

Co-Production of Ethanol and Cellulose Fiber from Southern Pine: A Technical and Economic Assessment

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Abstract

It has been shown previously that hemicellulose can be extracted from loblolly pine by dilute acid hydrolysis, and that the remaining wood mass can be delignified to produce high quality cellulose fiber. In the work reported here, we have evaluated the technical and economic feasibility of co-producing ethanol and cellulose fiber from loblolly pine. Our analysis indicates that ethanol can be produced at a break-even cost of between \$2.00 to \$2.50/gal, when the unit value of co-produced fiber remains the same. The cost for ethanol produced this way is more expensive than ethanol produced by complete hydrolysis of the carbohydrates in loblolly pine or other biomass feedstock.

Introduction

Ethanol from lignocellulosic biomass has the potential to contribute substantially to bioethanol for transportation (1-5). Current estimates of biomass available in the U.S. as bioenergy feedstock on a sustainable basis are 368 million t/yr of forest-derived biomass and 194 million t/yr of agricultural residue (6). One projection is that, nationwide, the amount of lignocellulosic biomass available from agriculture could increase to between 540 million and 900 billion dry metric tons/yr by 2050, while the amount of forest-derived biomass available would remain nearly constant (6).

In this paper, we consider options for co-producing ethanol, cellulose fiber, and power from a single biorefinery processing loblolly pine. The analysis is based on the assumptions that (a) an ethanol plant is built on the site of an existing kraft pulp mill, and that (b) it is fully integrated with the pulp mill with regard to mass and energy. We examine some of the technical issues of integrating production facilities, and estimate the break-even selling price of ethanol, fiber, and power. Two baseline cases are also considered: stand-alone production of cellulose fiber only, and stand-alone production of ethanol in a greenfield plant.

Basis

The basis for this study is a biorefinery complex that processes loblolly pine to produce ethanol and cellulose fiber, and power. The biorefinery consists of an ethanol plant fully integrated with a kraft pulp mill. In the biorefinery, wood is debarked and comminuted to produce 3-5 mm thick flakes (chips). Wood mass is extracted from the chips, and carbohydrates in the extract are converted to ethanol.

The wood consumption rate in the biorefinery considered here is not constant, but changes with product mix. We have employed the constraint that the rate of wood consumption is adjusted so that the digester capacity available in the pulp mill is utilized 100% for either acid prehydrolysis of hemicellulose or delignification of the wood chips after acid prehydrolysis. Without the ethanol plant, the kraft pulp mill processes 2700 dry metric tons/day of bark-free loblolly pine.

Some of the biomass input to the biorefinery is converted to waste, either from the acid prehydrolysis operations and fermentation (as ethanol plant residues) or from delignification (as black liquor). These wastes represent significant energy streams. The energy value of the ethanol plant residues is approximately equivalent to the ethanol product. The energy value of the black liquor is 10 to 20 times that of the ethanol produced. These biomass energy streams are dewatered and burned to generate high pressure steam. An extraction turbine is used to generate power. Process steam is extracted from the turbine at three pressures. The steam supply and demand for the entire plant are balanced by utilizing purchased biomass as fuel to generate steam and power, or by exporting excess biomass fuel. The power demand for the biorefinery is balanced by either purchasing power from the grid or by selling excess power.

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The conceptual process evaluated here follows qualitatively the process schemes outlined by Wooley et al. (7) and Hamelinck (8) up to the stage where cellulose would be hydrolyzed completely. In the conceptual process evaluated here, cellulose is recovered as fiber via alkaline delignification instead of being hydrolyzed to sugars. Figure 1 shows the components of the ethanol plant as integrated with a kraft pulp mill. Mass and energy flows between the ethanol plant and pulp mill are indicated.

