12-2007

Technical Evaluation of Hardwood Biorefinery Using the "Near-Neutral" Hemicellulose Extraction Process

Haibo Mao

Recommended Citation

Mao, Haibo, "Technical Evaluation of Hardwood Biorefinery Using the "Near-Neutral" Hemicellulose Extraction Process" (2007). *Electronic Theses and Dissertations*. 230.
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TECHNICAL EVALUATION OF A HARDWOOD BIOREFINERY USING THE "NEAR-NEUTRAL" HEMICELLULOSE EXTRACTION PROCESS

By
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A THESIS
Submitted in Partial Fulfillment of the
Requirements for the Degree of
Master of Science
(in Chemical Engineering)

The Graduate School
The University of Maine
December, 2007

Advisory Committee:

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By Haibo Mao
Thesis Advisor: Dr. Joseph M. Genco

An Abstract of the Thesis Presented
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A technical analysis was performed for a new process that produces ethanol and acetic acid from hardwood in addition to bleached hardwood Kraft pulp. The new process, termed the "near neutral" hemicellulose extraction process, involves the extraction of wood hemicellulose using green liquor prior to conventional Kraft pulping. This thesis assumes that the new process is located at an existing kraft pulp mill. Ancillary unit operations in the process include hydrolysis of the extracted carbohydrates using sulfuric acid, filtration of the extract to remove lignin that was extracted with the carbohydrates, liquid-liquid extraction of acetic acid and by-product furfural, liming of the hydrolyzed extract, separation of gypsum which is the product of the liming reaction, fermentation of C5 and C6 sugars and upgrading of the acetic acid and ethanol products by distillation. After the extraction step in the process, the final pH of the extraction liquor varies between 5 and 6 and preserves the yield and physical properties of the final pulp product which are equivalent to market Kraft pulp.

In the thesis reported here, a design model was developed using WinGEMS and ASPEN Plus software. The integrated mass and energy balances were obtained from the

computer model and used to size important process equipment in the process. Information from the process model and the flow sheet were used to estimate capital and operating cost for the process. A major economic factor in the analysis is whether a new extraction vessel is required or if an existing digester can be retrofitted into a vessel suitable for the extraction. The economic analysis was performed as a function of the size of the pulp mill being retrofitted to accommodate the hemicellulose extraction process. Alternative cases that were evaluated considered whether the utilities and waste water treatment systems were sufficient to accommodate the new process. In the economic analysis, the Discounted Cash Flow Rate of Return (DCFROR) was used to judge the economic merits of the new process. The rate of return on investment was found to vary between 9.9 and 14.0 percent depending upon the size of the pulp mill (750 to 1,500 tonne per day pulp production rate) for the case where the extraction vessel is available and the utilities and waste treatment facilities are sufficiently large to handle the additional requirements for the process. If a new extraction vessel must be purchased, the process is not economically justified regardless whether the utilities and waste water treatment facilities are sufficient to handle the new process.

A very important advantage of the "near-neutral" extraction process is that the recovery cycle is off-loaded because the amount of organic matter in the black liquor is reduced and less white liquor is needed for pulping. This change in operation would potentially allow a Kraft pulp mill to significantly increase its pulp production rate if the recovery cycle is the bottleneck in the plant. In the hemicellulose extraction process the methanol content of the black liquor is thought to be reduced by about 40%, while the TRS content is also diminished. These advantages result because of the lower white liquor charge and shorter pulping time during the modified Kraft cook. A major disadvantage of the process is that the production rates for the two co-products, ethanol and acetic acid, are low when compared to corn to ethanol processes. Less steam is produced in the recovery boiler because a portion of the organic matter in the wood chips is extracted. Consequently, additional steam must be supplied from a biomass boiler or by burning fossil fuels such as natural gas, coal or fuel oil. Lastly the near neutral extraction process is capital intensive unless an extraction vessel is available for use.

ACKNOWLEDGEMENTS

First and foremost I would like to express my deepest gratitude to my thesis advisor, Dr. Joseph Genco. This thesis could not be finished without his hard work, expertise and guidance. I would like to thank my thesis committee members, Dr Adriaan Van Heiningen, Dr. Hemant Pendse and Dr. Barbara Cole for their insight and assistance. I would also like to thank the U.S. Department of Energy and the New England Green Chemistry Consortium (NEGCC) for their financial support.

Lastly, I would like to give special thanks to my lovely wife Jie Luo whose patient love enabled me to complete this work.

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Chapter 1

BACKGROUND

1.1 Introduction

Interest in renewable resources as a source of energy and chemicals has increased because of potential worldwide shortages of petroleum and natural gas and growing environmental concerns regarding the accumulation of greenhouse gases in the environment. Rapid development in Asia has necessitated the need for additional energy resource to meet anticipated consumption. This is especially true for liquid fuels such as gasoline used in transportation. Although considerable sums of money have been invested in alternative energy research such as wind, geothermal and solar energy, none of the alternatives has had a major impact on the energy budget of the United States [Service, 2007].

The worldwide demand for an inexpensive stable source of energy can be satisfied in part by using bio-renewable energy. This idea of using renewable biomass is embodied in the concept of a biorefinery. The biorefinery is similar to a traditional petroleum refinery except that biomass would be used as the feedstock rather than by using oil. Feed stocks to the biorefinery that have been proposed are woody biomass, dedicated annual crops and municipal waste [Ragauskas, 2006]. Contrary to the conventional oil refinery which uses thermal processing, the biorefinery would be predicated on both the use of thermal and biological processes to convert starch, cellulose and lignin into the energy and chemicals rather than by using hydrocarbons available in oil. The concept of a biorefinery is being advanced by a number of researchers [Wising and Stuart, 2006; Pervaiz and Sain, 2006; Maybee and Saddler, 2006; Magdzinski, 2006].

One of the major products envisioned to be produced at a biorefinery is ethanol as recently discussed recently by Mitchell [2006] and earlier by Wooley and coworkers [1999].

1.1.1 Bio-Based Ethanol

A number of environmental, economic and political drivers have increased the focus on bio-ethanol production.

Environmental Drivers: Bio-ethanol is a sustainable energy source. Carbon dioxide (CO_2) emissions can be substantially reduced if bio-ethanol is used to supplement gasoline and diesel fuel in transportation fuels. Bio-ethanol has been shown to be a replacement for MTBE as an octane booster in gasoline and can potentially reduce groundwater and soil pollution.

Economical Drivers: If the price of oil continues to rise, bio-ethanol and other bio-fuels can potentially be produced at less cost than gasoline and diesel. Additionally, the production of bio-ethanol fuels such as ethanol stimulates economic development in rural agricultural areas.

Political Considerations: Bio-ethanol will reduce the world's dependence on fossil fuels. Bio-ethanol can be produced domestically from domestic resources rather than rely on oil from politically unstable regions of the world, although bio-based fuels can negatively impact the world's food supply.

In 2005, Brazil and the United States were the world's two leading producers of ethanol fuel; production rates were 4.35 and 4.30 billion US gallons per year respectively [Ethanol Fuel]. Virtually all of this ethanol was produced from common materials; in Brazil the preferred feedstock is sugar cane which is composed of sucrose, while in the

United States ethanol is produced from starch derived from corn. Future potential feedstocks being considered are lignocellulosic materials derived from corn stover, switch grass, wood and municipal waste.

The chemical processing involved in producing ethanol from sugar based feedstock is considerably simpler than that required for the conversion of corn into ethanol and from lignocellulosic materials such as woody biomass. Sugar based ethanol processes are relatively simple because the feedstock is present in dimeric form. For the use of corn, the starch must first be converted into simple sugars prior to conversion into ethanol. However both corn and sugar cane are in the human food chain and using foodstuffs to produce fuels raises ethical issues.

Ethanol from corn is the fastest growing chemical in the Unites States [Renewal Energy Association. http://www.ethanolrfa.org/industry/locations/] and currently there are more than 100 plants producing ethanol. Considering the lower energy density of ethanol, however, ethanol is still more expensive than gasoline derived from petroleum even with the federal government ethanol tax subsidies (see Table 1.1).

Table 1.1 Comparisons between Gasoline and Ethanol[1]

Item	**Density (kg/m^3)**	**High Heating Value (BTU/gallon)**	**$/Million BTU**	**Regular Price[2] ($/gallon)**
Regular Gasoline	737	125,000	20.0-24.0	2.5~3.0
Ethanol	789	84,600	23.6-29.5	2.0~2.5
1. Wikipedia, see ethanol item. 2. ICIS 2007 price quote. http://www.icispricing.com/				

On an equivalent BTU basis, the cost of ethanol should be 67% (1.7~2.0 \$/gallon) of the price of gasoline which is the ratio of the heating value of ethanol to that of gasoline ($\frac{84600\frac{BTU}{gallon}}{125000\frac{BTU}{gallon}} = 67\%$). At the present time the selling price of regular grade gasoline is about 2.50~3.00 dollars per gallon while the published manufacturing cost of ethanol from corn is about 1.5 dollar per gallon [Ethanol Market Price]. The goal set by the U.S Department of energy for ethanol from lignocellulosic material is 1.07 dollars per gallon by the year 2012 [Wooley, 1999]. Suggestions for possibly lowering the cost of bio-ethanol are to (a) lower the cost of transportation by building the bio-ethanol plant near the source of the biomass, (b) improve the ethanol fermentation yield, (c) increase the scale of production and (d) reduce the cost of the feedstock. One possibility is to use wood as the feedstock in ethanol plants and is the subject of this thesis.

1.1.2 Forest Products Industry

Recently the North American (NA) pulping industry has found it difficult to compete in the global economy. Global competitors like Brazil and Indonesia are using more advanced and cost effective technologies. To be more cost competitive the North American Forest Products Industry is hoping to increase revenue by producing bio-energy and bio-materials in addition to building and paper products [Van Heiningen, 2006]. In order to increase competitiveness, the North American Forest Products Industry is considering the production of highly desired liquid energy for domestic consumption. Consequently, a number of new biorefinery processes are being developed which use wood chips as the feedstock; for example, the Iogen Process, the Acid Catalyzed Organosolv Saccharification Process, and the Arkenol Process as derived by McColy and O' Connor [1999]. Notable among the advocates for the biorefinery is Adriaan Van

Heiningen of the University of Maine who proposes producing pulp and a number of by-products in an integrated manner.

1.2 Conceptual Biorefinery Processes

1.2.1 Conventional Kraft Pulp Mill

The three main constituents found in wood are cellulose, hemicelluloses and lignin and their contents are listed in Table 1.2. Wood also contains about 0.3 to 0.5% inorganics (Na, K, Ca, Ba, Cl, etc) as determined in an ash test. Additionally the wood contains about 3% to 8% extractives, which are low molecular weight compounds consisting primarily of fats (acids and alcohols), waxes and sterols in hardwoods and resins, terpenes, and phenolic compounds in softwoods [Sjostrom, E. 1981].

Table 1.2

Contents of Three Main Components of Wood (a)

Wood Components	**Hardwood (%)**	**Softwood (%)**
Cellulose	40-50	40-50
Hemicellulose	25-35	25-30
Lignin	20-25	25-35
(a) PULP & PAPER RESOURCES & INFORMATION SITE. http://www.paperonweb.com/wood.htm		

Figure 1.1 illustrates a typical conventional Kraft pulp mill process [Gullichsen, and Fogelholm, 2000]. In the conventional Kraft pulping process, primarily a mixture of sodium hydroxide (NaOH) and sodium sulfide (Na_2S) is used to convert wood chips into brownstock pulp in the pulping digester. Many complex chemical reactions occur in the pulping process, which is referred to as cooking. The cooking process is conducted under

elevated temperature and pressure conditions. During the cooking process approximately 40-50% of the wood mass is dissolved and forms black liquor, which is a mixture of the dissolved wood solids and the spent inorganic salts. The dissolved material consists primarily of degraded hemicelluloses, lignin and the extractives which are the degradation products of the reactions in the digester. Although a small portion of the cellulose is dissolved during the pulping process, it acts primarily as a tie substance and remains unchanged in the pulp except for a reduction in its molecular weight. The dissolved solids in the residual pulping liquor are referred to as black liquor and are separated from the pulp in external brown stock washers. The black liquor will contain about 50% of the wood solids that were entered into the process plus the spent cooking chemicals. Consequently, the black liquor will be combusted in a recovery boiler to produce steam and electricity. The pulping chemicals – sodium hydroxide (NaOH) and sodium sulfide (Na_2S) will be regenerated from the spent liquor in the recovery cycle. The products from the recovery boiler are primarily sodium sulfide (Na_2S) and sodium carbonate (Na_2CO_3). The sodium carbonate (Na_2CO_3) is converted into sodium hydroxide (NaOH) in the causticization process which uses lime (CaO) to convert sodium carbonate (Na_2CO_3) to sodium hydroxide (NaOH) and produces calcium carbonate ($CaCO_3$). The lime (CaO) is further regenerated from the precipitated calcium carbonate ($CaCO_3$) in a kiln operation termed lime burning. During the Kraft pulping process, although the wood chips lose almost all of the lignin and about half of their total solids content, they still can maintain their physical structure, but the structure has become so weak that they will break down to individual fibers. After a series of chemical and mechanical process such as washing, bleaching and drying etc, the fibers finished their mill life and can be sold in market as market pulp.

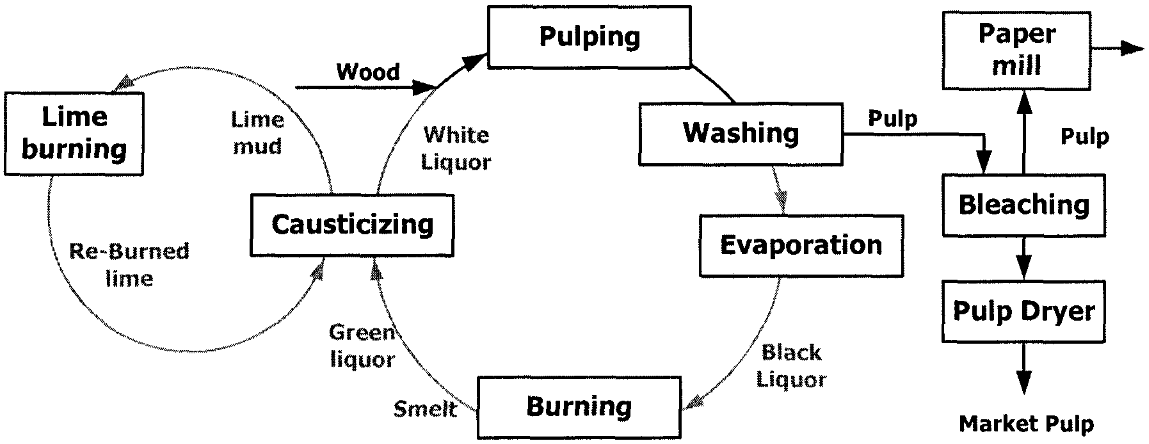


Figure 1.1 Conventional Kraft Pulping Processes [Gullichsen, 2000]

1.2.2 NREL Process for Producing Ethanol

A well known process for producing ethanol from bark-free, white wood was developed at the National Renewable Energy Laboratory (NREL). Details of this process are summarized by Wooley and coworkers [1999] and later by Mitchell [2006]. Figure 1.2 illustrates the basic unit processes in a wood to ethanol plant as envisioned by Wooley.

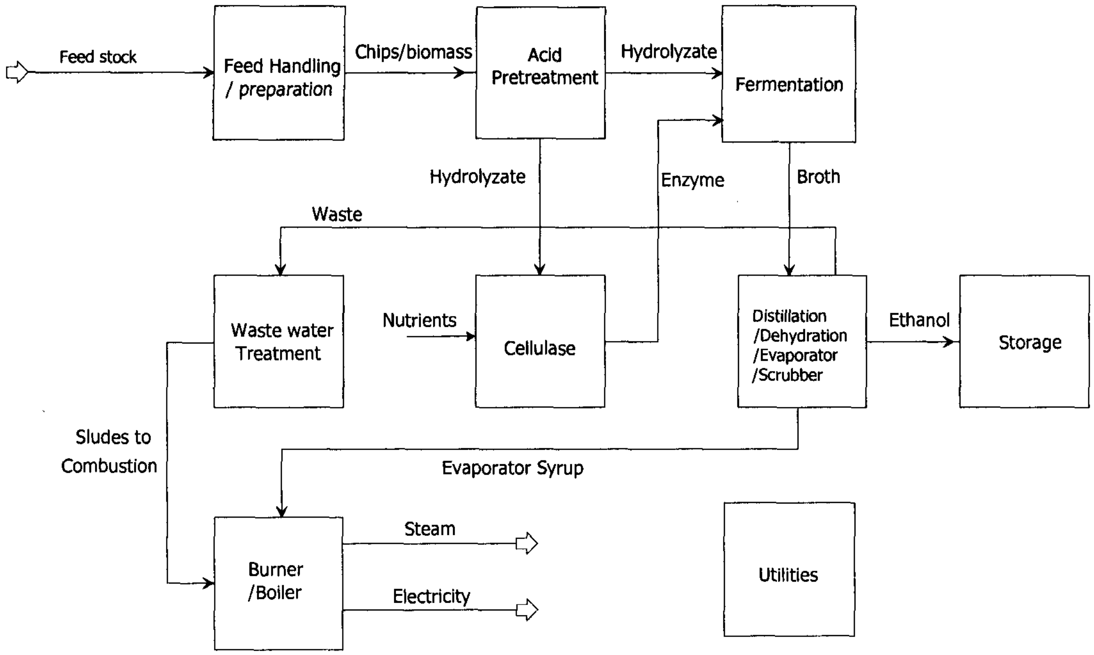


Figure 1.2 NREL Hardwoods to Ethanol Process [Wooley, 1999]

In the NREL process, wood chips are first upgraded in the feed handling and preparation section of the plant by removing metals, washing, screening and rechipping to achieve the appropriate size and degree of cleanliness. After the feed handling and wood preparation steps, the wood chips are processed in a pretreatment step where dilute sulfuric acid is applied in a high temperature environment. In the hydrolysis step most of the cellulose and hemicellulose in wood chips are hydrolyzed into mono-sugars. Following the acid hydrolysis step a portion of hydrolyzate is separated and sent into a cellulase production process where cellulase enzyme is produced. Then the remainder of the hydrolyzate is sent into the fermentation step where it is mixed with the cellulase enzyme and the mono-sugars in the hydrolyzate are fermented into ethanol by the cellulase enzyme. The products from the fermentation step termed broth, containing dilute ethanol, is discharged and sent to a ethanol recovery system where the broth is concentrated by evaporation and the ethanol separated by distillation and dehydration.

The ethanol product from the evaporation step is sent to a distillation system where the ethanol concentration is raised to the azeotropic composition; 95% ethanol and 5% water. The ethanol water mixture is further purified to 100% ethanol by dehydration. The residual lignin and unfermented hemicellulose from the evaporator are then conveyed into a furnace and boiler for steam and electricity production. Operation details on the process and an economic model are given by Wooley [1999]. Wooley's economic model was built used ICARUS software. In the NREL process the only products are ethanol and electrical energy. But unfortunately, the NREL process suffers from a very high capital investment and Wooley evaluated that the required selling price exceeds the expected market price ($2.5/gallon).

1.2.3 Co-Production of Ethanol and Cellulose Fiber

Another extensively discussed process to produce ethanol from lignocellulose feedstock is Co-Production of Ethanol and Cellulose Fiber Process developed at the Georgia Institute of Technology [Frederick, 2006]. The conceptual diagram for this process is shown in Figure 1.3. The debarked wood feedstock is pre-hydrolyzed with dilute sulfuric acid for a specified time (24-115 minutes) depending upon the mass fraction of wood removed. The prehydrolysis reaction is carried out at 150°C. Under these conditions Frederick estimates that about 6% - 18% of the debarked wood mass is extracted. The extracted material consists of soluble sugars; xylose, mannose, arabinose and galactose. The prehydrolysis reaction also converts some of the cellulose to glucose, and part of lignin is also solubilized. The hydrolyzate is fermented into ethanol after contaminants are removed that inhibit fermentation. The ethanol product is recovered by steam stripping and distillation. A portion of the biomass input to the biorefinery is converted to waste products. The waste products are generated either from the acid hydrolysis operations, the fermentation operation as ethanol plant residue, or from delignification as black liquor. The acid extracted wood chips are subsequently delignified to produce cellulose fibers. Compared to the NREL ethanol process, the Georgia Tech process is simpler and generates more revenue with the sale of two products, ethanol and wood pulp, but the process requires large amounts of sulfuric acid and the corresponding operation cost is high.

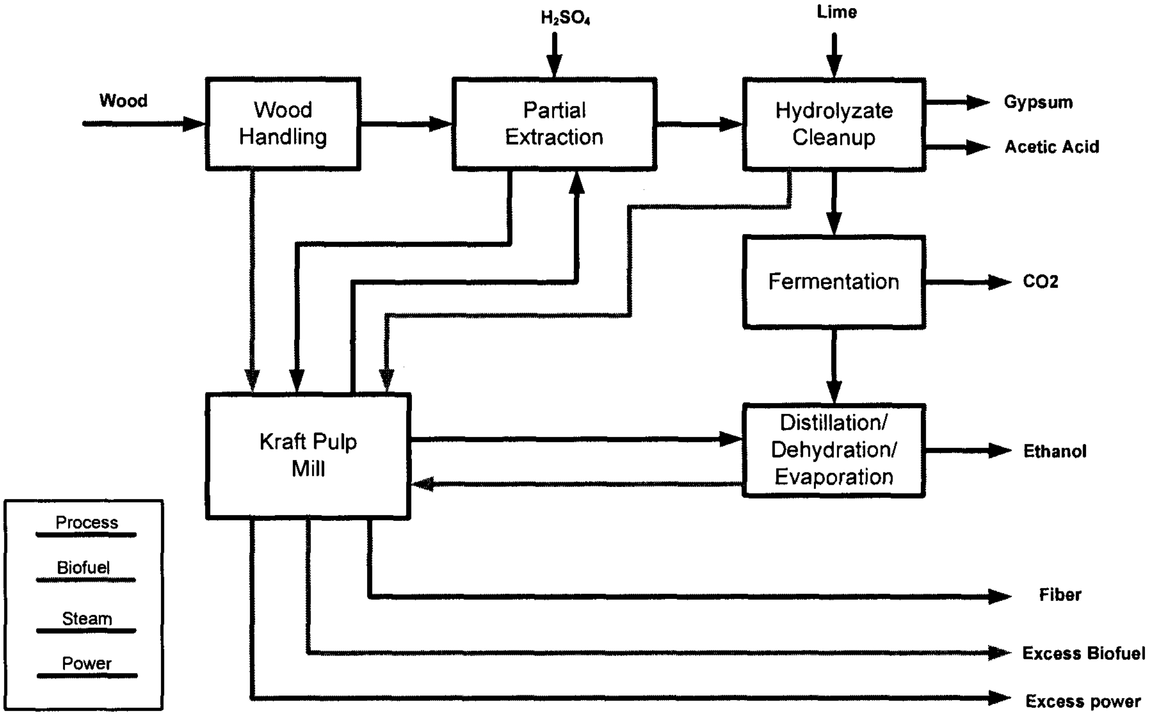


Figure 1.3 Conceptual Diagram of an Ethanol Plant Integrated with a Kraft Pulp Mill

1.2.4 IFBR Process with Products of Market Pulp, Ethanol and Acetic Acid

Professor Adriaan Van Heiningen at the University of Maine has proposed an Integrated Forest Biorefinery Concept (IFBR). This concept is illustrated in Figure 1.4. The Van Heiningen IFBR concept uses lignocellulosic feedstock rather than sugar based feedstock to produce a variety of new bio-products in a highly integrated and energy efficient manner. Potential new products include green power and steam, wood composites, liquid fuels, sugar based chemicals and polymers [Van Heiningen, 2006].

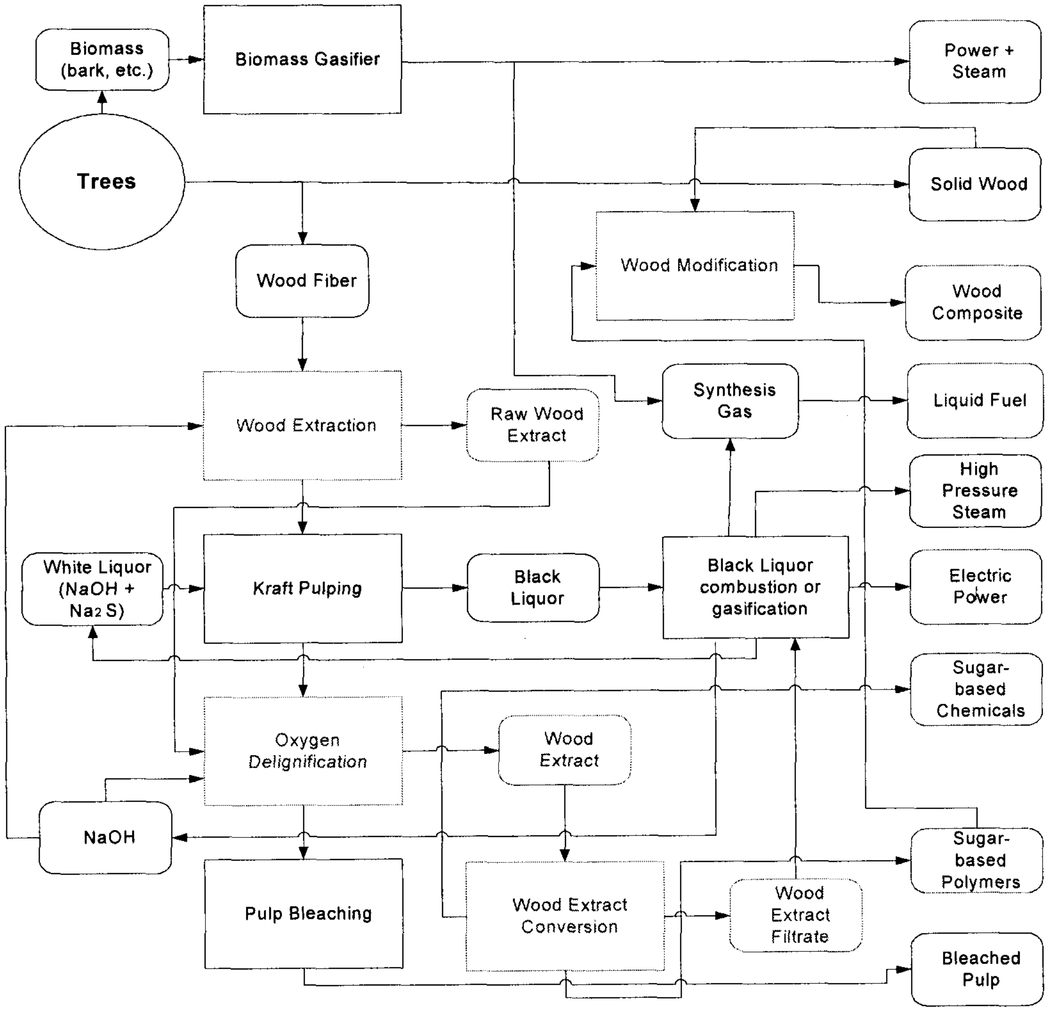


Figure 1.4 Integrated Forest Products Refinery Concept

In the IFBR concept, a portion of the hemicellulose polymers from hardwood chips, principally xylan, is extracted while maintaining pulp as the primary product. The site of the IFBR would be existing Kraft pulp mills. Although a variety of products are proposed, current IFBR research is focused on market pulp, ethanol and acetic acid at hardwood Kraft pulp mills. The biggest difference between the Van Heiningen IFBR process and a conventional Kraft pulp mill is that a hemicellulose extraction step is included prior to pulping. The process which produces ethanol and acetic acid from extracted hemicellulose is referred to as the "near- neutral" hemicellulose extraction process. In the extraction step, green liquor (GL) and anthraquinone (AQ) are used as the extraction chemicals in the process. The main chemical components of green liquor are sodium hydrolysis (NaOH) and sodium carbonate (Na_2CO_3) which acted to dissolve a portion of the hemicellulose polymers in the wood. Anthraquinone functions as a pulping catalyst to preserve the pulp yield following conventional pulping. By controlling the temperature and time of wood extraction, approximately 10% of the wood weight in the form of hemicellulose polymers and lignin are dissolved from the wood chips while maintaining essentially the same the pulp quality as conventional Kraft pulp. The hemicellulose polymers that are dissolved in the extraction liquid are then converted into ethanol and acetic acid co-products. A detailed diagram of IFBR process is shown in Figure 1.5 where the principal products are market pulp, ethanol and acetic acid.

