

KRAFT MILL BIOREFINERY TO PRODUCE ACETIC ACID AND ETHANOL: TECHNICAL ECONOMIC ANALYSIS

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The “near neutral hemicellulose extraction process” involves extraction of hemicellulose using green liquor prior to kraft pulping. Ancillary unit operations include hydrolysis of the extracted carbohydrates using sulfuric acid, removal of extracted lignin, liquid-liquid extraction of acetic acid, liming followed by separation of gypsum, fermentation of C5 and C6 sugars, and upgrading the acetic acid and ethanol products by distillation. The process described here is a variant of the “near neutral hemicellulose extraction process” that uses the minimal amount of green liquor to maximize sugar production while still maintaining the strength quality of the final kraft pulp. Production rates vary between 2.4 to 6.6 million gallons per year of acetic acid and 1.0 and 5.6 million gallons per year of ethanol, depending upon the pulp production rate. The discounted cash flow rate of return for the process is a strong function of plant size, and the capital investment depends on the complexity of the process. For a 1,000 ton per day pulp mill, the production cost for ethanol was estimated to vary between \$1.63 and \$2.07/gallon, and for acetic acid between \$1.98 and \$2.75 per gallon depending upon the capital equipment requirements for the new process. To make the process economically attractive, for smaller mill sizes the processing must be simplified to facilitate reductions in capital cost.

Keywords: Biorefinery; Kraft mill; Hemicellulose extract; Green liquor; Ethanol; Acetic acid

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INTRODUCTION

The concept of an Integrated Forest Products Biorefinery (IFBR) has been advanced by a number of investigators, who envision converting woody biomass, dedicated annual crops, and municipal waste into bio-energy and basic chemicals. One biorefinery concept involves extracting hemicelluloses, which normally end up in the black liquor of kraft pulp mills, prior to pulping, and using the extract for the production of ethanol and acetic acid (Van Heiningen 2006). The extracted liquor undergoes hydrolysis, separation of lignin, liquid-liquid extraction to separate acetic acid and furfural from monomeric sugars, fermentation, and distillation for the production of ethanol, acetic acid and furfural. A technical economic evaluation of the near-neutral hemicellulose extraction process was published by Mao and co-workers (Mao et al. 2008) assuming mixed southern hardwood chips as the feedstock and using 3% green liquor to extract the wood chips. The main purpose of the present work is to extend this analysis to an existing hardwood kraft mill located in the northeast with its supply of mixed northeast hardwood chips: birch, beech, maple, and poplar. In this analysis an attempt was made to determine the economy feasibility of building a commercial biorefinery that

is co-located at an existing kraft pulp mill and is fully integrated with the mill in terms of utilities and waste treatment. An attempt was made to maximize the production of ethanol by using a minimal amount of green liquor for hemicellulose extraction.

Contrary to the present study in which mixed northern hardwood chips are extracted at cooking temperature with a green liquor solution of low alkalinity to approximately neutralize the acids released upon treatment of the chip-liquor mass, pre-extraction of poplar wood chips at strong alkaline conditions (1-2 Molar NaOH at L/W of 4kg/L) and relatively low temperatures (50 – 90°C) was recently reported by Al-Dajani and Tschirner (2008). Under these conditions about 40-50 kg of hemicellulose oligomeric sugars could be extracted per ton of wood without detrimental effect on overall pulp yield when the extracted wood was subjected to modified kraft pulping. In a recent simulation of this process by Huang et al. (2010), the extracted hemicellulose sugars were converted to ethanol and the economics of ethanol production integrated in a kraft pulp mill were determined. A minimum selling price for ethanol of \$3.41/gallon for a wood feed rate of 2000 dry metric tonne/day was predicted. Since the hemicelluloses are extracted as oligomers they must be hydrolyzed to monomers before fermentation to ethanol. In the study of Huang et al. (2010) the hemicelluloses are first separated from the caustic solution using nanofiltration and then hydrolysed into monosugars using 1.1% sulfuric acid at 190 °C for 2 minutes. In the present study we used as input for the hydrolysis the recent results published by Um and van Walsum (2009) who investigated the acid hydrolysis of a concentrated mixed northern hardwood hemicellulose extract obtained by the same green liquor process as reported on in the present study.

Process Description

The conceptual biorefinery process is shown in Fig. 1, which illustrates the unit processes required for hemicellulose extraction and conversion to ethanol, acetic acid, and furfural. They include wood extraction for hemicellulose removal, flashing of the extract to produce preheating steam that is used to preheat the chips, recycling a portion of the flashed liquid extract back to the extraction vessel for the purpose of raising the solids content of the extract, acid hydrolysis using sulfuric acid for conversion of the oligomeric carbohydrates into monomeric sugars and cleavage of lignin-carbohydrate covalent bonds, filtration to remove precipitated lignin, liquid-liquid extraction followed by distillation to remove acetic acid and furfural from the sugar solution, liming to raise the pH to that required for fermentation of five and six-carbon sugars to ethanol, filtration of calcium sulfate, and finally distillation and upgrading the product to pure ethanol (99+%). It should be noted that glucuronic acid, which originates from 4-O-methyl- α -D glucuronoxylan, was not assumed to be converted to ethanol. Extraction of wood chips using 1% green liquor is considered to be the minimum amount of alkali required to preserve the properties of the kraft pulp. Evaporation to raise the carbohydrate content in the extract was found to be uneconomic compared to recycling liquor back to the extraction vessel and was not included in the process.

Process advantages

A major advantage of the process is that when sufficient alkali is used in the extraction step the pulp yield and physical properties of the brownstock pulp remain

essentially the same as that of conventional kraft pulp when compared to extraction with water. A second advantage of the “near-neutral” extraction process is that the lime kiln is off-loaded because less white liquor is needed for pulping, since the wood is partially cooked using green liquor. This change would allow a mill to potentially increase pulp production if the lime kiln is the bottleneck in the kraft process. Also, as the pH of the extraction liquor increases, the extent of removal of acetyl groups removed from hemicelluloses will increase and the concentration of sodium acetate in the extract, hence by-product acetic acid production will increase (Genco et al. 2008). Finally, a new feedstock stream of sugars is produced, which may be used for the production of biofuels and renewable chemicals.

Process disadvantages

Similar to all pre-extraction processes, since a portion of the wood is extracted, less organic solids are available to generate steam and electrical energy compared to a conventional kraft process. A disadvantage, when compared to auto hydrolysis-based water extraction, is that the concentration of carbohydrates in the extract is lower and will contain spent sodium salts originating from the green liquor. These two disadvantages raise the capital cost and have a negative aspect on the economic production of biofuels such as ethanol via biochemical processes. Also, the process involves several changes in pH which cause the operating cost to increase. Lastly, because green liquor is used as the final pH of the extract decreases, sodium carbonate (Na_2CO_3) decomposes to CO_2 . However pure water extraction also leads to CO_2 release due to decomposition of glucuronic acid, as shown by Leschinsky et al (2009).