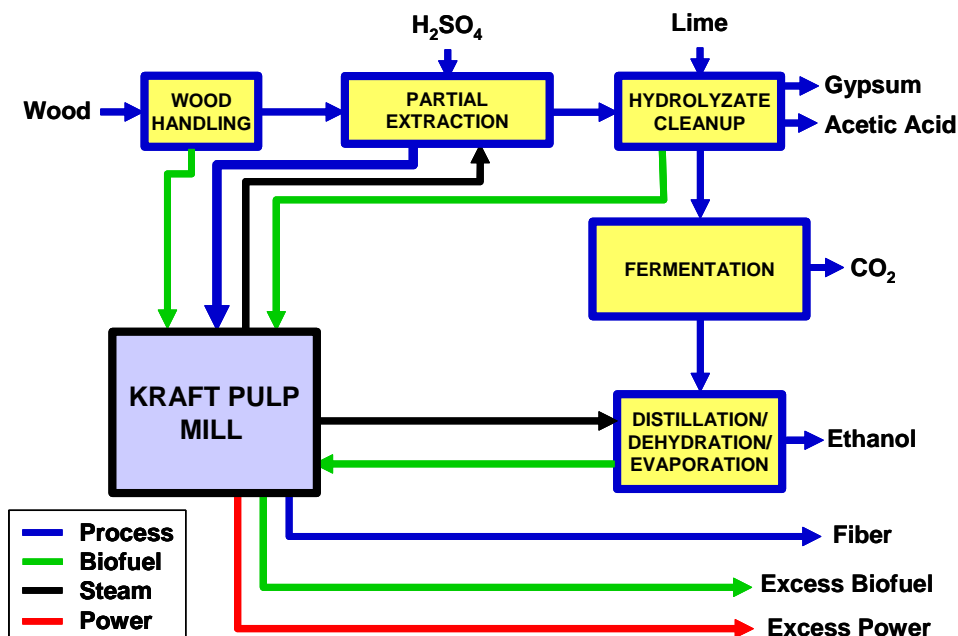


Figure 1. Conceptual diagram of an ethanol plant integrated with a kraft pulp mill.

Acid Prehydrolysis

Loblolly pine consists of nearly 65% cellulose and hemicellulose that can be converted to sugars, lignin as a third major component, and other constituents as shown in Table 1.

Table 1. Chemical constituents of loblolly pine.

Cellulose	43.6%
Hemicellulose convertible to sugars	
Mannan	10.8%
Galactan	2.2%
Xylan	6.6%
Arabinan	1.6%
Acetal	1.1%
Uronic anhydride	3.7%
Lignin	26.8%
Extractives	3.2%
Ash	0.4%
Total	100.0%

Prehydrolysis with dilute sulfuric acid was selected as the means of extracting hemicellulose from debarked wood chips. This technology is well established. It provides higher hemicellulose yields and less fermentation inhibitors than do other methods, although it produces gypsum as a low value by-product.

Dilute acid extraction of hemicellulose from loblolly pine yields soluble sugars (xylose, mannose, arabinose, and galactose). It also converts some of the cellulose to glucose, and part of the lignin is solubilized. Acetic acid is produced by cleavage of acetyl from the hemicellulose. Some of the pentose and hexose sugars are degraded to furfural, hydroxymethyl furfural, and other compounds.

In this study, we considered a biorefinery in which between 6% and 18% of the debarked wood mass was extracted with dilute (1.0%) sulfuric acid in water at 150°C, using a 3.0 acid solution/wood mass ratio. The duration of acid prehydrolysis was from 24 to 115 min, depending upon the mass fraction of wood removed. A proprietary model for the yield of wood mass removed versus acid concentration, temperature, and time, developed using data from several sources (9-11) and data reported in this paper were used to calculate the time required for prehydrolysis in each case. Figure 2 shows some of the results obtained from this model.

Hydrolyzate Conditioning

Degradation products of pentose and hexose sugars (primarily furfural and hydroxyl methyl furfural), acetic acid produced from cleavage of acetyl groups on hemicellulose, and other contaminants (terpenes, resin acids, etc.) are fermentation inhibitors. They must be removed from the hydrolyzate prior to fermentation. The contents of the prehydrolysis reactor are flashed to separate water, some of the acetic acid produced, most of the furfural and hydroxyl methyl furfural produced, and terpenes and other volatile matter from wood. The flashed vapor is condensed to provide process heat. The organic matter in the condensate is used as a process fuel. The remaining hydrolyzate solution is separated from the wood chips by filtration. The remaining acetic and sulfuric acids are removed by continuous ion exchange, using ammonia as regenerant. The product stream is neutralized with excess lime. This generates gypsum as a low value by-product.