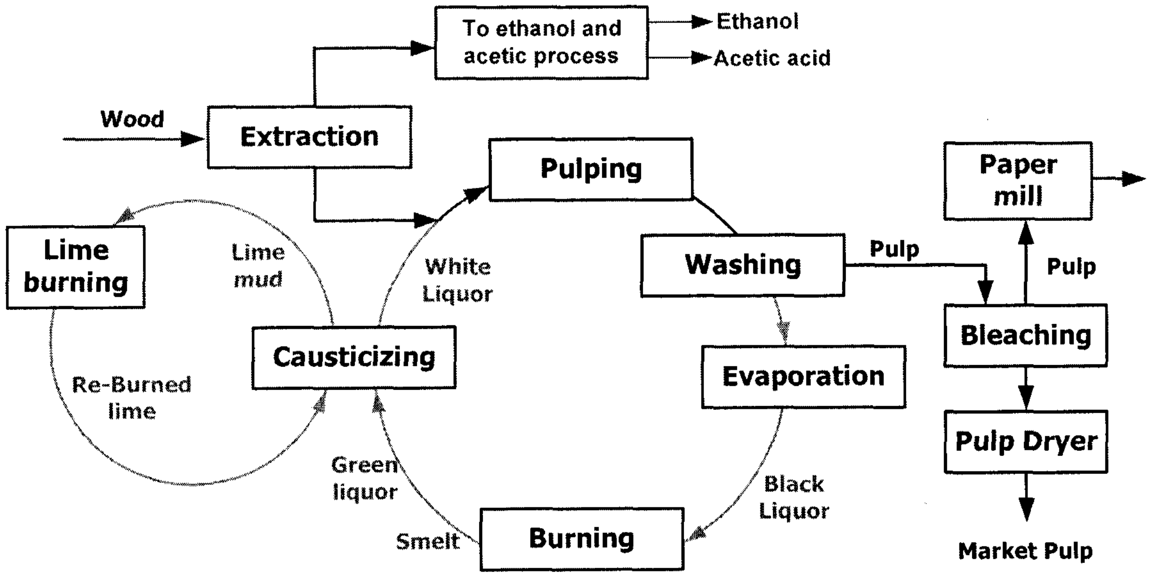


Figure 1.5 Current IFBR Process with Products of Pulp, Ethanol and Acetic Acid

In the hemicellulose extraction process, most of the hemicellulose polymers which are dissolved and converted into ethanol and acetic acid would normally be burned to retrieve energy in a conventional Kraft pulping process. The revenue associated with the sale of ethanol and acetic acid will make the IFBR concept more economically beneficial than producing solely Kraft pulp. A technical evaluation for producing ethanol from hardwood chips has been reported by Wooley [1999] and by Mitchell [2006]. The technical and economic feasibility of the hemicellulose extraction process is the subject of the work reported here.

1.3 Objective and Scope

The objective of the current work is to perform a technical and economic analysis of the hemicellulose extraction process proposed by Adriaan Van Heiningen in which the co-products are acetic acid and ethanol in addition to bleached hardwood Kraft pulp. This work compliments the work originally reported by Wooley and coworkers [1999] and later by Mitchell [2006] in which ethanol is produced from white wood using the NREL process. In Wooley and Mitchell's work the entire carbohydrate proportion of the wood is used to produce ethanol and the lignin fraction is burned to produce green power. This process differs from the current work where the main product from the mill is still hardwood Kraft pulp and the extracted materials are converted to ethanol and acetic acid. The acetic acid results from the acetyl groups on the hemicelluloses which are hydrolyzed during the extraction process and subsequently converted to acetic acid. In the NREL process the acetyl groups in the wood would either be burned or sent to the waste treatment plant.

The scope of the present project was to develop a computer model for performing an energy and material balance for the hemicellulose extraction process. In this work a conventional Kraft fiber line was used as the base case for comparison. Based on the material and energy results determined from the simulation model, the capital and operation cost for the proposed new hemicellulose extraction process was estimated from empirical equations published by Mitchell and from selected vender quotations. In this work, an incremental analysis was performed. In the incremental analysis the economics were considered for adding the new equipment to an existing Kraft pulp mill. The economic viability of the process was assessed by using the discounted cash flow rate of return on investment. Lastly, a discussion is presented delineating the advantages and disadvantages of the hemicellulose extraction process.

Chapter 2

BASE CASE – EXISTING KRAFT PULP MILL

An existing Kraft pulp mill was used as the site for the hemicellulose extraction process and thus served as the base case in the economic analysis. The Kraft or sulfate process uses a mixture of sodium hydroxide (NaOH) and sodium sulfide (Na_2S) to extract lignin from wood chips in digesters to produce pulp which is used in the papermaking process. The pulp may be bleached or unbleached and may be used at the same site in an integrated mill or alternatively sold on the open market. The process name is derived from the German word *kraft*, meaning strong or powerful because of the high tensile and tear strength of the product. The Kraft pulping process was developed by Carl Dahl in 1884 and now is used extensively throughout the world. Kraft pulp is utilized in approximately 80% of the production volume of paper [Kraft Process].

2.1. Process Overview

The basic unit processes comprising a bleached Kraft fiber line includes a wood yard, a Kraft pulping or cooking process, pulp washing, bleaching and drying. In addition to the fiber line it has pulp procession operations for removing shives or uncooked pulp, cleaning and screening operations for removing impurities in the pulp, and processes for recovery of the energy content in the dissolved wood solids. In addition, the pulping chemicals are regenerated from the spent liquor stream.

The basic process flow diagram for the existing Kraft pulp mill is shown schematically in Figure 2.1 where market pulp is produced. In the process raw wood is delivered to a wood yard for storage and wood processing. In the analysis presented here, the wood supply to the mill was assumed to be round wood. After the wood is debarked, chipped and screened the accepted chips are sent a continuous digester. The chips are steamed to remove air and preheat the chips to a high temperature. After preheating with steam, the wood chips at elevated temperature are sent into a large pressure vessel called a digester. In the digester the wood chips are impregnated or soaked in white liquor at a liquor wood ratio of four (4); that is four pounds of cooking liquor are added into the digester per pound of wood on a dry basis. After impregnation, the wood chips are then heated to the digester temperature for dissolution of the lignin. Then after delignification and carbohydrate degradation reactions, most of hemicellulose and lignin in the wood structure are dissolved into the spent liquor, which is called "black liquor". After leaving the digester, the wood chips are converted into individual fibers by application of mechanical energy, either in an outlet devise in the case of a continuous digester or a blow tank in a batch digester operation. Wood pulp from the digester are next processed to remove knots or uncooked chips that have very high lignin content, washed to remove black liquor and then screened to remove shives or oversized pulp particles, and sometimes cleaned to remove debris from the pulp.

Black liquor is sent into evaporators for concentrated and then sent into the recovery boiler for chemicals and energy recovery. Steam and electricity power are produced in the recovery boiler to meet the energy requirement of mill. In the model developed here excess energy over and above that required for satisfying the energy balance of the kraft mill are converted to electrical energy and sold on the open market as a source of revenue. It was assumed that both internal and external washing are performed in the process. Internal washing is performed in the bottom of the digester to remove dissolved wood solids and spent chemicals from the wood chips. External washing was assumed to be done in three stages of vacuum drum washing to again remove dissolved organic and inorganic wood solids from the fibers. After washing the wood pulp is then bleached to high brightness in a three stages ($DE_{OP}D$) or four stage ($DE_{OP}D_1D_2$) bleach plant for the production of market pulp. Typical bleaching sequence include application of chlorine dioxide (D_o) in the first stage followed by an extraction stage (E_{op}) reinforced with oxygen (O) and hydrogen peroxide (P) followed by a finally chlorine dioxide (D_1) stage. For very high brightness pulp a fourth chlorine dioxide (D_2) stage is sometimes added. In the bleach towers the lignin contend is decreased further and the brightness of the pulp increased. After bleaching, the wood pulp is formed into sheets, pressed, dried, and baled for sale on the open market.

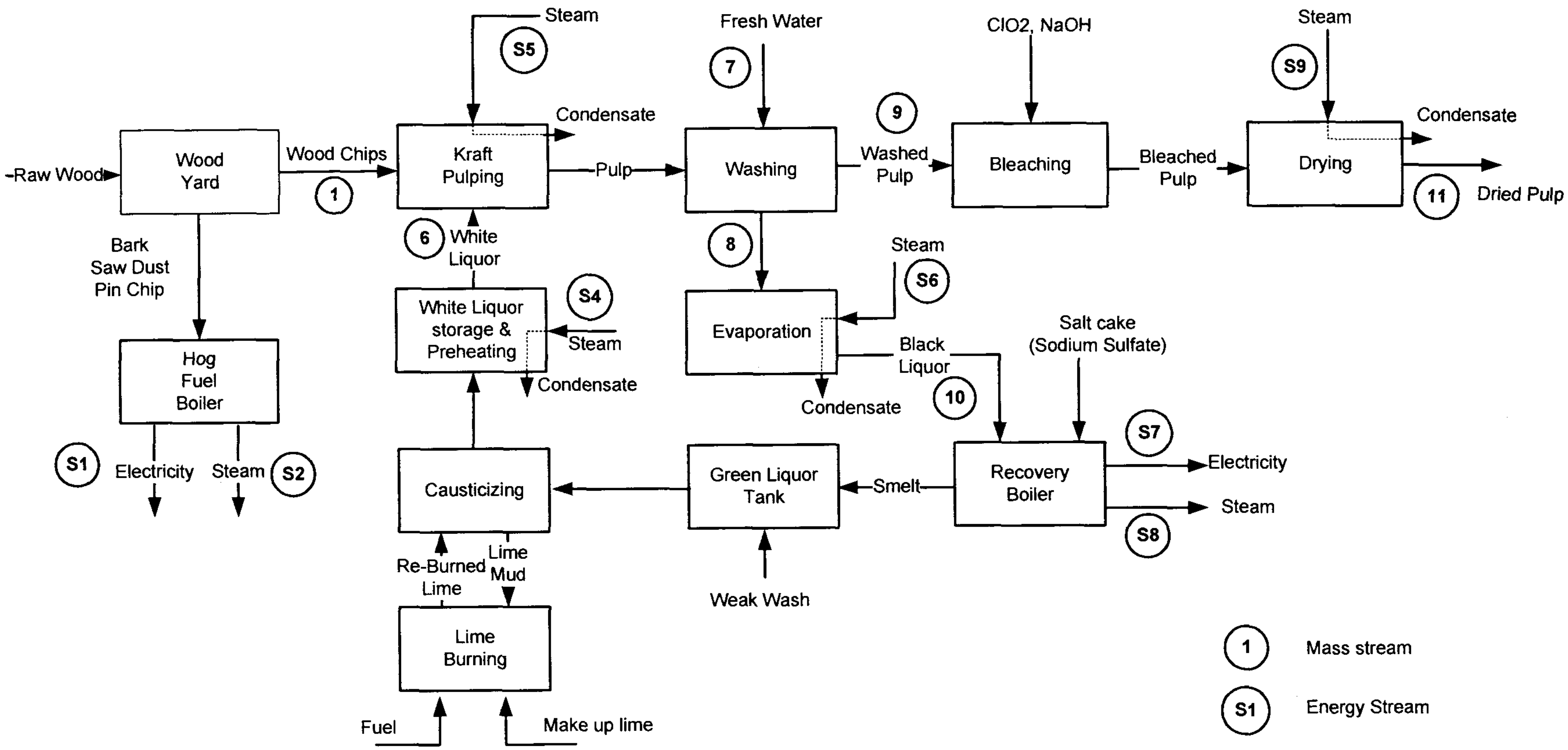


Figure 2.1 Process Flow Diagram of Base Case with Product of Market Pulp

2.2 Plant Size

The plant size must be specified to perform detailed material and energy balances for an existing Kraft pulp mill. In most circumstances, the cost of equipments does not scale linearly to the plant size; but rather the larger the plant size the lower the equipment cost per unit of capacity. However, savings from the lower unit equipment cost may be offset by the increased cost for long-distance feed stock collection and transportation. The larger the plant size, the greater the amount of feedstock required and the higher the cost of transportation to the mill site since the feedstock need to be collected over a greater area.

In previous research [Wooley 1999, Aden, 2002, and Mitchell, 2006], the quantity of feedstock was chosen as the basis for the plant size and the amount of product allowed to vary depending upon the feedstock. By contrast, in the current research it was assumed that the production rate of pulp had to be maintained constant both at the existing Kraft pulp mill and also in the case where the Kraft pulp mill was modified to accommodate the production of ethanol and acetic acid by the hemicellulose extraction process. Once the basis is fixed, any reasonable quantity can be selected as the plant size. In the base case, a production rate of 1,000 metric tonne per day of market pulp was chose as the production rate of the main product. In subsequent parametric studies discussed later, the size of the plant was changed accordingly to 750 and 1,500 tonnes per day of Northeastern bleached hardwood Kraft pulp. Results from the three plant sizes study were then plotted and curve drawn relating capital costs, operation costs and return on investment to plant size.

2.3 The Composition of Feedstock

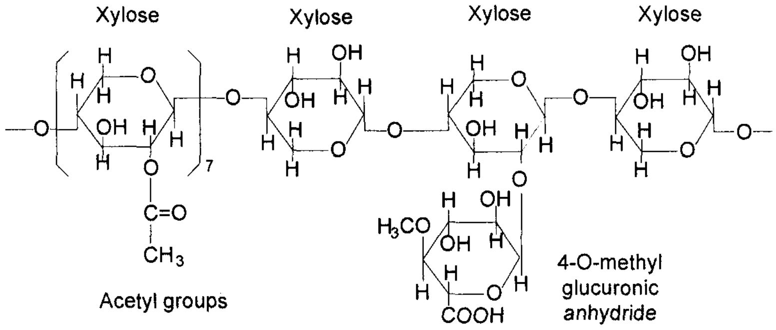
The characteristics of the feedstock have a significant impact on the overall mass and energy balance analysis for the process. Generally the composition of the feedstock and the pulp yield are the primary variables that will determine the amount of market pulp that can be produced from a given quantity of material. Also in the modified Kraft pulp mill case discussed in the next chapter, the feedstock composition and the amount of hemicelluloses extracted from the wood have a major impact on the amount of ethanol and acetic acid produced. The composition of feedstock can be determined from summative analyses once the species of feedstock is chosen. In the current research commercial mixed Northeast hardwood chips (birch, beech and maple) were chosen as the feedstock. A summative analysis on the feedstock is summarized in Table 2.1.

Table 2.1

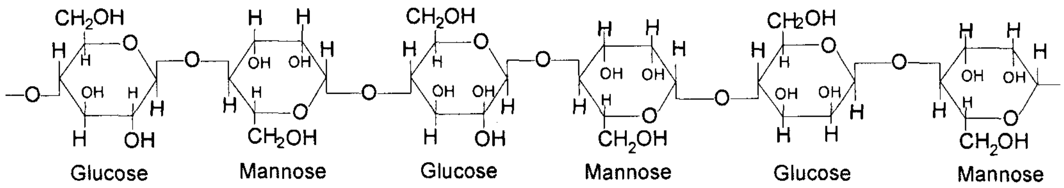
Composition of Feedstock [Van Heiningen, 2006]

Sample - Mixed Hard Wood		**% Weight of Dry Basis @**
Cellulose		42.6
Lignin		27.5
Hemicellulose	Acetyl Group	3.5
	4-O-MGA	4.6
	Arabinan	0.5
	Galactan	0.9
	Glucan	1.3
	Xylan	16.7
	Mannan	2.1
Ash		0.2
Total Weight of Dry Sample		100.0
@ Extractive free basis		

The composition of the feedstock shown in Table 2.1was used in the simulation model. In this analysis the mixed hardwood was assumed free of extractives. This assumption is equivalent to assuming that the extractives do not affect the hemicellulose extraction and the recovery of acetic acid and ethanol. The chemical structure of the main components, xylan and mannan, are shown in Figure 2.2 (A and B). The Glucuronoxylan has a backbone of ten (10) xylose units, approximately 7 of which are substituted at the number 2 and 3 position with acetyl groups. It is these acetyl groups that are cleaved during the hemicellulose extraction process that are converted to acetic acid. In addition there is one 4-O-methyl glucuronic anhydride unit for each 10 xylose units. The xylose and 4-O-methyl glucuronic acid units can be converted to ethanol by fermentation.



(A) Structure of Glucuronoxylan [Sjostrom, E., 1981]



(B)Structure of glucomannan [Sjostrom, E., 1981]

Figure 2.2 Chemical Structures of Xylan and Mannan

In the glucomannan polymer, the glucan to mannan ratio varies between 1:1 and 1:2. Also there are few, if any, acetyl side chains that can be cleaved during the extraction process. The mannose and glucose sugars can be converted to ethanol by fermentation.

2.4 Detailed Process Description

Preliminary material and energy balance calculations were performed using MathCAD as the process simulator. The bases for these calculations are summarized in Table 2.2. Performing the process simulation in MathCAD proved to be lengthy and onerous. Consequently the MathCAD simulation was abandoned and the simulation was conducted by using WinGEM version 5.3 computer packages.

Table 2.2

Design Basis for the Existing Kraft Pulp Mill Process

Item	Value
Bleached Pulp Production Rate	1,000 tonne/day
Feed Stock	
Consistency of raw wood	50%
Bark content	10%
Wood lost in debarking	0.5%
Temperature	20°C
Wood Preheating Temperature	80°C
Pulping Conditions	
Effective Alkali(EA)	15%
Sulfidity	30%
Liquid to wood ratio	4
Temperature	170°C
Heating ramping time	70 minutes
Steam condition	150 psig High Pressure steam
Target Kappa number	16
H Factor	1500 Hours
Kappa parameters A1, B1, n1	315, 45.6 and 0.3
Yield parameters A2, B2, n2	87.5, 4.25 and 0.4
Pulping yield	47%
Internal Chip Washing	
Diffusion washing	
Norden Number	3
External Drum Washer	
Stages	3
Dilution factor	3
Displacement ratio	3
Evaporator and Boiler	
Steam economy of multiple evaporator	4.2 lb water/ lb steam
Steam condition	72 psig Medium pressure steam

Table 2.2 Continued

Solid content of strong black liquor	75%
Net Heating Value of black liquor	12.76 MJ/kg
Bleaching Condition	
Yield	90%
Kappa number after bleaching	4
Pulp Drying Condition	
Steam condition	30 psig low pressure steam
Consistency of dry pulp	94%
Hog Fuel Boiler Condition	
High heating value of barks	21.05 MJ/kg
Energy efficiency for steam production	80%
Energy efficiency for electricity production	20%
General	
Density of pure water	1000 kg/m^3
Heat capacity of wood	0.3 $BTU/lb\cdot{}^{o}F$
Heat capacity of pure water	1.0 $BTU/lb\cdot{}^{o}F$

2.4.1 Wood Yard Process

The feed to the pulp mill was assumed to be 100% hardwood in the form of long logs which are stored in the mill yard. The moisture content of the feedstock was assumed to be 50%. The bark content of the wood was taken as 10% on a dry weight basis. The full length wood was assumed to be cut to four (4) foot lengths, debarked, chipped and screened. Oversized chips were re-chipped and re-screened in the wood yard. In the analysis, 100% of the bark was assumed to be removed in the debarking operation and 0.5% of the wood matter was lost during wood processing. The wood losses were assumed to occur as sawdust, pin chips and fines which together with the bark were sent to the Hog fuel boiler. For simplicity, it was assumed that the consistency of debarked wood chips was essentially unchanged during the wood processing operations.

2.4.2 Preheating and Pulping Process

Figure 2.3 illustrates the pulping process used in the computer simulation. The process configuration involves wood preheating, continue digester pulping, in digester chip washing and external drum washing.

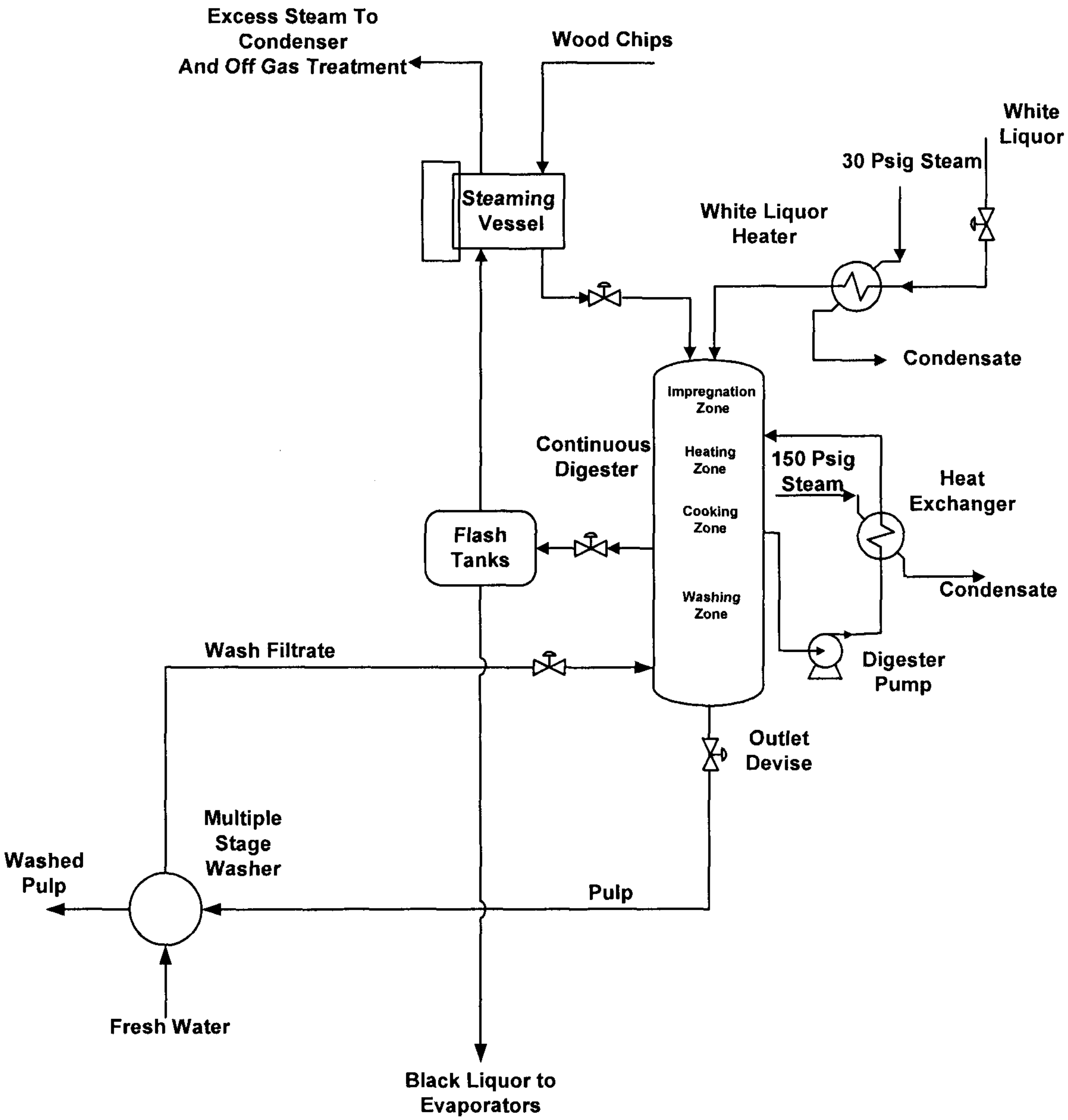


Figure 2.3 Configurations of Several Process Steps in an Existing Kraft Pulp Mill

Digester Operation. The wood chips after wood yard processing are preheated directly in a steaming vessel with low pressure steam that is recycled from the flash tanks. The temperature of the wood was assumed to be approximately 80°C. Following pre-steaming and air removal in the steaming vessel, the chips are then conveyed into a continuous pulping digester by re-circulating cooking liquor. In the digester, the chips are impregnated with the cooking liquor, heated to the cooking temperature of 170 °C, cooked for a predetermined time given by the H-factor and then washed counter-currently in the bottom zone of the digester by using wash water that is coming from an external multi-stage washer. In the process simulation, pulping was assumed to occur using a continue digester. It should be pointed out that the process could be done equally as well as used a batch digester.

In the digester, the chips maintain their wood structure during chemical pulping despite the loss of most of their lignin content and about half of their total solid mass. But the structure has become so weak that the chips will break down to individual fibers by modest mechanical action. Delignifying chemicals cannot easily penetrate directly to the compact lignin-rich middle lamella which binds cells together in wood. Chemicals travel mainly from the hollow fiber lumens through the semiporous cell walls towards the middle lamella, dissolving lignin and carbohydrates along the way. The material in the middle lamella is dissolved last [Gullichsen and Fogelholm, 2000]. The chips are separated into individual fibers by shear forces provided delignification is taken far enough which occurs upon discharge the chips from the bottom of the digester.

Cooking Liquor. The Kraft cooking liquor is a mixture of fresh white liquor, water in the chips, condensed steam and weak black liquor used to adjust the liquor-to-wood ratio (L/W). The liquor to wood ratio in commercial digesters varies from approximately 2.5 to as high as 4. The higher the liquor to wood ratio, the greater the amount of energy that will be consumed in heating the mass in the digester, but the better the degree of impregnation. It is highly desired for the wood to be completely impregnated to minimize pulp regents, or undercooked wood. The white liquor is strongly alkaline and typically has a pH of approximately 14. The active ingredients in the white liquor are sodium hydroxide (NaOH) and sodium sulfide (Na_2S). The white liquor also contains small amounts of a variety of salts such as Na_2CO_3, Na_2SO_4, $Na_2S_2O_3$, NaCl and $CaCO_3$ plus other accumulated salts. These non-process elements do not enter into the chemical reactions and act on as a dead load on the system and re-circulate through the recovery cycle. The non-process elements enter into the white liquor either as contaminants accompanying the raw materials or as a result of inefficiencies in the chemical regeneration cycle. The active species in the white liquor are the NaOH and Na_2S and to a lesser extent Na_2CO_3. All of the active species dissociate in water as they are strong electrolytes. The following equilibrium reactions prevail in white liquor [Gullichsen and Fogelholm, 2000].

$$NaOH \rightarrow Na^+ + OH^- \tag{2.1}$$

$$Na_2S + H_2O \rightarrow 2Na^+ + S^{2-} + H_2O \tag{2.2}$$

$$\mathrm{S}^{2-} + \mathrm{H_2O} = HS^- + \mathrm{OH}^- \tag{2.3}$$

$$Na_2CO_3 + H_2O = 2Na^+ + CO_3^{2-} + H_2O \tag{2.4}$$

$$CO_3^{2-} + H_2O = HCO_3^- + OH^- \tag{2.5}$$

A variety of chemical additives have been used in Kraft pulp [Francis, 2006, Wang, 2005]. In the study reported here it was assumed that anthraquinone was added at a level of 0.05% by weight to act as a pulping catalyst to increase pulp yield and selectivity [Sjostrom, 1981].