TECHNICAL ANALYSIS

Extraction Data Used in Design

Green liquor extraction data published by Genco et al. (2008) formed the basis for the technical economic evaluation presented here. Experiments were conducted with green liquor application rates of 0, 2, 4, and 6% based upon wood using total titratable alkali (Table 1).

Table 1. Chemical Composition of Green Liquor used in Design (Genco et al. 2008)

Chemicals	Value
Sodium hydroxide (NaOH)	9.0 g/l as Na_2O
Sodium sulfide (Na_2S)	29.1 g/l as Na_2O
Sodium Carbonate (Na_2CO_3)	70.0 g/l as Na_2O
TTA	108.1 g/l as Na_2O

In the experiments, 0.05% anthraquinone (AQ) (based on wood) was added during extraction to preserve the final pulp yield (Sjöström 1981). The extraction experiments were performed at a liquor-to-wood ratio of 4 for 110 minutes at 160 C in an electrically heated circulating digester. These conditions gave an H-factor of approximately 750 hours.

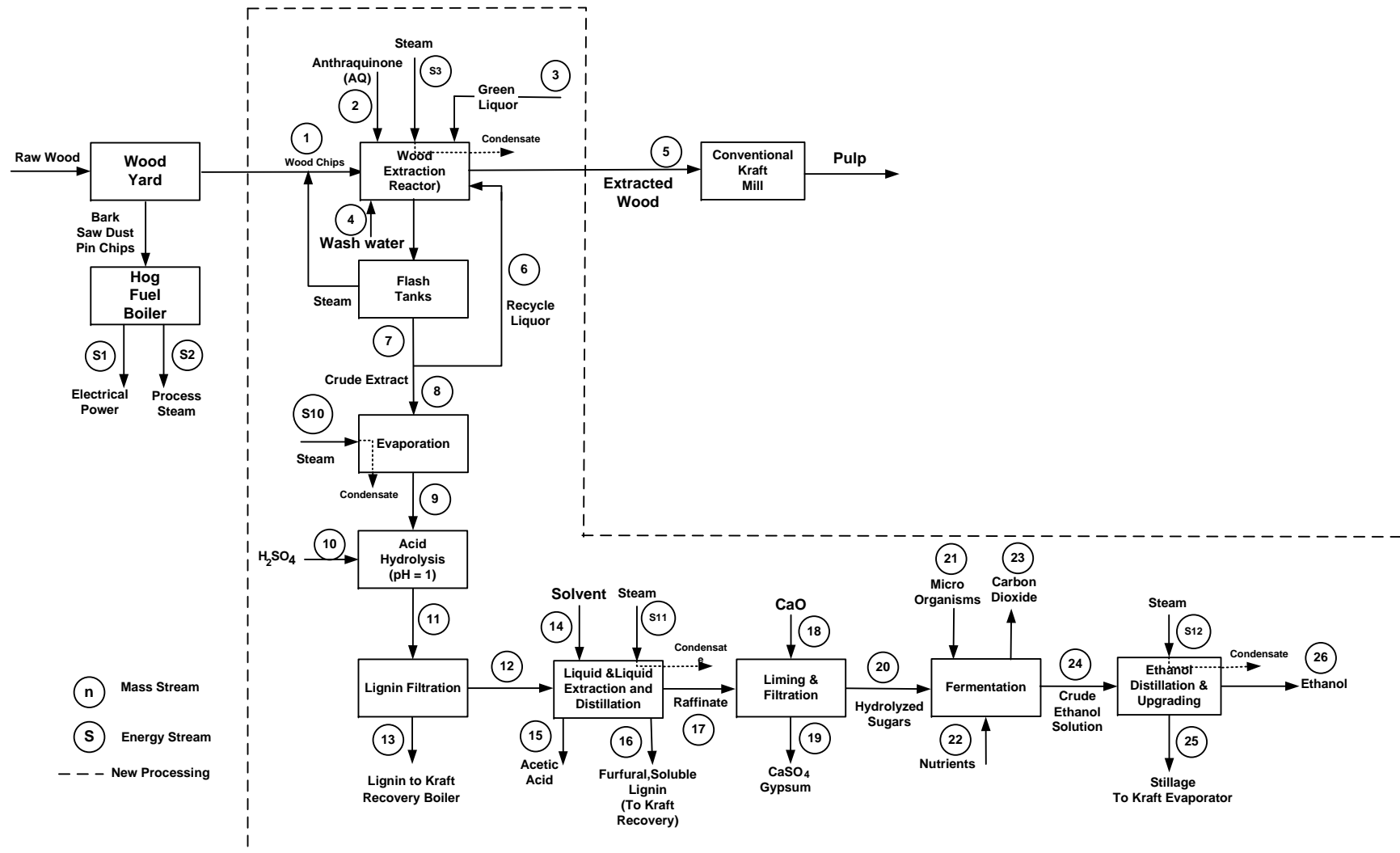


Fig. 1. Modified kraft pulp mill for the production of acetic acid and ethanol

The H-factor is based on an Arrhenius equation and combines the effects of time and temperature during the kraft process (Gullichsen and Paulapuro 1999). The H-factor was developed for correlating the kinetics of lignin reactions. It has been found that the H-factor can be used to correlate hemicelluloses extraction data using green liquor as the solvent. Conceptually, the H-factor is similar to the pre-hydrolysis P-factor used to correlate data on hemicelluloses removal by steam or water (Sixta 2006). Use of the H-factor as a correlating parameter for hemicellulose extraction is thought to work well because the xylan and mannan polymers are linked to lignin (Fengal and Wegener 1984). Thus, the removal of hemicelluloses is directly related to the removal of lignin and the data can be correlated by the H-factor.

The partially cooked chips following extraction were then cooked using either the soda process or the kraft process to give a final unbleached pulp of kappa number 16 to 18. Kraft cooks with 15% effective alkali (EA) were used as a control. For the partially macerated wood following green liquor extraction, the alkali used in the kraft pulping experiments was reduced to maintain a constant value of 15% for the combined value of the total titratable alkali (TTA) used in the green liquor extraction and the EA used in the kraft cook [$15\% = (TTA)_{GL} + (EA)_{Cook}$].

An existing kraft pulp mill producing bleached hardwood pulp was considered as the base case. For the IFBR version the pulp production was maintained constant and the hemicellulose extraction process was added to the kraft fiber line (Fig. 1). The methodology was an extension of that published by Mao et al. (2008). The feedstock to the biorefinery was assumed to be an equal mixture of birch, maple, and poplar of the composition used in the laboratory experiments reported by Genco et al. (2008). The extraction was assumed to occur in a separate impregnation vessel prior to the continuous digester for pulp production.

Process Simulation

The simulation model for the modified kraft pulp mill first was developed primarily using the WinGEMS computer code. The energy balance calculations associated with distillation and liquid-liquid extraction were performed using ASPEN-Plus software. Capital and operating cost for the process were estimated by standard methods (Turton et al. 2003; Peters and Timmerhaus 1991).