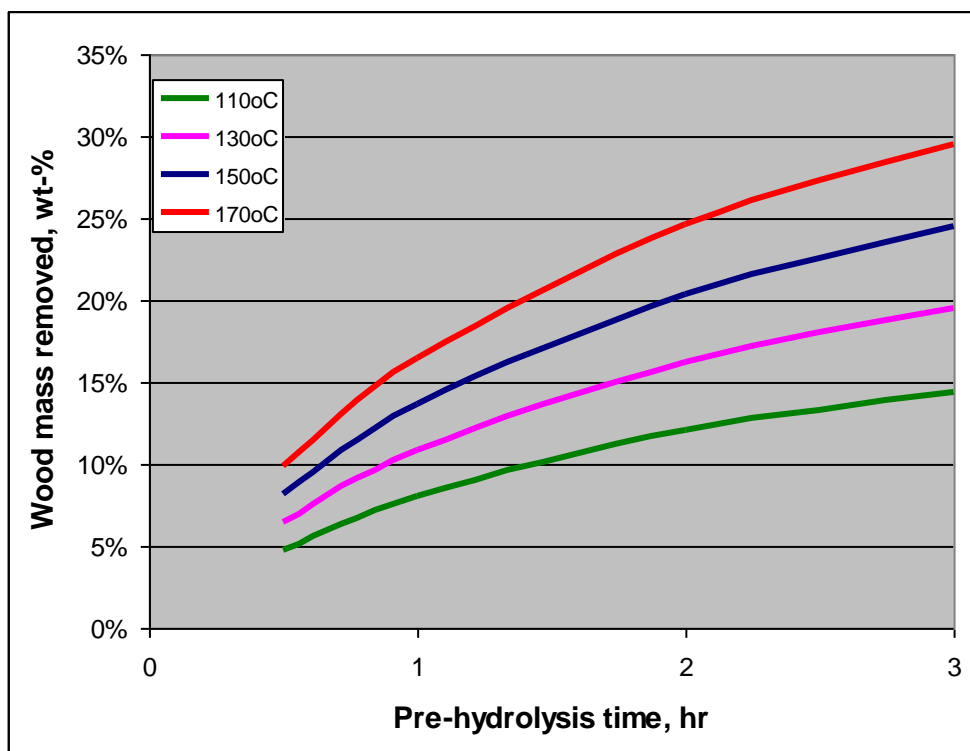


Figure 2. The relationship between wood mass removed, pre-hydrolysis temperature, and pre-hydrolysis time with 1% sulfuric acid applied based on dry wood mass, 3:1 liquor to wood ratio.

Fermentation

Fermentation is carried out after inhibiting contaminants have been removed from the hydrolyzate. Table 2 contains the stoichiometric factors and conversion efficiencies that were used in calculating the yield of ethanol produced

from extracted carbohydrates. The relatively high conversion efficiency used for pentose sugars is an optimistic estimate that assumes that on-going research (e.g. 12-14) will make it possible to ferment most of the pentose sugars together with glucose.

Table 2. Stoichiometric factors and conversion efficiencies for carbohydrates to ethanol.

Stoichiometric factors	
C5 carbohydrates to pentoses	1.136
C6 carbohydrates to hexoses	1.110
Pentoses to ethanol	0.511
Hexoses to ethanol	0.511
Conversion efficiencies	
Pentoses to ethanol	85%
Hexoses to ethanol	92%

Ethanol Recovery

The products from fermentation are an ethanol-water stream that contains unreacted sugars and suspended biomass, and carbon dioxide. Ethanol and water are steam stripped from the aqueous fermentation product to produce a 35 wt-% ethanol/65 wt-% water overhead product which is then distilled to 92.5 wt-% ethanol and dehydrated with molecular sieves.

The bottoms from the steam stripper are concentrated by multiple-effect evaporation to 50 wt-% solids and burned to generate steam.

Extraction of hemicellulose and ethanol production generates a significant quantity of aqueous waste. The ethanol plant wastes would normally be burned with other fuel in a biomass boiler, but could be burned in a recovery boiler if it had the capacity to process additional fuel input.

