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Preparation for Commercial Demonstration
Of Biomass-to-Ethanol Conversion Technology

FINAL REPORT

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**Preparation for Commercial Demonstration
Of Biomass-to-Ethanol Conversion Technology**

PROJECT OVERVIEW

Background

The objective of this program was to complete the development of a commercially viable process to produce fuel ethanol from renewable cellulosic biomass. The program focused on pretreatment, enzymatic hydrolysis, and fermentation technologies where Amoco has a unique proprietary position.

Assured access to low-cost feedstock is a cornerstone of attractive economics for cellulose to ethanol conversion in the 1990s. Most of Amoco's efforts in converting cellulosic feedstocks to ethanol before 1994 focused on using paper from municipal solid waste as the feed. However, while many municipalities and MSW haulers expressed interest in Amoco's technology, none were willing to commit funding to process development. In May, 1994 several large agricultural products companies showed interest in Amoco's technology, particularly for application to corn fiber. Amoco's initial work with corn fiber was encouraging. The project work plan was designed to provide sufficient data on corn fiber conversion to convince a major agriculture products company to participate in the construction of a commercial demonstration facility.

Summary of the Research and Development Plan

The work plan included steps to (1) develop the technology and know-how needed to make Amoco's process an attractive means of processing corn fiber feedstock, (2) develop engineering data at pilot plant scale to support process design and optimization, (3) prepare to produce enough byproduct animal feed from corn fiber to properly evaluate its commercial value, (4) assess the technical attractiveness of other feedstocks with business promise, and (5) strengthen alliance relationships to result in at least one industrial collaborator with a near term application.

The key goal was to develop a process to make ethanol at low cost, defined as less than \$0.85/gal. We targeted 25% corn fiber solids feed to the SSF process, a maximum of 10 IU of cellulase enzyme per gram of cellulose, complete SSF in approximately 48 hours residence time, and ethanol yields from starch, cellulose and xylans approaching 90% of theoretical. In addition, we believe that most of the protein in the feed corn fiber would have to be recovered in a form that could be sold for animal feed.

Accomplishments

The experimental program was completed. A design for a demonstration facility using corn fiber feedstock was developed, and capital and operating costs estimated. Ethanol costs are estimated to be about \$0.68/gallon for a corn fiber facility integrated with an existing corn to ethanol plant.

Amoco's proprietary pretreatment technology has been installed in the Alternative Fuels User Facility (AFUF) at NREL for use in confirming the design parameters in the one ton per day Process Development Unit (PDU) there. Amoco plans to produce sufficient solid product from corn fiber to test as an animal feed under the provisions of our CRADA with NREL.

A variety of feedstocks other than corn fiber were tested in the pilot scale pretreatment equipment, including bagasse, oat hulls, softwood from managed forest thinnings, rice straw, wheat straw, and barley straw. These supplement earlier data collected on hardwood sawdust and paper from municipal solid waste. Only the softwood failed to give highly reactive pretreated SSF feed material. These data have been used to provide preliminary designs for alternative demonstration facilities.

The business development effort resulted in a joint venture being created to pursue technology development. Stone & Webster Engineering Company joined with Amoco to form Swan Biomass Company.

DISCUSSION

The Statement of Work included three phases. The first phase focused on applying technology developed for hardwood and waste paper to corn fiber, a by-product in the production of corn starch. At the end of the first phase, the process economics were examined, and found to justify proceeding with the second phase, which scaled up the process developed in the first phase. Phase 3 was the generation of this final report.

The material in this report includes results from the experimental, modeling, scale-up and business development parts of the program. The report is organized by technology. The major divisions and subdivisions are related to the tasks and subtasks listed in the Scope of Work, but are not identical. For example, the text that follows does not identify the phase of the program at all. This report stresses results, observations, and particularly the conclusions, of the work accomplished under the program. Data are not included.

