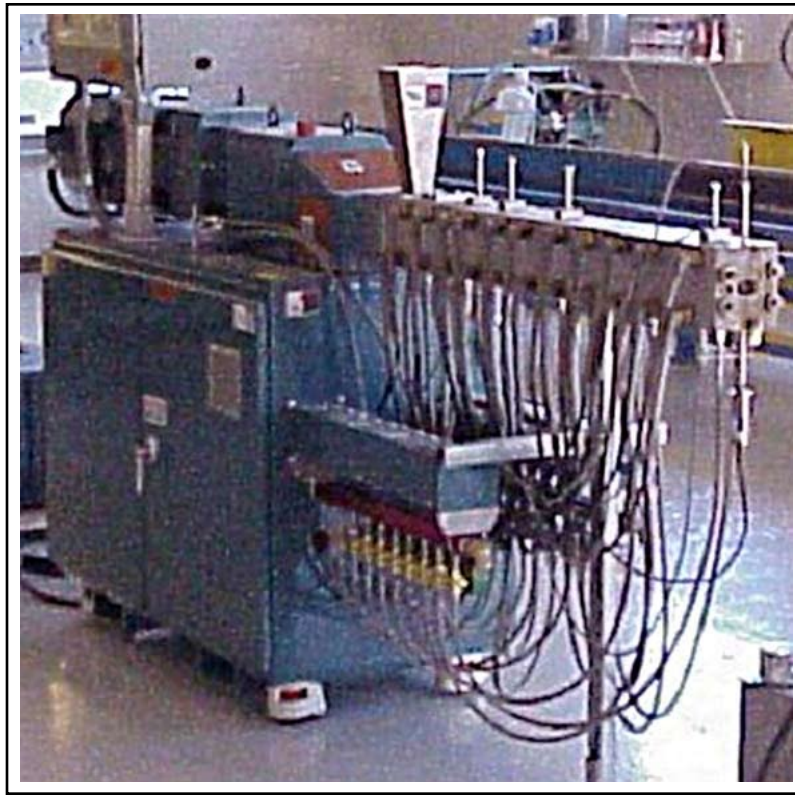

Figure 7. Twin-screw extruder.

Table 1. Effect of extrusion on maximum glucose availability from three grasses.

Grass	Control	Extruded
	(%)	
Big bluestem	21	36
Indian	23	32
Switch	21	25

Conversion

Another critical issue in production of ethanol from lignocellulose is low bulk density of biomass and presence of non-fermentable components such as lignin (Zaldivar *et al.*, 2001). The relatively light, fluffy nature of biomass requires that large volume of water be added to create a flowable slurry that can be processed through conventional reactors, piping, pumps, *etc*. Typically, slurries become too viscous to pump at 15–20% solids, restricting sugar concentrations, and subsequently ethanol titers to 3–5 wt % (Sedlak

and Ho, 2004; Hahn-Hägerdal *et al.*, 2005; Hamelinck *et al.*, 2005). In comparison, modern corn-ethanol facilities routinely achieve 15%+ ethanol in the fermented beer. Due to lower sugar and ethanol concentrations, biomass-ethanol plants would require substantially larger (2–4×) reactor capacities (increasing capital costs), would consume much more energy for distillation, and would have greater water and wastewater handling charges (increasing operating costs) (Hamelinck *et al.*, 2005). These higher process costs largely negate the feedstock cost advantages of biomass, and have impeded commercialization. Moreover, the increased demand for water may also affect the potential location of processing plants.

One approach to overcoming these limitations is to conduct saccharification and fermentation in a solid-state or high-solids environment, instead of traditional submerged bioreactors. Solid-state fermentation (SSF) is defined as a process in which microbes grow on moist solid substrate in the absence of free-flowing water. SSF has been evaluated for a number of applications, with reviews provided by Raimbault (1998), Pandey *et al.*, (2000) and Krishna (2005). Holker *et al.* (2004) note that microbes in nature typically grow on solid substrates, and that "cultivation of microorganisms in aqueous suspensions may rather impair their metabolic efficiency." They list a number of biotechnological advantages of SSF, but also point out that the main obstructions to industrial use as relating to the development of gradients during cultivation.