Experimental Delignification of Acid-Extracted Wood Chips

Ragauskas et al. (15) conducted a series of experiments in which wood mass was extracted from loblolly pine wood chips by dilute acid hydrolysis, and the wood chips were subsequently delignified to produce cellulose fiber. The results from that work are summarized here:

- Wood chips pre-hydrolyzed with dilute sulfuric acid to extract up to at least 12% of the dry wood mass can subsequently be delignified to produce cellulose fiber.
- Delignification of pre-hydrolyzed wood chips yields fiber with a lower lignin content than fiber from untreated wood chips delignified at the same conditions.
- During delignification, the lignin content of cellulose fiber from wood chips that have been pre-hydrolyzed with dilute sulfuric acid decreases more rapidly than for non-prehydrolyzed wood chips.
- The strength of handsheets made from fiber from pre-hydrolyzed wood was between 83 and 100% of the strength of handsheets made from fiber from untreated wood chips.

One important implication of these results is that shorter processing times would be required to achieve the same degree of delignification for wood chips pre-hydrolyzed with dilute sulfuric acid.

A proprietary model for yield and kappa number versus delignification conditions for pre-hydrolyzed loblolly pine chips was developed using published data from three sources (9-11) and data presented in this paper. A correlation developed previously by McDonough (16) was used to predict the yield of fiber and the carbohydrate-lignin selectivity when wood was delignified after acid prehydrolysis.

Table 3 shows the conditions employed during dilute acid prehydrolysis and kraft delignification. Table 4 compares the measured wood mass extracted and kappa numbers for the fiber produced with values predicted by the

proprietary extraction and delignification model in *BioRefOpt*TM. The agreement between the data and predicted values is sufficient for use of the model in preliminary process design calculations.

Table 3. Acid pre-hydrolysis and kraft delignification conditions employed.

Acid Prehydrolysis Conditions	
Temperature;	150°C
Time, hr:	0.5, 1.0
H ₂ SO ₄ , wt-% of dry wood	0, 0.2, 0.5%
Liquor/Wood Ratio	5:1
Post Extraction Washing?	yes
Kraft Delignification Conditions	
Maximum temperature:	165°C
H-factor:	1294
Sulfidity:	30%
Effective alkali charge, wt-% of dry wood	16%
Ratio of liquor to wood	4:1

Table 4. Comparison of measured and predicted wood extracted by pre-hydrolysis and kappa number of cellulose fiber produced by delignifying the wood after prehydrolysis. The pre-hydrolysis and delignification conditions are those in Table 3.

Duration of Pre-hydrolysis, hr	H ₂ SO ₄ charge, wt-% dry wood	Mass % Wood Extracted		Kappa Number ^a	
		Measured	Predicted	Measured	Predicted
0.5 hr	0.0%	5%	4.5%	24.4	23.5
0.5 hr	0.2%	5%	6.0%	21.0	22.0
0.5 hr	0.5%	8%	6.7%	19.7	21.4
1.0 hr	0.0%	8%	7.5%	21.4	20.7
1.0 hr	0.2%	10%	10.0%	16.8	18.9
1.0 hr	0.5%	12%	11.1%	17.5	18.2

^a1 kappa number unit is equivalent to approximately 0.15 wt-% lignin in the fiber produced.

Results

Distribution of Wood Mass

Prehydrolysis of loblolly pine chips with dilute H₂SO₄ removes hemicellulose from wood, but it also degrades part of the cellulose to glucose and removes acid-soluble lignin and some of the extractives (17). Figure 4 shows the calculated distribution of wood components between the acid hydrolyzate, fiber mass, and black liquor solids as a function of fractional wood mass removed during acid prehydrolysis. These results are for loblolly pine prehydrolyzed and delignified at the conditions indicated in Figure 3.

After acid prehydrolysis the extent of alkaline hydrolysis of cellulose increases during kraft delignification (18) This is indicated by the decreasing fraction of cellulose in wood that is retained in the fiber mass as well as the increasing amount of cellulose degradation products in black liquor (see Figure 4). The amount of hemicellulose retained as fiber also decreases, albeit more slowly, with increasing wood mass extracted.

