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Perspectives on the SERI Alcohol Fuels Program

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PERSPECTIVES ON THE SERI ALCOHOL FUELS PROGRAM

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ABSTRACT

The production of alcohols from lignocellulosic biomass has moved from a long-range technology a few years ago to one with a real near-term potential for commercial development. SERI's 1 ton/day gasifier produces a medium-Btu gas used to make methanol with only a small water shift. Recent catalyst research has produced materials that make methanol and mixtures of higher alcohols that will enhance the value of methanol as a fuel extender. Three processes have emerged as candidates for early development. They are (1) a high-temperature, dilute-acid, plug-flow approach similar to the Dartmouth reactor; (2) steam explosion pretreatment followed by hydrolysis using the RUT-C30 fungal organism; and (3) direct microbial conversion of cellulose to ethanol using bacteria in single or mixed cultures.

INTRODUCTION

The current U.S. energy consumption, primarily in the form of fossil fuels, is approximately equal to the net annual storage of solar energy in biomass in the United States. We consume about 75 quads of energy (1 quad equals 1 quadrillion Btu), which is equivalent to approximately 5 billion tons of dry biomass per year. It has been suggested that biomass can provide 10-15 quads of energy by the year 2000. Whether biomass will become a major source of energy and chemical feedstock depends on the management of water, land, nutrient, and organic resources, both now and in the future. Resource management ultimately depends on philosophical and policy issues; this paper deals only with the practical questions of the conversion of biomass into useful fuels and chemicals.

NATURE OF THE TECHNOLOGY

"Biomass" is an umbrella term for perhaps the most technically, economically, and socially complex solar energy option. The term is ambiguous in that it hides the scope of biomass resources, as well as the technology required for conversion of biomass into useful fuels and chemicals. While many people believe that biomass offers the potential for a substantial reduction in consumption of fossil fuels, a clear strategy for realizing this potential has yet to be developed.

Biomass is a diverse resource in terms of its availability and its physical and chemical characteristics. It is generally bulky and expensive to transport and, therefore, has a collection area limited by economics. Unlike coal, petroleum, or natural gas, biomass is only a feasible source of energy when it is produced, converted, and utilized on a local basis. Production of fuels and chemicals from biomass is often competitive with production of food and fiber. The use of lignocellulosic biomass as the feedstock will minimize the competition with food, and the development of tree (energy) farms will reduce the impact on fiber production.

THE SERI ALCOHOL FUELS PROGRAM

The Solar Energy Research Institute has been assigned the lead role by the Department of Energy in directing the national program for production of alcohol fuels. The principal objectives of the program are (1) to develop the conversion technology for transforming lignocellulosic biomass into fuel alcohols, and (2) to provide a mechanism for the early transfer of mature processes to the private sector. The program consists of a mixture of in-house research activities and subcontracted research.

Figure 1 shows the general conversion pathways for producing alcohols from biomass. The Alcohol Fuels Program is conducting or funding research only in pathways 3 and 4. The starch and sugar bioconversion processes (pathways 1 and 2) are considered commercially proven and therefore require no federally funded research and development support. Research on pathway 5 is being conducted at SERI by Biomass Program researchers and therefore will not be discussed in this presentation.

Cellulosic materials are found in municipal solid waste, woody biomass, and crop residues; these are all potential feedstocks for bioconversion and thermoconversion processes. In the first part of this presentation any reference to feedstock, unless otherwise specified, will include all of these materials. Later specific processes using specific feedstocks will be discussed.

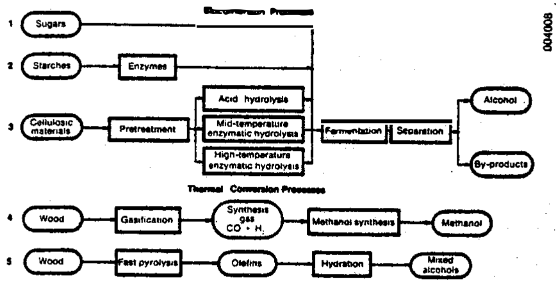


Figure 1. Conversion Pathways for Producing Alcohols from Biomass

Figure 2 shows the work breakdown structure for the SERI Alcohol Fuels Program, which contains four major elements:

- Management
- Ethanol production
- Methanol production
- Process development.

Each of these elements is subdivided into support units or technologies that are described briefly below.