The continuous digester process was modeled as having four zones; an impregnation zone, a heating zone, a cooking zone and a washing zone. The different zones in the digester have different functions in the process. In the impregnation zone, wood chips are impregnated or soaked with cooking liquor. The quantity of white liquor used in cooking liquor was determined by the chemicals charge based on wood. The chemical properties and composition of Kraft cooking liquors are defined as [Gullichsen, J and Fogelholm, 2000]:

$Total\ Alkali$: $All\ Na^+\ compounds$

$(NaOH, Na_2S, Na_2CO_3,\ \ Na_2SO_4, Na_2S_2O_3, Na_2SO_4, etc)$

$Active\ ALkali, AA$: $NaOH + Na_2S$

$Effective\ Alkali, EA$: $NaOH + \frac{1}{2}Na_2S$

$Sulfidity$: $100 \times Na_2S/(NaOH + Na_2S)$

$Causticity$: $100 \times NaOH/(NaOH + Na_2CO_3)$

$Reduction$: $100 \times Na_2S/(Na_2S + Na_2SO_4)$

Technically the effective alkali (EA) and the sulfidity (S) of the white liquor are used to control the chemical charged. Once the chemical charge is decided, the quantity of pulping chemical used in the digester can be determined. After the impregnation zone, wood chips enter into the heating zone. In this zone, the wood chips and liquor are heated to the pulping temperature by re-circulating the liquor through a series of indirect heat exchangers. Heating was assumed to occur in an upper and lower heating zone. Figure

2.4 illustrates the heating schedule of the pulping process which was assumed to be linear with time. High pressure steam was assumed to provide the energy for heating the chips and liquor. The equation for the energy balance in for heating zone is listed in Equation 2.6.

$$\textit{Enthalpy change} \text{ from steam} =$$

$$\left[\frac{dH}{dt}\right] = F_{wood} \times Cp_{wood} \times \Delta T + F_{Liquor} \times Cp_{liquor} \times \Delta T \tag{2.6}$$

where F_{wood} and F_{Liquor} are the mass flow rates of the wood and cooking liquor respectively, Cp_{wood} and Cp_{Liquor} are the respective heat capacities and ΔT is the temperature change.

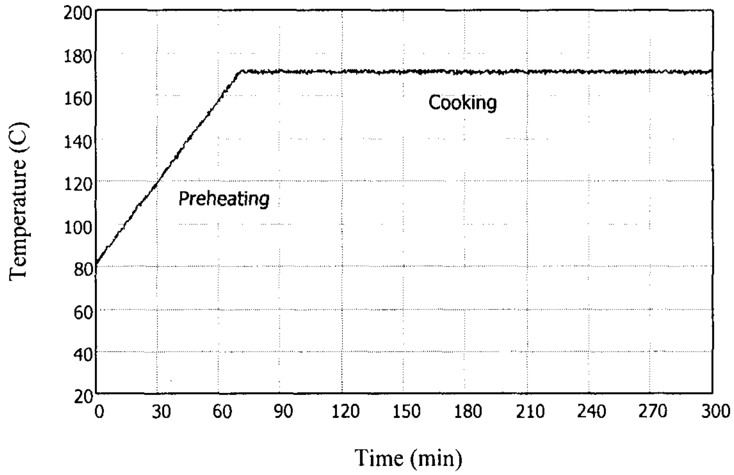


Figure 2.4 Heating Schedule of Hardwood Pulping

The parameter used to estimate the degree of pulping in the digester was the H-factor which is defined by Equation 2.7.

$$H = \int_{0}^{t_{max}} \exp\left(43.20 - \frac{16113}{T(K)}\right) dt \tag{2.7}$$

where T is the temperature in degrees Kelvin and t_{max} is the maximum time of cooking in hours. The exponential term represents the relative reaction rate defined by

Vroom [1957]. Based upon Equation 2.8 and a desired H factor, the residence time for cooking was estimated. The kinetic pulping model proposed by Hatton [1973] was used to estimate Kappa number and yield in the digester. Hatton's equations are illustrated in Equations 2.8 and 2.9.

$$Kappa = A_1 - B_1 \times \log(H) \times EA^{n_1} \tag{2.8}$$

$$Yield = A_2 - B_2 \times \log(H) \times EA^{n_2} \tag{2.9}$$

where A_1, A_2, B_1, B_2, n_1 and n_2 are empirical constants which are listed in Table 2.2. EA is the effective alkali. In the analysis presented here, the empirical constants were estimated from experimental data for the Kappa number and pulp yield provided by Van Heiningen [2006]. The empirical constants are shown in Table 2.2. Once the kappa number and yield are determined, the composition of cellulose, hemicellulose and lignin in fiber can be decided from a simple material balance (see Equation 2.10~2.12). In Equation 2.12, the cellulose is treated as a tie substance and assumed not to be dissolved.

$$X_1^p + X_2^p + X_3^p = 100\% \tag{2.10}$$

$$X_1^w + X_2^w + X_3^w = 100\% \tag{2.11}$$

$$\frac{X_1^w}{Yield} = X_1^p \tag{2.12}$$

where: X_1^p *and* X_1^w = content of cellulose in pulp and wood.

X_2^p *and* X_2^w = content of hemicellulose in pulp and wood.

X_3^p *and* X_3^w = content of lignin in pulp and wood.

$Yield$ = overall pulping yield

In the digester following the cooking zone, the chips pass into a counter-current diffusion washing zone. Wash liquor from an external washer enters the bottom of the digester and flows countercurrent to the chips where dissolved solids are removed by diffusion. At the interface between the cooking and the washing zone black liquors are extracted using screens in the digester and sent to a series of flash tanks. In estimating the washing efficiency in the digester (Figure 2.5), the Norden washing model was used [Genco, 1998].

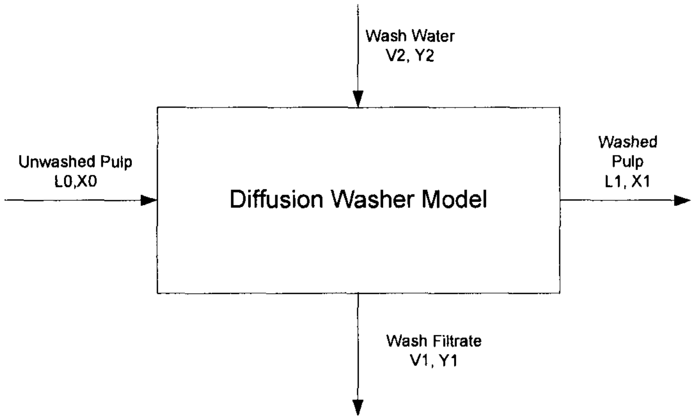


Figure 2.5 Internal Diffusion Washing Model

Washing Norden efficiency. The Norden model consists of writing material balance for the total mass and for the black liquor solids which are removed from the chips.

Solids $$L_0 \times x_0 + V_2 \times y_2 = L_1 \times x_1 + V_1 \times y_1 \qquad (2.13)$$

Total $$L_0 + V_2 = L_1 + V_1 \qquad (2.14)$$

where: L_0 =Flow rate of liquor in unwashed pulp, tonne liquor/tonne pulp.

x_0 = Weight fraction of dissolved solids in the liquor of unwashed pulp.

L_1 = Flow rate of liquor in washed pulp, tonne liquor/tonne pulp.

x_1 = Weight fraction of dissolved solids in the liquor of washed pulp.

V_2: = Flow rate of liquor in wash water, tonne liquor/tonne pulp.

y_2: = Weight fraction of dry solids in wash water.

V_1: = Flow rate of liquor in wash filtrate, tonne liquor/tonne pulp.

y_1: = Weight fraction of dry solids in wash filtrate.

The Norden efficiency (E) relates the equilibrium number of washing stages to the flow rates of unwashed pulp (L_0), washed pulp (L_1) and washed water (V_2) and their compositions.

$$E = \frac{\ln\left[\frac{L_0 \cdot (x_0 - y_1)}{L_1 \cdot (x_1 - y_2)}\right]}{\ln\left(\frac{V_2}{L_1}\right)} \tag{2.15}$$

The black liquor solids fraction inside the pulp (X_1) and the liquor flow rate of chips (L_1) discharged from digester were estimated using Equation 2.13 to 2.15.

After pulping in the digester, the liquid from the digester is sent into flash tanks for energy recovery. The cooked wood chips are conveyed through an outlet devise which fiberizes the chips into pulp and then sent to an external multiple stage washers for further washing to remove the dissolved solids from the pulp. In the external washing model, three stages of brown stock washing were assumed to take place using drum washers.

2.4.3 Flash Tanks Process

The hot black liquid going to the flash tanks has a high temperature and thus contains considerable sensible heat which is recovered in the form of steam in the flash tanks. In most circumstances the pressure in the flash tank is controlled by a pressure valve which sets the enthalpy of the steam and the solids concentration of the black liquor. The low pressure steam from the flash tanks is sent into a pre-steaming vessel for heating the incoming wood chips. The flash tank model is illustrated in Figure 2.6.

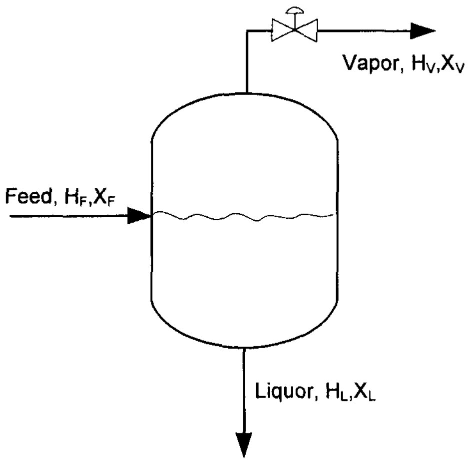


Figure 2.6 Flash Model

The total and solids material balances are shown in Equations (2.16~2.18). In the model, the black liquor solids were assumed to be a non-volatile and thus act as a tie substance.

$$\text{Overall material Balance: } Feed = Liquor + Vapor \tag{2.16}$$

$$\text{Overall solids balance: } Feed \times X_F = Liquor \times X_L \tag{2.17}$$

$$\text{Overall energy balance: } Feed \times H_F = Liquor \times H_L + Vapor \times H_V \tag{2.18}$$

where: X_F *and* X_L = solids content in feed and liquor.

H_F, H_L *and* H_V = Enthalpy of feed, liquor and vapor respectively.

These three equations are solved to give the flow rate and concentration of black liquor going to the evaporators. After leaving the flash tanks, the hot liquid is sent to the evaporators for further concentration.

2.4.4 External Multiple Stage Washing Process

The main function of the external washing process is to remove additional wood solids and spent chemicals from the pulp. Here a three-stage external drum washer model was used to simulate external washing (see Figure 2.7).

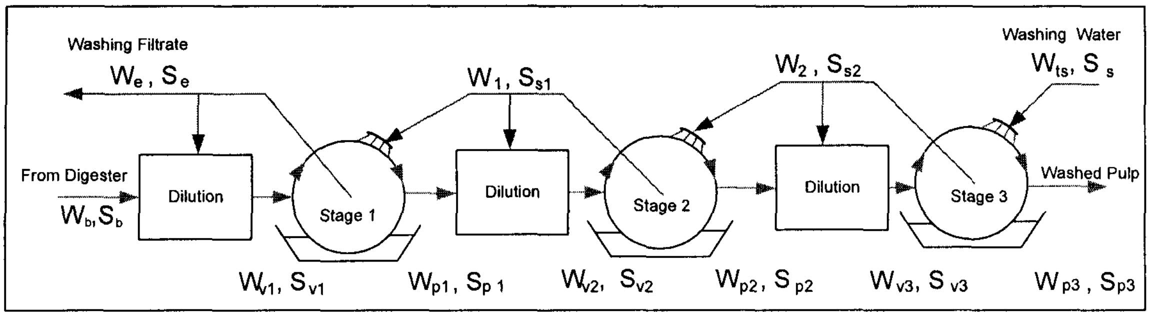


Figure 2.7 Three Stages External Drum Washing Model

The water balance equation involved in the drum washer is listed in Equation 2.19. [Smyth, 1982]

$$W_B \times (1 - S_B) + W_{TS} \times (1 - S_S) = W_E \times (1 - S_E) + W_{P3} \times (1 - S_{P3}) \tag{2.19}$$

where: W_B and S_B = mass and solid content of the pulp coming from the digester.

W_{TS} and S_s = mass and solid content of the incoming washing water. (For pure water S_s=0)

W_E and S_E= mass and solid content of the wash filtrate.

W_{p3} and S_{p3} = mass and solid content of the washed pulp came from the third stage of washing.

In Equation 2.19 the liquor streams (W_B, W_{TS}, W_{P3}) have the units of kg liquor per kg of pulp. Similarly the dissolved solids (S_B, S_{TS} and S_{P3}) have the units of kg BL solids per kg of pulp. The equation for the dissolved solids balance is shown in Equation 2.20.

$$W_B \times S_B + W_{TS} \times S_S = W_E \times S_E + W_{P3} \times S_{P3} \tag{2.20}$$

The dilution factor (D) gives the net amount of water added to the washing system per pound of pulp. From the water and dissolved solids balances (Equation 2.20 and

2.21), the mass of liquor with the pulp (W_{p3}) and the dissolved solids content in the washed pulp (S_{p3}) can be determined.

$$D \text{ (Dilution factor)} = W_{TS} \times (1 - S_s) - W_{p3} \times (1 - S_{p3}) \qquad (2.21)$$

The washed pulp is then sent into the bleach plant and the wash filtrate goes back to the digester for internal washing and then goes to the flash tanks (Figure 2.3).

2.4.5 Evaporator Process

The main function of the recovery boiler is to recovery the thermal energy content of the dissolved wood solids and to reconstitute the cooking chemicals in the black liquor. However the black liquor from the flash tank is very dilute (8% to 15% dissolved solid content) and commonly is concentrated prior to burning in the recovery boiler in order to get higher energy efficiency in the recovery recycle. The black liquor is often concentrated to 70% solids content or greater for safety reasons to avoid explosions in the recovery boiler. Here it was assumed that a six-effect evaporator was used to concentrate the black liquor from approximately 15% to 75% solids content. The use of a six effect evaporators improves the overall energy efficiency of the recovery boiler. Commonly the steam economy for a six effect evaporator is about 4 to 5 pounds water per pounds steam [Geankoplis, 2003] and after concentration in a multiple-effect evaporator the dissolved solid content in black liquor is about 75%. Here it was assumed that in the low solids content section of the evaporator that is the first four (4) effects, the steam economy of the evaporator was 4.5 pounds of water per pound steam. In effects five (5) and six (6), that is the high solids content section of the evaporator, the steam economy was assumed to be 0.9 pounds of water per pound steam. The overall steam economy of the six effect evaporator was 4.2 pounds of water per pound steam.

2.4.6 Recovery Boiler Process

The concentrated black liquor from the evaporators is sent into the recovery boiler. The dissolved organic contents in the black liquor is burned in the recovery boiler and the energy released used for steam production and molten salts called smelt, exits the furnace at approximately 370 °C. The smelt consist primarily of molten sodium carbonate (Na_2CO_3) and sodium sulfide (Na_2S) together with molten non process elements.

The higher heating value (HHV) of the black liquor was estimated by using the empirical equation given by Gullichsen [2001].

$$HHV = 25.04C_C + 0.1769C_S - 2.582C_{Na} + 48.92C_H + 42.31 \pm 0.41 \qquad (2.22)$$

where: HHV = the higher heating value of black liquor, (MJ/kg) dry solids.

C_C = the carbon content of dry solids, kg Carbon / kg dry solids.

C_S = the sulfur content of dry solids, kg Sulfur / kg solids.

C_{Na} = the sodium content of dry solids, kg Sodium / kg solids.

C_H = the hydrogen content of dry solids, kg Hydrogen / kg solids.

The typical higher heating values of black liquors are listed in Table 2.3 [Gullichsen, 2001]. Also Gullichsen gives an equation for estimating the Net heating value (NHV) of black liquor (see Equation 2.23).

Table 2.3

Typical Higher Heating Value of Black Liquor [Gullichsen, 2001]

Species	**Typical**		**Range**	
	MJ/kg	**BTU/lb**	**MJ/kg**	**BTU/lb**
Nordic softwood	14.2	6100	13.3-14.8	5700-6350
Nordic hardwood	13.5	5800	13.0-14.3	5550-6150
North American softwood	14.2	6100	13.3-15.0	5700-6450
North American hardwood	13.9	5975	13.0-14.8	5550-6350
Tropical hardwood	14.1	6050	13.4-14.8	5750-6350
Bagasse	14.8	6350		
Bamboo	14.1	6050		
Straw	14.7	6325		

$$NHV = HHV - I_{25}\left[(18.015/2.016)\,C_H + (1-x)/x\right] - (78/32)\Delta h_R \times C_s \times \eta_{red} \qquad (2.23)$$

where: NHV = the net heating value of black liquor, (MJ/kg) dry solids

I_{25} = the heat of evaporation of water at 25°C (2.433 MJ/kg)

x = Dry solids concentration, kg dry solids/ kg fuel (75%)

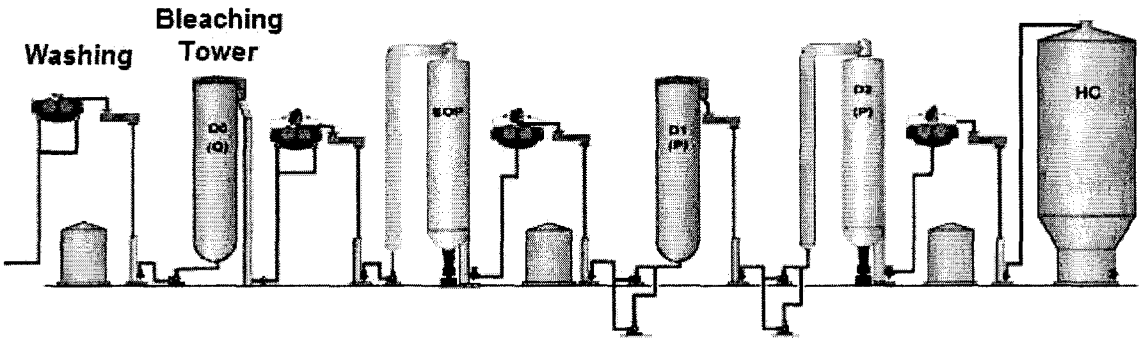
Δh_R = The heat of reduction (13.1 MJ/kg for Na2S)

η_{red} = The reduction efficiency in the smelt.

It was assumed that the recovery boiler produced steam at intermediate (120 psig) and low pressures (72 psig) which are the two pressure levels used in the process. Steam from the recovery boiler is used to satisfy the steam requirements for the pulp mill. Since market pulp was assumed to be the primary product from the mill, any excess steam was converted into electrical energy and sold via the electrical grid. The smelt leaving the boiler was sent to a smelt tank where it dissolves. The smelt solution is then clarified to remove grits and debris, and then sent to the causticization process. The chemical recovery system was not included in the process simulation since the focus of the research reported here was the fiber line.

2.4.7 Bleaching Process

The objective of bleaching is to improve the brightness and cleanliness of the pulp by the use of strong oxidizing agents. This occurs either by removing or brightening the colored substances in the pulp. Lignin which accounted about 90% of the dark color associated with unbleached pulp is degraded during the bleaching process. The pulp was assumed to be bleached to 89 ISO brightness using a short sequence $D_0E_{OP}D_1D_2$ bleaching process (see Figure 2.8). The active oxidizing agents in the bleach plant are chlorine dioxide (ClO_2), oxygen (O_2) and hydrogen peroxide (H_2O_2). In the D_0 or first stage, 100% chlorine dioxide (ClO_2) is used to reduce the kappa number from 16, leaving the digester following washing, to approximately 4 leaving the D_0 stage. In the E_{OP} stage the pulp is extracted with caustic (NaOH), reinforced with oxygen (O_2) and hydrogen peroxide (H_2O_2). Lastly the pulp is brightened to 89 ISO using two additional stages. After the D_2 bleaching stage, the pulp is washed one last time and then sent to high consistency (HC) storage. From the high consistency storage system, the pulp is sent to the sheet forming, pressing and drying processes [Metso Bleaching Process, 2007].



D – Chlorine Dioxide (ClO_2); O – Oxygen (O_2); E-alkaline (NaOH) extraction;

P- Hydrogen peroxide (H_2O_2).

Figure 2.8 Typical Chloride Dioxide Bleaching Sequence with Drum Washers after Each Bleaching Stage

2.4.8 Pulp Forming, Pressing and Drying Processes

Market pulp is primarily sold in sheet form in 500 pound bales. Pulp from the high consistency chest is sent to a pulp machine, often a cylinder or Fourdrinier machine where the pulp is formed, pressed and dried. The primary reason for drying the pulp is to decrease the water content and reduce the cost of transporting the pulp. The paper machine consists of two parts, the wet end which involves forming and pressing and then the drying process. Often the drying is done in a tunnel dryer or air float dryer. The consistency of pulp following the bleaching process is about 10% to 20%. On the paper machine the consistency is lowered to about 1% to 2% so that the pulp can be formed into lap or sheets. The consistency of the pulp leaving the former going to the press was assumed to vary between 10% and 15% and leaving the press to be approximately 20%. In the dryer section the sheet pulp was assumed to be dried from approximately 20% to 94% solids using low pressure steam.

The mass of water that is evaporated from the pulp when the consistency change from C_1 to C_2 is

$$\Delta X = \frac{1}{C_1} - \frac{1}{C_2} = \frac{Kg\ Water}{Kg\ Pulp} \tag{2.24}$$

where ΔX is the mass of evaporated water (kg water/kg pulp) and the consistencies (C_1) and (C_2) are given in terms of the fraction weight. An approximation to the rate of energy input to the dryer $\left(\frac{dH^T}{dt}\right)$ for an adiabatic process is given by Equation (2.25). The energy required in the drying process will depend upon the flow rate of pulp (P^0, kg/hr), the fractional efficiency of the dryer (η) and the enthalpy of evaporation (ΔH_{vap}, KJ/kg).

$$\frac{dH^T}{dt} = \left[\frac{P^0 \times \Delta X \times \Delta H_{vap}}{\eta}\right] = \left(\frac{Joules}{hr}\right) \tag{2.25}$$

Equation (2.26) neglects sensible heat and assumes adiabatic operation of the dryer. Following the drying process the pulp is wrapped, baled, sent to a warehouse and later sold on the open market.

2.4.9 Hog Fuel Boiler

In most Kraft pulp mills, a Hog fuel is used to burn wood yard residuals such as bark, saw dust, chips fines and other biomass to recover energy. A typical steam production system for a Hog fuel boiler is shown in Figure 2.9. Similar to the recovery boiler, the steam produced in the Hog fuel boiler is used to first meet the requirement of the mill. In our model, any excess steam is converted into electrical power and conveyed into the power grid and revenue generated from the sale of excess power.

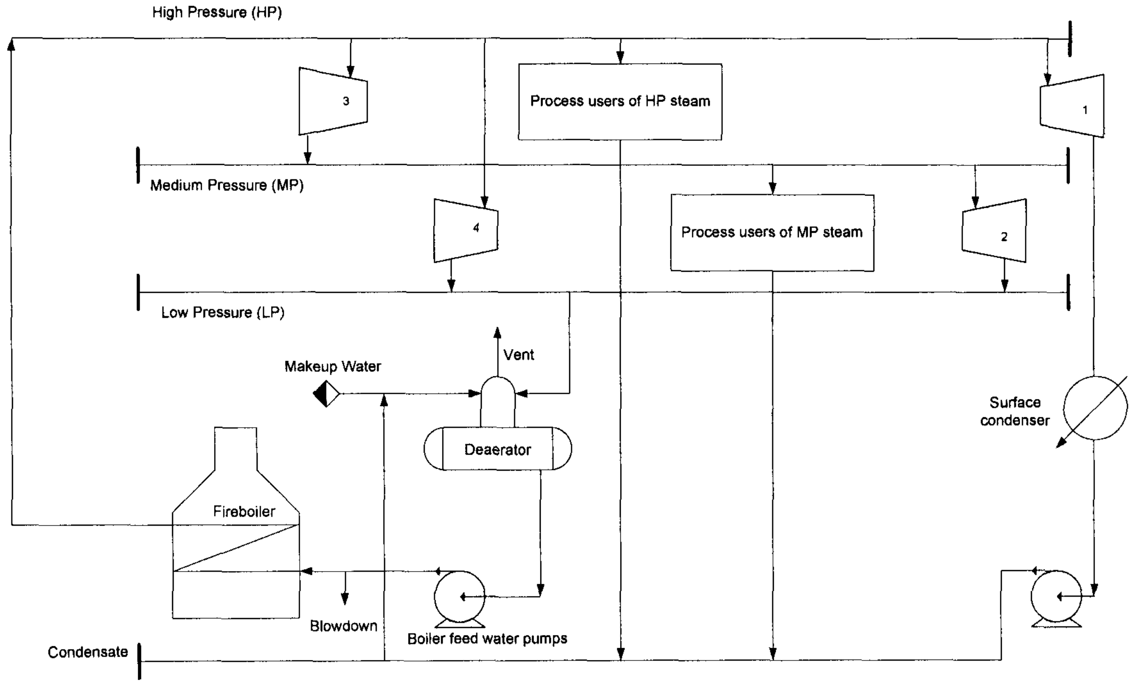


Figure 2.9 Typical Steam Producing System [Turton, et. al. 1997]

The overall energy efficiency for conversion of biomass to electricity is a very important parameter to quantify the Hog fuel boiler. It was reported that the overall energy efficiency for biomass to electricity is typically lower than large central station fossil power plants [Tiangeo, 2005]. The reason for the low efficiency is due to smaller facility sizes and lower fuel quality because of the comparatively high moisture in many cases. Figure 2.10 illustrates the overall efficiency versus net power output for several technology classes. From Figure 2.10, it is clear that the efficiency of conversion is generally independent of the type of fuel. Efficiency for conversion of biomass to electricity in existing biomass based power systems ranges from 10% to about 28%; see purple line in Figure 2.10. Here it was assumed that the energy conversion efficiency in both the Hog fuel and recovery boilers was 20%.

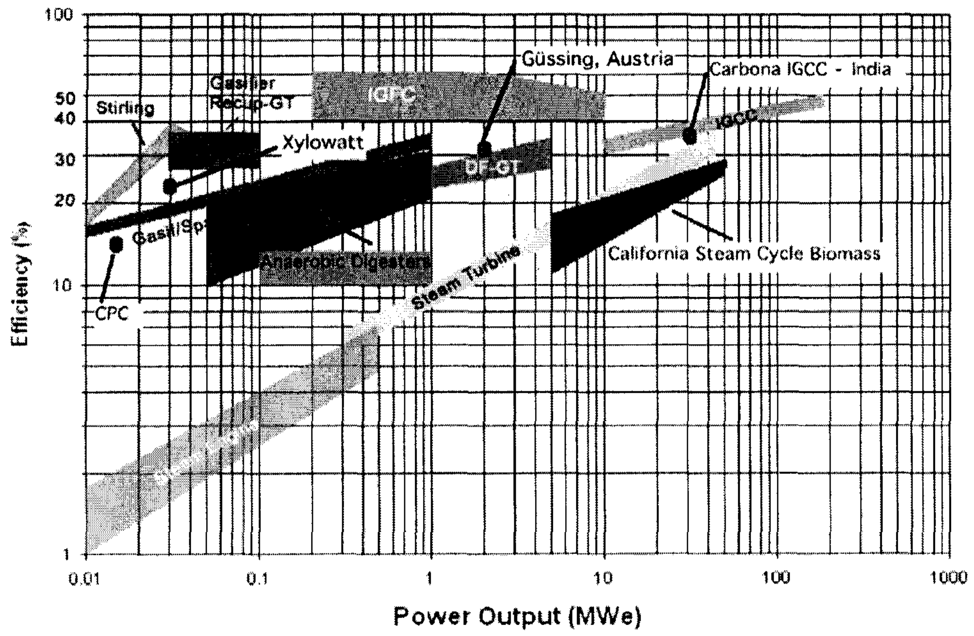


Figure 2.10 Efficiency vs. net Electrical Power Output for Several Prime Movers [Valentino, 2005]

IGFC-Integrated Gasifier Fuel Cell, DF-GT- Direct Fired Gas Turbine (Simple cycle)

IGCC – Integrated Gasifier Combined Cycle

2.5 WinGEMS Simulation

The material and energy balance calculation were performed using WinGEMS and MathCAD simulation software. Preliminary calculations were performed using MathCAD software. The MathCAD model proved to be tedious, hard to debug, and had long run times. Consequently process simulation work was not pursued using MathCAD. WinGEMS was introduced for simplicity and to achieve consistent results. The WinGEMS program proved to be easy to use with many advanced features and had capabilities that allowed the users to readily build steady-state and dynamic simulations with a wide variety of uses and applications. WinGEMS is particularly suited to the process simulation for the paper industry and handles solids processing very well. The Wingems program has a graphical user interface with simple blocks and streams tools which are used to construct complicated process models. It also has a project-orientation design mode that places all aspects of the simulation (diagram layout, simulation values, execution information and input/output configuration) into a single project file. WinGEMS also permits automatic data exchange with Microsoft Excel spread sheets and complete unit independence which allows the user to specify the units for any given value. Lastly WinGEMS allows the used to development their own estimation properties. Unfortunately, WinGEMS is not particularly well suited to handling liquid vapor equilibrium and thus distillation models were simulated using ASPEN Plus.