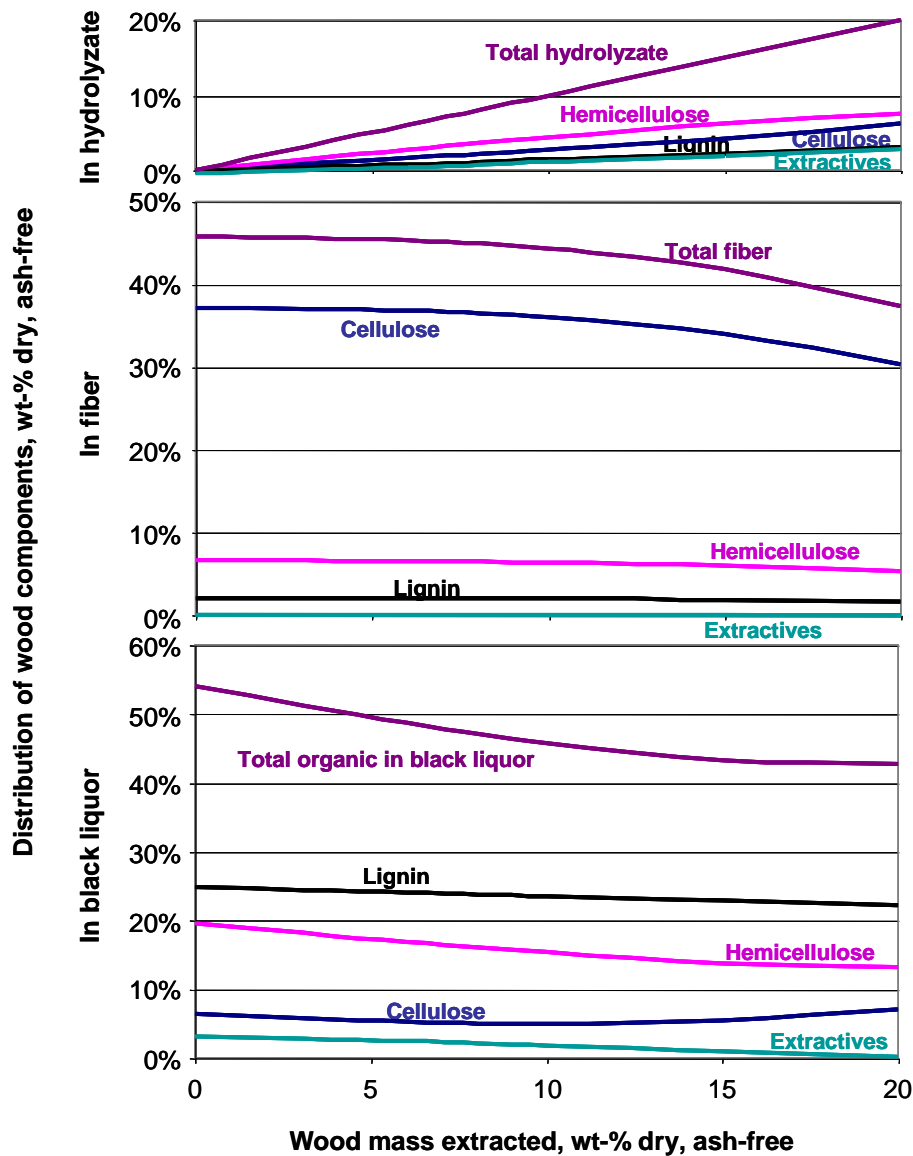


Figure 4. Distribution of wood components between prehydrolyzed, fiber mass, and black liquor for loblolly pine subjected to partial carbohydrate extraction and subsequent kraft delignification.

Utilization of Pulp Mill Equipment

In the cases of co-production of ethanol and cellulose fiber, it may be more cost-efficient to utilize pulp mill and bleach plant equipment in part for ethanol production rather than construct entirely separate equipment for that purpose. The most expensive additional equipment would be pressure vessels for extraction of hemicellulose prior to delignification. This is because no matter how much hemicellulose is extracted, all of the wood has to be processed in the extraction vessels. Other parts of the ethanol plant need to process only the biomass extracted, the ethanol produced, and the residual matter from ethanol production. The size of the equipment required for these operations will depend mainly on the amount of wood extracted and not on the total amount of wood processed.