Management

The management element provides the technical management, cost control, and reporting for the program. In addition, the technical evaluation and planning unit supports the program with engineering and analysis activities that provide technology oversight and direction.

Ethanol Production

The ethanol production element is supported by both in-house and subcontracted research. Its principal objective is to develop the research data necessary to improve the cost-effectiveness of ethanol production processes. Research activities concentrate on the operations that appear to offer the best opportunity to reduce the costs of producing ethanol. Specific research areas are

- Acid hydrolysis processes
- Enzymatic hydrolysis processes
- Genetic engineering
- Pretreatment research
- Separation research
- By-product research
- Parametric and sensitivity analyses.

Methanol R&D

The methanol production element consists of three areas of research activity: gasification research, synthesis and catalysis, and methanol fuels cells. The principal activity of the gasification research task is the development of the down-draft, fixed-bed oxygen gasifier. The advantage of this design is simplicity of operation and the production of a relatively clean synthesis gas for methanol synthesis. The synthesis and catalysis research group is developing a homogeneous bimetallic catalyst for converting syngas into methanol and other low-molecular-weight alcohols. The goal of this research is to catalyze with high selectivity, which requires lower temperatures and pressures for operation than conventional heterogeneous catalysts. The fuel cell research studies use methanol as a fuel through an in situ membrane bound catalyst to convert the methanol to hydrogen and carbon dioxide.

Process Development

The process development element contains four activities: process research, process evaluation and testing, integrated experiments, and engineering R&D.

The process research subtask will identify efficient and economically feasible processes through integration of novel conversion unit processes into flowsheets for evaluation and testing. The process evaluation and testing subtask will evaluate specific flowsheets and perform bench- and pilot-scale experiments to develop sufficient data to determine commercial feasibility. The startup and operation of the biotechnology high bay at SERI's Field Test Laboratory Building during FY 1984 will provide a focal point for testing process options to establish the commercial feasibility of selected

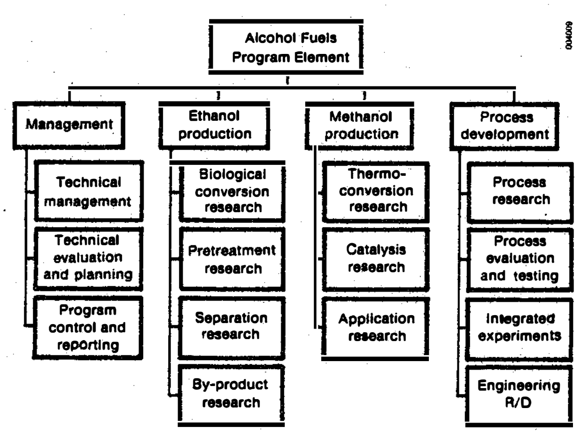


Figure 2. FY 1984 WBS Alcohol Fuels Program Element

cellulose-to-ethanol technologies. The integrated experiments subtask is expected to identify one or more processes that warrant an integrated experiment. Costs for such experiments will be shared with industrial partners. The experiments will test specific processes in a site-specific commercial environment to provide realistic scale-up information for the private sector. The engineering R&D subtask will assess the economic and engineering impact that process improvements developed in other areas of the program will have on the overall systems. Engineering activities have the potential to improve the economics and reduce the financial risk associated with development of a new technology.

SPECIFIC RESEARCH ELEMENTS

SERI Gasifier

Numerous types of reactors are available to gasify biomass; air, oxygen, ambient pressure, high pressure, up draft, down draft, fixed bed, and fluidized bed are among the most common parameters used in developing a gasifier reactor design. SERI researchers have designed a down draft, fixed bed, pressurized oxygen gasifier that produces a clean, medium-Btu gas.

Figure 3 shows a schematic drawing of the SERI gasifier, which is a 1 ton/day experimental unit that is similar in design to the models developed in Europe during World War II. The principal advantage of this configuration is the production of a very clean synthesis gas (a very low level of tar and char is found in the product stream). Also, because the product gas is discharged under pressure, it will require less compression prior to entering a methanol or ammonia synthesis system. The resulting gas can be converted to methanol, ammonia, methane, or gasoline. The gas can also be used directly in industrial pipelines and in turbines for peak power generation. Table 1 shows biomass gasification reactions and chemicals that can be obtained from the process.