2.5.1 Component and Their Definitions

The components that were used in the WinGEMS model simulation are listed Table 2.4.

Table 2.4

Components used in WinGEMS model and Their Definitions

Category	Name of Components	Formula and Comments
General	Mass flow rate, temperature	
	Consistency	Suspension solids
Suspension solids	Bark, cellulose, hemicellulose, lignin, inerts, calcium oxide, calcium carbonate, calcium carbonate	
Dissolved solids	Hydrogen ion, sodium, hydroxide, hydrosulfide, calcium, sulfite, sulfate, thiosulfate, carbonate, chloride, AQ, arabinan, galactan, mannan, glucan, xylan, acetyl group, 4-o-MGA, arabinose, galactose, glucose, mannose, xylose, 4-o-MGA acid, dissolved wood, dissolved lignin, acetic acid, ethanol, enzyme, chlorine dioxide, furfural, bicarbonate, degradation products	
Gases	Oxygen, nitrogen, carbonate dioxide, sulfur dioxide, water vapor, methanol	
Derived components	Effective alkali	$=NaOH + \frac{1}{2} Na_2S$
	Effective alkali	$=NaOH + \frac{1}{2} Na_2S$
	Sulfidity	$=Na_2S / (NaOH + Na_2S)$
	pH	= -log[H] if less than 7 14+log[OH] if larger than 7
	Dissolved inorganics, dissolved organics, total dissolved solids, total suspension solids, water, total titratable alkali, density, total volume flow, total enthalpy	

2.5.2 WinGEMS® Model and Simulation Results

WinGEMS version 5.3 was used for modeling both the Kraft mill base case and also the hemicellulose extraction process. The configuration of the existing Kraft pulp mill case is shown in Figure 2.11. For both the existing Kraft mill case as well as the hemicellulose extraction process three pulp mill sizes were considered; a small mill having a pulp production of 750 tonne per day, a medium size mill of 1,000 tonne per day and lastly a large pulp mill having 1,500 tonne per day production rate. For each of these three cases, rigorous mass balance and energy balances were determined using WinGEMS simulation model. The output for each case was sent into an Excel spread sheet. Typical results for selected streams for the 1,000 tonne per day base case are illustrated in Tables 2.5 and 2.6.

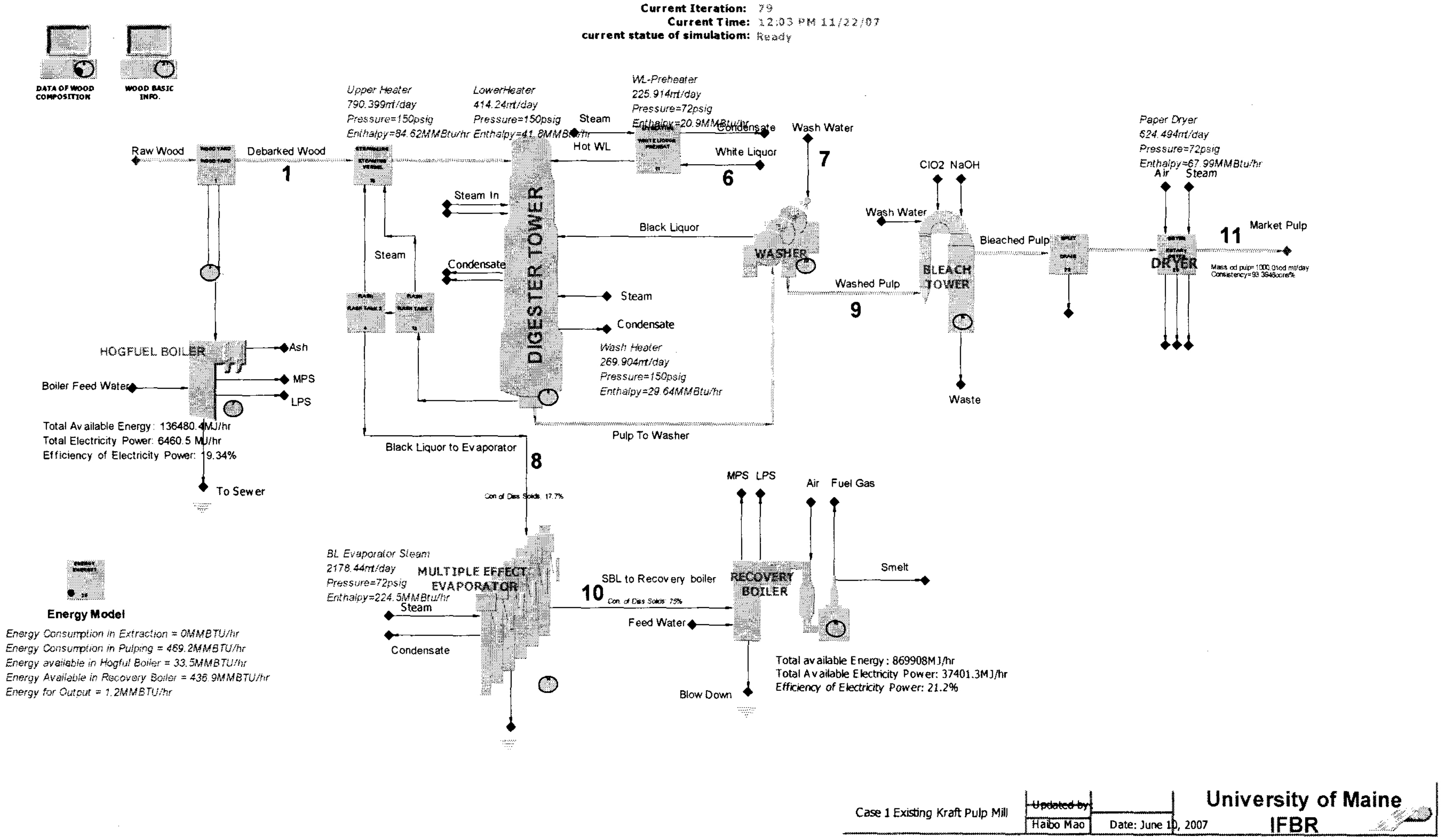


Figure 2.11 WinGEMS Model of Existing Kraft Pulp Mill Case

Table 2.5

Mass Balance of Existing Kraft Pulp Mill Case

<table>
<tr><th colspan="9">Case 1. Mass Balance for Existing Kraft Pulp Mill – 1,000 Tonne/day Pulp Production</th></tr>
<tr><th>Description</th><th>Stream Number</th><th>Total Flow Rate (Tonne/day)</th><th>Consistency (%)</th><th>Concentration (%)</th><th>Suspension Solids (Tonne/day)</th><th>Dissolved Solids (Tonne/day)</th><th>Water (Tonne/day)</th><th>Temp (°C)</th></tr>
<tr><td>Debarked Wood</td><td>1</td><td>4342</td><td>50.0</td><td>0.0</td><td>2171</td><td>0.0</td><td>2171</td><td>20</td></tr>
<tr><td>White Liquor</td><td>6</td><td>3193</td><td>0.0</td><td>17.3</td><td>0.0</td><td>552.4</td><td>2640</td><td>45</td></tr>
<tr><td>Wash Water</td><td>7</td><td>10543</td><td>0.0</td><td>0.0</td><td>0.0</td><td>0.0</td><td>10543</td><td>20</td></tr>
<tr><td>Wash Filtrate</td><td>8</td><td>9271</td><td>0.0</td><td>17.8</td><td>0.0</td><td>1648.0</td><td>7623</td><td>102</td></tr>
<tr><td>Washed Pulp</td><td>9</td><td>8504</td><td>12.0</td><td>0.02</td><td>1020</td><td>1.4</td><td>7482</td><td>22</td></tr>
<tr><td>Black Liquor</td><td>10</td><td>2199</td><td>0.0</td><td>75.0</td><td>0.0</td><td>1648.0</td><td>549</td><td>102</td></tr>
<tr><td>Dried Pulp (Air dried)</td><td>11</td><td>1071</td><td>93.4</td><td>8.0</td><td>1,000</td><td>5.6</td><td>65.1</td><td>42</td></tr>
</table>

Note: Refer to Figure 2.1 and 2.11 for Stream Number.

Table 2.6

Energy Balance for 1000 Tonne/day Existing Kraft Pulp Mill Case

<table>
<tr><th colspan="6">EXISTING KRAFT PULP MILL CASE</th></tr>
<tr><th colspan="2">Stream Number</th><th>Flow Rate (Tonne/day)</th><th>Pressure (psig)</th><th>Temp (°C)</th><th>Enthalpy (MMBTU/hr)</th></tr>
<tr><td rowspan="6">Energy Consumption</td><td>S4 W. L. Preheater</td><td>192</td><td>72</td><td>160</td><td>20.9</td></tr>
<tr><td>S5 Upper Heater</td><td>770</td><td>150</td><td>186</td><td>84.6</td></tr>
<tr><td>S5 Lower Heater</td><td>380</td><td>150</td><td>186</td><td>41.8</td></tr>
<tr><td>S5 Washer Heater</td><td>270</td><td>150</td><td>186</td><td>29.6</td></tr>
<tr><td>S6 Evaporator</td><td>2,060</td><td>72</td><td>160</td><td>224.0</td></tr>
<tr><td>S9 Steam Dryer</td><td>625</td><td>72</td><td>160</td><td>68.0</td></tr>
<tr><td rowspan="8">Energy Production</td><td colspan="5">Hog Fuel Boiler</td></tr>
<tr><td>S1 Elec. Energy (KW)</td><td colspan="4">5,621(a)</td></tr>
<tr><td>S2 Med. Pres. Steam</td><td>119</td><td>150</td><td>186</td><td>13.1</td></tr>
<tr><td>S2 Low Pres. Steam</td><td>187</td><td>72</td><td>159</td><td>20.4</td></tr>
<tr><td colspan="5">Recovery Boiler</td></tr>
<tr><td>S7 Elec. Energy (KW)</td><td colspan="4">21,429(a)</td></tr>
<tr><td>S8 Med. Pres. Steam</td><td>1,302</td><td>150</td><td>186</td><td>143.0</td></tr>
<tr><td>S8 Low Pres. Steam</td><td>2,704</td><td>72</td><td>159</td><td>294.0</td></tr>
<tr><th colspan="6">SUMMARY</th></tr>
<tr><td colspan="4">Steam Consumption in Extraction</td><td>Not Applicable</td><td>MMBTU/hr</td></tr>
<tr><td colspan="4">Steam Consumption in Pulping</td><td>469.2</td><td>MMBTU/hr</td></tr>
<tr><td colspan="4">Steam Available in Hog fuel Boiler</td><td>33.5</td><td>MMBTU/hr</td></tr>
<tr><td colspan="4">Steam Available in Recovery Boiler</td><td>436.9</td><td>MMBTU/hr</td></tr>
<tr><td colspan="4">Steam Form for Output</td><td>1.2</td><td>MMBTU/hr</td></tr>
<tr><td colspan="2" rowspan="2">Total Energy Output</td><td colspan="2">As electricity</td><td>27.1(a)</td><td>MW</td></tr>
<tr><td colspan="2">As steam</td><td>462.7</td><td>MMBTU/hr</td></tr>
</table>

(a) Electricity energy was calculated by assuming the efficiency for conversion of thermal to electrical energy was equal to 20%.

2.6 Summary

A detailed description is presented in this chapter for a fiber line that is located at an existing Kraft pulp mill. This Kraft fiber line served as the base case for comparison to similar cases in which the fiber line was expanded to incorporate the hemicellulose extraction process at a hardwood kraft mill. Material and energy balance calculations were performed for the base case using the WinGEMS simulation program. Such calculations are critical for estimation of capital, operating costs and profitability. The recovery cycle was not included in the process simulation since the main focus of this research was the Kraft fiber line and how the economics of a Kraft mill changes with the incorporation of the hemicellulose extraction process.

Chapter 3

MODIFIED KRAFT PULP MILL CASE

- THE HEMICELLULOSE EXTRACTION PROCESS

This chapter describes the modification of an existing Kraft pulp mill to facilitate production of market hardwood Kraft pulp, as well as ethanol and acetic acid using the hemicellulose extraction process. Modifications to the existing fiber line involved insertion of an extraction vessel between the pre-steaming vessel and the pulping digester, equipment for hydrolysis and fermentation of the extracted carbohydrate polymers and lastly processes for the separation of the various by-products and waste materials. The objective of this chapter is to illustrate the unit processes required for the production of ethanol and acetic acid and to summarize the estimation of the material and energy balance required for equipment sizing and a process economic evaluation. The pulp production rate was maintained constant at 1,000 tonne per day. The wood supply was commercial mixed Northeast hardwood chips and included a mixture of birch, beech, maple and poplar. In addition to the main by-products of ethanol and acetic acid, the modified Kraft pulp mill also produces methanol, furfural, carbon dioxide and gypsum. All of these products were treated as waste material in the process economics.

3.1 Solvent Selection

A limited number of solvents are available for use in the extraction process. The first criterion is that the solvent must be water bared so that the solvent does not have to be recovered separately. Also, it is highly convenient if the solvent was either an intermediate or a makeup chemical to the Kraft pulping process. This limited the number of choices to either green liquor or white liquor which are common chemicals in the liquor cycle of Kraft pulp mills, or makeup chemicals to the recovery cycle. Makeup chemicals include sodium carbonate (Na_2CO_3), sodium hydroxide ($NaOH$), sodium bisulfate ($Na_2S_2O_3$) or even water.

Pure Water as a Solvent. Water has been widely used in pre-hydrolysis of wood in the production of alpha-cellulose [Smook, G., 2002]. Consequently, water is often sited as a solvent for use in a biorefinery to remove hemicelluloses [Sung-Hoon Yoon, 2006, Tunc, 2007].

In the production of alpha-cellulose, the hemicelluloses and lignin are considered waste materials and are removed. In the production of alpha-cellulose by the Kraft process, a pre-hydrolysis plus displacement steps are performed that remove approximately 90% of the hemicelluloses from the wood before kraft cooking. These carbohydrates would of course permit larger quantities of ethanol and acetic acid to be produced, but the low pH following the extraction process would lower the pulp yield and its quality. In the present study, one objective was to maintain the same pulp quality and yield and use the pulp in the production of paper. Consequently, pure water was not chosen as the solvent for a market hardwood Kraft pulp mill. In the production of dissolving pulps, water would be the natural solvent to select.

Green Liquor as a Solvent. After due consideration of the possible candidates, green liquor was selected as the solvent because it is produced in the liquor cycle and off-loads the evaporation, recovery boiler and lime kiln. Also, it has been shown by Van Heiningen that extraction with green liquor will maintain the same pulp quality and the yield as pulping with conventional white liquor provided that anthraquinone is used as a pulping catalyst. To maintain the same pulp yield and physical properties in the final pulp product, Van Heiningen has shown that it is critical that the pH of the extraction liquor is close to a neutral condition. Maintaining the pH of the extract close to a near-neutral condition also has the advantage that it avoids precipitation of lignin in the extraction portion of the process.

3.2 Process Description

3.2.1 General Description and Design Basis

The basic idea for the modified Kraft pulp mill case is to extract a portion of the hemicellulose polymers from the wood feedstock prior to Kraft pulping. The extracted hemicelluloses would then be converted into ethanol and acetic acid while using the residual wood to produce market Kraft pulp.

Green liquor, a mixture of sodium carbonate (Na_2CO_3) and sodium hydroxide (NaOH), is an intermediate in the production of Kraft pulping liquor and was selected as the extraction agent. In some kraft pulp mills an on-site idle Kamyr continuous digester may be modified to an extraction vessel. A more likely situation is that an impregnation vessel which existed in the mill could be converted into an extraction vessel. Two cases will be evaluated; one in which a new extraction vessel is purchased and the alternative case, where an existing vessel is modified and used for the hemicellulose extraction.

Approximately ten percent (10%) of the mass of the wood chips will be extracted in the extraction step. The extract will be send to the ethanol and acetic acid production process. A scheme for the entire process is shown in Figure 3.1. The processing of the extracted wood is shown in black color and represents a conventional Kraft pulp mill process. The unit processes that marked with blue color are required for hemicellulose extraction and conversion to ethanol and acetic acid. Unit processes include (1) wood extraction for hemicellulose removal, (2) recycling a portion of the extract back to the extraction vessel for the purpose of raising the solids content of the extract, (3) evaporation to further thicken the extract, (4) sulfuric acid hydrolysis for conversion of complex carbohydrates into simple sugars, (5) filtration to remove precipitated lignin, (6) liquid-liquid extraction followed by distillation to remove acetic acid and furfural from the sugar solution by the Lenzing Process or alternatively by stripping and sorption with activated carbon [Sherman, 1979], (7) liming to raise the pH required for fermentation and removal of excess sulfate ion, (8) fermentation of mono-sugars and glucuronic acid into ethanol, and (9) distillation and dehydration of the product into pure ethanol (99+%). The design basis is summarized in Table 3.1 and includes the design conditions and parameters used in the modified Kraft pulp mill case.

Table 3.1

Design Basis for the Modified Kraft Pulp Mill Process

ITEM	VALUE
Bleached Pulp Production Rate	1,000 tonne/day
Feed Stock	
Consistency of green wood	50%
Bark content	10%
Wood lost in debarking	0.5%
Temperature	20°C
Wood Preheating Temperature	80°C
Extraction Conditions	
Solvent composition	Green Liquor (See Table 3.2)
AQ usage in extraction	0.05%
Extraction temperature	160 °C
Liquid to wood ratio	4 (4 kg liquid to 1 kg of wood)
Heating ramping time	60 minutes
Residence time	110 minutes
Temperature of wash water	20°C
Dilution factor of internal washing	0 (No net water add in)
Norden number of internal washing	3
PH of extract	6
H factor	800 hours

Table 3.1 continued

Amount extracted	10.1% (See Table 3.3)
Pulping Conditions	
Effective Alkali	12%
Sulfidity	30%
Liquid to wood ratio	4
Temperature	170°C
Heating ramping time	About 7 minutes
Steam condition	150 psig High Pressure steam
Final Kappa Number	16
H Factor	700 Hours
Kappa parameter A_1,B_1, n_1	315, 45.6 and 0.3
Yield parameter A_2,B_2, n_2	87.5, 4.25 and 0.4
Pulping yield	52.3%
External Washer	
Stages	3
Dilution Factor	3
Norden Efficiency	3
Evaporator and Boiler	
Steam economy of multiple evaporator	4.2 lb water/ lb steam
Steam condition	72 psig Medium pressure steam
Solid content of strong black liquor	75%
Net heating value of black liquor	13.32 MJ/kg
Bleaching Condition	
Yield	98%
Kappa Number after bleaching	4
Paper Drying Condition	
Steam condition	30psig low pressure steam
Consistency of dry pulp	94%
Hog Fuel Boiler Condition	
High heating value of biomass	20.05 MJ/kg
Energy efficiency for steam production	80%
Energy efficiency for electricity production	20%
Flash tank condition	
Pressure of flash tank	20 psig
Acid Hydrolysis	
pH of hydrolyzate	1
Hydrolysis efficiency	90%
Liquid-Liquid Extraction Efficiency	90%
Fermentation Efficiency	90%
Density of Pure Water	1000 kg/m^3
Heat Capacity of Wood	0.3 BTU/lb × °F
Heat Capacity of Water	1.0 BTU/lb × °F

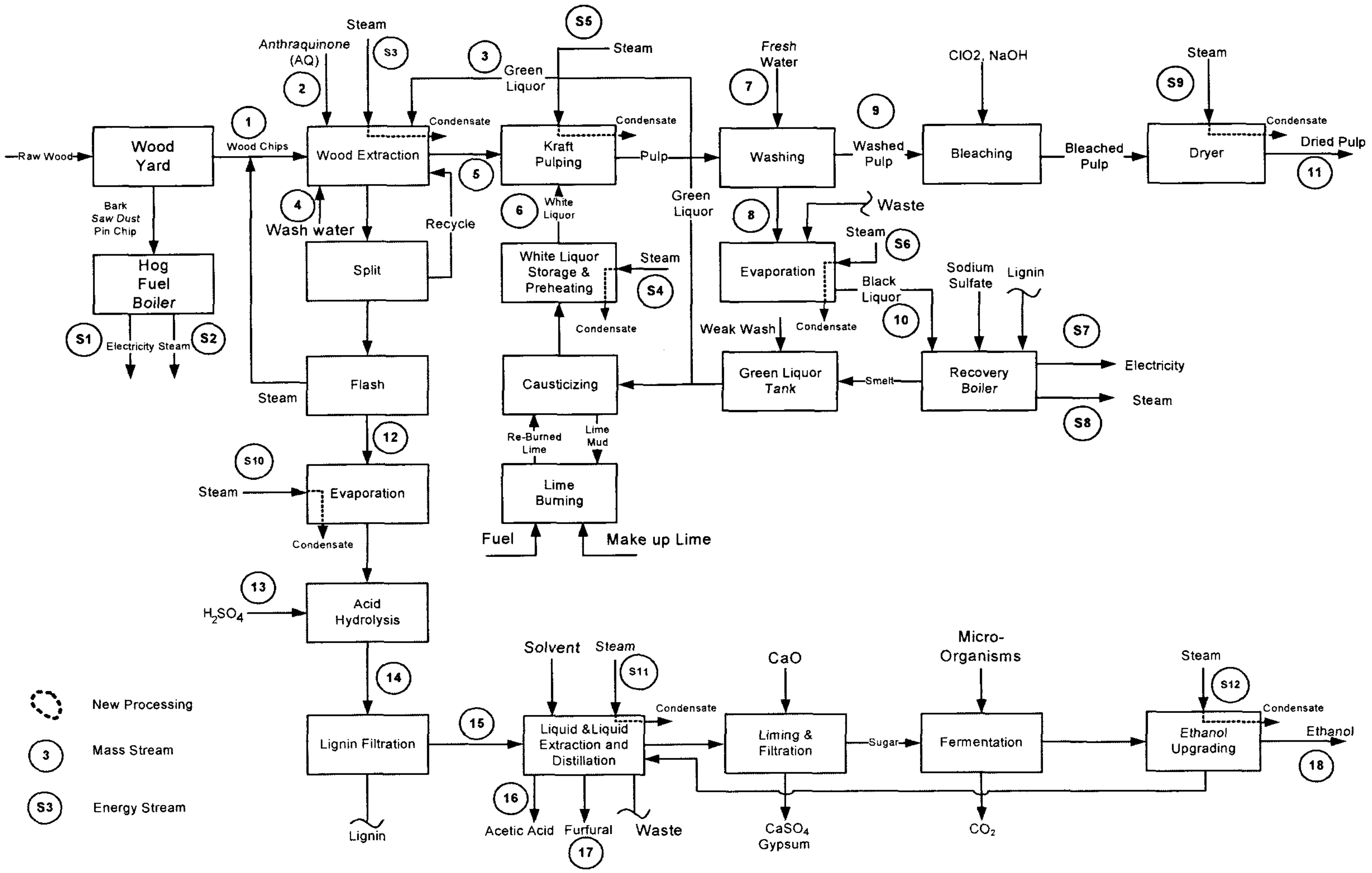


Figure 3.1 Process Flow Diagram of Modified Kraft Pulp Mill Case with Product of Market Pulp, Ethanol and Acetic acid

3.2.2 "Near-Neutral" Extraction Process

It was assumed that the wood extraction and pulping were conducted in an extraction vessel and a continuous Kamyr digester (see Figure 3.2). Prior to pulping, commercial mixed Northeast hardwood chips (birch, beech and maple) are being fed to a continuous extraction vessel at the rate of about 2,100 tonnes per day (dry basis, for 1,000 tonnes per day pulp production rate case). It was assumed that all of the wood handling facilities exist and operate normally.

Preheating and Impregnation. After the wood yard the screened chips traveled from the chip bins, through a low pressure feeder valve to a steaming vessel where they are heated from ambient temperature to approximately 80 °C in 15 minutes – the same temperature and same time as in the existing pulp mill case. Heating is done by direct low pressure steam injection. After preheating in the steaming vessel, the chips then go to a chip chute where they are contacted with pre-heated green liquor and anthraquinone (AQ). The chips then pass through a high pressure feeder and are conveyed hydraulically into the top of the extraction vessel using green liquor in a flow loop (not shown in Figure 3.2). In the extraction vessel the chemical AQ serves as a pulping catalyst to preserve pulp yield and the green liquor serves as the extraction agent. The composition of green liquor used in extraction vessel is listed in Table 3.2.