Technical Program

The steps envisioned for a commercial process for converting corn fiber into ethanol are similar to those developed for converting waste paper or hardwood, where Amoco had developed its experience. But the process changes needed because of the new feedstock are not trivial. Paper and wood contain no starch, while starch is a major component of corn fiber. Also, paper does not contain enough hemicellulose to make conversion of xylose critical to the economics of paper conversion, but hemicellulose is the largest single component of corn fiber. Corn fiber contains substantial amounts of protein, which must be recovered in an economically acceptable form, and this need complicates conversion strategies.

Pretreatment is a critical unit operation, and enough preliminary work had been done to show that optimal operating conditions are far different for corn fiber than for waste paper. The process must convert most of the hemicellulose in corn fiber to xylose and arabinose, and avoid producing reversion products such as furfural that inhibit enzyme or yeast performance. Most of the starch will be converted to a soluble form by the pretreatment as well, and formation of hydroxymethylfurfural (HMF), a reversion product of glucose, must be avoided. Starch and cellulose require different enzymes to hydrolyze them to glucose, a step required to make them fermentable. Problems with the performance of cellulase (for cellulose conversion) on corn fiber were encountered in preliminary work. SSF utilizing both glucose and xylose is new technology that works well on simple sugar solutions, but must be proven on corn fiber hydrolyzate. Some enhancement of the genetically modified yeast's ability to ferment xylose may be needed.

1.0 Enzymatic Hydrolysis

Corn fiber is produced in wet milling of corn, and is the residue after processing to remove corn oil, germ and much of the starch. The fiber from most mills will be similar, but not identical; not only will each mill operate slightly differently, but the corn varieties can also be different. Amoco used corn fiber from two mills in its initial work, the Cardinal mill owned by Casco in Ontario, Canada, and the Cargill mill in Eddyville, Iowa. No significant differences were observed in the behaviors of the two feeds; both mills used the same variety of corn.

The cellulose in corn fiber responds as expected for a well-pretreated substrate, and its response to cellulase is predictable using Amoco's model that was developed for steam exploded wood. The starch in corn fiber responds to amylase as expected; it was not clear if amylase would be needed, but if it is used, its cost will be less than one cent per gallon of ethanol. There are no interferences between enzymes. Exogenous β -glucosidase is not needed. Xylanase is effective at high doses, but its use is not economically justified.

2.0 Fermentation

Ethanol yields from glucose were high, generally about 90%. Fermentation at up to 25% solids proceeded rapidly at high glucose concentrations, but not when the glucose concentration was low and acetic acid level (generated by contaminants) was high. The recombinant yeast 1400 (pLNH33) developed by Purdue ferments both xylose and glucose, but must be used at lower temperatures (30°C) than baker's yeast. This plasmid-bearing yeast has not yet been successfully used at pilot plant scale; ethanol yields in the laboratory are high, over 90% from both glucose and xylose. There is some concern about the stability of the plasmid in continuous operations, and it may be necessary to add fresh yeast to maintain xylose conversion in SSF.

3.0 Pretreatment Evaluation

The primary goals of pretreatment are cellulose reactivity enhancement and hemicellulose and starch hydrolysis, measured by soluble xylose and glucose release, respectively. Generation of large quantities of inhibitors that suppress reactions of either yeast or cellulase must be avoided. Amoco's pretreatment technique achieves the conditions required to balance the competing requirements of increased cellulose reactivity and low inhibitor formation.

3.1 Corn Fiber

The Amoco pretreatment appears to be a very attractive process for corn fiber. Corn fiber can be processed at high rates and meet the goals of pretreatment: all of the starch and 85% of the xylan are solubilized, and less than 3 mg reversion inhibitors/g dry solids are generated. Most of the sugars are solubilized to oligomeric form rather than to monomers during pretreatment, but the oligomers appear to degrade to monomer form during SSF.

3.2 Other Feedstocks

In addition to these feedstocks, Amoco also tested the pretreatment of rice straw, wheat straw, barley straw, bagasse, young softwood trimmings, and oat hulls. Rice straw was of interest because the City of Gridley, California was seeking help in developing a project to use rice straw. Recent changes in California law require that open field burning, the conventional method for destroying the rice straw, be eliminated. The rice industry in California's Central Valley needs to find other ways to deal with their problem, and conversion to ethanol seems attractive if the straw can be utilized as feedstock. Wheat and barley straws were of interest to the province of Manitoba, which is seeking to become a supplier of ethanol for Canada and the U.S. based on agricultural wastes. Bagasse is of interest in Hawaii and several foreign countries, most notably Brazil. The young softwood trimmings were of interest to U. S. Forest product companies, and oat hulls were of interest to potential customers in Canada.