Ethanol from Cellulose

There are two ways to produce ethanol from cellulose: acid hydrolysis and enzymatic hydrolysis. Each process has numerous variable parameters, including acid, operation temperature, reactor configuration, microbial systems, and pretreatment. In this presentation only one of the many variation will be discussed for each general method: (1) a high-temperature, dilute-acid hydrolysis process, and (2) a base-case enzymatic hydrolysis process that employs steam explosion as the pretreatment. These cases were selected based on recent research results and because both have been subjected to extensive parametric analyses by our in-house modeling group.

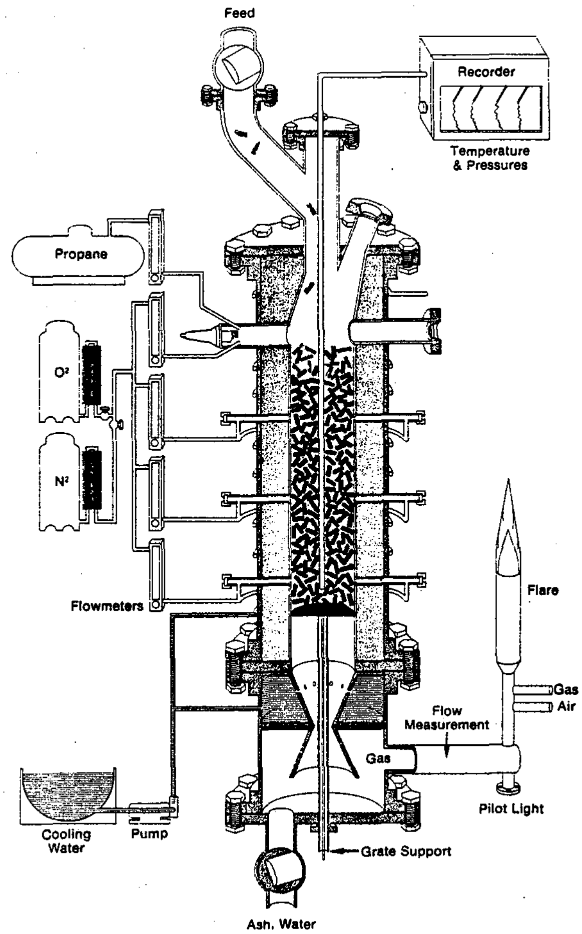


Figure 3. SERI Oxygen Biomass Gasifier

Acid Hydrolysis Process

The process for the conversion of a lignocellulosic biomass feedstock to fuel ethanol is shown schematically in Figure 4. The process employs a plug-flow reactor in the hydrolysis unit that operates at 240°C, 1% acid, and a 7-second residence time. The substrate is ground aspen wood, which is loaded into the reactor as a 15% solids slurry with water. The unreacted solids are pressed and burned to provide heat for the process. The liquid stream containing the soluble sugars is neutralized using calcium hydroxide and treated to remove any materials that would be toxic to the fermentation organisms. Standard fermentation and distillation follow to convert the glucose sugars to ethanol and to purify the ethanol to fuel quality. The base-case design was sized to produce 50 million gal/yr of anhydrous ethanol from aspen wood; the cost estimates were based on a Gulf Coast location and constant 1983 dollars.

Table 1. Reactions and Chemicals Produced from Biomass Gasification

Biomass O_2 Gasification:

$$CH_{1.4}O_{0.6} + 0.2\ O_2 \rightarrow CO + 0.7\ H_2$$

Water/Gas Shift: $CO + H_2O \rightarrow CO_2 + H_2$

Methanol: $CO + 2H_2 \rightarrow CH_3OH$

Fertilizer: $3H_2 + N_2 \rightarrow 2NH_3$

M Gas: $CH_3OH \xrightarrow{\text{Zeolite}} (CH_2)_n + H_2O$

Methane: $CO + 3H_2 \rightarrow CH_4 + H_2O$

The 50 million gal/yr size reflects the dispersed nature of biomass and assumes a maximum collection radius of 25 miles. The base-case estimate for the selling price of ethanol from the system as configured was $2.00/gal.

Parametric analyses were performed for several operating conditions and system configurations. The items determined to be the dominant cost-controlling factors are (1) feedstock cost, (2) solids loading in the reactor, and (3) xylose sugar utilization.

Feedstock Cost. The cost of the feedstock is the dominant factor in determining the cost-effectiveness of production of ethanol in the acid hydrolysis process. Figure 5 shows the relationship of the selling price of ethanol in $/gal versus the cost of the aspen wood. This relationship dictates the necessity of reducing the cost of the feedstock or increasing the yield for the process in order to reduce the production cost per unit of ethanol.