Table 3.2

Composition of Green Liquor

Chemicals	Amount Used	Extended Condition
Total Titratable Alkali	3% on wood as Na2O	AA on Wood as Na2O = 1.05% Sulfidity = 76.4% Reduction Efficiency = 97.3% Causticizing Efficiency = 11.4%
NaOH	9.0 g/L as Na2O	
Na_2S	29.1 g/L as Na2O	
Na_2CO_3	70.0 g/L as Na2O	
Na_2SO_4	0.8 g/L as Na2O	

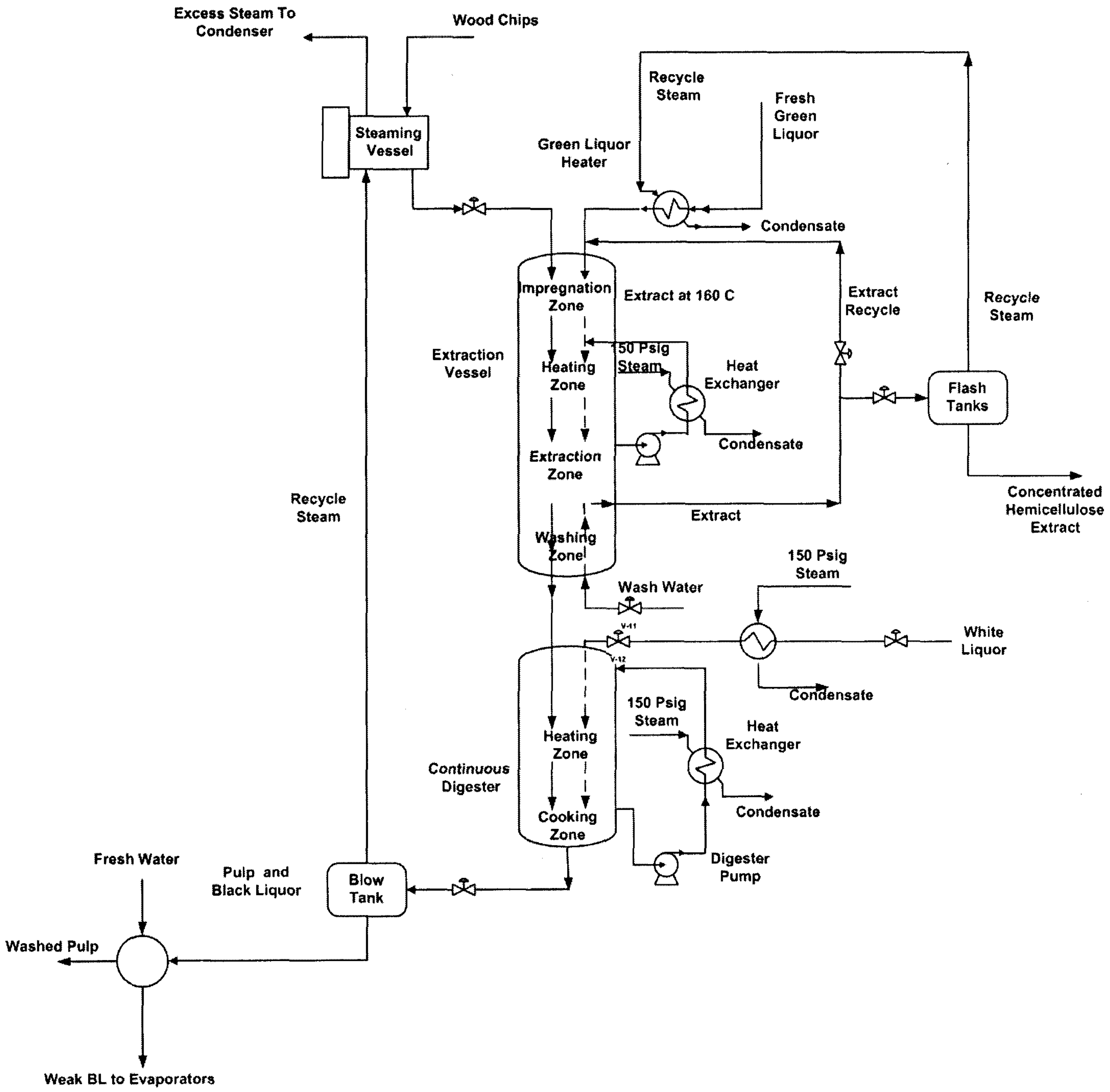


Figure 3.2 Schematic Diagram for Near Neutral Hemicellulose Extraction and Pulping System

Wood Extraction. After the preheated wood chips reach the extraction vessel, they are further heated in the heating zone of the vessel to the desired extraction temperature of 160 °C. In this analysis it was assumed that the heating was done in 60 minutes by indirect steam heating using external heat exchangers. Physically the extraction vessel is equipped with several sets of screens located on the walls of the vessel and concentric pipes to move liquor in and out of the vessel. The screens are used to extract liquor from the vessel and concentric pipes return the circulating liquor to the vessel at the location of the screen. The wood extraction will be conducted at a temperature of 160 °C for 110 minutes to give an H-factor of approximately 800 hours. After the extraction process, the wood chips are washed with fresh water to remove the extracted liquor. The washing takes place in the bottom of the extraction vessel by displacing extraction liquor. Following washing the chips are removed from the extraction vessel and conveyed (hydraulically) to the pulping digester by using white liquor. For simplicity the white liquor recirculation loop is not shown in Figure 3.2. The entire heating schedule for wood extraction and pulping is shown schematically in Figure 3.3, which plots the temperature of the wood versus time. Van Heiningen has presented data on the mass extracted (weight %) for southern hardwood versus the H-factor which is defined by Equation 2.8. The Van Heiningen data are illustrated in Figure 3.4.

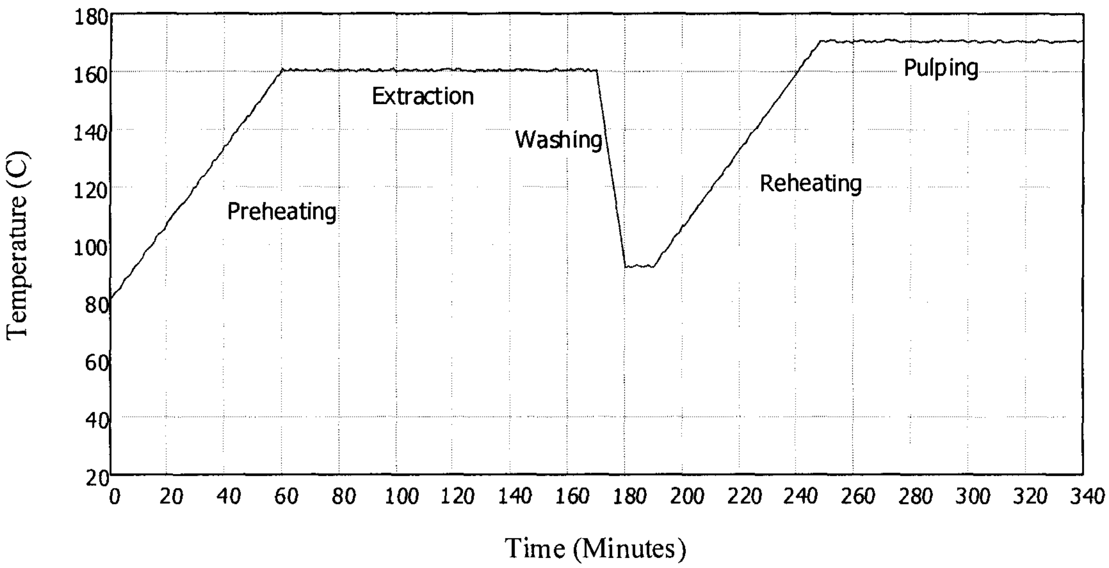


Figure 3.3 Schematic Diagram of Heating Schedule for Wood Extraction and Pulping

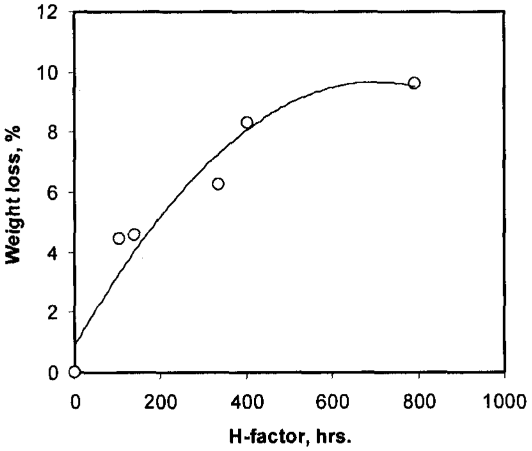


Figure 3.4 Weight Losses vs. H Factor in Extraction Vessel [Van Heiningen, 2007]

The composition of the extract on an inorganic free basis is illustrated in Table 3.3 based on Van Heiningen's data. The sodium sulfide (Na_2S) content in the green liquor was assumed to be converted to sodium sulfate (Na_2SO_4) as shown in Equation 3.1. This assumption is consistent with the results of laboratory analysis. The final pH following the extraction will be approximately 5.5 to 6.0. Under these conditions the sodium carbonate (Na_2CO_3) presents in the green liquor was assumed to be converted to sodium bi-carbonate ($NaHCO_3$).

$$Na_2 S \xrightarrow{Oxidized} Na_2SO_4 \tag{3.1}$$

$$Na_2CO_3 + H_2O \Leftrightarrow NaHCO_3 + NaOH \tag{3.2}$$

The sodium acetate results from acetyl group side chains (Figure 2.2) that are readily cleaved off from the xylan polymers by hydrolysis reaction.

Table 3.3

Composition of Wood Extract (a)

[Van Heiningen, 2006]

Extraction Component	% Weight
Arabinan	0.1
Galactan	0.3
Mannan	0.2
Glucan	0.4
Xylan	3.4
Lignin	1.3
4-O-m Glucuronic Acid	2.4
Acetyl group	2.0
Total	10.1
(a) Inorganic free basis	

Washing Zone. After wood extraction, the chips will enter into an internal washing zone which is located in the bottom of the extraction vessel. It is very important that the chips are washed after the extraction with clean water (neither black liquor nor white liquor) to recover the extract and avoid contamination with lignin and additional sodium salts. Also it is desirable to wash with hot water, if possible, to avoid cooling the chips. In the internal washing zone extracted wood will be washed by pure water to decrease the amount of extracted hemicellulose that remains in wood chips. After internal washing, the extracted liquor and dissolved wood solids will leave the extraction vessel and go to a series of flash tanks for downstream processing into ethanol and acetic acid. The extracted wood chips, following through the washing zone, are conveyed to a second hydraulic digester where the wood chips are cooked into unbleached pulp by removing residual lignin. White liquor is used to convey the chips from the extraction vessel to the pulping digester. The white liquor can be entered at a variety of locations to permit modified continuous cooking and countercurrent washing in the pulping digester (Figure 3.5)

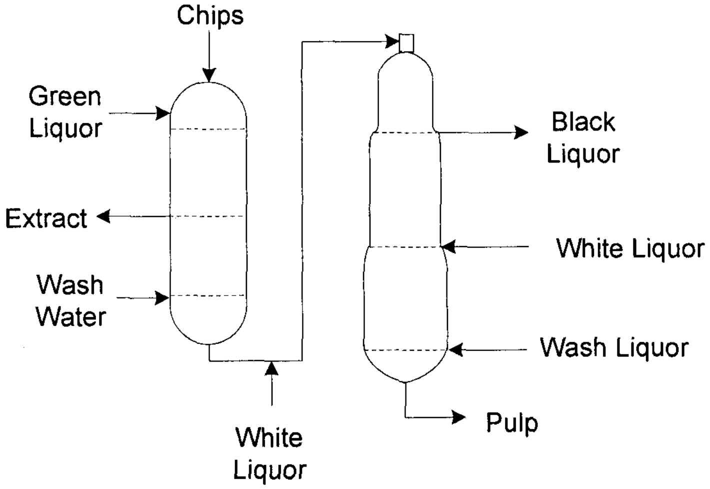
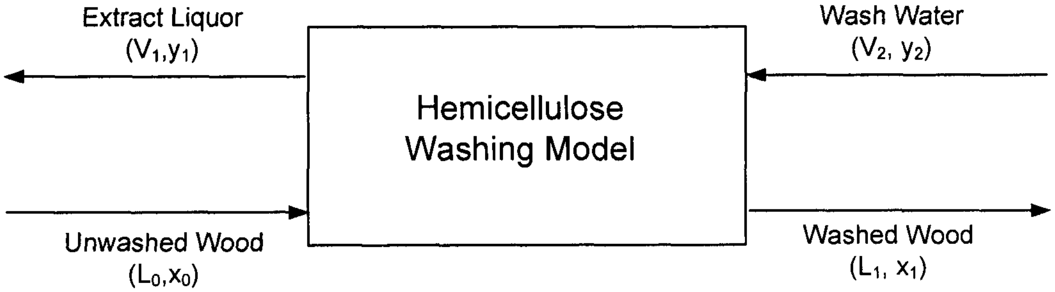


Figure 3.5 Extraction and Pulping with Alkali Concentration Profiling

Washing Study. Different wash conditions were applied to the hemicellulose extraction process for washing study. The wash model is illustrated in Figure 3.6. The main concerns in the internal washing are the hemicellulose recovery efficiency for the ethanol process and the dissolved solids content in the extract (y_1). In the following study, the dilution factor varied from negative one (-1) to positive two (2) and the Norden efficiency varied from 2 to 4.



Solids balance: $L_0 \times x_0 + V_2 \times y_2 = L_1 \times x_1 + V_1 \times y_1$

Total balance: $L_0 + V_2 = L_1 + V_1$

Norden Efficiency:

$$E = \frac{\ln\left[\dfrac{L_0 \cdot (x_0 - y_1)}{L_1 \cdot (x_1 - y_2)}\right]}{\ln\left(\dfrac{V_2}{L_1}\right)}$$

Dilution Factor: $D = L_1 \times (1 - x_1) - V_2 \times (1 - y_2)$

Total Variables: L_0, x_0, L_1, x_1, V_1, y_1, V_2, y_2, D, E

D.F = 10(Total variables) – 4(Equations) = 6

Given: L_0, x_0, V_2, y_2, D, E

Figure 3.6 Hemicellulose Washing Model

Figure 3.7 shows the relationship between the hemicellulose recovery efficiency and different internal washing conditions. Figure 3.8 shows the dissolved solids content in extract changes with dilution factor and washing Norden efficiency.

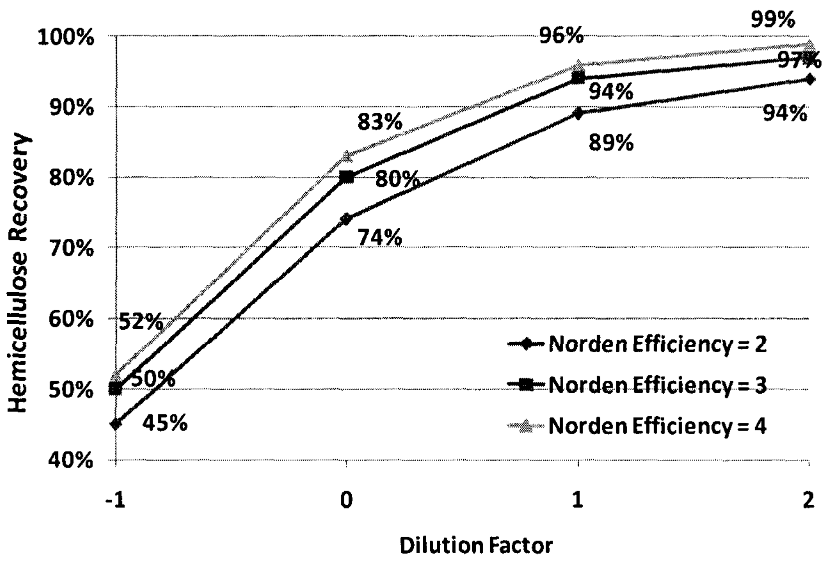


Figure 3.7 Hemicellulose Recovery Efficiency verse Different Dilution Factor

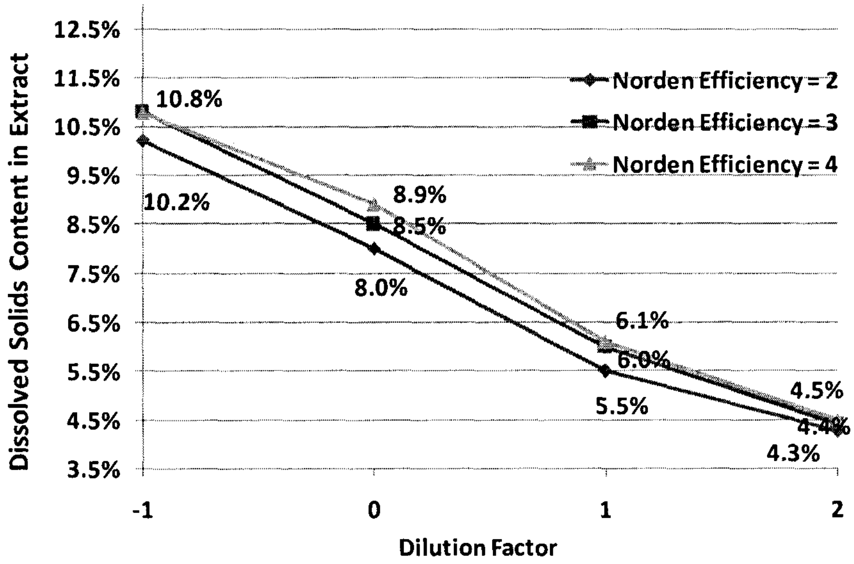


Figure 3.8 Dissolved Solids Content verse Different Dilution Factor

It is clear that for a better washing, a high dilution factor is required in the internal washing stage. The Norden efficiency does not appear to significantly influence the results. The high dilution factor will require more wash water and results in lower solids content in the extract; however a greater amount of extracted hemicellulose is recovered.

In the internal washing design, a dilution factor zero (0) and Norden efficiency three (3) are picked up as the washing conditions. Under the design condition, 80% of the extracted hemicellulose is recovered at a dissolved solids content of 8.5%. To recovered 97% of the hemicellulose at a Norden efficiency of 3 would required a dilution factor of 2 (kg H2O/ kg wood) and would lower the dissolved solids content to 4.4%.

3.2.3 Liquor Flashing and Evaporators

General Considerations. There are two considerations regarding removal of the liquor extract from the extraction vessel. First, since the organic solids content in the extract is low, it is desirable to raise the solids content of the organic portion of the extract. This is being done to minimize downstream processing in the hydrolysis reactor; which requires addition of sulfuric acid and then disposal of gypsum. Secondly, depending upon the design of the extraction vessel, there is minimum liquor to wood ratio that is required to fill the extraction vessel for movement of the chips. Meeting the liquor to wood ratio in the extraction vessel necessitates recycle of extract to the extraction vessel. Also, the optimum temperature in the hydrolysis reaction was determined to be approximately 126 °C. For these reasons, the flash tank was operated at 20 psig and the liquor was recycled prior to going to the flash tank (Figure 3.2). An alternative would be to send all of the extract to the flash tank, recovery additional steam which would be contaminated with methanol and total reduced sulfur (TRS) and then recycle concentrated liquor back to the vessel. In this alternative, the recycle liquor would also have to be reheated. In our analysis, we chose the first alternative in which the liquor is recycled prior to flashing.

Flash Tanks. The liquor extract leaving the extraction vessels has a pressure of approximately 110 psig. It is sent to a flash tank which is operated at 20 psig pressure to recovery energy and lowers the temperature of the extraction liquor. After liquor recycle and flashing, the extraction liquor may be further concentrated in a set of evaporators by using low pressure steam to raise the solids content. Highly concentrated liquid would reduce the size of the down stream equipment but this alternative would require additional equipment cost for evaporators. In this study, liquor evaporation was conducted as an optional process. An economic hydrolysis was performed to investigating whether additional evaporator of the extract is economically justified. Three cases were considered.

Case A. No addition evaporation and process the extract at 8.5% solids

Case B. Evaporate the extract from 8.5% to 20% solids, and

Case C. Evaporate the extract from 8.5% to 30% solids.

The conclusion from the analysis was that additional evaporator is not justified economically. Details of this analysis are given in chapter 4. Too high salt concentration for fermentation is another very important reason why no concentration is needed. The extraction liquor leaves the evaporators or flash tank in a temperature of approximately 126 °C which is the temperature of saturated steam at 20 psig and goes to the hydrolysis section of the plant for acid hydrolysis of the carbohydrate.

3.2.4 Acid Hydrolysis

General Description. Sulfuric acid (H_2SO_4) is used to hydrolyze the concentrated extract rich in hemicelluloses. The hydrolysis reactions are conducted in two parallel batch hydrolysis tanks which are operated as a continuous stirred tank reactor (Figure 3.9).

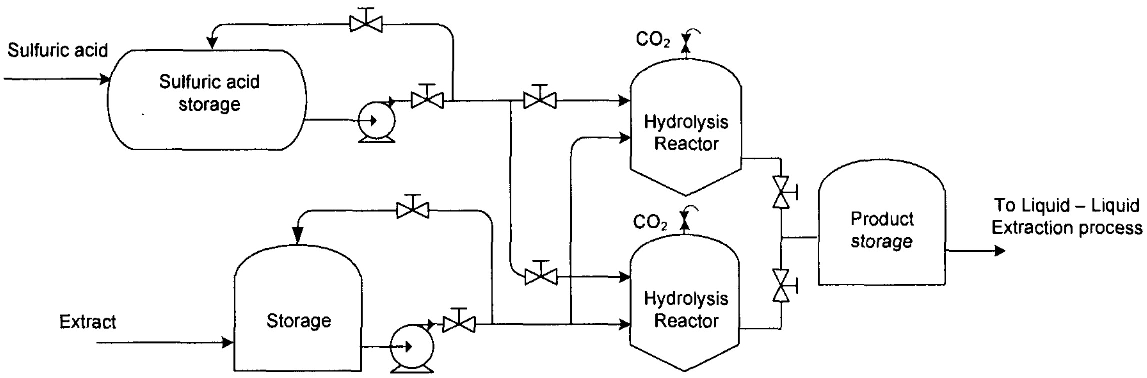


Figure 3.9 Schematic Diagram for Acid Hydrolysis

The batch hydrolysis reactors will be operated to give a continuous flow of hydrolyzate going to the liquid -liquid extraction section of the plant. The pH value in the acid hydrolysis tanks will be controlled by the amount of acid entered into the hydrolysis reactors. The low pH value will convert all of the sodium acetate in the extraction liquor into acetic acid. Sodium bicarbonate ($NaHCO_3$) and residual sodium carbonate (Na_2CO_3) will be decomposed to carbon dioxide (CO_2), water and sodium sulfate (Na_2SO_4).

It was assumed that all of the lignin in the extract is precipitated because of the low pH. Carbon dioxide will be removed from the hydrolysis tank as an off gas. No effort was made to recover the carbon dioxide. The sodium sulfate (Na_2SO_4) is extremely soluble in water and remains in the hydrolyzate and must be removed by liming. For purpose of economy and to minimize the amount of gypsum produced it is desirable to minimize the amount of sulfuric acid that is used in the hydrolysis reactions. The kinetics of the hydrolysis reaction are extremely important and will discuss in detail.

Sulfuric Acid Consumption. The sugar hydrolysis reactions are catalyzed by acid and require low pH and elevated temperature. Acid consumption is a very important consideration in the sugar hydrolysis reactions. Sulfuric acid is added because the sulfate ions can be removed by liming with calcium oxide or slaked lime ($Ca(OH)_2$). This alternative may not be economic since sulfuric acid may have to be purchased by the mill. In bleached pulp mills, sulfuric acid is available as a by-product in the generation of chlorine dioxide (ClO_2), a common bleaching agent. During the extraction process acetyl groups are cleaved from the xylan polymer and enter into the hydrolyzate as sodium acetate. In the hydrolysis process sodium acetate is converted into acetic acid. Also, the glucuronic acid groups on the xylan polymer will be cleaved and will be present as the sodium salt of the glucuronic acid. In the hydrolysis reactor free glucuronic acid will be formed and will consume protons donated by the sulfuric acid. Also the bicarbonate will consume protons by decomposition to carbon dioxide (see Equation 3.3 and 3.4)

$$NaHCO_3 + H^+ \rightarrow H_2O + CO_2 \uparrow + Na^+ \tag{3.3}$$

$$R-OONa + H^+ \rightarrow ROOH + Na^+ \tag{3.4}$$

where R= C_2H_3 for acetic acid and $C_6H_9O_5$ for glucoronic acid.

Figure 3.10 illustrates the consumption of sulfuric acid by a sample of the wood extract. These data were generated by titrating 50 ml of extraction liquor with 1N H_2SO_4 to lower the pH to 1. The sulfuric acid consumption per cubic meter of extract solution was estimated to be 0.057 tonne 100% H_2SO_4 (see Equation 3.5).

H_2SO_4 Consumption =

$$29ml\ H_2SO_4 \times \frac{1mole}{2L} \times 98\frac{g}{mole} \times \frac{1}{50\ ml\ Extract} = 0.0284\frac{tonne}{m^3\ Extract} \tag{3.5}$$

The usage of sulfuric acid calculated for WinGEMS model is $0.0284 \times \frac{tonne}{m^3} \times 3010\frac{m^3}{day} = 85\frac{tonne}{day}$.

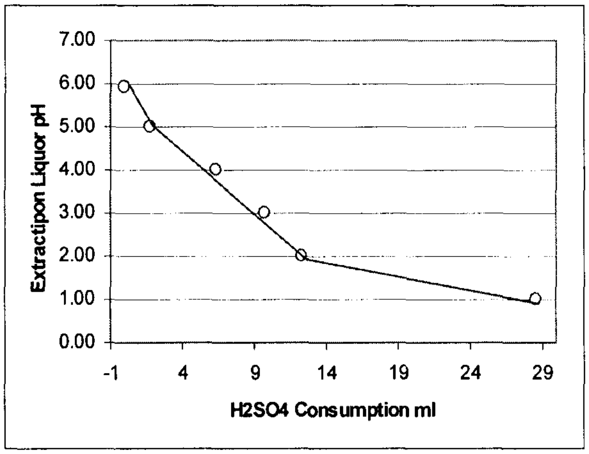


Figure 3.10 Experimental Data for Sulfuric acid Consumption by

Titrating Extraction Liquor to pH =1 [Van Heiningen, 2007]

Just for acidification to pH = 1, the acid usage is equal to 0.05 mole H_2SO_4 per liter of extract ($pH = -\log[0.05\frac{mole}{L} \times 2] = 1$) and which is equal to 0.0049 tonne acid per cubic meter of extract ($0.05\frac{mole}{Liter} \times 98\frac{g}{mole} = 0.0049\frac{kg}{L} = 0.0049\frac{tonne}{m^3}$), so comparing with experimental data most of acid is needed for buffer. After the acid hydrolysis, most of the dissolved lignin will be precipitated and removed by filtration. In this analysis, it was assumed that 100% of the lignin was precipitated and removed from the extract by filtration.

Hydrolysis Kinetics. A carbohydrate hydrolysis model has been developed by Garrote and co-workers [2001] based on earlier work by Carrasco [1992]. In this work, Garrote describes the kinetics for the decomposition of xylan oligomers to xylose and the side reaction of xylose to furfural. In Garrote work, Eucalyptus wood samples were extracted with water to obtain a liquid extract which was subsequently hydrolyzed using sulfuric acid. In the hydrolysis model, furfural is further decomposed into a variety of degradation products. Lastly, acetyl groups on the xylan polymer are converted into acetic acid. The hydrolysis reactions are written schematically in Equation 3.6~ 3.9.

$$xylooligomers \xrightarrow{k_1} xylose \tag{3.6}$$

$$xylose \xrightarrow{k_2} furfural \tag{3.7}$$

$$fulfural \xrightarrow{k_3} degradation\, products \tag{3.8}$$

$$acetyl\, group \xrightarrow{ka} Acetic\, acid \tag{3.9}$$

In the work reported here, it was assumed that the sodium acetate follows similar kinetics to those for the conversion of acetyl groups into acetic acid. More likely however, this reaction is instantaneous.

In the Garrote model, the reaction rate coefficients (k_i) were shown to follow an Arrhenius Equation $k_i = A_i e^{-Eai/RT}$, where (A_i) and (E_i) are the frequency factor and activation energy respectively. Garrote shown that the rate constants (k_i) for each of the chemical reaction are dependent upon on the temperature (T), the sulfuric acid concentration (C) and activation energy Ea_i (see Equation 3.10 and 3.11).

$$k_i = a_i \times C^{n_i} \times \exp\left(-\frac{Ea_i}{R \times T}\right) \tag{3.10}$$

or

$$\ln(k_i) = \ln(a_i) + n_i \times \ln(C) - \frac{Ea_i}{R \times T} \tag{3.11}$$

In Equation 3.10 and 3.11, (a_i) and (n_i) are empirical constants, and (C) is the concentration of sulfuric acid (mole/L).

Garrote presents data for the hydrolysis products. These data were analyzed to determine the kinetic coefficients for the four hydrolysis reactions (see Equations 3.6 to 3.9). Table 3.4 listed the parameters derived from experimental data and used in the hemicellulose hydrolysis model. Details of this analysis are summarized in Appendix A.

Figures 3.11~3.13 illustrate how the concentration of the products change with reaction time. In this illustration the reaction temperature was fixed at 126°C and the acid concentration was 0.5% after conversion of the bi-carbonate to carbonate and the conversion of sodium acetate to acetic acid. In the analysis conducted, the sulfuric acid concentration was varied from 0.5% to 4%. Referring to Figure 3.11, a maximum in the xylose concentration occurs at 1.3 hours. In Figure 3.12, if the sulfuric acid concentration is raised to 4% then the maximum concentration occurs at 0.3 hours.