Extraction Process

The charge of green liquor used in the pre-extraction was assumed to be about 1% as TTA . Extraction was assumed to occur in a continuous digester. Extraction conditions, pulp yield, extract composition, and pulp physical properties were assumed to be similar to those determined in the laboratory experiments. Nine percent (9%) of the wood was assumed to be removed during the extraction process in accordance with the laboratory data (Genco 2008). The charge of effective alkali (EA) in the modified Kraft cook was reduced by 1% (as Na_2O on original dry wood) compared to the base case for the conventional kraft cooking to give the same bleachable grade hardwood pulp (17 Kappa number). The liquor-to-wood ratio was assumed to be four (4) and was similar to the conditions used in the laboratory experiments (Genco 2008). An anthraquinone charge of 0.05% (on wood) was included in the green liquor extraction process. Wood

chips are pre-steamed in a steaming vessel for 15 minutes, then heated to the extraction temperature of 160 °C in 55 minutes, and extracted for 110 minutes at 160 °C. This gave a total H-factor of 750 hours during the cooking process. The extract composition based on wood is illustrated in Table 2. The liquid containing the extracted hemicellulose and lignin are separated from the chips, and the chips are conveyed into the pulping digester.

Alkaline Pulping Conditions

The pulping conditions were assumed to be 14% EA in the pulping portion of the cook at a total H-factor of 1,350 hours, including approximately 750 hours in the extraction vessel. The liquor-to-wood ratio was taken to be 4.0. The pulp yield was taken to be 47% and was the same as for the conventional kraft process. The final pulp was assumed to have a kappa number of 17 and TAPPI viscosity of 37 cp. The kraft control was assumed to use 15% EA, 30% sulfidity, and H-factor of about 1,350 hours. The pulp production rate was assumed to be unchanged.

Table 2. Wood Components Removed During Extraction Used in Process Design; (% Extracted) based on 1% Green Liquor Charge

Item	Amount (Based on Wood)
Extraction Yield	9.0%
Fermentable C5 and C6 Sugars	3.5%
Acetate Extracted	2.5%
Lignin Extracted	1.5%
Non-Fermentable Sugars	1.5%
Biomass Extracted (ODMTPD)	108
pH of Extract	3.4

Plant Sizes

Several pulp mill sizes were considered in the design. These included a small plant producing 550 tonne per day representative of older bleached kraft mills in the northeast, a 750 tonne per day pulp representative of a more modern mill, a large plant having a capacity of 1,000 tonne per day, and a state of the art 1,500 tonne per day kraft mill.

Concentration of Extract

The composition and quantity of the extract used in the economic analysis is given in Table 3 for the case of the 1,000 tonne per day pulp mill, assuming a four-to-one liquor-to-wood ratio, with a dilution factor equal to zero and a Norden washing number in the digester equal to 3. Following extraction, the extract liquor at high temperature (160 °C) and elevated pressure (110 psig) is sent to a flash tank to recovery steam and lower the temperature (130 °C) and pressure (20 psig). The solids content removed from the digester was set at 8.5% and was achieved by recycling solids from the blow tank back to the digester in Fig. 1. It is undesirable to use multiple effect evaporation to

concentrate the extract, since it requires large amounts of steam and the capital cost of the evaporator.

Reverse osmosis was thought to be unnecessary, since Zacchi and Axelsson (1989) showed that 8.5% was close to the optimum concentration for the extract prior to fermentation. This level of solids content can be achieved by recycle. One advantage of using reverse osmosis to concentrate the extract is that the concentration of the salts remains constant and is not concentrated by the evaporation or recycles options. In the reverse osmosis option the cost of removing water must be balanced against the cost of providing additional reactor volume for fermentation and the added cost of ethanol distillation.

Extract Composition

The dissolved organic content in the extract removed from the digester was estimated to be 7.48%, with the remainder being inorganic salts (Table 3). The fermentable 5- and 6-carbon sugars were estimated to be 2.9%, while the non-fermentable sugars, primarily glucuronic acid, were estimated to be 1.24%. The acetate portion of the extract was 2.08%. The remainder of the extract was lignin (1.24%) and dissolved salts (0.51%).

Table 3. Composition of Extraction for 1,000 Tonne per day Pulp Mill Production

Characteristics of Extract	Value
Flow Rate	2,673.7 tonne/day
Suspended Solids Content	0%
Dissolved Organics	7.48%
Fermentable Sugars	2.909%
Acetate	2.077%
Lignin	1.247%
Non-fermentable Sugars	1.247%
Dissolved Inorganics	0.51%
[Na] ⁺	0.229%
[CO ₃] ²⁻	0.191%
[SO ₄] ²⁻	0.003%
[S _x O _y]	0.044%
Water	2,460.2 tonne/day

Acid Hydrolysis and Lignin Removal

The hydrolysis of the component carbohydrates was assumed to follow the kinetics specified by Garrote et al. (2001) for hydrolysis of extract from eucalyptus using sulfuric acid. Complete hydrolysis was shown to occur at a pH of 1.0 at 126°C. This required addition of sulfuric acid to make a 2.84% solution sufficient to lower the pH, decompose any remaining carbonate, and conversion of acetate to acetic acid by addition of hydrogen ion. A hydrolysis time of 1.3 hours was needed for complete hydrolysis of the xylan oligomers. At these conditions it was assumed that all the extracted lignin is

precipitated and can be separated from the liquor by pressure filtration. This assumption has been verified experimentally.

Acetic Acid and Furfural Recovery

Following lignin separation a liquid-liquid extraction process was used to extract acetic acid and furfural from the mixture liquor (Fig. 2). Seader and Henley (2006) discuss the recovery of acetic acid from water using liquid-liquid extraction with ethyl acetate as the solvent. Ethyl acetate is a solvent used commercially to remove acetic acid from water (<http://www.ddpsinc.com/ProcessProfiles/pp50.html>). Process simulation studies were conducted using ASPEN in which guaiacol was used as a model compound for soluble lignin. It was found that guaiacol is readily extracted by ethyl acetate. This was also found to be the case in laboratory studies. Other solvents can be chosen, but ethyl acetate was felt to be adequate for a preliminary design study.

Physical properties for acetic acid, furfural, and ethyl acetate are summarized in Table 4. Sugar feed from the hydrolysis reactor is sent to the extraction column, where ethyl acetate is used as the solvent to extract acetic acid furfural, small quantities of water, and soluble lignin. The “raffinate” from the extraction column is composed of an aqueous mixture of sugars, which goes to the liming process. The organic or “extract” phase from the liquid/liquid extraction column then goes to a solvent recovery column where the ethyl acetate solvent is recovered and recycled back to the extraction column after makeup ethyl acetate is added. The bottoms product from the solvent recovery column contains water, soluble lignin acetic acid, and furfural. Residual water, acetic acid, and furfural are removed by successive distillation. The bottoms product from the acetic acid/furfural splitter column containing sodium salts, traces of acetic acid, and furfural are recycled back to the evaporators in the kraft process (Fig. 1). The recovery efficiency for acetic acid and furfural was estimated to be about 90%. The extracted acetic acid and furfural can be further purified by distillation (not shown) and are sold as final products of 99% purity.