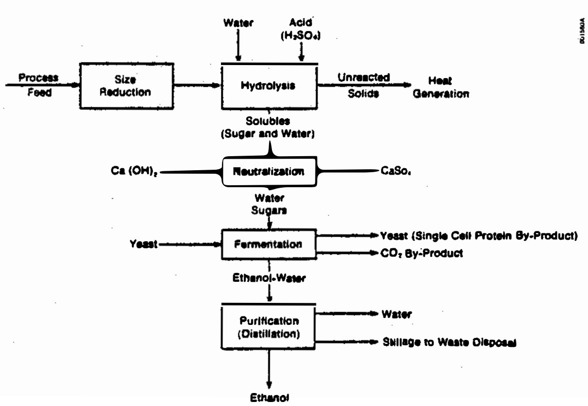


Figure 4. Cellulose-to-Ethanol Overall Processing Plan

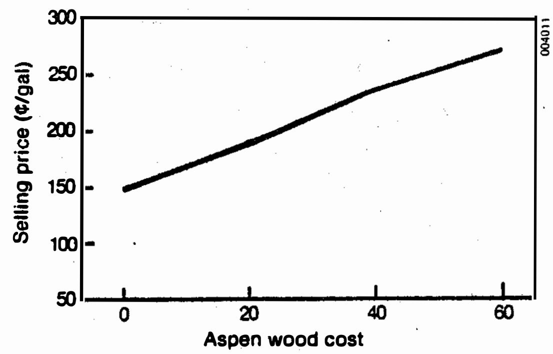


Figure 5. Selling Price of Ethanol vs. Cost of Aspen Wood

Solids Loading. The amount of water in the process streams has a large effect on the process economics. The presence of large amounts of water increases the steam requirements as well as the equipment size and capital cost of the plant. In addition, low solids loading yields a dilute sugar stream to the fermenter section, resulting in a low ethanol concentration in the beer and increased energy costs for the distillation section. Figure 6 shows the effect of solids loading on the selling price of ethanol. The optimum solids loading appears to be about 30%. This is the target value in our current process design; however, equipment for handling solids at this level may be difficult to obtain.

Xylose Sugar Utilization. Process changes that favor the use of the xylose sugars in the feedstock can greatly reduce the selling price of ethanol. One approach being studied is to develop, through genetic engineering techniques, a yeast that can ferment both xylose and glucose in the same fermentation vessel. This research issue is being pursued with vigor because meeting this goal has the potential to reduce the selling price of ethanol to about $1.10/gal. A more imminent alternative is to convert the xylose to furfural and use the by-product credit to subsidize the selling price of

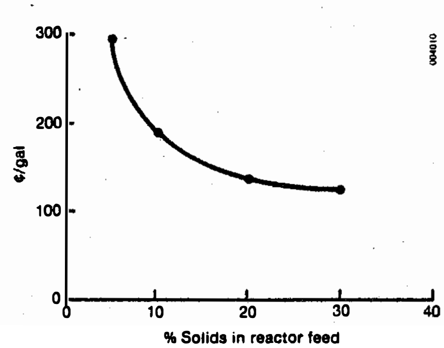


Figure 6. Cost of Ethanol vs. Percentage of Solids in the Reactor Feed

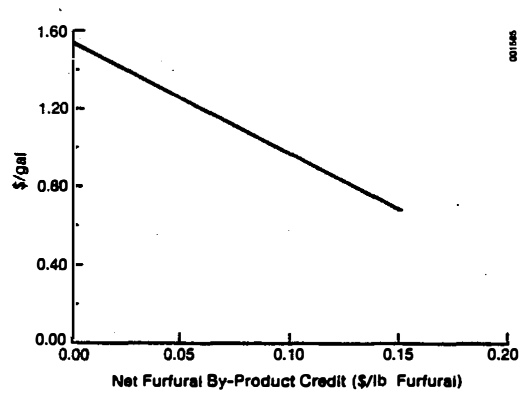


Figure 7. Selling Price of Ethanol as a Function of the Net Furfural By-Product Credit

ethanol. Figure 7 shows the effect of a furfural by-product credit on the selling price of ethanol. The current market price for furfural is about \$0.60/lb; as shown in Figure 7, a net selling price for furfural of \$0.10/lb could reduce the selling price of ethanol to less than \$1.00/gal. With the current demand for furfural, one or two plants of the size in this study would saturate that market. However, there is a large potential market for derivatives of furfural based on well-known chemical processes if the price of furfural were low enough to encourage the chemical industry to change feedstocks.