To overcome the issue of gradient development in SSF, several reactor designs have been proposed to address the key factor of adequate mixing. These have ranged from static trays (Rajagopalan and Modak, 1995) and deep static beds (Chinn *et al.*, 2003) to rotating drums (Hardin *et al,* 2001) and helical blade mixers (Schutyser *et al.*, 2003). Unfortunately, many of these designs are not amenable to scale-up or continuous material flow desired in industrial scale facilities (Mitchell *et al.*, 2000). We have developed two continuous-flow, solid-state or high-solid bioreactor designs that successfully overcome many of these performance issues. The plug-flow, rotating solid-phase bioreactor (Fig. 8) was used to ferment fodder beet pulp with *Saccharomyces cerevisiae* to 8–9 % ethanol in 36–48 h (Gibbons *et al.*, 1984; Gibbons and Westby, 1986a, b and c). This same reactor was subsequently used to ferment sweet sorghum pulp to 6% ethanol in 72 h (Gibbons *et al.*, 1986), while *Kluyveromyces marxianus* produced 7% ethanol in 48–72 h from Jerusalem artichoke pulp (Gibbons, 1989). The high-solids, diffusion fermentor (Fig. 9) was able to convert beet cubes to 9% ethanol with retention times of 264 h for liquid and 72 h for beets (Gibbons and Westby, 1986d; Gibbons and Westby, 1987 a and b; Gibbons *et al*, 1988). Due to their design, construction, and continuous-flow operation, we believe that one or both of these designs will be scaleable for industrial production of ethanol from pretreated biomass, using a combination of cellulase enzymes and appropriate yeast.

To most effectively accomplish simultaneous saccharification and fermentation in the same vessel we will explore the use of thermotolerant yeast. This will allow enzymes to operate at closer to optimal temperatures, while reducing both enzyme repression and catabolite inhibition (Zaldivar *et al.*, 2001). Use of thermotolerant yeast would also provide the added benefits of reducing cooling costs and discouraging contamination (Banat *et al.*, 1998).

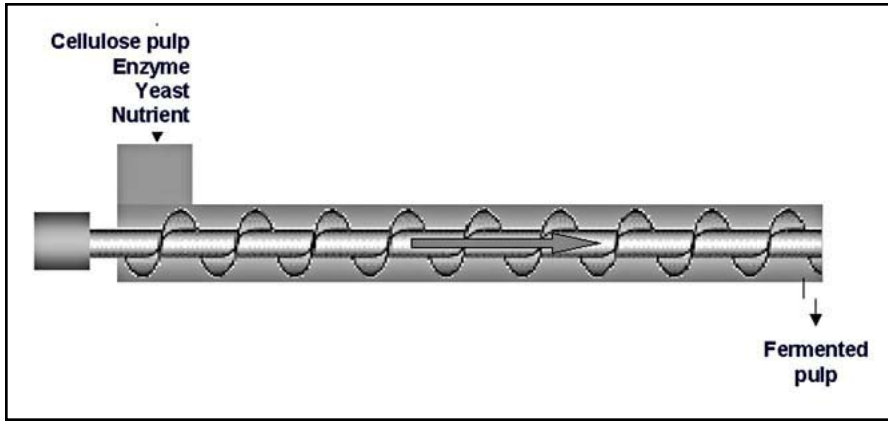

Figure 8. Solid-state bioreactor.

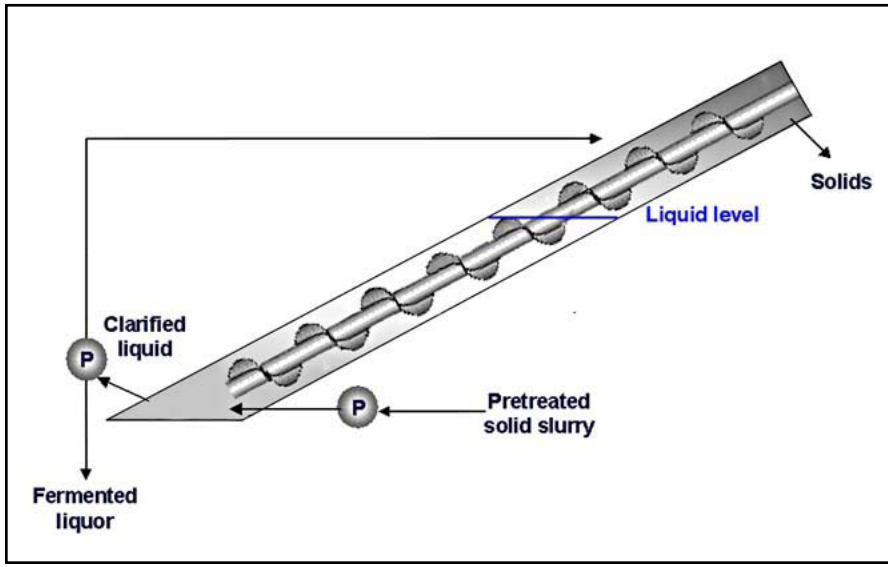

Figure 9. High-solids bioreactor.

Acknowledgments

The author thanks Drs. Julson, Muthukumarappan, West, Raynie, Krishnan, and Dalaly for their contributions to this presentation. Funding for this work was provided in part by the SDSU Agricultural Experiment Station, the Sun Grant Initiative, and the South Dakota Corn Utilization Council.

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