Table 3.4

Parameter Derived from Experimental Data for Hydrolysis Model

Kinetic Coefficients (For Equation 3.6~3.11)	**Parameters**	**Value**
k_1 (hr^{-1})	a_1	Exp(36.66)
	n_1	1.0
	Ea_1	108.0KJ/mole
k_2 (hr^{-1})	a_2	Exp(31.51)
	n_2	0.71
	Ea_2	109.03KJ/mole
k_3 (hr^{-1})	a_3	Exp(20.79)
	n_3	0.34
	Ea_3	70.88KJ/mole
k_a(hr^{-1})	a_a	Exp(26.80)
	n_a	1.18
	Ea_a	73.37 KJ/mole

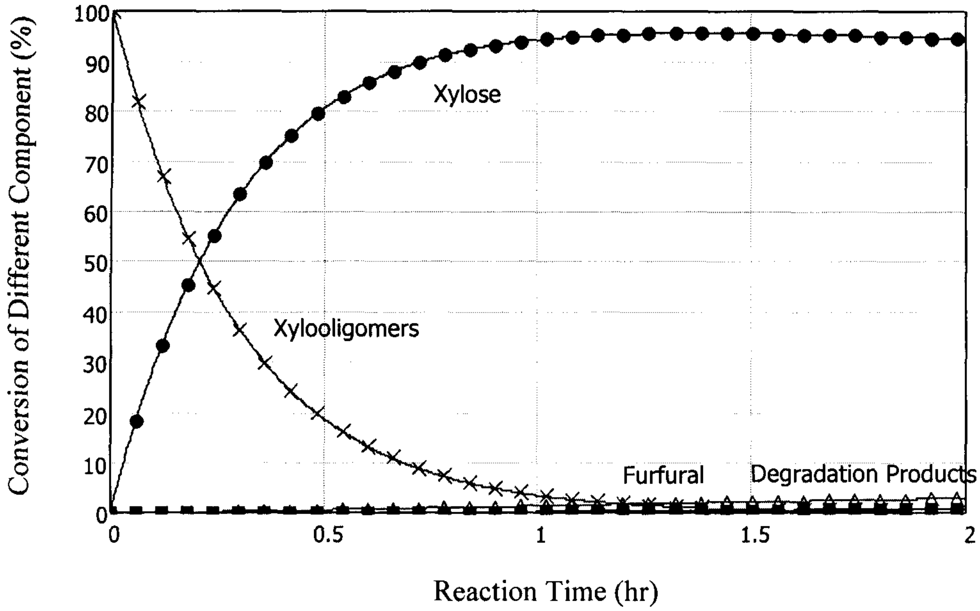


Figure 3.11 Hydrolysis Reaction of Xylooligomers

(Reaction Temperatures = 126°C, Concentration of H_2SO_4 = 0.5%)

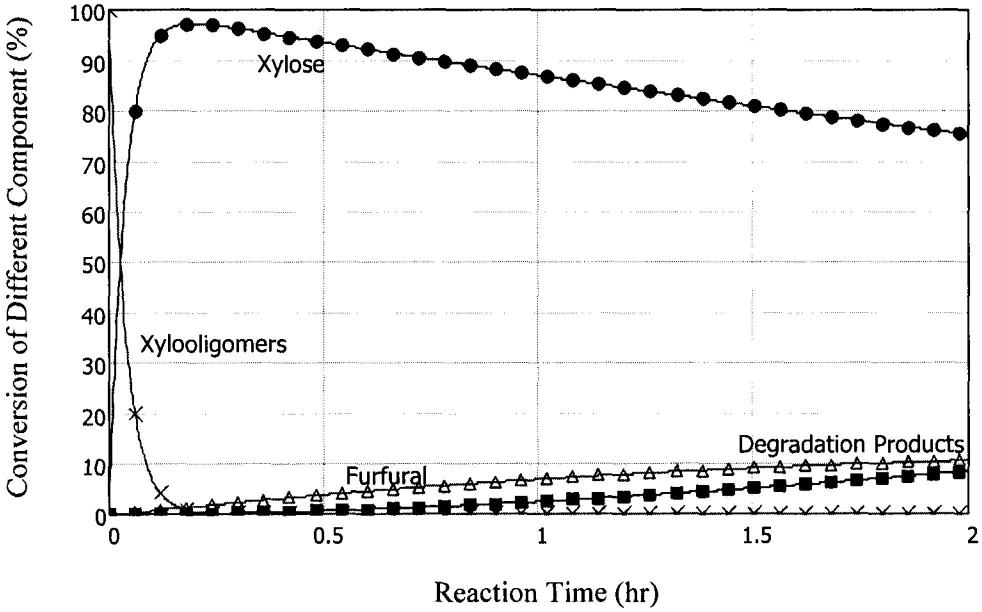


Figure 3.12 Hydrolysis Reaction of Xylooligomers

(Reaction Temperatures = 126°C, Concentration of H_2SO_4 = 4%)

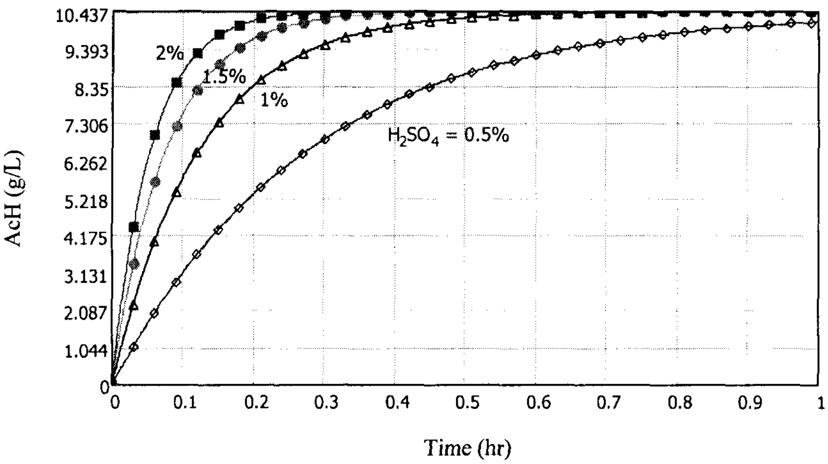


Figure 3.13 Acetic Acid Generation from Xylooligomers Hydrolysis Reaction

(Temperature= 126°C, Concentration of H_2SO_4 = 0.5%)

The conditions for the xylan hydrolysis reaction were optimized by varying the concentration of sulfuric acid and the optimum time determined to produce the maximum xylose concentration. This analysis is summarized in Figure 3.14. It is clear from Figure 3.14 that the higher the sulfuric acid concentration and the higher the temperature, the shorter the reaction time to achieve a maximum xylose concentration.

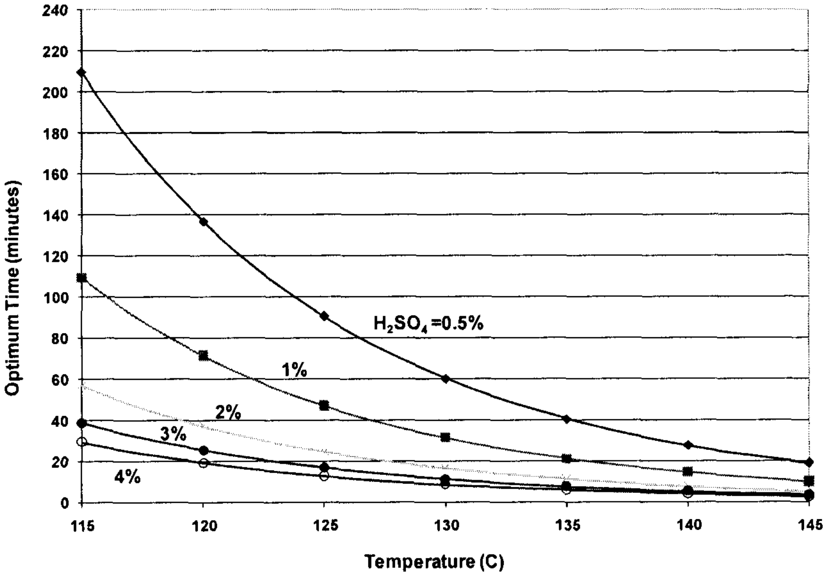


Figure 3.14 the Optimum Time of Xylose Concentration vs. Hydrolysis Temperature

The concentration of furfural varied with acid concentration and hydrolysis temperature are shown in Figure 3.15. From the Figure 3.15 it is clear that low concentrations of furfural are produced at low temperature and high concentration of acid.

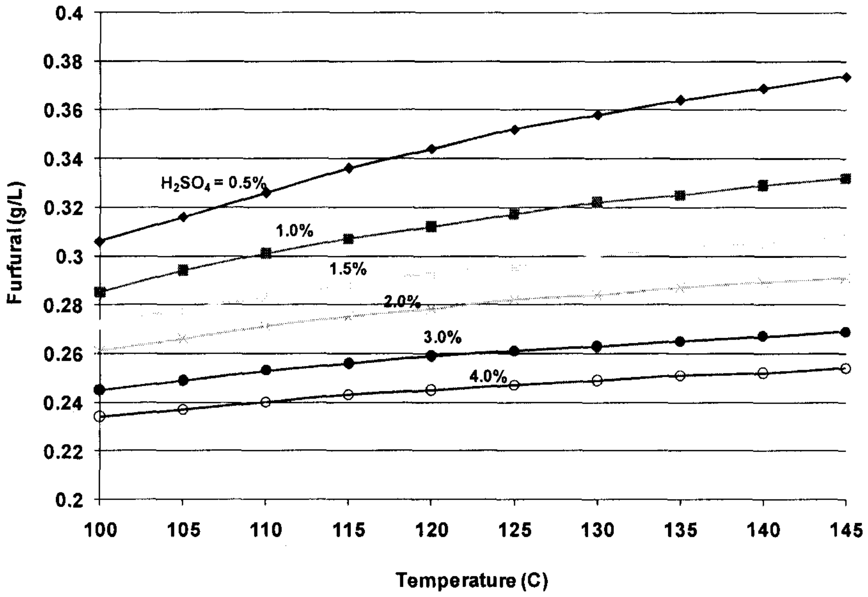


Figure 3.15 Furfural Generation vs. Acid Hydrolysis Condition

Application to Industrial Processing. For the purpose of industrial design, the Garrote's data suggest that short resident time, high temperature and low sulfuric acids are desired. The short resident time will minimize capital investment in the equipment while the low sulfuric acid concentration minimizes the formation of gypsum. The high temperature will require addition steam and may require more costly materials of construction. It is highly desirable to minimize the concentration of furfural since it is an inhibitor in the fermentation of component sugars to ethanol. Also the less sulfuric acid is used, the lower will be the operating cost for the acid and the lower will be the cost for liming and gypsum disposal. Based on this analysis a temperature of 126 °C and a liquor

Table 3.5

The Properties of Possible Solvent [Jones, 1967]

pH of 1 and a reaction time of 1.3 hours was selected as the conditions for the hydrolysis reactor.

3.2.5 Liquid – Liquid Extraction

In the acid hydrolysis step, a considerable quantity of acetic acid will be generated and can be sold as a by-product from the process. Also, acetic acid must be removed because it will inhibit the fermentation of C5 and C6 sugars to ethanol. Similarly, the by-product furfural which is formed in the hydrolysis step in the process must be removed since it is toxic to yeast and micro-organisms used in the fermentation process.

Separation by Liquid-Liquid Extraction. There is a large body of literature that describes the removal of acetic acid from dilute aqueous solutions by extraction with a suitable solvent [King, 1958, Jones, 1967, Geankoplis, 2003]. In this method the acetic acid is removed and the solvent is separated from the acetic acid by distillation. The solvent is then recycled to the extraction step and the acetic acid is upgraded. Quite often the acetic acid will form an azeotrope with the solvent and the design engineer is faced with the problem of breaking an azeotrope. Thus, it is critical to select a suitable solvent that avoids an azeotrope if possible. Table 3.5 lists a variety of solvents that have been used to separate acetic acid from water in aqueous solutions. Table 3.5 also gives the normal boiling point of the solvent and the boiling point of the azeotrope.

present), water, acetic acid and furfural are separated in a series of distillation columns. Furfural is further rectified in a vacuum distillation to 99.5% as a saleable product. The purity of the acetic acid after the rectified column is thought to be 99+%. Acetic acid would be sold as a by-product. The methanol and furfural would be incinerated, most likely in the lime kiln. Waste water from the process would be sent to the waste treatment system. Details of Aspen model of the Lenzing process is illustrated in Appendix B.

Table 3.6

Boiling Point and Chemical Formula of Component Present in the Hydrolyzate

Chemical Species	Chemical Formula	Boiling Point (°C)
Methanol	CH_3OH	86
Water	H_2O	100
Furfural	$C_5H_4O_2$	132
Acetic acid	CH_3CH_2OH	168
Ethyl acetate	$C_4H_8O_2$	77
Undecane	$C_{11}H_{24}$	192

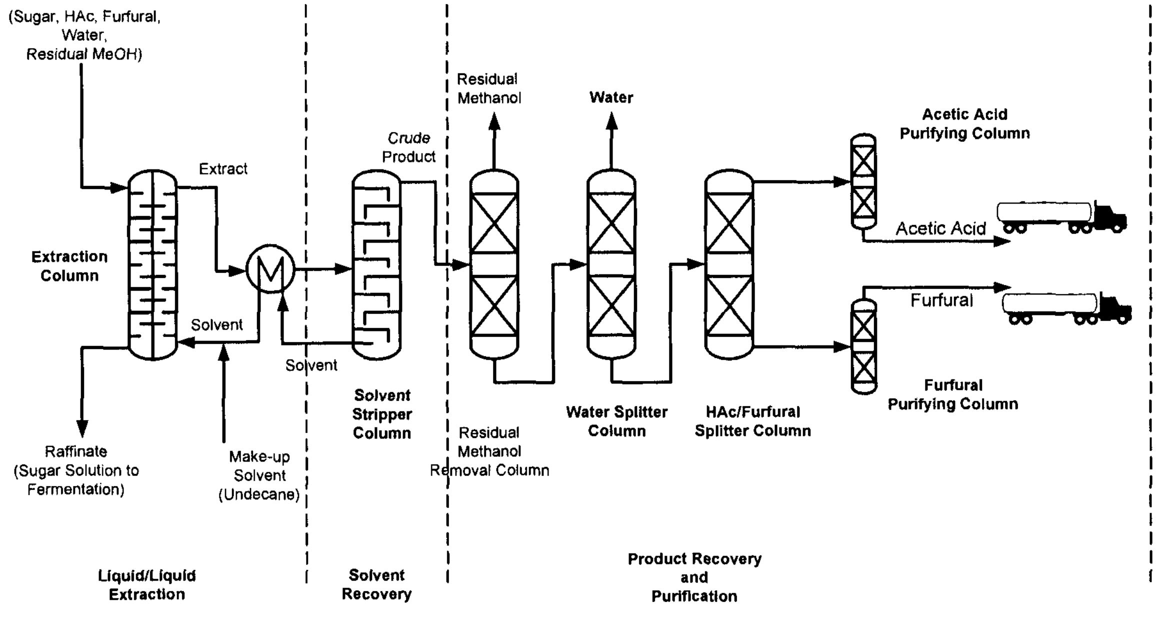


Figure 3.16 Lenzing's Process for Acetic acid and Furfural Recovery

[Lenzing Technology, 2006]

3.2.6 Liming Process

The raffinate from the Lenzing containing the component sugar is sent to the liming process (Figure 3.17).

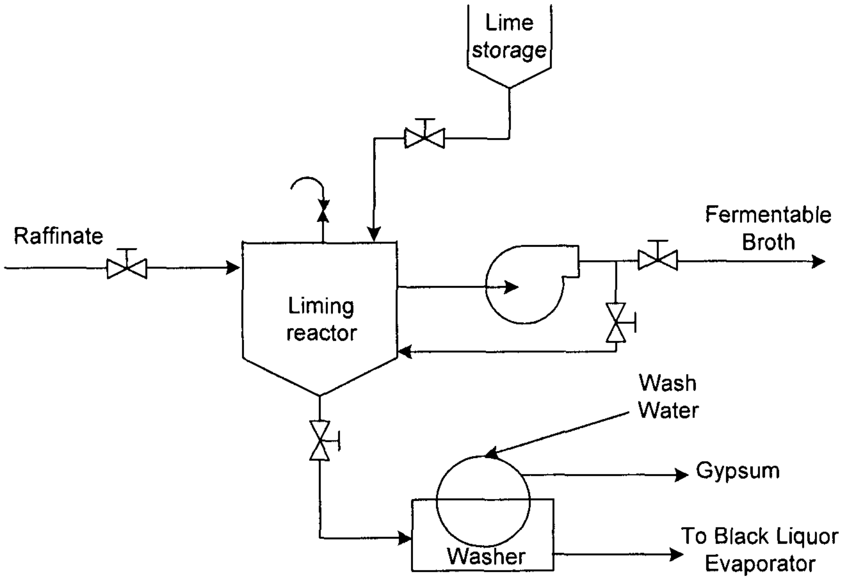


Figure 3.17 Schematic Diagram for Liming

In the liming process the pH of the raffinate is raised from a value of approximately 1 to about 6 by the addition of lime (calcium oxide, CaO). The objectives of the liming process, are to (1) raise the pH of the raffinate solution, (2) precipitate sulfate ion as gypsum ($CaSO_4 \cdot 2H_2O$), and to detoxify the hydrolyzate. The gypsum is then removed by filtration [Martinez, 2001]. Sulfate ion needs to be removed from the hydrolyzate because it inhibits fermentation of sugars to ethanol. The chemistry of the liming process is shown in Equation 3.12.

$$CaO + 2H^{+} + SO_4^{2-} + H_2O \rightarrow CaSO_4 \cdot 2H_2O \downarrow \tag{3.12}$$

The resulting gypsum is collected in the bottom of a settling tank and removed in a filter press. The gypsum is washed and exported at about 79% solids and is available as a by-product for sale or disposal to a landfill. After the liming process, the concentration of sulfate ion in the fermentation broth has been sufficiently lowered to the micro-organism tolerance level, and the pH value of the liquor is back to neutral. The broth liquor is now ready for fermentation.

3.2.7 Ethanol Fermentation

If the sugar concentration in the fermentation broth is too low it may need to be concentrated. In this case an evaporator or membrane separation process would be used to raise the sugar concentration to a more desirable level. Here we assume the sugar concentration in the fermentation broth is suitable and an evaporator system is not required.

Ethanol fermentation inhibitors such as furfural and hydroxyl methyl furfural in acid hydrolyzates have been recognized for at least 50 years. Most of the furfural was extracted in liquid-liquid extraction section and it can also be further removed by yeasts [Azhar, 1981]. In a high cell densities environment the toxicity effects of above organics can be alleviated. It was reported that the large yeast inocula along with various other treatments such as activated charcoal, and anion exchange can be used to improve the fermentability of acid hydrolyzates [Jeffries, 1988].

Fermentation to Ethanol. Fermentation is then carried out after inhibiting contaminants have been removed or lowered to a tolerance concentration. The ethanol fermentation process is sketched in Figure 3.18 following the design given by American Process Inc [API, 2007]. Commonly the fermentation step is performed in a five (5)-stage semi-continuous process. Micro-organisms such as E-coli B (KO11) [Lwaford, 1997, Balasubramanian, 2001] or Z. mobilis [Wooley, 1999] would be used to convert five and six carbon sugars into ethanol and carbon dioxide. The micro-organism is prepared in a skid using fresh culture and seeded with a recovered culture and with residual nutrients. The fermenters are periodically disinfected with 50% ethanol from the sugar ethanol column. Acetic acid product is used for the broth pH adjustment and nutrients are added into the first fermenter. CO_2 is removed from the fermenters and collected for recovery. After the five (5) stage fermentation process the ethanol product is very dilute. The broth from the last fermentation process will be sent into a sugar column for ethanol upgrading (See Figure 3.19). After ethanol upgrading in the sugar column the unfermented sugar will be recycled back to the five (5) stage fermentation process for additional fermentation.

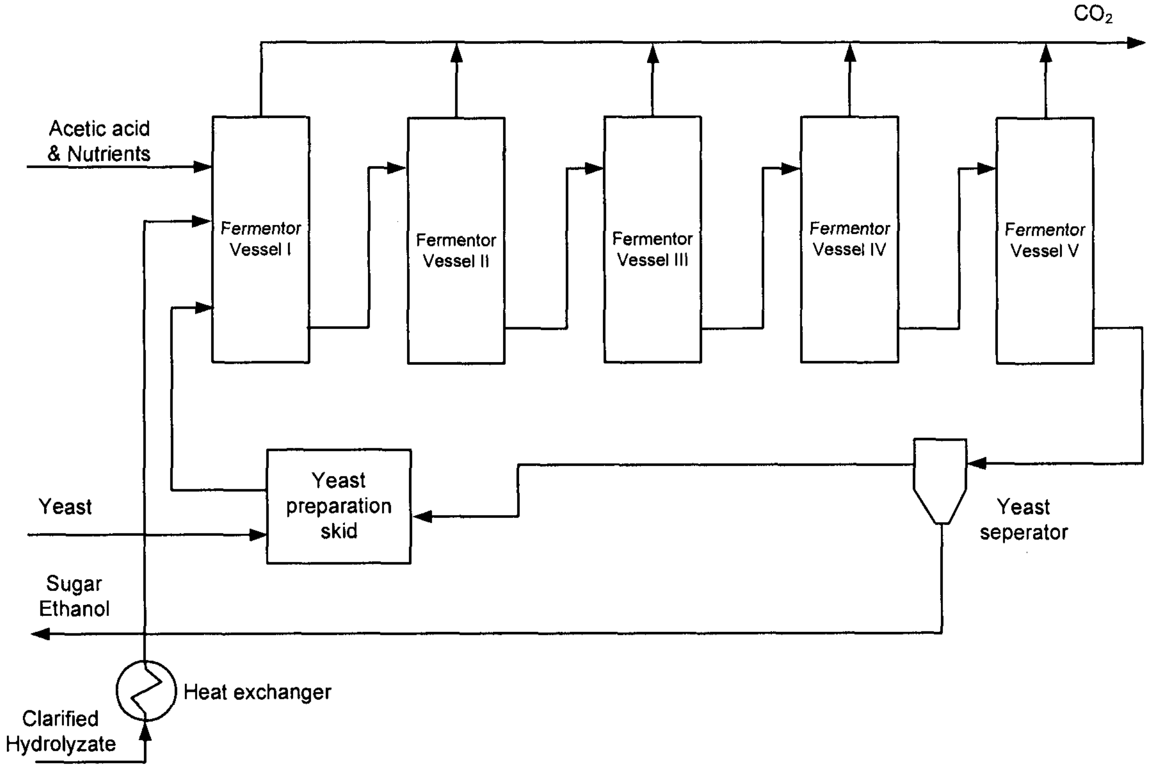


Figure 3.18 Ethanol Fermentation Process [API, 2007]

Fermentation Chemistry. Theoretical yields for the fermentation of pentose and hexose sugars to ethanol have been reported [Olsson 1996, Aden, 2002, Wooley, 1999, Frederick, 2006]. In the analysis reported here, it was assumed that the fermentation took place under anaerobic conditions and approximately 90% of hexose and pentose sugars in the feed are converted into ethanol. It was further assumed that no aerobic fermentation is carried out. Equation 3.13 shows the anaerobic fermentation of glucan and mannose to ethanol. Equation 3.14 and 3.15 are the anaerobic fermentation of xylose and glucuronic acid to ethanol respectively. It should be pointed out that anaerobic fermentation of glucuronic acid leads to the formation of acetic acid. Consequently the acetic acid broth is sent to the Lenzing process for recovery. Table 3.7 listed the conversion efficiencies used as the basis for process design for the ethanol fermentation step.

$$C_6H_{12}O_6 \xrightarrow{Enzyme} 2C_2H_5OH + 2CO_2\uparrow \tag{3.13}$$

Glucose and Mannose Ethanol Carbon Dioxide

$$3C_5H_{10}O_5 \xrightarrow{Enzyme} 5C_2H_5OH + 5CO_2\uparrow \tag{3.14}$$

Xylose Ethanol Carbon Dioxide

$$C_6H_{10}O_7 \xrightarrow{Enzyme} C_2H_5OH + CH_3COOH + 2CO_2\uparrow \tag{3.15}$$

Glucuronic Acid Ethanol Acetic Acid Carbon Dioxide

Table 3.7

Sugar Fermentation Efficiencies to Ethanol

Sugar Category	Overall Fermentation Efficiencies	Weight Efficiency (g/g)
Pentoses to ethanol (Xylose)	90%	0.460
Hexoses to ethanol (Glucose and Mannose)	90%	0.460
Glucuronic Acid	90%	0.213

3.2.8 By-Product Recovery and Upgrading

Figure 3.19 illustrates the by-products recovery and upgrading process. The product discharged from ethanol fermentation step included very dilute ethanol and is sent into a sugar column to do an initial ethanol distillation. Then the overhead products from the sugar distillation columns, which contain approximately 50% ethanol, will be sent to a conventional ethanol rectification column where it is rectified to the azeotropic composition of 95%. The ethanol product from the rectification column is then dehydrated using a molecular sieve column to raise the ethanol concentration to 99%. Finally the product ethanol is cooled and sent to storage for sale.

The bottom products from the sugar column will be sent into a glucuronic acid fermentation system where the glucuronic acid is fermented into acetic acid and ethanol. The broth from the glucuronic acid fermentation process is sent to an acid acetic distillated column where the ethanol is stripped from the acetic acid. The concentration of ethanol leaving the acetic acid column was assumed to be about 50% and is mixed with the ethanol coming from the sugar column. This mixed ethanol stream is then sent to an ethanol rectification column where 95% ethanol leaves the top of the column and is sent to dehydration. The bottom products from the both of acid and ethanol rectification columns, both rich in acetic acid, are mixed and recycled back to the Lenzing process (see Figures 3.16 and 3.19). In the Lenzing process, previously discussed, the acetic acid, trace methanol and furfural are extracted and purified by distillation.

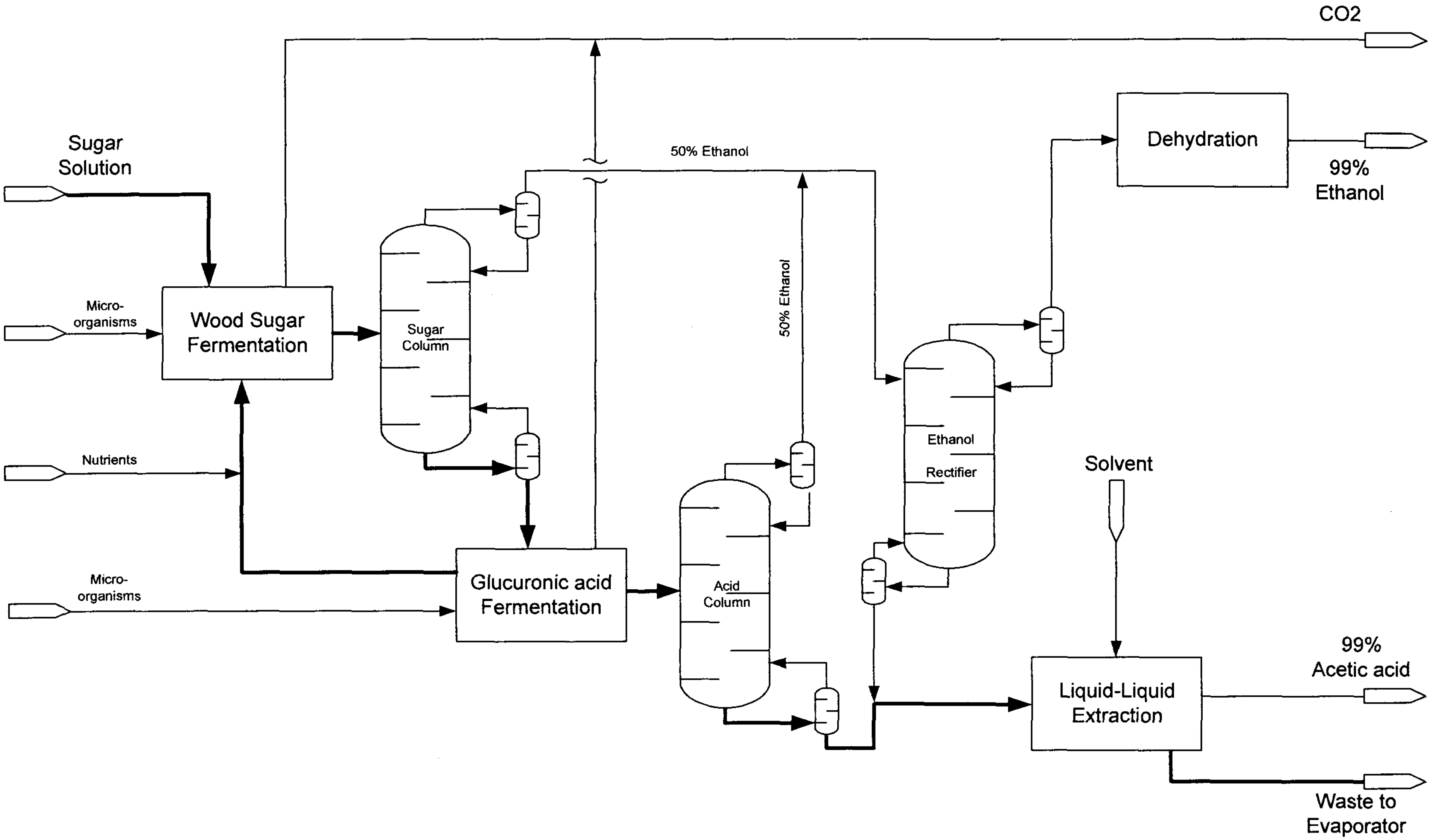


Figure 3.19 Processes for Fermentation and Upgrading Ethanol

3.3 WinGEMS Model for Modified Kraft Pulp Mill Case

A detailed description of the WinGEMS model of the existing kraft pulp mill case was included in Chapter 2.5. Here the same principle was used to model the modified Kraft pulp mill case. It should be mentioned that the WinGEMS software does not deal with the equilibrium of thermodynamics. Consequently, energy balances involving liquid and vapor equilibrium such as liquid extraction and the distillation process could not be simulated in the WinGEMS model. Therefore these energy balances were modeled using ASPEN plus software or were approximated by scaling the data presented by Wooley [1999] and Aden [2002]. Both Wooley and Aden used ASPEN plus for modeling ethanol production from hardwood. The configuration of the entire WinGEMS model is illustrated in Figure 3.20. The results from the mass and energy balance for the 1,000 tonne per day case using the WinGEMS simulation model are summarized in Tables 3.8 and 3.9.