The recovery efficiency for acetic acid and furfural was estimated to be about 90% based upon discussions with Lenzing Ltd. and from the process simulation studies performed using ASPEN (<http://www.lenzing.at/chemicals/en/products/2753.jsp>). The extracted acetic acid and furfural can be further purified by distillation (not shown) and are sold as final products as 99% purity. *E. coli* [KO-11], the micro-organism used to ferment xylose to ethanol, is tolerant to low levels of soluble lignin (Walton 2009).

Table 4. Properties Used in Design of Liquid/Liquid Extraction Process

Name	Formula	MW (g/mole)	B.P (C)	Density (gm/cm ³)
Water	H ₂ O	18.0	100	1.00
Furfural	C ₅ H ₄ O ₆	96.1	162	1.16
Acetic Acid	CH ₃ CH ₂ OH	60.0	118	1.05
Ethyl Acetate	C ₄ H ₈ O ₂	88.1	77	0.90

Liming and Gypsum Removal

After liquid- liquid extraction, calcium oxide (CaO) is used to “lime” the extract liquor. The main function of liming is to adjust the pH to a near-neutral condition for ethanol fermentation. The lime also acts as a bactericide. The calcium precipitates the sulfate ions as gypsum [CaSO₄•2H₂O] to a concentration level that can be tolerated by the fermentation culture. Gypsum is removed by using plate and frame filtration.

Fermentation and Ethanol Recovery

In the fermentation step it was assumed that C5 and C6 organics can be fermented simultaneously by using *E. coli* (KO11) that was purchased (Wooley et al. 1999; Aden et al. 2002; Amartey and Jeffries 1996). The *E. coli* [KO11] organism used to convert xylose to ethanol that forms the basis for making the cost estimate was thought not to ferment 4-O-methyl- α -D-glucuronic acid. Thus no credit was taken for fermenting glucuronic acids. The efficiency of converting C5 and C6 sugars into ethanol was set at 90% of the theoretical yield based upon the work of Wooley et al. (1999). Ethanol was processed after fermentation by pre-distillation to 50% purity and then further distillation to 95%, which is the azeotrope concentration. The ethanol is then further concentrated to 99.9% by using molecular sieve technology. Stillage from ethanol purification and upgrading is returned to the kraft recovery process. Additional background can be found on the web (http://www.ethanolindia.net/molecular_sieves.html).

Ethanol and Acetic Acid Production Rates

Figure 3 illustrates the estimated production rates for ethanol, acetic acid, and furfural as a function of the production rate for the kraft mill using Northeast hardwood chips, assuming that the plant operates 350 days per year (96% capacity factor). For a 1,000 tonne per day pulp mill the production rate for ethanol would be approximately 31.6 tonne/day (3.70 million gallons per year of 100% ethanol) and 50.0 tonne per day of acetic acid (4.41 million gallons per year of 100% acetic acid). In addition about 1.08 tonne per day of furfural are produced (0.084 gallons per year).

Energy Consumption

The addition of the hemicellulose extraction process to a kraft pulp mill reduces the energy that is obtained from the residual pulping liquor. The net energy output is illustrated in Fig. 4 in terms of millions of BTU per hour as equivalent steam. The net energy output of the mill is plotted as a function of pulp mill size when using mixed northeastern hardwood chips. A comparison is made to the kraft mill base case where no hemicelluloses are pre-extracted. On average, the modified kraft mill would produce approximately 30 to 40% less steam than the conventional kraft mill because about 10% of the wood mass is extracted and the energy content of this mass appears as the energy content of the ethanol and acetic acid. Also, additional energy is required for distillation in both the production of ethanol and acetic acid; predominately in the form of steam required for distillation (Mao 2007).

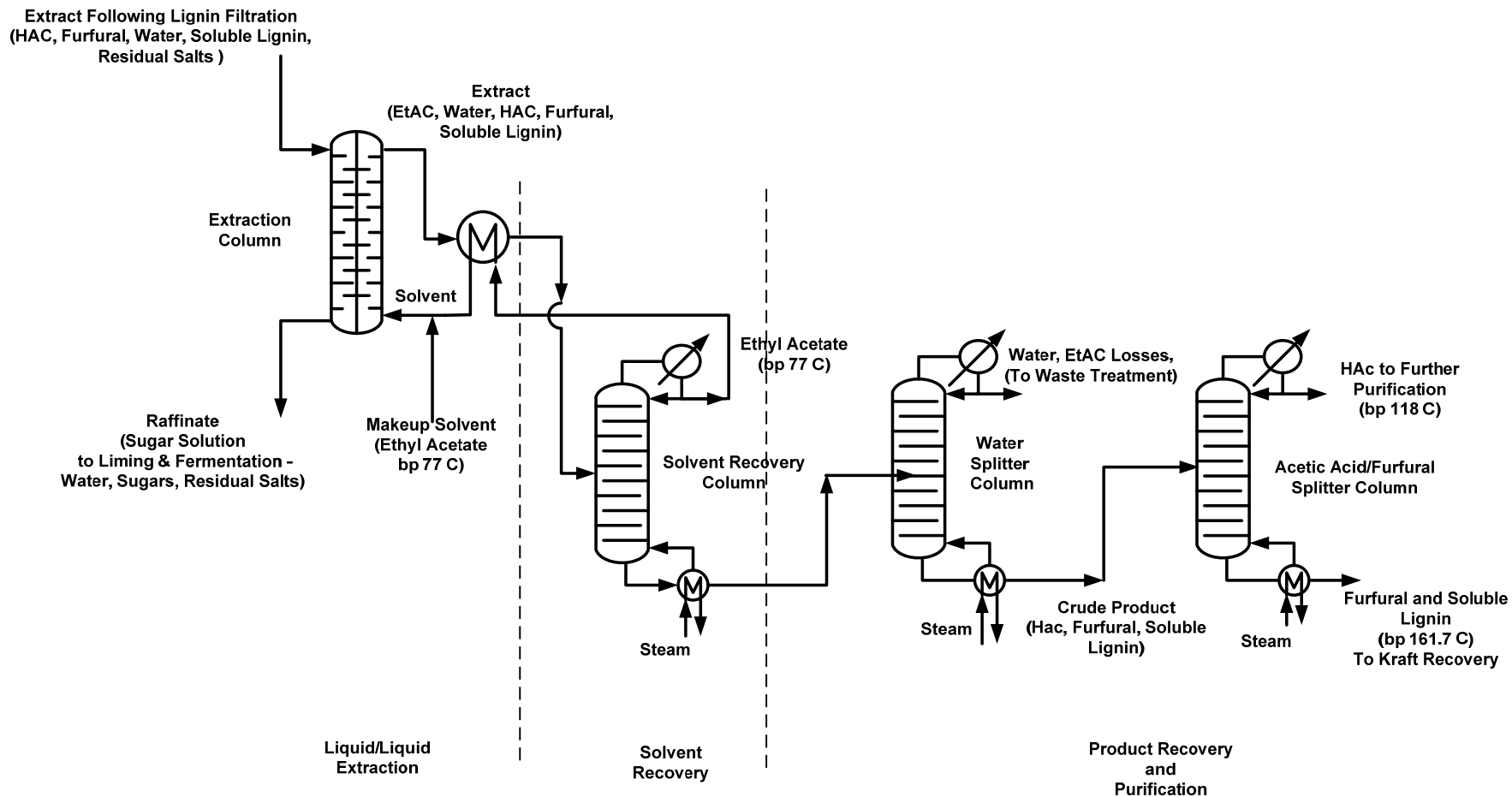


Fig. 2. Liquid-liquid extraction process for separation of acetic acid and furfural from mixed sugar feed