The variety of feedstocks provided a chance to evaluate the Amoco pretreatment process over a range of materials with potential for commercial application. The results validated the expected broad utility of the technology.

3.2.1 Bagasse

Bagasse appears to be a good feedstock candidate for the Amoco biomass to ethanol process. Hemicellulose can be removed effectively under relatively mild conditions, and the levels of reversion inhibitors can be kept low.

3.2.2 Straws

The experiments with rice, wheat and barley straws must be considered only to be scouting tests of their suitability as feedstocks. Rice straw will likely be the first of these materials to undergo extensive testing because of funding available through the City of Gridley. The first requirement is to determine how to feed straws at high rates. The simplest method is likely grinding the straw, either with or without water. Other possible techniques would involve equipment modifications.

Although generally successful in producing feedstocks that can be readily converted to ethanol in SSF, the experiments may not have covered the range of optimal operating conditions for any of the straws; this was most clear in the case of barley straw, which will require significantly more severe conditions than those tested to reach acceptable levels of hemicellulose conversion.

Rice straw contains large amounts of silica, which is fine and highly dispersed. This material must be removed at some step in the processing, or captured during combustion if the solid residue from ethanol manufacture is burned as fuel.

3.2.3 Softwood

None of the tests on this feedstock produced satisfactory material for SSF processing. Given the range of the variables explored and the reactivity results, it is not certain that the current Amoco pretreatment can produce a substrate from this feedstock reactive enough to make ethanol production attractive.

3.2.4 Oat Hulls

The experiments with oat hulls were only extensive enough to make a cursory evaluation of Amoco's technology applied to this feed. It appears that oat hulls would be a very attractive feedstock for the Amoco ethanol process.

4.0 Pilot Plant SSF Operations

Amoco built a pilot plant to extend the technology for producing ethanol from biomass to steady-state flow systems. The plant included equipment for feedstock handling, pretreatment, SSF, stripping of ethanol from the product slurry, and separation of the solids from the slurry product. The SSF section included facilities for growing yeast, and for adding enzyme, base and acid. The SSF tanks were connected in series, and each had a volume of 2000 liters.

Forty five runs were completed in 1994. The first nine of these runs were on water or Avicel, primarily designed to test mechanical equipment and to verify operability. The next twelve runs utilized sulfite pulp or paper; these runs were not integrated with the pretreatment section. Some runs with paper utilized phosphoric acid in one of the SSF tanks for pretreatment. The final 24 runs used corn fiber feed, and included integrated operation of pretreatment and SSF. The stripping section was never employed.

For the corn fiber runs, eighteen were batch experiments, some of them run simultaneously. There were two fed-batch tests, and four 3-stage CSTR experiments. One of the latter tests was aborted very

shortly after start up. The Purdue recombinant yeast Strain 1400 (pLNH33) was utilized in eight runs.

The first 14 runs with corn fiber, which included 12 batch runs and the 2 fed batch runs, were made prior to the beginning of the program reported here. This means that 6 batch runs and 4 continuous runs were performed under the contract.

4.1 Pre-Contract Batch (and Fed-Batch) Operations

Runs 22 through 35 were complete before the contract work started. In retrospect, the value of these tests was limited by several factors:

- The quality of the pretreatment was not monitored carefully enough during these tests.
- The full importance of inhibitors on yeast was not yet recognized.
- The full importance of temperature control was not yet recognized.

In addition, most runs were badly contaminated. The source of contamination was not tracked down.

It appears that the limit on ethanol yield in these batch runs was contamination. As long as glucose level was significantly above zero, ethanol production was rapid; amylase may slightly augment this early conversion, but only slightly. The highest yields were achieved in runs without amylase. Ethanol yields in this time span are very high, based on the glucose converted. When contamination was avoided, ethanol continued to be produced from cellulose; about 10 to 15% higher yields were achieved over the next day or so. No uncontaminated runs went beyond 48 hours, so the limits on yield are not known.