In this study, we divided assignment of the pulping digesters to delignification or pre-extraction. We assigned the capacity of each in accordance to the amount of wood mass extracted prior to delignification, with the constraint that the digester capacity is utilized 100%. Figure 5 shows the relative utilization of the digesters for each purpose.

In practice, corrosion resistance is an issue that needs to be considered before process equipment designed for alkaline delignification is converted to mildly acidic pre-hydrolysis applications.

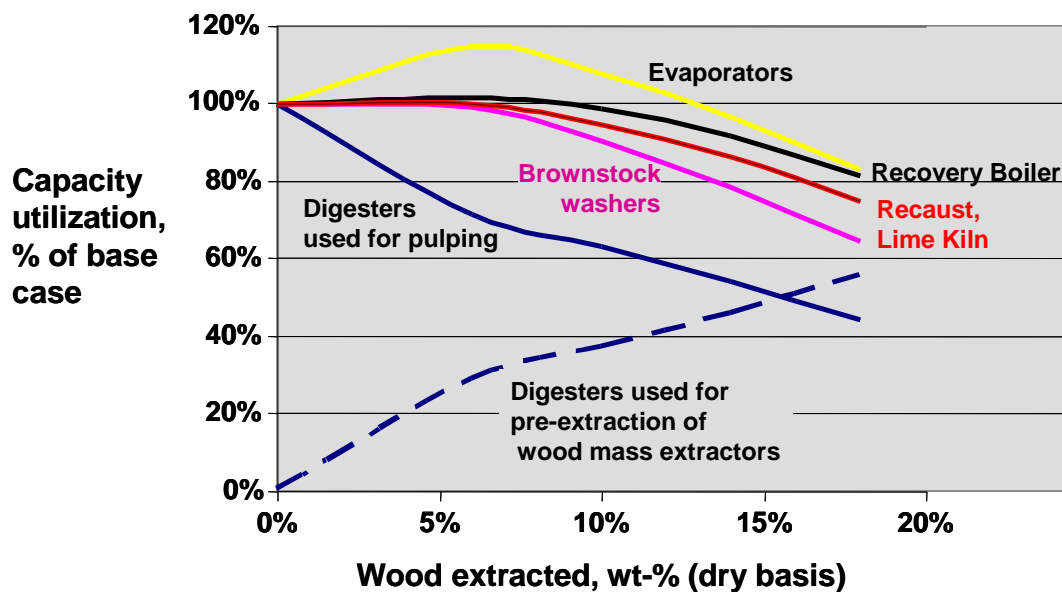


Figure 5. Utilization of the capacity of pulp mill equipment for delignification versus wood mass extracted for ethanol production. The pulping digester capacity utilized for extraction of wood mass for ethanol production is also shown.

Production Capacity for Ethanol and Fiber

One result of dividing the digester capacity between pre-extraction and delignification is that, as more wood mass is extracted, less wood is consumed and less cellulose fiber is produced (see Table 3). Another result is that most of the other equipment in the pulp mill is under utilized (see Figure 5). The black liquor evaporators are the exception. Because of the additional water input to the pulp mill from the wet, pre-extracted chips, the evaporation requirement first increases above the base case (cellulose fiber only), but then decreases. In sizing the equipment required for ethanol production from pre-extracted wood mass, we assumed that underutilized black liquor evaporation capacity would be used to concentrate aqueous waste from ethanol production. Similarly, we assumed that any underutilized recovery boiler capacity would be used to burn concentrated ethanol plant waste. It was assumed that additional evaporation equipment and a biomass waste boiler steam generation would be purchased to provide the evaporation capacity and steam generation capacity needed beyond the available capacity provided by the black liquor evaporators and recovery boiler.

Table 3 shows the wood consumed and the products resulting from the various cases analyzed. The left and right columns contain results respectively for production of cellulose fiber but no ethanol, and ethanol but no fiber. These two cases serve as bounds with which to compare the cases where both ethanol and cellulose fiber are produced. Table 4 shows how the energy input as wood, fuel oil, and power is distributed among the products of the biorefinery.