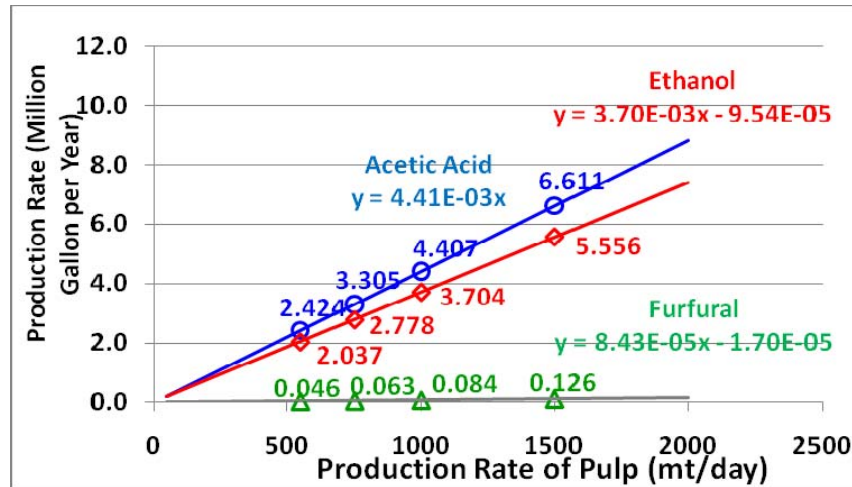


Fig. 3. Products rate versus plant size for mill using northern hardwood chips

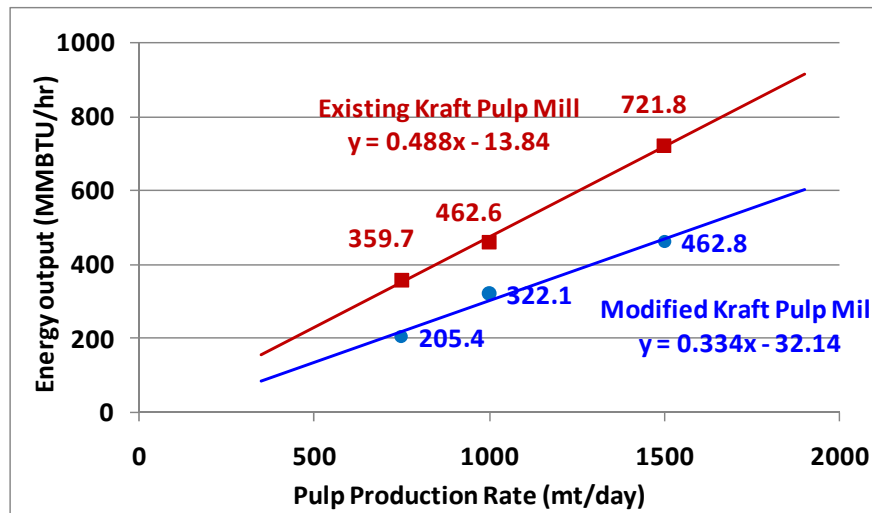


Fig. 4. Energy output versus plant size for kraft mill using mixed northeastern hardwood chips

ECONOMIC ANALYSIS

Basis for Analysis

In the economic analysis it was assumed that an extraction vessel of some type was available at the site and the plant operated as a single fiber line in a continuous fashion. The extraction vessel may be an idle digester that could be connected in series with the primary digester. A more likely situation in a single fiber-line pulp mill is that

an impregnation vessel is available that could be upgraded into an extraction vessel, since the wood must be impregnated with the pulping liquor in either case.

Similarly, some mills would have sufficient waste treatment and utilities available to accommodate the new process, while other mills would have to expand the waste treatment and utility systems to account for the additional processing. Four cases were considered depending upon whether an extraction vessel was assumed to be available (Cases 1 and 2) or whether it must be purchased (Cases 3 and 4). Two sub-cases were considered, depending on whether the utilities and wastewater treatment systems have to be upgraded (Cases 1 and 3) or are sufficient to handle the additional processing (Cases 2 and 4).

Capital Cost Estimate

This capital cost estimate was based on information provided by Mitchell (2006), who corrected capital cost data originally presented by Wooley (1999) for a white wood to ethanol plant. Mitchell broke the biorefinery into various sections corresponding to the unit processes involved in the plant. The total installed equipment cost of the unit processes in the white wood to ethanol plant was obtained by multiplying the cost of purchased equipment by an installation factor; which amounted to about 3.55. The installation factor covered building alterations, installation labor and materials, process piping, instrumentation, engineering services, and other construction expenses. Mitchell (2006) used the CEPCI index to correct Wooley's data to 2007 dollars for the various unit processes comprising the biorefinery. A 15% contingency factor was applied to the estimated capital cost obtained from Mitchell's cost curves to correct to 2008 costs and account for uncertainties in the analysis. In making the capital cost analysis reported here, 20% of the cost of a new continuous digester was applied to the project for modification of the impregnation vessel and/or connecting two continuous digesters in series. Vender estimates were obtained for the cost of a new extraction vessel. For those cases requiring a new extraction vessel, the full cost was applied.

Estimation of Cost of Manufacture

Raw materials

The raw materials used for the mill operation and waste material produced were determined from the WinGEMS and ASPEN plus computer simulation model and will depend upon plant size. Values for the unit costs for the raw materials determined from the material an energy balance are summarized by Mao (2007). The added wood costs were taken to be \$60 per dry tonne to account for the decrease in pulp yield.

Fixed operating costs

Fixed operating cost includes labor cost (*LS*), overhead for maintenance (*OM*), maintenance per se (*M*), taxes and insurance (*TI*), and capital recovery (*CR*). The labor costs were estimated by correcting the data of Wooley (1999) for the production of ethanol from white wood and were treated as a fixed expense.

Capital recovery

Capital recovery is the yearly cost (R_C , dollars per year) for borrowing money at an interest rate (i) and repaying the borrowed capital exclusive of the value of the land (FCL_L) in the form of an annuity over (n)-years.

$$R_C = FCL_L \times \left[\frac{i(1+i)^n}{(1+i)^n - 1} \right] = FCL_L \times CRF \quad (1)$$

A capital recovery factor (CRF) of 16.5% was used in the current analysis. The capital recovery factor was obtained by assuming that 100% of the capital investment was borrowed at a 10% rate of interest (i) over a ten (10) year period (n).