Mass Balance. For the case of a 1,000 tonne per day Kraft pulp mill, extracting approximately 10% of the wood, approximately 39.5 tonne per day of ethanol and 45.1 tonne per day of acetic acid can be produced. The production of furfural which amounts to approximately 0.9 tonne per day was assumed to be burned in the lime kiln. If a market can be found for the furfural it can of course be sold, but in the current analysis it was assumed to be burned.

Energy Balance. An energy balance for the 1,000 tonne per day modified Kraft mill is illustrated in Table 3.9. Relative to the base case, in the modified Kraft mill additional energy is consumed in the extraction vessel because the wood has to be heated and the chips then washed in the extraction vessel and again reheated in pulping digester (see Figure 3.3). Additional energy is also required in the ethanol separation and distillation processes (12.7 MM BTU/hr) as well as in the Lenzing process (11.8 MM BTU/hr). It was assumed that in the fermentation processes, the energy requirements are small and are assumed to be zero. In actuality heat from the metabolism of micro-organisms must be removed.

Since organic matter is removed from the wood, the energy content in the black liquor will be lowered accordingly. Steam generation occurs in both the Hog fuel boiler from combustion of bark and wood waste and in the black liquor recovery boiler. The results of the simulation for the 1,000 tonne per day pulp mill gives the estimated steam generation in the Hogfuel boiler to be 116.1 MM BTU/hr and that in the recovery boiler to be 416.1 MM BTU/hr. The energy balance was done in a manner that sufficient steam was produced first to satisfy the steam requirements in the Kraft mill; and then excess energy in the wood waste, bark and black liquor is converted into electrical energy. The efficiency for the conversion of energy in the form of bark, wood waste and black liquor was assumed to be 20% overall efficiency.

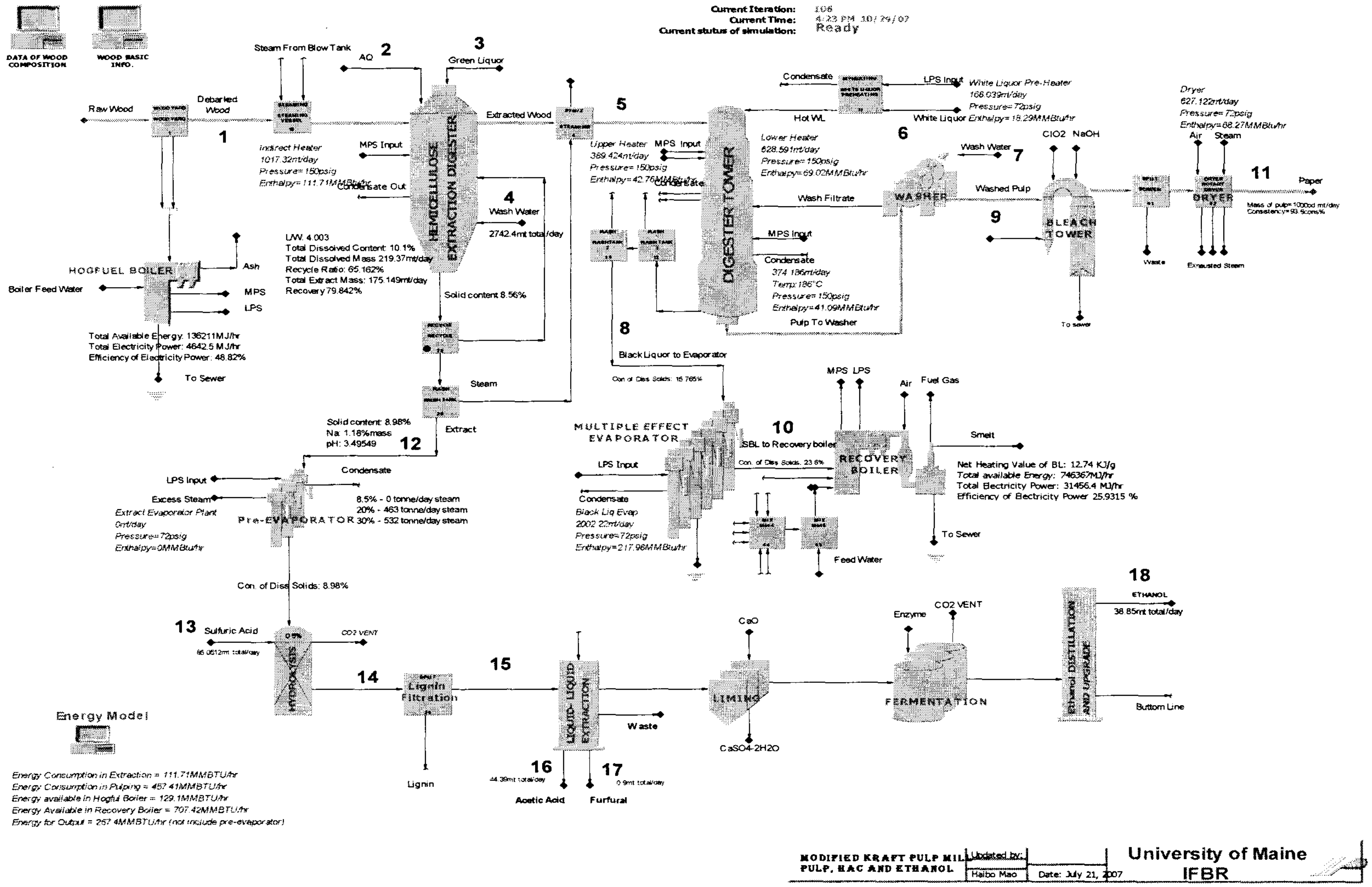


Figure3.20 WinGEMS Model of Modified Kraft Pulp Mill with Products of Pulp, Ethanol and Acetic Acid

Table 3.8

Mass Balance of 1000 Tonne/day Modified Kraft Pulp Mill Case

MODIFIED KRAFT PULP MILL CASE								
Description	**Stream Number**	**Total Flow Rate (Tonne/day)**	**Consistency (%)**	**Concentration (%)**	**Suspension Solids (Tonne/day)**	**Dissolved Solids (Tonne/day)**	**Water (Tonne/day)**	**Temp (C)**
Wood to digester	**1**	**4334**	50.0	0.0	2167	0.0	2167	20
Anthraquinone	**2**	**11**	0.0	10.0	0.0	1.1	9.8	0
Green Liquor	**3**	**657**	0.0	16.2	0.0	106.4	550.2	20
Wash Water	**4**	**2746**	0.0	0.0	0.0	0.0	2746.6	20
Extracted Wood	**5**	**4917**	39.7	2.1	1952.7	63.5	2901.2	92
White Liquor	**6**	**2296**	0.0	17.3	0.0	397.5	1898.9	45
Water	**7**	**10543**	0.0	0.0	0.0	0.0	10542.6	20
Wash Filtrate	**8**	**8638**	0.0	15.7	0.0	1353.0	7285.1	101
Washed Pulp	**9**	**8503**	12.0	0.02	1020.4	1.7	7481.3	23
Black Liquor	**10**	**1804**	0.0	75.0	0.0	1353.0	451.0	101
Dried Pulp	**11**	**1069**	93.6	17.2	1000.0	11.8	56.9	42
Dilute Extract	**12**	**3172**	0.0	8.5	0.0	268.0	2903.5	127
Sulfuric Acid	**13**	**87**	0.0	93.0	0.0	81.2	6.1	20
Hydrolyzate	**14**	**3235**	0.7	9.1	22.8	292.8	2919.7	126
Aqueous solution	**15**	**3213**	0.0	9.1	0.0	292.8	2919.7	126
Acetic Acid	**16**	**45.1**	0.0	100.0	0.0	45.1	0.0	93
Furfural	**17**	**0.92**	0.0	100.0	0.0	0.9	0.0	93
Ethanol	**18**	**39.5**	0.0	100.0	0.0	39.5	0.0	25

Note: Refer to Figure 3.1 and 3.20 for Stream Number.

Table 3.9

Energy Balance for 1000 Tonne per Day Modified Kraft Pulp Mill Case

MODIFIED KRAFT PULP MILL CASE					
Stream Number		**Flow Rate (Tonne/day)**	**Pressure (Psig)**	**Temp (C)**	**Enthalpy (MMBTU/hr)**
Energy Consumption	**S3 Extraction**	770	150	186	84.6
	S4 W. L. Preheater	143	72	160	15.6
	S5 Upper Heater	378	150	186	41.5
	S5 Lower Heater	589	150	186	64.7
	S5 Washer Heater	374	150	186	41.1
	S6 B.L. Evaporator	1919	72	160	209.0
	S9 Steam Dryer	627	72	160	68.2
	S10 Extract Evaporator	0.0	72	160	0.0
	S11 HAC Separation	107	150	186	11.8
	S12 EtOH Distillation	115	150	186	12.7
Energy Production	**Hog Fuel Boiler**				
	S1 Elec. Energy (KW)	768 (a)			
	S2 Med. Pres. Steam	542	150	185	59.5
	S2 Low Pres. Steam	520	72	158	56.5
	Recovery Boiler				
	S7 Elec. Energy (KW)	17520 (a)			
	S8 Med. Pres. Steam	1627	150	185	178.6
	S8 Low Pres. Steam	2184	72	158	237.5

SUMMARY			
Steam Consumption in Extraction		84.6	**MMBTU/hr**
Steam Consumption in Pulping		440.1	**MMBTU/hr**
Steam Available in Hog Fuel Boiler		116.1	**MMBTU/hr**
Steam Available in Recovery Boiler		416.1	**MMBTU/hr**
Steam Form for Output		7.4	**MMBTU/hr**
Total Energy Output	**As Electricity**	18.3 (a)	**MW**
	As Steam	300.0	**MMBTU/hr**

(a) Electricity energy was calculated by assuming the efficiency for conversion of thermal to electrical energy was 20%.

3.4 Energy Consumption and Effect on Operation of the Lime Kiln

In the "near neutral" extraction process less white liquor is required in the cooking step. This will result in a corresponding decrease in the amount of calcium carbonate ($CaCO_3$) that needs to be removed in the white liquor clarifier and decomposed to lime in the kiln. This reduction in flow of $CaCO_3$ has a significant effect on the amount of energy required to operate the lime kiln. This is because the hemicellulose extraction process uses green liquor (Na_2CO_3 and Na_2S) as the solvent and the green liquor does not go to the causticization and lime cycles. Figure 3.21 shows the comparison of cooking conditions in the existing and modified Kraft pulp mill cases.

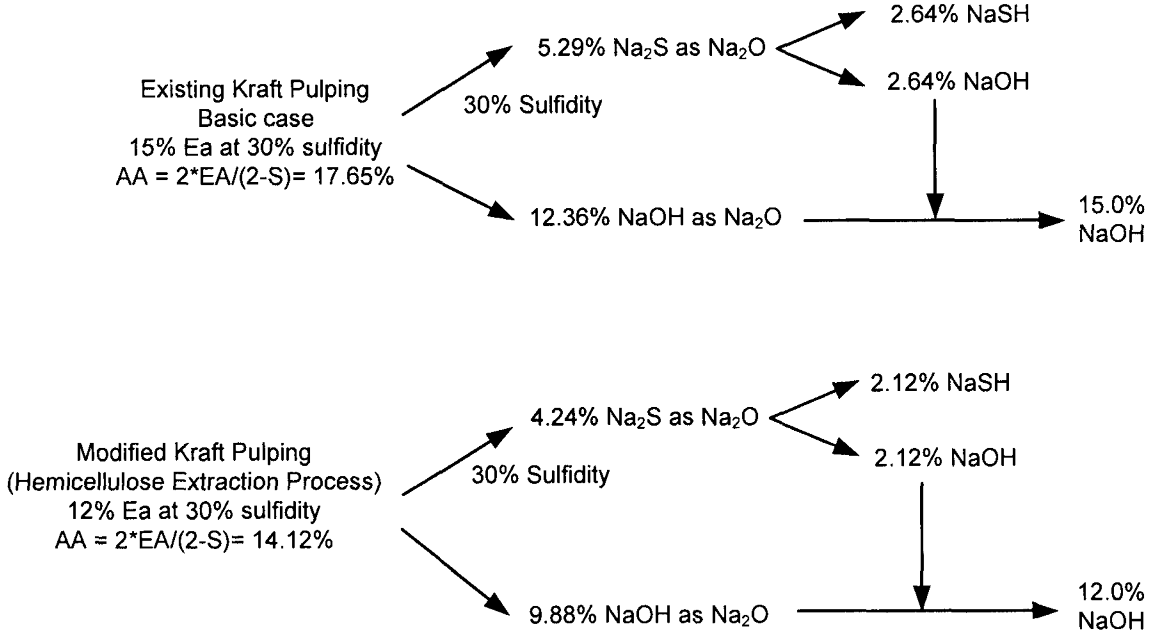


Figure 3.21 Cooking Condition Comparisons between Existing Kraft Pulp and Modified Kraft Pulp Case

Assuming 15% EA and 30% sulfidity used in the existing pulp mill and correcting for the hydrolysis of sodium sulfide, 12.36% NaOH is required on a Na_2O basis for the pulping process. This may be compared to 9.88% NaOH again calculated as Na_2O in the modified Kraft mill assuming 30% sulfidity and 12% EA. Thus, there is reduction in effective alkali calculated on a Na_2O basis between the modified and the existing Kraft pulp mill. This is a distinct advantage of using green liquor rather than sodium hydroxide (NaOH) or white liquor in the pre-extraction step.

Oil Savings in Lime Kiln. Gullichsen and Fogelholm [Gullichsen, 1999] estimated that the oil consumption required to heat and decompose one tonne of CaCO3 (dry lime mud basis) is 0.085 tonne of oil.

$$CaCO_3 \xrightarrow{Energy} CaO + CO_2 \tag{3.16}$$

Since in the near neutral hemicellulose extraction process less lime mud goes to the kiln, there will be a savings of about 9.3 tonne of fuel oil per day for a 1,000 tonne per day pulp mill assuming an overall pulp yield of 47% based on 80% Causticizing efficiency in lime kiln.

$$\text{Oil Savings} = \frac{1000\frac{tonne}{day}Pulp}{47\%\,Yield} \times (12.36 - 9.88)\% \times$$

$$\frac{\frac{0.87kg}{s}oil}{10.21\frac{kg}{s}CaO} \times \frac{MW_{CaCO_3}}{MW_{NaOH}} \times \frac{1}{Causticizing} = 9.3\ \text{tonne/day} \tag{3.17}$$

At a fuel oil price of about \$2.2 per gallon (\$598/tonne) the oil saving are approximately \$2 million dollars per year.

$$Total\ saving = \frac{9.3tonne}{day} \times \frac{\$598}{tonne} = 2.0\ \text{million dollar per year} \tag{3.18}$$

The savings in oil in the lime kiln of approximately \$2 million dollars per year helps offset the loss of steam which is used to manufacture the new products.

Reduction in Steam Generation. The addition of the hemicellulose extraction process to a Kraft pulp mill reduces the energy which is obtained from the residual pulping liquor. In this study no attempt was made in the present analysis to optimize the energy use by performing a pinch analysis [Turton 2003]. The net energy output is illustrated in Figure 3.22 in terms of millions of BTU per hour as equivalent steam and electrical energy as a function of the pulp mill size. A comparison is made to the base Kraft mill case where no hemicelluloses are pre-extracted which is shown on the bottom line of Figure 3.22. A more clear quantity comparison of energy requirement and production between existing Kraft pulp mill and modified kraft pulp mill for a 1,000 tonne per day pulp production rate is illustrated in Tables 3.10. On average, the modified Kraft mill would produce approximately 35% less steam than the conventional Kraft mill because 10% of the wood mass is extracted and additional energy is required for the pre-evaporation and distillation operations. Also, energy is lost during the extraction process because the extraction liquor is removed from the digester and flashed.

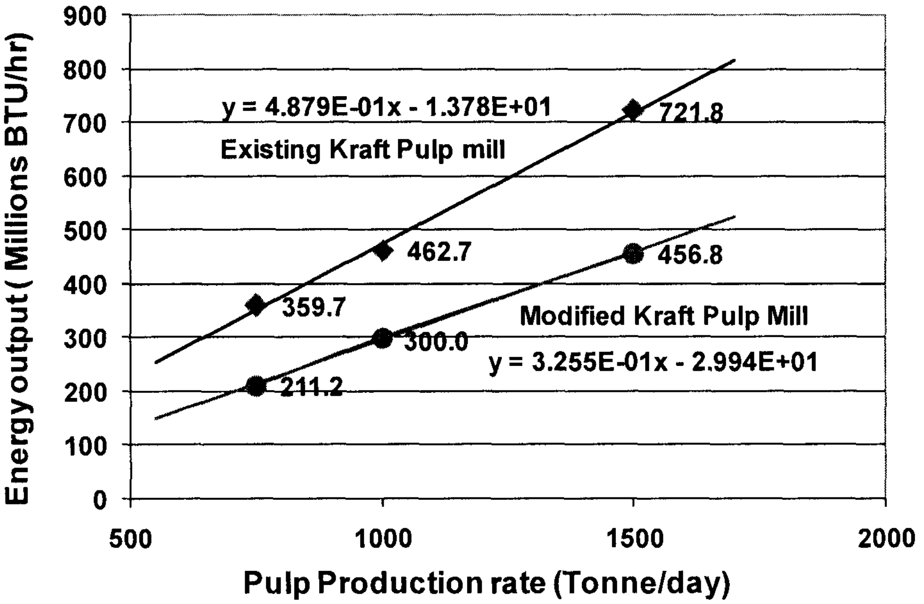


Figure 3.22 Energy Output vs. Plant Size

Table 3.10

Energy Comparison for 1000 Tonne per Day base case and

Modified Kraft Pulp Mill Case

Energy Balance Relative to Base Case				
Stream Number and Description		**Existing Kraft Pulp Mill Case**	**Modified Kraft Pulp Mill**	**Units**
Steam Required (Enthalpy)	**S3 Extraction**	0.0	84.6	**MMBTU/hr**
	S4 WL Preheater	20.9	15.6	**MMBTU/hr**
	S5 Upper Heater	84.6	41.5	**MMBTU/hr**
	S5 Lower Heater	41.8	64.7	**MMBTU/hr**
	S5 Washer Heater	29.6	41.1	**MMBTU/hr**
	S6 BL Evaporator	224.3	209.0	**MMBTU/hr**
	S9 Steam Dryer	68.0	68.2	**MMBTU/hr**
	S10 Extract Evaporator	0.0	0.0	**MMBTU/hr**
	S11 HAC Separation	0.0	11.8	**MMBTU/hr**
	S12 EtOH Distillation	0.0	12.7	**MMBTU/hr**
Total Steam Production (Enthalpy)	**Hog Fuel Boiler**	129.4	129.1	**MMBTU/hr**
	Recovery Boiler	802.5	720.1	**MMBTU/hr**
Steam Required in Extraction		0.00	84.6	**MMBTU/hr**
Steam Required in Pulping		469.2	440.1	**MMBTU/hr**
Steam Required in Ethanol Process		0.0	24.5	**MMBTU/hr**
Oil Savings in Lime Kiln		0.0	(15.3)	**MMBTU/hr**
Net Energy Output	**As steam**	462.7	300.0	**MMBTU/hr**
	As Electricity	27.1	18.3	**MW**

Note: Oil saving in existing Kraft pulp mill case is zero, and in modified Kraft pulp millcase is positive 15.3 MMBTU/hr.

3.5 Production Rate

The production rate of byproducts – ethanol, acetic acid and furfural as a function of the production rate of the Kraft pulp mill is shown in Figure 3.23. The data in Figure 3.23 were obtained by using the WinGEMS computer model. Pulp production rates between 550 and 1,500 tonne per day were analyzed to determine anticipated production rates for ethanol, acetic acid and furfural. From Figure 3.23 it is clear that the larger the pulp mill, the larger will be the production of the by- products. The production rate of ethanol for the 1,000 tonne per day pulp production rate would be approximately 39.5 tonne/day (4.62 million gallons per year of 100% ethanol) and 45.1 tonne per day of 100% acetic acid (3.97 million gallons per year). In addition about 0.92 tonne per day of furfural are produced (320 tonne per year). For even the 1,500 tonne per day Kraft mill, the amount of ethanol produced is relatively small (7 million gallons per year). Modern corn to ethanol plants under construction typically produces 100 million gallons per year [Renewal Energy Association]. Similarly, for comparison purposes, a modern acetic acid plant would have a production rate of 500,000 tonne per year, which is about 30 times larger than the capacity of the 1,000 tonne per day pulp mill [Acetic Acid Facts]. Although these are small plants relative to the size for a new corn to ethanol plant, production of ethanol and acetic acid represents significant sources of revenue for the pulp mill.

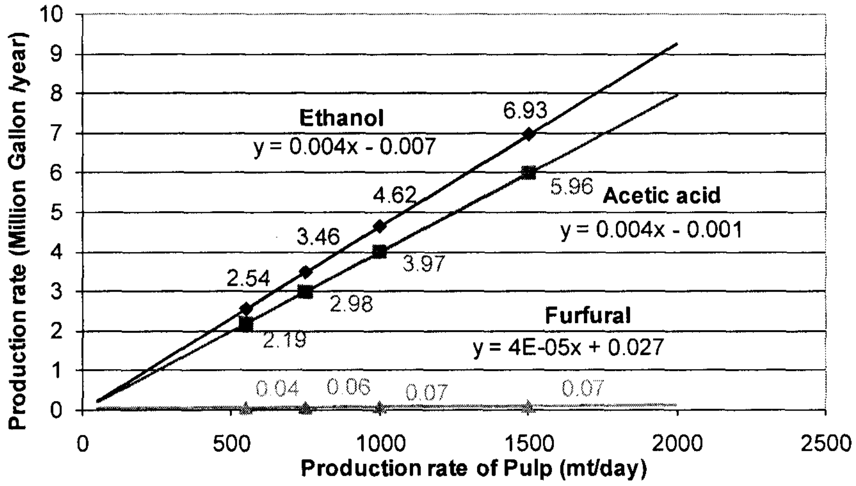


Figure 3.23 Production Rates of Ethanol, Acetic Acid and Furfural

3.6 Process Advantage and Disadvantage

There are several important advantages associated with the "near- neutral" hemicellulose extraction process. Firstly, the quantity and quality of the pulp is unchanged compared to pulp obtained from a conventional Kraft process. This point is amply illustrated in Figures 3.24 with data obtained from Van Heiningen [Van Heiningen, 2007]. Figure 3.24 shows that pre-extraction with modified kraft pulp cooking condition (3% green liquor +0.05% AQ at 160°C for 110 minutes followed by modified kraft cooking at 12% EA and 30% sulfidity) gives the same yield (blue triangular symbols), based on original wood, as a conventional Kraft pulping process when the pulping is conducted at 15% EA and 30% sulfidity (red star symbols). Secondly, the physical properties of pulp produced by the hemicellulose extraction process pulp are as good as or slightly better than that of the Kraft pulp produced using conventional methods. This is illustrated in Figure 3.25 which shows that the tear-tensile strength of the pre-extracted and conventional Kraft pulps.

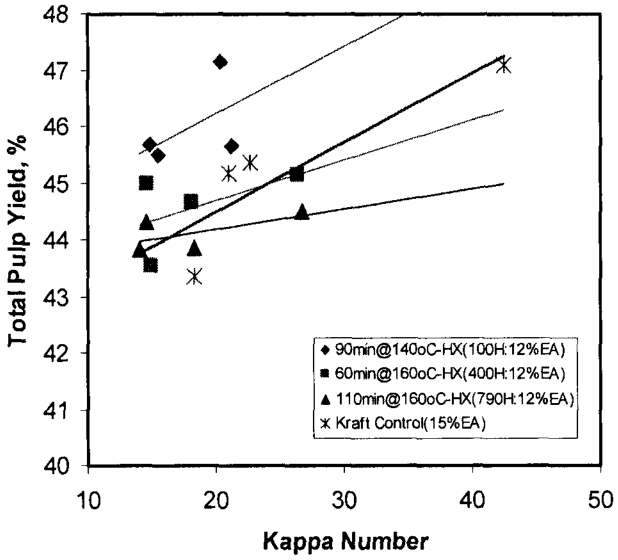


Figure 3.24 Yield vs. Kappa number

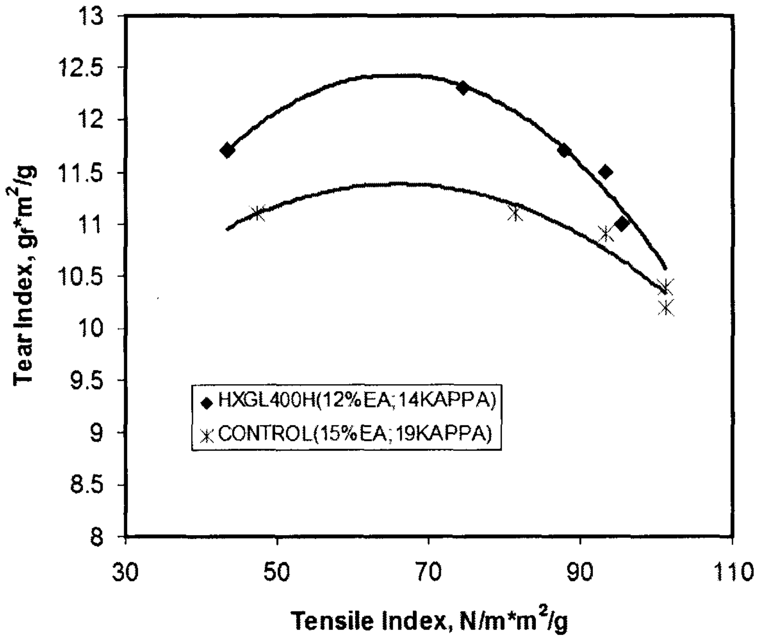


Figure 3.25 Tear Index vs. Tensile Index

As previously discussed, a third advantage of the "near-neutral" extraction process is that the recovery cycle is off-loaded because the amount of organics in black liquor is reduced and less white liquor is needed for pulping. This change would allow a mill to significantly increase its pulp production rate if the recovery cycle is the bottleneck.