Higher cellulase doses led to high yields at 20 hours; it is not clear if this higher yield could be sustained at longer times.

To this point, lower solids concentrations have outperformed higher solids runs. The best run was the first 30 hours of the fed batch run 26, where the yield at the end of the batch mode was 57% of theoretical. Yeast have not survived at 25% solids, except in the laboratory; however, high solids was always accompanied by severe contamination and low glucose levels.

The first test of strain 1400 (pLNH33) was disappointing, but not surprising in hindsight. No xylose conversion was observed; the temperature was too high for effective xylose fermentation.

4.2 Batch Operations under Contract

The batch runs conducted under the contract began to focus on the shortcomings of the previous batch runs. The first three, runs 36, 37 and 38 sought to explore the effects of pretreatment on SSF behavior and the effect of cellulase dose. They reverted to the bakers' yeast to avoid complications caused by simultaneously testing a new organism, along with the effects of pretreatment and cellulase. The utility of these runs was limited by the use of pH = 4 and a temperature of 37°C.

The next test was the first three-stage CSTR run in the pilot plant. This was followed by two more batch runs, the first runs at pH = 5 and 30°C. Runs 40 and 41 were run under identical conditions, using Purdue yeast; they both suffered from a severe lag in yeast performance. Runs 42, 43 and 44 were CSTR runs.

The final batch run was the last operation in the pilot plant before Amoco left the facility. The primary purpose of the run was to try to show that Purdue yeast would ferment xylose satisfactorily.

4.3 Continuous Operations

Run 39, which started August 16, 1994, was the first pilot plant test where the SSF reaction was carried out in constant-flow stirred tank reactors; unfortunately, the temperature and pH were too high. This test was followed by two batch runs, then three more CSTR runs, and then a final batch run. All of these runs were made at pH = 5 and a temperature of 30°C.

The CSTR runs utilized three 2000 liter tanks in series to perform SSF. These runs were initiated by loading 10% solids and enzymes into all three tanks, inoculating the first tank with yeast, then beginning the addition of 25% solids feed to the first tank 24 hours later, and simultaneously starting slurry flow between tanks. Enzyme dosage in all cases was 1.8 FPU cellulase/g solids (about 15 FPU/g cellulose) and 25 ml glucoamylase/kg solids (about triple the usual dose in the corn ethanol business).

Each of the continuous runs became contaminated shortly after starting solids addition, and none can be judged entirely successful.

4.5 Results of Contract Pilot Plant Runs

The corn fiber pilot plant work completed before the contract (but after the proposal was written) allowed the runs under the contract to focus more carefully on viable operating parameters and to test key factors. Nevertheless, the first four runs under the contract suffered from a poor choice of pH and temperature. These runs

still helped establish relationships between pretreatment results and SSF operation, and showed that arabinose consumption is due to contaminants rather than the yeast.

The experiments failed to prove or disprove the utility of the recombinant yeast strain 1400 (pLNH33). If xylose was being converted to ethanol, it was at a slower-than-expected rate. In all cases, contamination prevented the results from being clear. Final ethanol yields were always low, even when based on glucose conversion only, and despite high glucose conversions. Contaminant bacteria varied from run to run, some using arabinose, some xylose and some ethanol as substrate. Acetic acid was the most commonly observed byproduct of contamination; lactic acid was not monitored, however.

The three runs made under constant flow conditions, using three SSF reactors in series, were likewise contaminated. These runs proved that 25% solids could be tolerated in the feed to the first tank; enough cellulose hydrolyzes very quickly to reduce the slurry viscosity to tolerable levels. The runs also showed that the yeasts do not adapt as quickly as might be wished to large changes in glucose levels; there can be a significant lag in fermentation when the glucose level is boosted by the addition of fresh feed, for example. The yeasts then seem to flourish until the glucose level drops to steady-state levels, when contaminants begin to take over.