Depreciation

Yearly, depreciation charges for the k -th year (d_k) were estimated for the process by using a straight line method over a ten year period (N_D).

$$d_k = \left(\frac{FCL_L}{N_D} \right) \quad (2)$$

Miscellaneous operating expenses

Other fixed costs used in the analysis are summarized by Wooley (1999). These included costs associated with maintenance (M), overhead on maintenance (OM), taxes and insurance (TI) and the capital recovery (R_C)

Yearly operating cost

The yearly operating cost or cost of manufacturing (COM_k) was estimated from Equation (3).

$$COM_k = [RM + U + LS + M + OM + TI + R_C]_k \quad (3)$$

In equation (3), (RM) is the sum of all raw materials, (U) is the utilities cost, (LS) is the labor and supervision, (M) the cost for maintenance, (OM) the overhead on maintenance, (TI) is the taxes and insurance, and (R_C) is the recovered capital.

Discounted cash flow rate of return on investment

A profitability analysis was performed using the discounted cash flow rate of return (DCFROR) method for judging the viability of prospective investments. The discounted cash flow rate of return on investment (DCFROR) is the discount rate at which the net present value (NPV) at the end of the project goes to zero (Turton et al. 2003; Peters and Timmerhaus 1991). In the discounted cash flow rate of return on investment, the interest rate (i) is found, so that the negative cash flows are just balanced by the positive cash flows. In the discounted cash flow rate of return on investment, the interest rate (i) is found so that the negative cash flows (CF_k) for year (k) are just

balanced by the positive cash flows for the investment and the net present value (*NPV*) becomes zero.

$$NPV(i) = \sum_{k=0}^{k=N=Termination} \left[\frac{CF_k}{(1+i)^k} \right] = 0 \quad (4)$$

$$CF_k = [R - COM]_k * (1-t) + d_k * t \quad (5)$$

In equation (5), the cash flow will depend upon the revenue (R_k) and the cost of manufacturing (COM_k) for the k^{th} year and the tax rate (t).

Selling prices and plant revenue

The extraction process was assumed to be constructed over a two year period. The selling price of ethanol was taken to be \$2.00 dollars per gallon, while the selling price of acetic acid was assumed to be \$4.00 dollars per gallon (Mao et al. 2008). Additional wood is required in the process, since the experimental data showed that the overall pulp yield drops by approximately 2%, from 48% to 46%, and the pulp production rate remained constant. Revenues from the process are shown in Table 5 and are the same for all the four cases evaluated. The revenues will vary with the volume of products produced and their selling prices. Revenues from the biorefinery in Table 5 include the revenue penalty associated with less steam being produced. No penalty was assessed for any possible loss of pulp yield.

Table 5. Revenues to Biorefinery for Northeastern Mixed Hardwood

Mill Size (mt/day)	Million Dollars/year			
	Acetic Acid	Ethanol	Lost Steam	Total
550	9.7	4.1	-1.89	11.88
750	13.2	5.6	-2.58	16.19
1000	17.6	7.4	-3.44	21.59
1500	26.4	11.1	-5.17	32.39

Capital Cost for Different Cases Investigated

The total estimated project costs for the cases considered in this analysis are summarized in Fig. 5. This figure gives the capital investment as a function of plant size and whether an extraction vessel is available and whether the utilities need to be upgraded or are sufficient for the new process. From Fig. 5 it is quite clear that the total capital cost will depend upon the plant size and the situation with regard to the availability of an extraction vessel and the utilities. It is apparent that the cases with the highest capital investment are those that require the purchase and installation of an extraction vessel and where the waste water treatment and utilities need to be upgraded.

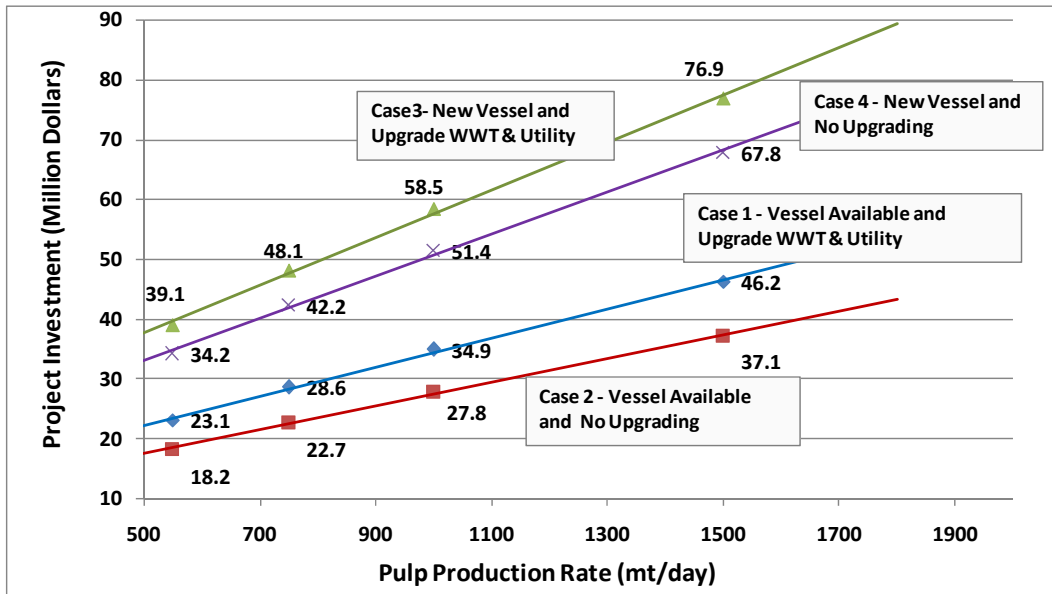


Fig. 5. Total project investment for cases investigated

Yearly Operating Cost

It was assumed that the investment was completely borrowed and repaid over the life of the project, which was taken to be ten (10) years. The annual operating costs for the different scenarios are illustrated in Fig. 6. It is clear that the projects with the high capital investment invariably lead to high annual operating cost; and results from the application of the capital recovery factor (CRF) to the total capital investment. Projects with high capital investment will result in high annual charges for repaying the capital investment.