Enzymatic Hydrolysis Process

There are three principal methods for the enzymatic hydrolysis of lignocellulosic biomass to produce ethanol: (1) separate hydrolysis and fermentation, (2) simultaneous saccharification and fermentation (SSF), which combines the hydrolysis and fermentation reactions into one step, and (3) direct microbial conversion, in which bacterial species grow directly on the substrate to convert the feedstock to ethanol in one step. The results described below are from a base-case study conducted at SERI using the Chem Systems model, which was developed under a subcontract to SERI; the data include recent research results from Lawrence Berkeley Laboratories.

The base-case flowsheet consists of steam-explosion pretreatment, enzyme production by a fed-batch fermentation of the RUT-C30 strain of the fungus *Trichoderma reesei*, hydrolysis of the cellulose to glucose by enzymes followed by fermentation of the glucose in a separate process step, and vapor reuse distillation. A block diagram flowsheet for this process is shown in Figure 8. The operating conditions for the base case were:

- Feedstock - Aspen wood chips at \$30/ton

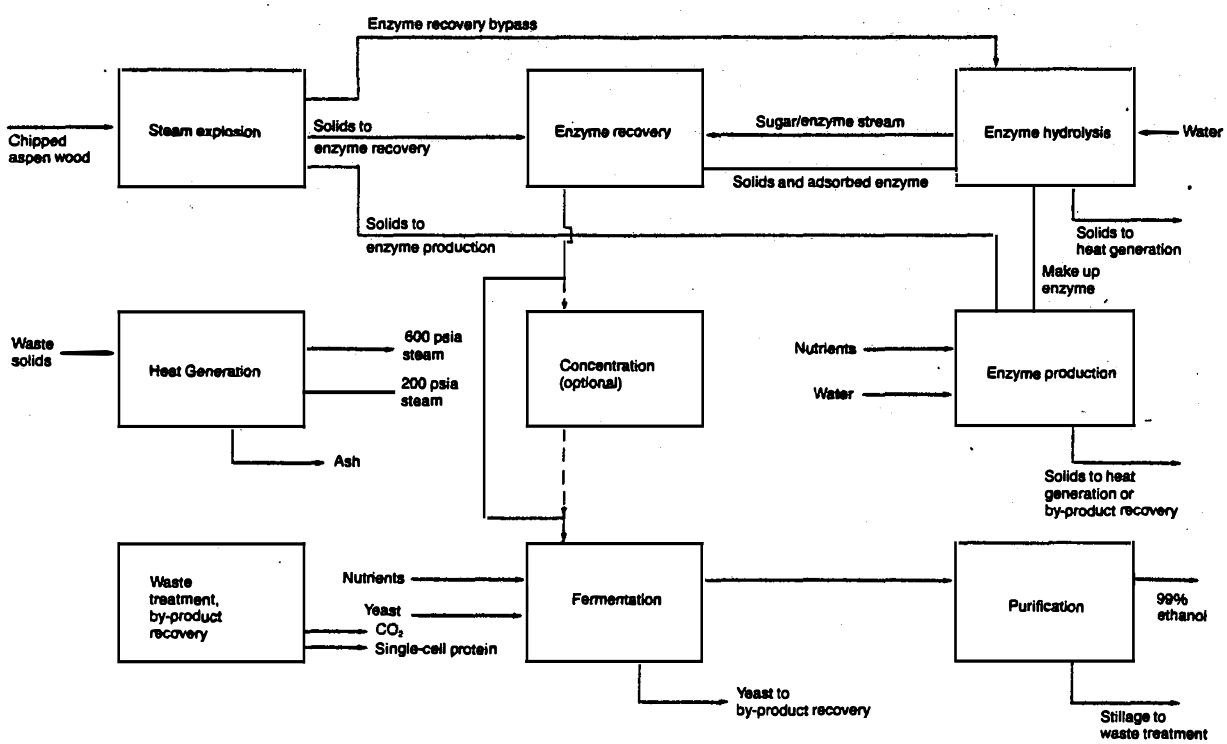


Figure 8. Process Block Diagram Including Enzyme Recovery

- Pretreatment
  - Steam: 400 lb/ton of wood at 560 psig and 247°C
  - Cook time: 5 seconds
- Substrate loading - 20 wt %
- Enzyme loading - 25 FPU/g of substrate (to yield 80% conversion of cellulose to glucose).