Economic Assessment

For the cases where ethanol was produced from hemicellulose extracted from wood, a break-even selling price for ethanol, was calculated by forcing the incremental profit from the ethanol plant to be zero. This imposes all additional capital and operating costs beyond those of the original pulp mill on the ethanol plant. In the case where

ethanol is produced in a stand-alone, greenfield plant from the completely hydrolyzed wood carbohydrates, a break-even selling price for ethanol was calculated by forcing the net profit from the ethanol plant to be zero.

The revenues and costs for each scenario and the break-even selling prices for ethanol determined under these assumptions are shown in Table 5. These results show that the break-even price of ethanol depends strongly on the annual capital recovery rate. It may depend strongly on the cost of wood and fuel oil, and the value of power, as these variables are the most dominant ethanol-related costs or revenues.

Figure 6 shows the sensitivity of the break-even price for ethanol to four variables: the cost of wood, the cost of power, the cost of fuel oil, the selling price of excess biofuel, and the annual capital recovery factor. The results are for the case where 10% of the wood mass is extracted from loblolly pine. These results show that the break-even price of ethanol depends strongly on the annual capital recovery rate and on power costs. The slope of the break-even ethanol price versus the value of power is negative because the biorefinery is a net producer of power. The other three variables have only a small impact on the break-even price of ethanol.

Table 3. Wood consumed and products generated from the various cases analyzed.

Bark-free wood extracted for ethanol production	0%	6%	10%	14%	18%	71.2%
Wood purchased (bark-free basis), t/a	923,145	888,773	816,548	786,608	683,365	1,007,400
Ethanol produced, t/a	0	19,904	31,741	41,724	48,335	252,204
Unbleached fiber produced, t/a	422,374	406,817	360,080	330,825	271,077	0
Gypsum produced, t/a	0	7,991	7,668	38,653	35,218	83,680
Exportable power, MWe	19.4	29.9	28.4	27.8	25.3	-4.2
Exportable wood waste, t/a	79,254	13,918	42,479	93,233	113,888	470,410

Table 4. Distribution of Energy Value Among Products

Bark-free wood extracted for ethanol production	0%	6%	10%	14%	18%	71.2%
Energy input rate (as MW)						
Wood (incl bark)	638.0	614.3	564.4	543.7	472.3	696.3
Fuel oil	21.5	20.9	19.2	18.5	16.1	
Power						4.2
Total	659.5	635.2	583.6	562.2	488.4	700.5
Energy output rate (as MW)						
Ethanol	0	20.4	32.5	42.7	49.5	258.2
Unbleached fiber	206.1	198.5	175.7	161.4	132.3	
Exportable power	19.4	29.9	28.4	27.8	25.3	
Exportable wood waste	53.2	9.3	28.5	62.6	76.4	315.8
Total	278.7	258.1	265.1	294.5	283.5	573.9
Energy output, % of input						
Ethanol	0.0%	3.2%	5.6%	7.6%	10.1%	36.9%
Unbleached fiber	31.3%	31.3%	30.1%	28.7%	27.1%	
Exportable power	2.9%	4.7%	4.9%	4.9%	5.2%	
Exportable wood waste	8.1%	1.5%	4.9%	11.1%	15.7%	45.1%
Total	42.3%	40.6%	45.4%	52.4%	58.0%	81.9%

Table 5. The costs and income by item for the various cases in Table 3. These results are for a 15% annual capital return factor.

Main Products	Ethanol + Fiber					Ethanol
	0%	6%	10%	14%	18%	
Wood mass extracted						71.2%
Break-even price for ethanol, \$/gal		\$2.03	\$2.16	\$2.22	\$2.52	\$1.14
Costs (\$million/a)						
Wood (\$63.80/ODt)	\$64.856	\$67.097	\$64.384	\$64.909	\$59.141	\$63.688
Power (\$60.00/MWh)						\$2.036
Fuel oil (\$65/bbl)	\$7.027	\$6.837	\$6.281	\$6.051	\$5,259	-
Chemicals	\$15.867	\$15.234	\$13.568	\$13.582	\$11.316	\$3.982
Fixed Operating Costs ^a		\$0.849	\$1.619	\$1.779	\$2.465	\$12.863
Capital Recovery (15%)		\$9.282	\$7.439	\$6.816	\$4.148	\$28.535
Total Cost (\$/a)	\$87.750	\$99.299	\$93.291	\$93.139	\$82.329	\$111.104
Revenue (\$million/a)						
Ethanol value at break-even price		\$13.545	\$22.985	\$31.039	\$40.811	\$96.155
Bleached fiber (\$270/ODt)	\$140.791	\$135.606	\$120.027	\$110.275	\$90.359	
Excess biomass fuel (\$29.70/ODt)	\$2.378	\$0.418	\$1.274	\$2.797	\$3.417	\$14.112
Excess power (\$60.00/MWh)	\$9.402	\$14.471	\$13.749	\$13.461	\$12.210	
Gypsum (\$10/ODt)	\$0.000	\$0.080	\$0.077	\$0.387	\$0.352	\$0.837
Total revenue	\$152.571	\$164.119	\$158.111	\$157.959	\$147.149	\$111.104
Profit (= total revenue – total cost)^{a,b}	\$64.820	\$64.820	\$64.820	\$64.820	\$64.820	\$0.000