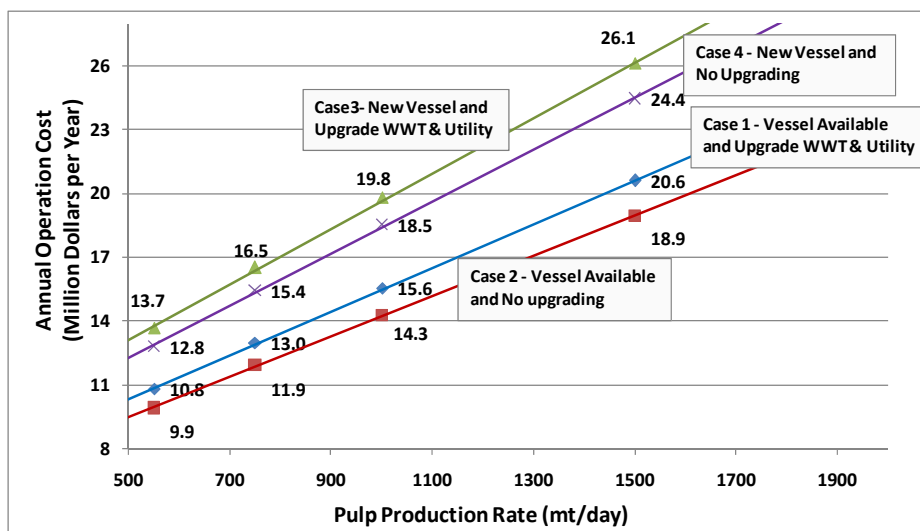


Fig. 6. Annual operating cost for cases investigated

Unit Production Cost.

The unit production costs for the 1000 tonne per day pulp mill case are given in Table 6. The unit production costs were estimated from the operating cost by assigning a portion of the operating cost to the production of both ethanol and acetic acid. Production costs were proportioned based upon the amount of product produced on a mass basis. Using this simplified method of proportioning the operating costs resulted in a greater proportion of the operating cost being allocated to the acetic acid because of its greater production rate. For the northeastern hardwood case, assuming a pulp production rate of 1,000 tonne per day, production costs for ethanol varied between \$1.63 and \$2.07/gallon, depending upon the extraction vessel being available and whether the waste treatment system and utilities needed to be upgraded. Similarly for the acetic acid the unit production cost varied between about \$1.98 and \$2.75 per gallon.

Table 6. Unit Production Cost for 1000 Tonne per Day Pulp Mill for Cases Investigated

Case	Ethanol (\$/gallon)	Acetic Acid (\$/gallon)
Case 1 - Vessel Available with Upgrading	1.63	2.16
Case 2- Vessel Available and no Upgrading	1.49	1.98
Case 3-New Vessel Upgrading	2.07	2.75
Case 4-New Vessel and no Upgrading	1.94	2.57

Table 7 lists the unit production cost as a function of plant size for Case 2, extraction vessel available and on upgrading of utilities required, which is the most economical case. The production cost of ethanol would vary between \$1.32 to \$1.89 per gallon, while for acetic acid it varied between \$1.75 and \$2.51 per gallon. These estimates vary strongly as a function of size. Huang and co-workers (2010) estimate the minimum selling price for ethanol produced in a kraft mill biorefinery at \$3.41/gallon that uses 2,000 dry tonne per day of wood. Huang postulates that the \$3.41/gallon price can be reduced to \$1.86/gallon if 56% more ethanol is produced by converting the cellulose in the short fiber fraction of the pulp into ethanol.

Table 7. Unit Production Cost as a Function of Size for Case 2, Vessel Available and No Utilities Upgrading

Pulp Mill Size (Tonne per Day)	Ethanol (\$/gallon)	Acetic Acid (\$/gallon)
550	1.89	2.51
750	1.66	2.21
1000	1.49	1.98
1500	1.32	1.75

Discounted Cash Flow Analysis

The results of the profitability analysis are summarized in Fig. 7. In the discounted cash flow rate of return method, a project was judged to be a good, neutral, or poor by comparing the calculated discounted rate of return (i) to the cost of capital (i_c), which in the present study was taken to be 10%. The cost of capital (i_c) is the minimum rate of return that is considered acceptable assuming a very low risk on the enterprise. Similarly at 0% rate or return, the positive cash flows to the investment just equal the negative cash flows to the project.

$i \gg i_c$ (Very Good Project Investment)

$i = i_c$ (Project Investment is Neutral)

$i \ll i_c$ (Poor Project Investment)

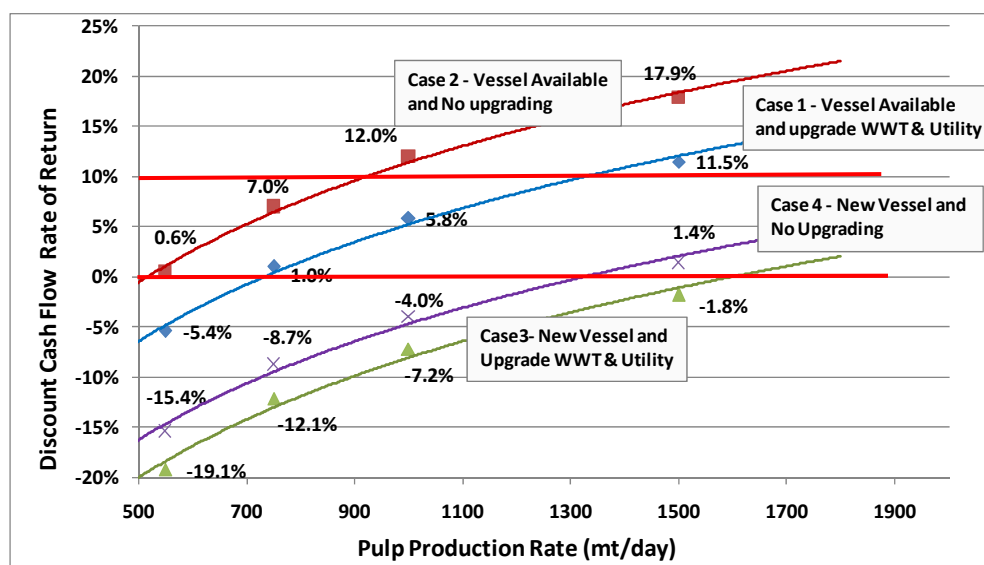


Fig. 7. Discount cash flow rate of return for different cases

It is clear from Fig. 7 that the larger the plant size, the more profitable the investment. The condition leading to the highest discounted cash flow rate of return is Case 2, which minimizes the capital investment. For Case 2 the design condition assumes that the extraction vessel is available and no upgrading is required for the utilities and waste water treatment systems. In kraft pulp mills where these conditions are fulfilled, the rate of return can be as high as 18% for the large 1,500 tonne per day pulp mill case. For Case 2, the most profitable case, the cost of capital (10%) is reached for a 900 tonne per day pulp mill. Under no conditions did it prove profitable to install the hemicellulose extraction process where a new extraction vessel is required. As a general rule, as the capital investment increases, the discounted cash flow rate of return on investment decreased. For the cases where a new vessel is required, the discounted cash flow rate of return is invariably negative except for very large pulp mill sizes (Fig. 7).