Any future pilot plant work needs to recognize the following:

- It is important to carefully control the quality of pretreatment,
- pH must be kept around 5 when using corn fiber, and
- Contamination control is difficult and critical to producing useful results.

Nothing in the work completed suggests that the problems encountered cannot be solved.

5.0 Modeling

5.1 Kinetics Modeling

Amoco kinetic and process models were adapted to corn fiber and other agricultural wastes in order to examine the design and costs for projected commercial facilities using the technology developed under this program.

Yeast kinetics for the seed fermenters were derived by Purdue for strain 1400; these apply only to glucose fermentation and yeast growth, and do not deal with xylose fermentation. Fermentation was not modeled in the SSF system; it was not necessary because cellulose hydrolysis is the rate-controlling step. Both glucose and xylose conversions were based on Purdue and Amoco laboratory results.

5.2 Process Design

A corn fiber conversion plant was designed to be built adjacent to an existing ethanol plant. The fiber plant would share a number of utilities and other facilities already in place.

A block flow diagram of the plant design is shown in Figure 5.2. The numbers correspond to stream numbers in the computer spreadsheet model. Corn fiber is taken from the existing presses in the wet milling operation and fed into the pretreatment reactor with steam and acid. The exit stream from pretreatment is flashed; recovered steam is used in distillation. A Doering mixer is used to push slurry into the SSF feed pump. There are 3 stages of SSF in series, each with one day residence time. Air, acid, enzyme and yeast are added to the first reactor; carbon dioxide from the reactors is scrubbed to recover evaporated ethanol. Slurry from the third stage is sent over a cross-flow filter, and some of the liquid (which contains ethanol) is recycled to dilute the pretreated slurry. The purpose of this recycle is to raise the ethanol concentration in the product so that distillation costs remain reasonable. The product slurry from the third stage is sent to distillation, and the ethanol product is dried using molecular sieves. The fusel oils and denaturant are added to the product, and the product is sent to storage. The water and solids from the still bottoms are sent to solids separation (vacuum filter or centrifuge), and the solids are sent to existing driers in the corn mill. The water goes through aerobic digestion; any methane is used for process fuel. Some of the water is recycled to dilute the pretreated solids, the rest is sent to water treating in the existing plant.

5.3 Spreadsheet Results

5.3.1 Base Case

The economics calculated by this spreadsheet are what Amoco refers to as "square case" economics that are useful in comparing projects. The basis is a discounted cash flow analysis, using costs as they are today, without inflation. A 15% rate of return is assumed.

The capital cost for the facility in 1994 dollars was \$41.8 million. The most expensive areas of the plant are the SSF section

and distillation; other significant areas of cost are the pretreatment and anaerobic digestion.

The cost of ethanol for this base case design is \$0.68/gallon.

5.3.2 Sensitivities

Cellulase use is not strongly justified. The cost of the enzyme barely offsets the extra income generated from the additional ethanol produced when cellulase is used in the process. The major reasons for continuing to use cellulase would be (1) to demonstrate that SSF with cellulase is a viable process if a corn fiber plant is the first commercial or demonstration operation, and (2) to capture better economics if the cost of cellulase decreases significantly.

If the yeast could be genetically modified to ferment arabinose, as well as xylose and glucose, the cost of ethanol could be cut about \$0.06/gallon, or just under 10%. If it proves possible to grow enough yeast in the SSF tanks so that some of the seed fermentation equipment can be eliminated and the purchase of molasses and corn steep liquor becomes unnecessary, ethanol cost of production would decrease \$0.07/gallon.

There are significant economies of scale in the base case design. For example, if the feed rate is reduced from 750 tons per day of corn fiber to 500 tons per day, the ethanol cost would rise \$0.07/gallon to \$0.75/gallon.

5.3.3 Rates of Return

A second spreadsheet was used to examine the economics of commercial application of the technology more closely. This model contains no details of the flowsheet, but does look at the effects of parameters such as inflation rate, federal and state ethanol subsidies, construction time, when construction starts, sustaining capital, and so on. It produces annual cash flow information, and summarizes the results as the discounted cash flow rate of return and present value for one or many commercial plants.

The base case produces an internal rate of return (ROR) of 22.2% and a net present value (NPV) of \$14 million.