^a For this study, a value of cellulose fiber, defined as the difference between the selling price and the fixed operating costs plus capital recovery for producing it, was assumed to be \$270/ODt.

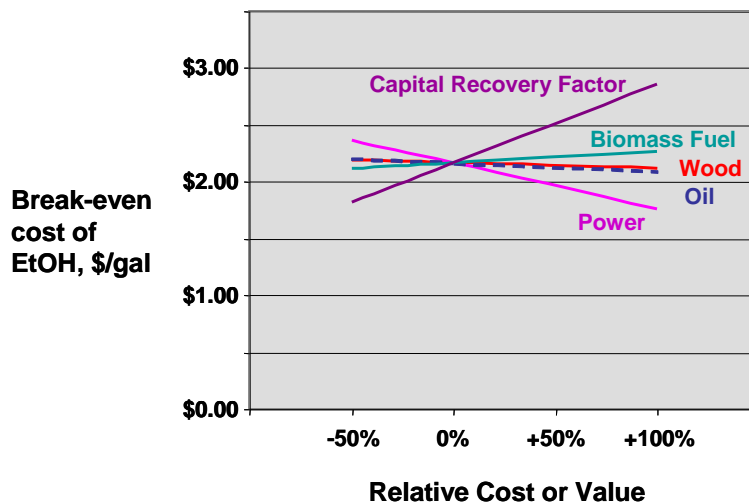


Figure 6. Sensitivity of the break-even price for ethanol to the cost of wood, the cost of power, the selling price of excess biofuel, and the annual capital recovery factor.

The estimated break-even price of producing fuel-grade ethanol by fermentation of sugars from various feedstock and the capital investment required has been reported by a number of investigators. Table 6 compares some recent results. They indicate that ethanol produced from carbohydrates from loblolly pine is comparable with ethanol from other feedstock in terms of break-even unit price and capital investment required. Co-production of ethanol and cellulose fiber may be less attractive.

Table 6. Comparison of results this and other studies for production of ethanol by fermentation using various feedstocks.

Feedstock	Ethanol 10 ⁶ gal/yr	Ethanol Yield gal/metric ton biomass	Breakeven Price, \$/gal	Total Installed Cost, \$10 ⁶
Dry Milled Corn (19)	25	114	\$0.88	\$31.40
Corn Stover (19-21)	25-69	72-90	\$1.07-1.50	\$42-218
Yellow Poplar (7)	52	68	\$1.44	\$273
Spruce (22)	67	84	\$1.97-2.08	\$113-119
So. Pine, hydrolysis of carbohydrates (23)	84	93	\$1.07-1.74	\$190
So. Pine, pre-extraction of carbohydrates for ethanol	6-16		\$2.03-2.52	\$66-28

Conclusions

Ethanol from loblolly pine is very likely to be competitive with ethanol from other sources when the carbohydrate content of the wood is utilized fully for ethanol production. High conversion of cellulose to sugars via enzymatic hydrolysis is needed to improve the profitability of ethanol produced via this route.

Co-production of ethanol and fiber may be profitable, but will be less so than production of ethanol only. More rapid, efficient, and selective hemicellulose extraction methods are needed to improve the profitability of co-production of ethanol and fiber.

Agents for more rapid and efficient conversion of pentose sugars are required in both cases.

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