CONCLUSIONS

In the present analysis, the extraction and pulping were assumed to be conducted using continuous processing and extraction data presented previously (Genco et al. 2008). The assumption inherent in the analysis is that an existing impregnation vessel can be converted into an extraction vessel. Based upon the design study the following conclusions are drawn:

1. For a 1,000 ton per day pulp mill, the production cost for ethanol is estimated to be between \$1.63 and \$2.07/gallon; and for acetic acid between \$1.98 and \$2.75 per gallon depending upon equipment available for use with the new process.
2. For northern hardwood, the rate of return on investment varies directly as a function of plant size and capital investment.
3. Installing a new extraction vessel reduces the discounted cash flow rates of return considerably, especially for small plant sizes and becomes negative when the waste water treatment plant and utilities must be upgraded.
4. There are several advantages to the new process. First, two new by-products from the pulping process are generated. Secondly, the pulp yield and pulp quality are preserved, except at very low levels of green liquor addition. Thirdly, the recovery boiler and lime kiln are off-loaded, depending upon the amount of green liquor used in the extraction. Off-loading the recovery cycle allows a potential increase in production rate if this section of the mill is the bottleneck for the production rate.
5. Even for the 1,500 tonne per day kraft mill, the amount of ethanol produced, 5.6 million gallons per year, is relatively small when compared to a modern corn to ethanol plant, which typically produces 50-100 million gallons per year (<http://www.ethanolrfa.org/industry/locations>). Similarly, for purposes of comparison, a modern acetic acid plant would have a production rate of 500,000 tonne per year, which is about 17 times larger (29,000 tonne per year) than the capacity of the 1,500 tonne per day pulp mill (<http://www.the-innovation-group.com/ChemProfiles/Acetic%20Acid.htm>).
6. Although these wood-derived chemical production rates are relatively small, the production of ethanol and acetic acid could potentially represent positive revenue for a kraft pulp mill operator.
7. It is clear from the above analysis that for a biorefinery concept predicated on producing ethanol and acetic acid at existing kraft mills, the processing must become simpler to reduce the capital expenditure. This will improve annual operating cost and the discounted cash flow rate of return, which is unacceptably low except for very large mills that have an existing extraction vessel that can be modified appropriately and sufficient utilities and waste treatment facilities exist to accommodate the additional processing.

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REFERENCES CITED

- Aden, A., Ruth, M., and Ibsen, K. (2002). *Lignocellulosic Biomass to Ethanol Process Design and Economics Utilizing Co-Current Dilute Acid Pre-hydrolysis and Enzymatic Hydrolysis for Corn Stover*, NREL technical report, NREL/TP-510-32438, 27-36.
- Al-Dajani, W. W., and Tschirner, U. W. (2008). "Pre-extraction of hemicelluloses and subsequent kraft pulping. Part 1: Alkaline extraction," *Tappi J.* 7(6), 3-8.
- Amartey, S., and Jeffries, T. (1996). "An improvement in *Pichia stipitis* fermentation of acid-hydrolyses hemicellulose achieved by over liming (calcium hydroxide treatment) and strain adaptation," *World Journal of Microbiology & Biotechnology* 12, 281-283.
- Fengel, D., and Wegener, G. (1984). "Wood – Chemistry, Ultra-structure, Reactions," Walter de Gruyter, Berlin 167-171.
- Garrote, G., Dominguez, H., and Parajo, J. C. (2001). "Generation of xylose solutions from *Eucalyptus globulus* wood by auto-hydrolysis-post-hydrolysis processes kinetics," *Bioresource Technology* 79, 155-164.
- Genco, J. M., Mao, H., van Heiningen, A., Zou, H., Luo, J., and Pendse, H. (2008). "Technical economic evaluation of a northern hardwood biorefinery using the "near-neutral" hemicellulose pre-extraction process," 2008 TAPPI Pulping Conference, Portland, Oregon (August, 2008).
- Gullichsen, J., and Paulapuro, H. (eds.), (1999). "Chemical Pulping, Book 6A, Papermaking Science and Technology", Tappi, Atlanta, A291-A292.
- Huang, H-J., Ramaswamy, S., Al-Dajani, W. W., and Tschirner, U. W. (2010). "Process modeling and analysis of pulp mill-based integrated biorefinery with hemicellulose pre-extraction for ethanol production: A comparative study," *Bioresource Technology* 101, 624-631.
- Leschinsky, M., Sixta, H., and Patt, R. (2009). "Detailed mass balances on the autohydrolysis of eucalyptus globulus at 170 °C," *BioResources* 4(2), 687-703.
- Mao, H. (2007). *Technical Evaluation of a Hardwood Biorefinery Using the "Near-Neutral" Hemicellulose Extraction Process*, Master's Thesis, University of Maine.
- Mao, H., Genco, J. M., van Heiningen, A., and Pendse, H. (2008). "Technical economic evaluation of a hardwood biorefinery using the 'near-neutral' hemicellulose pre-extraction process," *J. Bio-based Materials and Bio-energy* 2(2), 1-9.
- Mitchell, J. (2006). *Production of Ethanol from Hardwood*, M.S. Thesis, University of Maine.

- Molecular technology, http://www.ethanolindia.net/molecular_sieves.html.
- Peters, M. S., and Timmerhaus, K. D. (1991). *Plant Design and Economics for Chemical Engineers*, 4th Ed., McGraw Hill, New York.
- Seader, J. D., and Henley, E. J. (2006). “*Separation Process Principles*,” 2nd Ed., John Wiley, New York, 296.
- Sixta, H. (ed.), (2006). “*Handbook of Pulp*,” Wiley-VCH, Vol. 1, 343-345.
- Sjöström, E. (1981). “*Wood Chemistry-Fundamentals and Application*,” Academic Press, New York, 139-140.
- Turton, R., et al. (2003). *Analysis, Synthesis, and Design of Chemical Processes*, 2nd Ed., Prentice Hall, Upper Saddle River, N.J.
- Um, B.-H. and van Walsum, P. (2009). “Acid hydrolysis of hemicellulose in green liquor pre-pulping extract of mixed northern hardwoods,” *Appl. Biochem. Biotechnol.* 153, 127-138.
- Van Heiningen, A. (2006). “Converting a kraft pulp mill into an integrated forest biorefinery,” *Pulp and Paper Canada* 107(6), 38-43.
- Wooley, R., et al. (1999). *Lignocellulosic Biomass to Ethanol Process Design and Economics Utilizing Co-Current Dilute Acid Prehydrolysis and Enzymatic Hydrolysis Current and Futuristic Scenarios*, NREL/TP-580-26157 (July 1999).
- Walton, S. (2009). “*Biological Conversion of Hemicellulose Extract into Value-added Fuels and Chemicals*,” PhD Dissertation, University of Maine (December).
- Zacchi, G., and Axelsson, A. (1989). “Economic evaluation of pre-concentration in production of ethanol from dilute sugar solutions,” *Biotechnology and Bioengineering* 34, 223-233.
- <http://www.ddpsinc.com/ProcessProfiles/pp50.html>
<http://www.ethanolrfa.org/industry/locations/>
<http://www.lenzing.at/chemicals/en/products/2753.jsp>
<http://www.the-innovation-group.com/ChemProfiles/Acetic%20Acid.htm>

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