The base case for the enzymatic process was also sized to 50 million gal/yr and was subjected to the same constraints as the acid hydrolysis case. The base case estimate for the selling price of fuel-grade ethanol from the process as configured was $2.30/gal.

The most cost-sensitive factors identified by parametric analyses completed on the base-case enzymatic hydrolysis process were feedstock cost, enzyme recycle, and xylose utilization.

The feedstock cost had approximately the same effect on the selling price of ethanol as in the acid hydrolysis case. However, the conversion yield in the enzymatic processes is anticipated to be higher than the acid hydrolysis case, and the effect of feedstock will not dominate the cost. For example the feedstock cost in the acid hydrolysis base case was approximately $0.75/gal, while for the enzyme case it was about $0.50/gal (based on cellulose conversion only).

The process variable with the largest effect on the selling price of ethanol was enzyme recycle. Figure 9 shows the relationship between enzyme recycle and the selling price of ethanol. It is clear that enzyme recycle has a dramatic effect on the process economics; however, Figure 10 shows the effect of several other process options, and again the recycle option is clearly dominant. Conversion of xylose to ethanol also provides a substantial reduction in price of ethanol, while the remaining changes in operating conditions produce only small reductions in selling price.

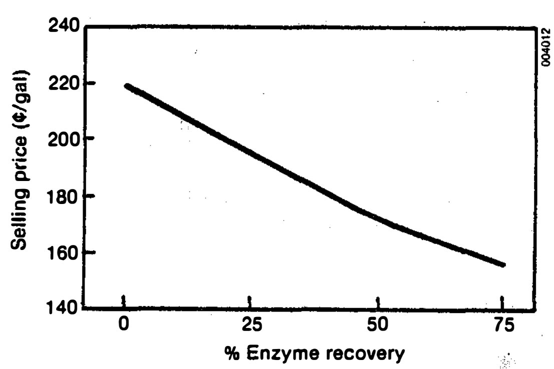
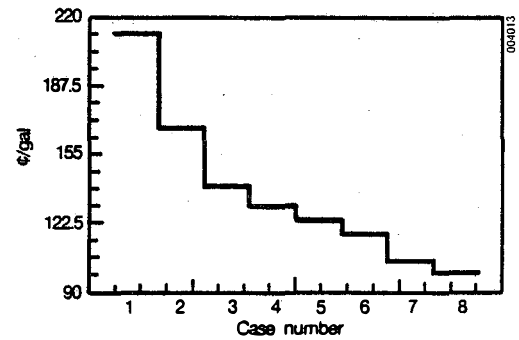


Figure 9. Selling Price of Ethanol vs. Percentage of Enzyme Recycle



1. Base case
2. Plus 60% enzyme recovery
3. Plus xylose utilization
4. Plus reduced enzyme load (15 FPU/g)
5. Plus 90% conversion
6. Plus 25 wt% solids load
7. Plus 50% explosion cost
8. Plus 50% enzyme production capital cost

Figure 10. Ethanol Selling Price vs. Process Improvements

CONCLUSIONS

The technology for the conversion of biomass to alcohols has indeed developed rapidly in the last few years. Several systems will probably be ready for large-scale demonstration in the next year or two. In order to assess the readiness of these technologies, two approaches have been used: (1) evaluation by commercial engineering companies and (2) modeling studies to identify the cost-sensitive parameters in the candidate processes.

SERI has enlisted the assistance of several consulting firms to review the current state of the art of cellulose conversion technology by completing feasibility studies for each process that has commercial potential. The firms selected were Stone and Webster, A. D. Little, Chem Systems, and Badger Engineering. Each of these companies will develop a flow sheet using the best available data for the process being evaluated. Then capital costs will be estimated, heat and material balances will be calculated, and a cost of production determined. Each engineering firm will also suggest areas for further research to reduce the cost of production based on their evaluation and feasibility study results.

The use of parametric analysis as a tool to evaluate process options in biomass conversion technology has proved to be a valuable asset to development of research strategy for the Alcohol Fuels Program. These results must be kept in perspective because the estimated values for the production of ethanol shown in this presentation are accurate to only ±35% at best. The real value in this exercise comes from the comparison of various process options and plant configurations and using the results of these studies to identify the research and process activities that have potential for cost reductions.