Some of the more important sensitivities have been examined; results are shown in Table 5.3.3.

The continuation of the federal ethanol subsidy has the biggest effect on the NPV of the sensitivities examined. On the other hand, this event has only small effect on the rate of return, since its impact is out in the future. Delaying start of production increases the impact the subsidy's demise has on the economics.

Table 5.3.3
Economic Sensitivities

Case	ROR, %	NPV, \$MM
Base	22.2	14
Maintain federal subsidy after 2000	25.8	26
1997 start of construction	20.5	9
with maintenance of federal subsidy	25.3	22
50% equity, remainder borrowed at 9%	31.9	19
Illinois site (st. tax cr. is \$0.15/gal)	21.4	12

Financing part of the plant cost significantly increases the rate of return on the owner's capital, but only modestly increases the NPV.

5.4 Other Feedstocks

The models make it reasonably simple to examine commercial use of other feedstocks to make ethanol, provided a minimal amount of laboratory and pilot plant data are available. Such data are available for a number of feedstocks, particularly those discussed in Chapter 3 above. Two examples will be presented here, bagasse in Hawaii and rice straw in Gridley, California.

5.4.1 Bagasse Processing

The bagasse conversion plant that was designed was to be located in Hawaii adjacent to an existing sugar refinery. The plant shares a number of utilities and other facilities already in place. A block flow diagram of the plant design is shown in Figure 5.4.1.

There are several differences between the block flow diagram for this plant and the one for corn fiber. First, there is no ethanol or thin stillage recycle; ethanol concentration in the product liquid is high enough that ethanol recycle is not necessary. Fresh water is injected into both the pretreater and the Doering mixer instead. Second, the entire distillation bottoms is sent to anaerobic digestion instead of just the liquid. There is no need to avoid anaerobic bacteria in the solids product with bagasse, since the solids will be burned for fuel and not sold as an animal feed. Third, there are no fusel oils generated from bagasse. Otherwise, the flow sheets are identical.

The capital cost for the facility in 1994 dollars was \$90 million. Like the corn fiber plant, the most expensive areas of the plant

are the SSF section and distillation; other significant areas of cost are the pretreatment and anaerobic digestion.

The cost of ethanol for this base case design is \$1.06/gallon. The ethanol price would increase \$0.12/gallon if enzyme was purchased rather than manufactured on site. Building a grass-roots plant would raise the capital cost to \$133 million and the cost of ethanol to \$1.23/gallon. The combination of building a grass-roots plant and buying enzyme would boost the ethanol price to \$1.35/gallon. Running the plant on bagasse (without sugar in the feed), but maintaining the \$40/ton price for the feedstock, would raise the cost of ethanol to \$1.17/gallon.

5.4.2 Rice Straw Processing

The rice straw conversion plant that was designed was to be located in the area of Gridley, California adjacent to an existing electric power plant using biomass as fuel. The plant shares utilities and other facilities already in place. A block flow diagram of the plant design is shown in Figure 5.4.2.

There are several differences between the block flow diagram for this plant and the one for corn fiber. First, there is a shredder block, that represents a flail to break up the rice straw bails rather than a size-reduction device. Water is added to the straw, after breakup, because the straw is very dry as-received, and water is needed in pretreatment. There is no fusel oil stream because none are generated from rice straw. And as with bagasse, the entire still bottoms is sent to aerobic digestion, since the solid product is a boiler fuel, not an animal food.

The capital cost for the facility in 1994 dollars was \$52.4 million; it is assumed that \$20 million of this capital is secured from DOE or a combination of government entities. The most expensive areas of the plant are the SSF section and distillation and other significant areas of cost are the pretreatment, enzyme plant and anaerobic digestion.

The cost of ethanol for this base case design is \$0.99/gallon. The ethanol price would increase to \$1.12/gallon if only \$10 million in government capital funding was available, and to \$1.26 if no government support was available. Building a grass-roots plant without government incentives would raise the cost of ethanol to a prohibitive \$1.66/gallon.

One way to reduce ethanol costs is to take advantage of economies of scale, and to build a larger commercial plant. For example, a 750 tpd feed rate would lower the cost of ethanol by about \$0.05/gallon, and raising feedrate to 1000 tpd would drop the cost of ethanol \$0.12/gallon from the base case.

6.0 Pretreatment Scale Up at NREL

The Amoco pretreater was disconnected from the old pilot plant facility in December, 1994 and shipped to Golden, Colorado. It was installed in early January, 1995 in the Alternative Feedstocks User Facility building at NREL.

The limits on throughput had been demonstrated shortly before the machine was moved. Once the equipment was in Golden, the heat needed to provide pretreatment temperatures at high throughput was provided by installing a circulating hot oil system, and larger acid and steam supply systems were purchased and installed. The machine started up on April 11, 1995, and a series of high-throughput tests was performed.

The Amoco Pretreatment Reactor (APR), supplied pretreated corn fiber to the NREL Process Development Unit from April 26 through May 9, 1995 at rates up to 180 lb/hr. The feedstock from a local corn wet mill was drier than the feedstock normally run in Canada, and solids levels were about 45%. The feed rate was very close to the 1 ton/day (dry) overall capacity of the PDU.

The quality of the pretreated fiber at the higher rates was excellent. High reactivity was attained with low concentrations of reversion inhibitors.

The metallurgy of the pretreater continues to be tested by Amoco at NREL. The Carpenter 20 parts that were sufficiently resistant to acid at low feed rates were worn away in the early NREL tests. Hastelloy and Incoloy parts in contact with acid held up well.

Scale up of pretreatment for commercial application will likely require tests in a vendor shop. It is not yet certain if sufficient data can be collected at the current small scale to design commercial equipment.

7.0 Business Development

The feedstock flexibility of the Amoco biomass-to-ethanol process provides an opportunity to assess a wide variety of feedstocks, and thus substantially improve the opportunity for successful commercialization. Figure 7.0.1 illustrates as the upper four boxes the variety of feedstock classes that were shown to work in the pretreating section of the process and to produce an intermediate useful for fermentation. In general, only changes in those process parameters under operator control were necessary to begin processing one feedstock rather than another.

Figure 7.0.1

Technology Market Overview

The market for biomass-to-ethanol conversion technology was analyzed to determine whether the technology being developed would have a combined market of sufficient size to justify its commercialization. What the specific requirements of each market would be that would influence its relative competitiveness was also addressed. Broad surveys were used to complement intensive assessment conducted in collaboration with industrial, academic, and governmental experts in the municipal waste, forest product, agriculture, and agricultural processing segments of the economy. The study of potential markets was limited to the production of ethanol in the United States.

General Findings

It was found that a multi-sector market for the conversion of waste biomass was possible, with a growth potential of 20+ billion gallons per year. Figure 7.0.2 provides a profile of the relative importance and growth potential of the identified market segments

Figure 7.0.2

Waste-Based Ethanol

Potential Supply

based on waste biomass alone. Summary descriptions of each segment are provided below.

Agricultural Processing Waste

The market for converting agricultural processing waste appears to be the one with the most near term potential for substantial ethanol production. In the course of producing refined products for market, the agricultural processing industry disposes of substantial quantity of waste biomass. Corn refining, to produce sweeteners (high fructose corn syrup), starches, and sometimes ethanol, is representative of this industry. It disposes of its corn fiber waste as animal feed (distillers dried grain and solubles, or DDGS). The market for DDGS values the product only based on its protein content--the residual starch, hemicellulose, and cellulose are not valued and add to shipping costs for the product.

To the corn refiner, conversion of the residual starch, hemicellulose, and cellulose in corn fiber to ethanol represents an opportunity to take advantage of a low value stream, and to manufacture a product with a 15+ percent return on invested capital. The cost of ethanol manufacture using Amoco technology is about one third of that of ethanol manufacture from a new facility using conventional technology and generating the same level of profitability. The forces encouraging the development of the corn fiber market segment are dominantly profit driven. Although ethanol currently benefits from a federal subsidy and some state subsidies, plants built with Amoco's current technology would be expected to be competitive even if the subsidies are removed at the end of the decade.

A similar market for Amoco technology can be envisioned in other sectors of the agricultural processing industry (wheat and other cereal grains, fruit and vegetable processing, etc.) But the size and character of these market segments have not yet been analyzed in detail.

Agricultural Field Waste

The market for technology to produce ethanol from agricultural field waste is likely to grow more slowly at first than, but ultimately to catch up with, the market for the conversion of agricultural processing wastes. In addition, once it is established and its characteristics become known, this market is likely to be the precursor for an "energy crop" industry in the next century.

The initial market for biomass-to-ethanol technology is expected to be generated from the imposition of government mandates, in general based on environmental/health considerations. The central theme in this market is the need of the farm community to dispose of wastes (straw, tree prunings, sugar cane bagasse, etc.) remaining after a

harvest in preparation for the next growing season. The traditional disposal technique has been open field burning, but this method has been banned in some areas and is expected to be phased out over the next few years in many others.

In some cases, it is possible to plow field waste back into the ground, but in others it is not. Biomass-to-ethanol technology can be used to remove the cellulose and hemicellulose fractions of this biomass and then convert them to ethanol, leaving the lignin fraction which is a high energy content, low sulfur, low alkali powder.

Projects based on biomass-to-ethanol technology applied to agricultural field waste conversion have tended to be associated with existing power facilities that can convert the residual lignin to electricity, thus reducing the capital requirements for infrastructure and boiler installation. Farmers' cooperatives or associations are also viewed as important stake-holders, since project profitability depends on the continuing availability of low cost feedstock, and the cost of waste streams has a tendency to increase once it has an established value in use. The potential size of this market segment is large (\$15+ billion potential investment in California alone). However the structure of owners' groups can become complex as the multiple stake-holders sometimes necessary to insure success are included.

Municipal Waste/Waste Paper

The market for waste paper conversion, although appealing from the perspective of a highly visible problem that could potentially be converted into an asset, was found to be smaller than its media image. Application sites were primarily located in large municipal areas with high land, construction, labor, and utility costs. Permitting and other governmental processes are such that predevelopment time and costs are expected to be considerable. A powerful, established waste management industry has made substantial investments in landfills with capacity to accommodate future growth. Recycling mandates and policies have been established that make the entry of any new means of creating value out of the waste stream, like the manufacture of transportation fuels, difficult. For these reasons it was projected that this feedstock would not contribute substantially to growth in the biomass to ethanol industry in the coming decades.

Forest Product Industry Wastes

The character of the market for biomass-to-ethanol technology in the forest product industry is similar to that for agricultural field wastes and municipal wastes from small cities: for the most part it is likely, near term, to depend on the existence of an infrastructure including a solids fired boiler for acceptable profitability. Most waste from the forest product industry is likely to be either collected and processed by one facility in a location to satisfy the needs of a group of mills, or to be used as supplemental feed for a facility processing agricultural field wastes or perhaps municipal wastes to ethanol.

"Energy Crops"

Longer term biomass-to-ethanol technology may undergo cost reductions sufficient to allow the widespread use of grown crops as feedstock for the manufacture of fuels and chemicals. In the short term the most likely use of crops as feedstock will develop as a supplemental feed to facilities based on the availability of agricultural processing or field wastes. For instance, switch grass might be grown on land with low productivity located near a corn refinery, and be used to supplement corn fiber as a feedstock for the biomass-to-ethanol unit. Over time however energy crops are likely to grow to the point where they make a major contribution to renewable fuels production as indicated in Figure 7.0.3.

Figure 7.0.3

Biomass-Based Ethanol

Potential Supply

Business Relationships

During the course of this study a variety of collaborations were established to evaluate various market and technology factors. Most of these collaborations were short term, but an ongoing working relationship developed between Amoco and Stone & Webster Engineering Corporation. As the study progressed it became apparent that it would be desirable to have an aggressive,

committed engineering firm involved in the technology and market development effort. To enable the commercial application of Amoco's biomass-to-ethanol technology to proceed most effectively, Amoco and Stone & Webster formed SWAN Biomass Company. That entity now is responsible for the combined commercialization program.