Environmental advantages of the extraction process are that the methanol content of the black liquor is reduced by about 40%, while its TRS content is also diminished because of the lower white liquor charge and shorter pulping time during the modified Kraft cook. Finally, a new feed stock stream of sugars is produced which may be used for the production of biofuels and renewable chemicals.

Also there are several disadvantages for the “near-neutral” hemicellulose extraction process. In the current research the production rate of the two co-products ethanol and acetic acid is low. Within the organic in wood chips is extracted, less steam was produced in recovery boiler. Finally it needs additional project investment for the “near-neutral” hemicellulose extraction process.

Chapter 4

ECONOMIC EVALUATION OF THE HEMICELLULOSE EXTRACTION PROCESS

4.1 Introduction

This chapter summarizes the results of an economy analysis performed for the hemicellulose extraction process. This analysis is predicated on the results of the mass and energy balance calculations performed for the existing and modified Kraft pulp mill cases previously discussed and cost curves developed by Wooley [1999] and later upgraded by Mitchell [2006]. Wooley presents a detailed economy model for a hardwood to ethanol process starting with hard wood chips. Capital and operating cost as well as the profitability analysis presented by Wooley were updated to 2006 costs by Mitchell [2006] who considered a variety of scenarios depending whether the plant was built at a green field site or located at an existing Kraft mill. Of particular interest are capital cost curves generated by Mitchell for the various areas of the hardwood to ethanol plant as a function of the amount of wood being processed.

Estimating Capital Cost. Wooley and Mitchell divided the hard wood to ethanol plant into the following nine (9) areas or unit processes; feed handling (A100), acid pretreatment and detoxification (A200), fermentation (A300), cellulase production (A400), distillation/dehydration/evaporation and scrubbing (A500), waste water treatment (A600), product storage (A700), lignin combustion and turbo-generation equipment (A800), and utilities (A900) sections. Several of the same unit processes employed in the hard wood to ethanol are similar to those found in the hemicellulose extraction process. This similarity permitted scaling capital cost data originally presented by Wooley and Mitchell to the present research. Processes common to both the hard wood to ethanol and the hemicellulose extraction processes are the feed handling, acid pretreatment and hydrolysis sections, lignin filtration, liming and gypsum filtration, C5 and C6 fermentation, ethanol distillation and upgrading, storage, waste treatment and utility sections of the plant. New areas in the hemicellulose extraction process that required new capital cost curves were the (1) wood extraction vessel and affiliated liquor flashing operations, and (2) the liquid-liquid extraction and distillation processes (Lenzing Process) to separate sugars from the hydrolyzate and to recover the furfural, acetic acid and methanol by-products. Unit processes present in the hard wood to ethanol plant but not applicable to the hemicellulose extraction process were excluded from the analysis.

Assumptions Inherent in the Analysis. Although preliminary in nature, using this approach was thought to make the economy analysis realistic and credible. Assumptions inherent in the economy analysis are (1) the hemicellulose extraction process with the new products of ethanol, acetic acid and furfural is fully integrated with the existing Kraft pulp mill that continues to produce pulp at the same rate, (2) the mass and energy flow in the modified plant is fully integrated with regard to the wood supply and no additional wood is necessary, (3) the operation of the hemicellulose extraction process does not negatively impact the operation of the Kraft mill, and (4) reductions in steam generation brought about by the hemicellulose process can be made up by firing either biomass to a biomass boiler or by firing the normal fuel used in the mill in an industrial boiler. These assumptions permitted the economic performance of the existing pulp mill to be uncoupled from that of the hemicellulose extraction process in the modified Kraft pulp mill and greatly simplified the analysis.

4.2 Project Cost

4.2.1 Estimation of Capital Cost

In chemical process design, equipment cost is often estimated by using the exponential scaling expression which is broadly applied in chemical engineering economic analyses [Turton, 2003]. The basic premise behind the exponential scaling law is that if the original cost of a piece of equipment is known, then the cost of the new equipment can be estimated by comparing the sizes of the new and original equipment raised to some exponential power.

$$NewCost(C_P) = OriginalCost\left(\frac{New\,Size}{Original\,Size}\right)^{\exp} = C_0\left(\frac{A}{A_0}\right)^{\exp} \tag{4.1}$$

where (C_0) is the original cost of the equipment at size (A_0) and (C_P) is the new capital cost at size (A). This law is sometimes referred to as the six-tenths rule because the exponent (exp) is often approximately 0.6.

The scaling exponent (exp) is commonly obtained from either standard reference books, vender quotes or by assuming the six-tenths scaling rule applies. Sometimes in order to get the equipment cost more conveniently, the exponential scaling expression is cast in an alternative form in which the original size (A_0) of the equipment and the original cost (C_0) are combined into a single constant ($K = \frac{C_0}{{A_0}^{exp}}$) as shown in Equation (4.2). The size of the basic equipment in the hemicellulose extraction process was estimated based on the detailed mass and energy balance data obtained from the WinGEMS simulation model. In the economy analysis three plant sizes were evaluated;

750, 1,000, and 1,500 metric tones per day pulp production (P_{pulp}) and corresponded to small, medium and large Kraft pulp mills. Material and energy balances were determined for the three plant sizes.

$$C_p = K \times A^{\exp} \tag{4.2}$$

In estimating capital cost, the production capacity of the pulp mill (P_{Pulp}) was used in place of the size parameter (A) in Equation (4.2). Similarly the cost of the equipment in the various sections of the hemicellulose extraction process ($C_{Plant\ Section}$) was uses in place of the cost parameter (C_P). Thus, Equation (4.2) becomes

$$C_{Plant\ Section} = K_{Plant\ Section} \times P_{Pulp}^{\ \exp} \tag{4.3}$$

A value of ($K_{Plant\ Section}$) was determined as a function of plant size and used to estimate the capital cost. This was done by using the exponential scaling exponents published by Wooley [1999] and Mitchell [2006]. An overall flow diagram for the modified Kraft pulp mill is illustrated in Figure 4.1. Capital cost equations of the form given by Equation 4.3 were developed for the nine major sections of the process illustrated in Figure 4.1. The scaling equations of published by Mitchell are summarized in Table 4.1 where (P_{HW}) represents the flow rate of hardwood consumed.

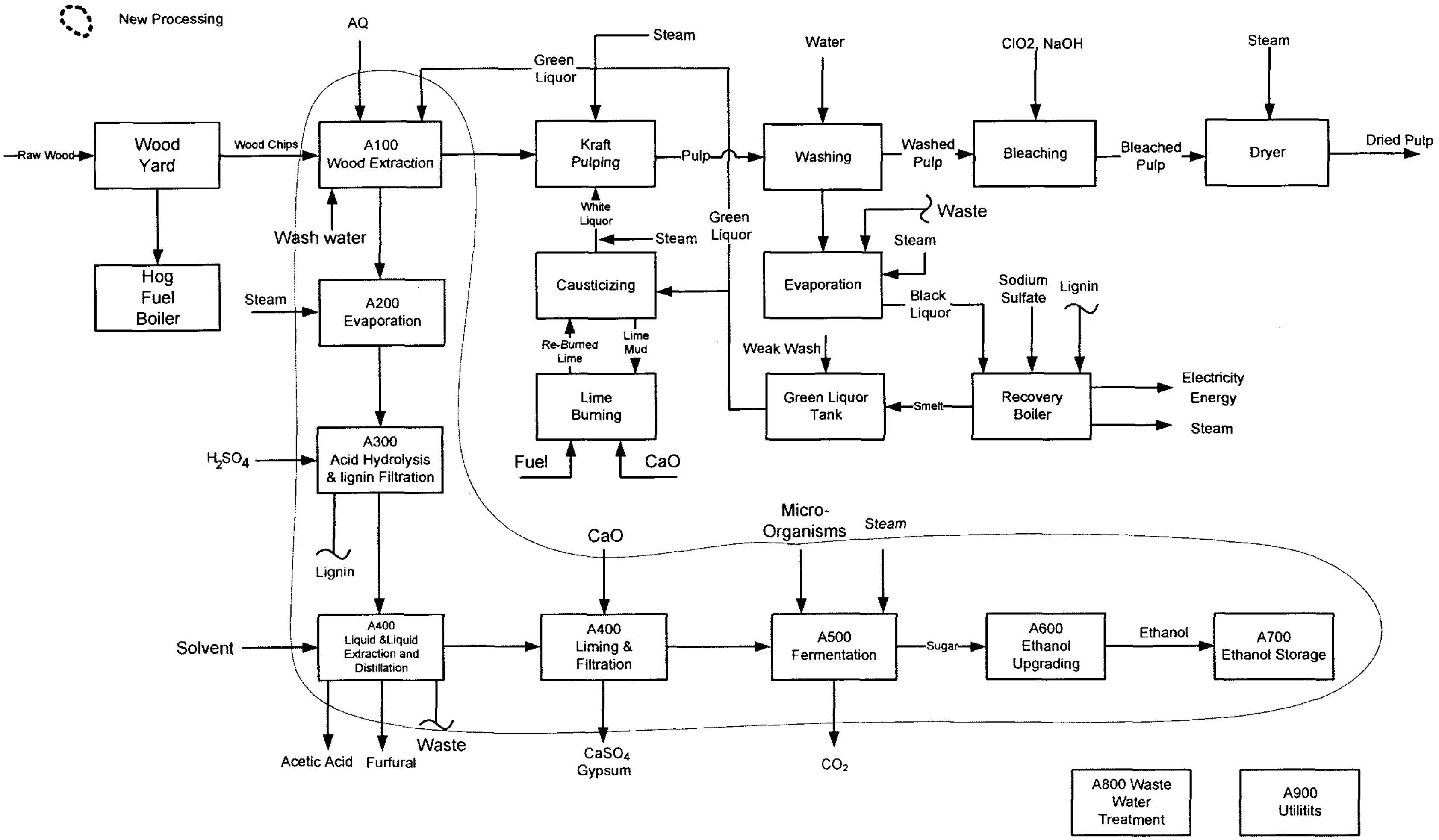


Figure 4.1 Schematic Diagram of Hemicellulose Extraction Process Showing the Area Code of the Plant Used in the Capital Cost Equations

Table 4.1

Equations for Estimating Installed Equipment Cost for 26 Million Gallon per Year Hardwood to Ethanol Plant from Wooley and Mitchell's Work$^{(a.b)}$

Plant Section	2005 Installed Equipment Cost Equation
Feed Handing (A100)	$CT_{A100} = 62709\times (P_{HW})^{0.5929}$
Pretreatment/Detoxification (A200)	$CT_{A200} = 154923\times (P_{HW}))^{0.6929}$
Fermentation (A300)	$CT_{A300} = 10559\times(P_{HW}))^{0.9568}$
Cellulase Production (A400)	$CT_{A400} = 31641\times (P_{HW})^{0.8264}$
Distillation (A500)	$CT_{A500} = 86294\times (P_{HW}))^{0.7068}$
Waste Water Treatment (A600)	$CT_{A600} = 128499\times (P_{HW}))^{0.5963}$
Storage (A700)	$CT_{A700} = 13625\times (P_{HW}))^{0.6610}$
Boiler/ Turbo-generator (A800)	$CT_{A800} = 217961\times (P_{HW})^{)0.7165}$
Utilities (A900)	$CT_{A900} = 20234\times (P_{HW})^{0.7568}$
Total Installed Equipment Cost	$TC_{\text{installed}} = 591236\times (P_{HW}))^{0.7343}$
(a) Wooley [1999] and Mitchell [2006]. (b) Size parameter is the hard wood feed to the process.	

In the Wooley and Mitchell work, the main products produced are ethanol and electricity. In the current work main products from the hemicellulose extraction process are bleached market hardwood Kraft pulp and by-products are ethanol and acetic acid. Rather than using the flow rate of hard wood (P_{HW}) as the size parameter, the ethanol production rate (P_{EtOH}) was chosen as a more convenient size parameter for using in the capital cost equations.

Using the ethanol production rate as the size parameter, Equation 4.3 can be written as Equation 4.3A.

$$C_{Plant\ Section} = K^{*}_{Plant\ Section} \times P_{EtOH}^{\exp^{*}} \tag{4.3A}$$

where K^* and $\exp^*$ are the new capital cost parameters.

In addition to the plant areas selected by Wooley and Mitchell, the hemicellulose extraction area of the plant, referred to as the "extraction vessel" and a new evaporation area were added to the analysis. Table 4.2 lists the capital cost equations for the various areas of the hemicellulose extraction process based upon the pulp production rate and ethanol production rate.

Table 4.2

Exponential Scaling Expression for Different Plant Section

Plant Section(1)	**Area Number in Wooley Report**	**Installed Equipment Cost based on Pulp Mill Size (dollars)(2)**
A100 Extraction Vessel	N/A	$CA_{A100} = 161{,}572\ (P_{Pulp})^{0.650}$
A200 Evaporation	N/A	$CA_{A200} = 876{,}317\ (P_{EtOH})^{0.36}$
A300 Acid Hydrolysis	A200	$CA_{A300} + CA_{A400} = 1{,}453{,}100 (P_{EtOH})^{0.683}$
A400 Liquid Extraction(3)		
A500 Fermentation	A300	$CA_{A500} = 285{,}906\ (P_{EtOH})^{0.965}$
A600 Ethanol Upgrading	A500	$CA_{A600} = 670{,}763\ (P_{EtOH})^{0.707}$
A700 Ethanol Storage	A700	$CA_{A700} = 119{,}319\ (P_{Pulp})^{0.626}$
A800 Waste Water Treatment	A600	$CA_{A800} = 946{,}720\ (P_{EtOH})^{0.593}$
A900 Utilities	A900	$CA_{A900} = 224{,}863\ (P_{EtOH})^{0.747}$

Note: (1) A100 section was obtained from a vender quote. A200 section scaled from data provided by Peters and Timmerhaus [Peters, 1991], A300-900 sections from Wooley. (2)The Wooley's Cost expression is based on 2005 dollars. The hemicellulose extraction vessel is in terms of 2006 dollars. (3) It is assumed A400 section can be estimated by Wooley's A200 section Pretreatment/ Detoxification.

Cost of Extraction Vessel. The cost of an extraction vessel was assumed to be similar to that of a continuous digester and was based upon a vender quotation. The scaling parameter for the extraction vessel was based on its volume (V_{Ext}).

$$C_{p,Ext} = K_{Ext} \times V_{Ext}^{exp} \tag{4.4}$$

The vender quoted 12.5 million dollars for a digester vessel that processes sufficient wood to produce 1,000 tonne per day of pulp. The vender also quoted the scaling exponent (exp) to be equal to 0.65. The parameters used to estimate the volume of the digester vessel was 48% pulp yield, at a liquor to wood ratio of 2.5 (2.5 kg of liquor to 1 kg of wood) and a residence time (t_R) of 180 minutes, that is 40 minutes heating time (t_H) , 110 minutes for pulping (t_P) and 30 minutes for chip washing (t_W). The flow rate of wood required for pulp is

$$F_{Wood} = \left(\frac{P_{pulp}}{Y_P}\right) = \left(\frac{1{,}000}{48\%}\right) tonne/day = 2083\ tonne/day \tag{4.5}$$

where (P_{pulp}) and (Y_P) are the pulp production rate and pulp yield for a 1,000 tonne per day mill. The total flow rate of liquor to the digester (F_{Total}) is equal to the sum of the flow rate of wood plus the pulping liquor.

$$F_{Total} = F_{Wood} + F_{Liquor} = F_{Wood}\left(1 + R_{\frac{L}{W}}\right) = 7291\ tonne/day \tag{4.6}$$

The digester volume was estimated from the total residence time (t_R) and the total mass flow rate (F_{Total}).

$$V_{Digester} = F_{Total} \times (t_R) = 1947\ m^3 \tag{4.7}$$

Lastly the volume of the extraction vessel (V_{Ext}) was assumed equal to the volume of an equivalent digester ($V_{digester}$).

Under these assumptions the constant (K_{Ext}) for the cost Equation 4.4 becomes Equation 4.9. The extraction condition of current research which is proposed in chapter 3 is 47% overall pulp yield ($Y_P{}^*$), 98% bleach yield ($Y_{bleach}{}^*$), 180 minutes residence time ($t_R{}^*$) and Liquor to Wood ratio 4 ($R_{\frac{L}{W}}{}^*$). Based on this condition the volume of a new extraction vessel ($V_{ext}{}^*$) for a pulp production rate of 1,000 tonne per day pulp mill is shown in Equation 4.10.

$$V_{Digester} = V_{Ext} = 1947m^3 \tag{4.8}$$

$$K_{Ext} = \left(\frac{\$12.5{\times}10^6}{V_{Ext}^{0.65}}\right) = \$9.09{\times}10^4/m^3 \tag{4.9}$$

$$V_{ext}{}^* = t_R{}^* \times \left(\frac{P_{pulp}{}^*}{Y_P{}^* {\times} Y_{Bleach}{}^*}\right) \times \left(1 + R_{\frac{L}{W}}{}^*\right) = 2400m^3 \tag{4.10}$$

The final installed cost for the new extraction vessel($V_{Ext}{}^*$) is

$$C_{P\,Ext}(\$) = \$9.09{\times}10^4{\times}(V_{Ext}{}^*)^{0.65} = \$14.32{\times}10^6 \tag{4.11}$$

Equation (4.11) which is based on the volume of the extraction vessel was transformed to the production rate of pulp which is a more appropriate scaling parameter.

$$C_{p,Ext} = 0.16 \times P_{Pulp}{}^{0.65}\ Million\ dollars \tag{4.12}$$

The installed equipment cost of a new extraction vessel is illustrated in Figure 4.2 and 4.3. The equipment cost of evaporator based on heat exchange area is illustrated in Figure 4.4. In the Figure 4.4 four common types of evaporator are shown. In the current research the horizontal tube type was chosen because it was the cheapest. It is very important to mention that the cost of extraction vessel is estimated based on the feedstock that it processed. For other area the equipment cost is based on the ethanol production rate.

Capital cost data can be corrected for inflation by using an appropriate cost index (I). The correction factor is assumed to be a linear function of the time index.

$$C_p(Time2) = C_p(Time\,1) \times \left(\frac{I_{time\,2}}{I_{time\,1}} \right) \tag{4.13}$$

Typical indices used for correcting capital cost estimates are the Chemical Engineering Plant Cost Index (CEPCI), the Marshal and Swift index (MS) and the Engineering New-Record Construction Index [Turton et. al, 2003]. In Equation 4.13 C_p (time2) is the purchased cost of equipment at time two (2) while C_p (time 1) refers to the purchased cost of the same equipment in the base year (time 1). In the economy evaluation performed here for the hemicellulose extraction process, capital cost estimates were corrected to 2006 (time 2) while time one (1) refers to 2005, the year chosen by Mitchell [2006] in his analysis. Thus Equation (4.13) becomes

$$C_p(2006) = C_p(2005) \times \left(\frac{I_{2006}}{I_{2005}} \right) \tag{4.14}$$

After the capital equipment is purchased, additional funds are required for its installation. The installation cost of equipment (C_I) was acquired by multiplying the purchased equipment cost by an installation factor ($f_{installation}$). Thus the installation cost can be expressed as the following Equation 4.15.

$$C_I(2006) = C_p(2006) \times f_{installation} \tag{4.15}$$

The general scaling equation for the installed equipment cost in year 2006 $C_I(2006)$ is given by the Equation 4.16.

The estimation for total installed equipment Cost (TC) was obtained by summing the equipment cost for the various areas of the plant (Equation 4.17).

$$C_I(2006) = C(time1) \times \left(P_{pulp}\right)^{\exp} \times \left(\frac{I_{2006}}{I_{2005}}\right) \times f_{installation} \tag{4.16}$$

$$TC(2006) = \sum_i C_{I\,i}(2006) \tag{4.17}$$

where i is the section number and TC represents the total equipment cost.

Table 4.3 lists the total installed equipment Cost (TC) for the different section of the hemicellulose extraction process for the 1,000 tonne per day pulp production case. Here a contingency of 15% of the installed equipment cost was added to adjust the total installed equipment cost. Figure 4.5 and Figure 4.6 illustrate the installed equipment cost for the different areas of the process. Curves are presented using both the pulp (P_{Pulp}) and ethanol (P_{EtOH}) production rates respectively.

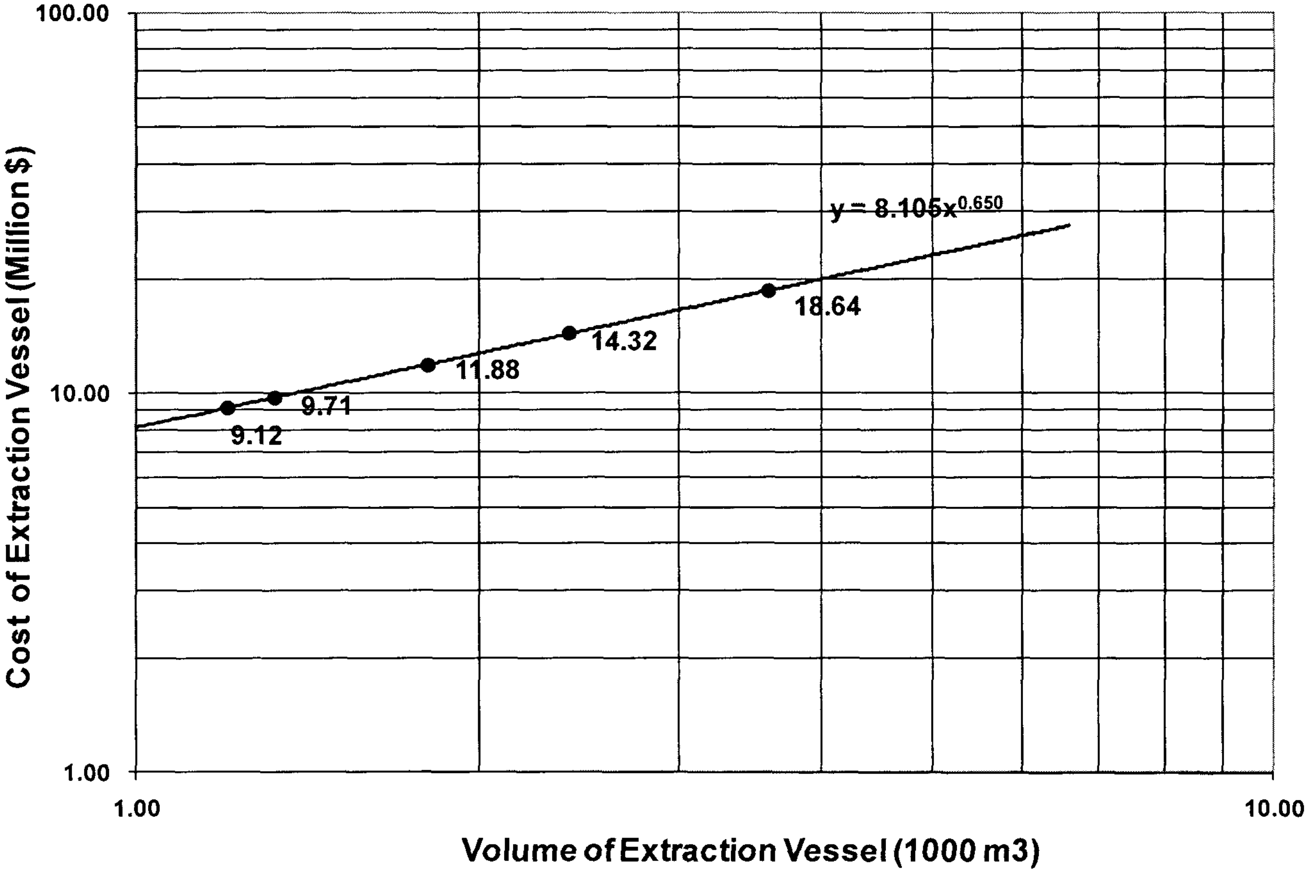


Figure 4.2 Installed Equipment Cost of a New Extraction Vessel vs. Volume of the Extraction Vessel

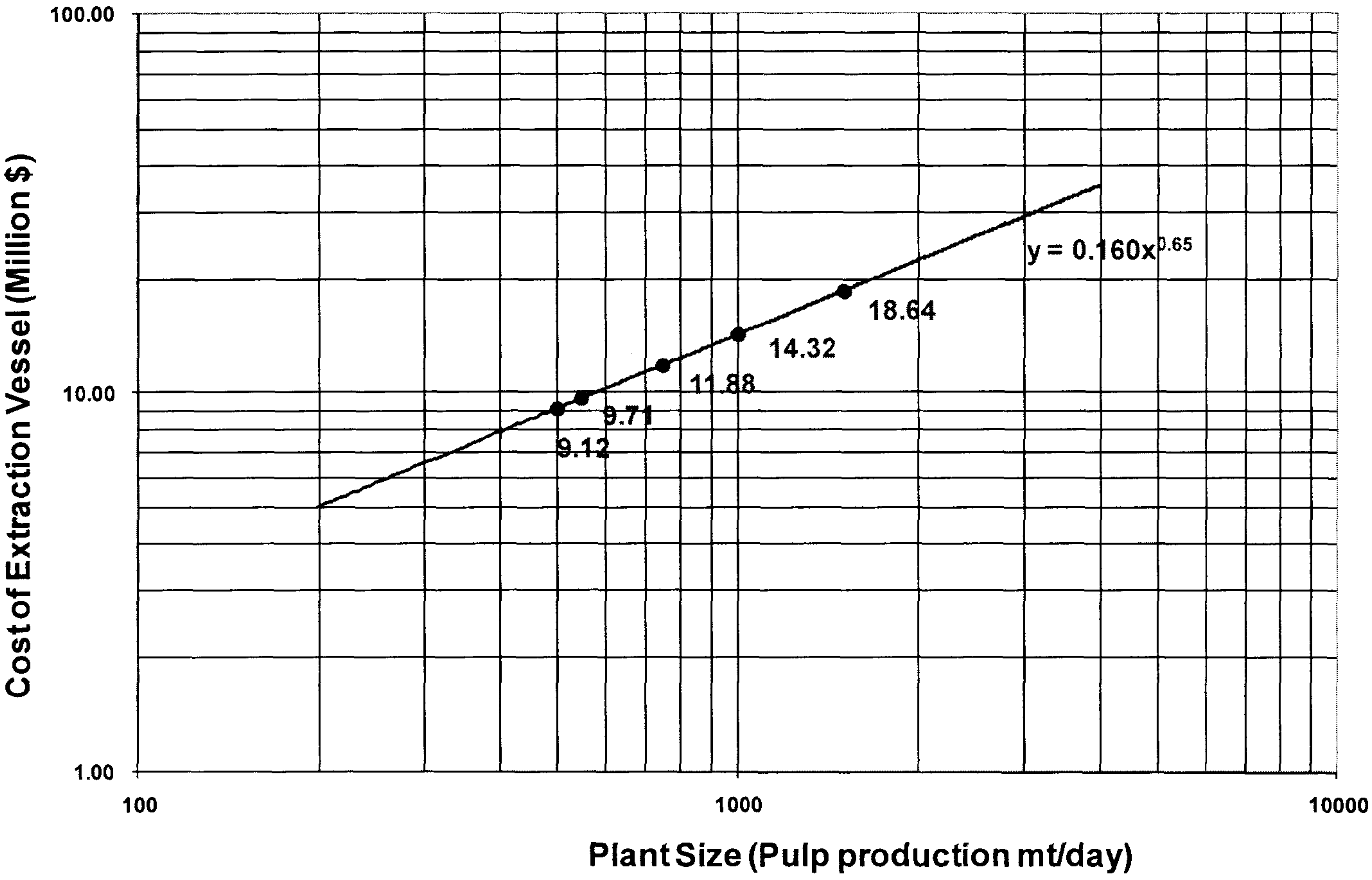


Figure 4.3 Installed Equipment Cost of a New Extraction Vessel vs. Plant Size

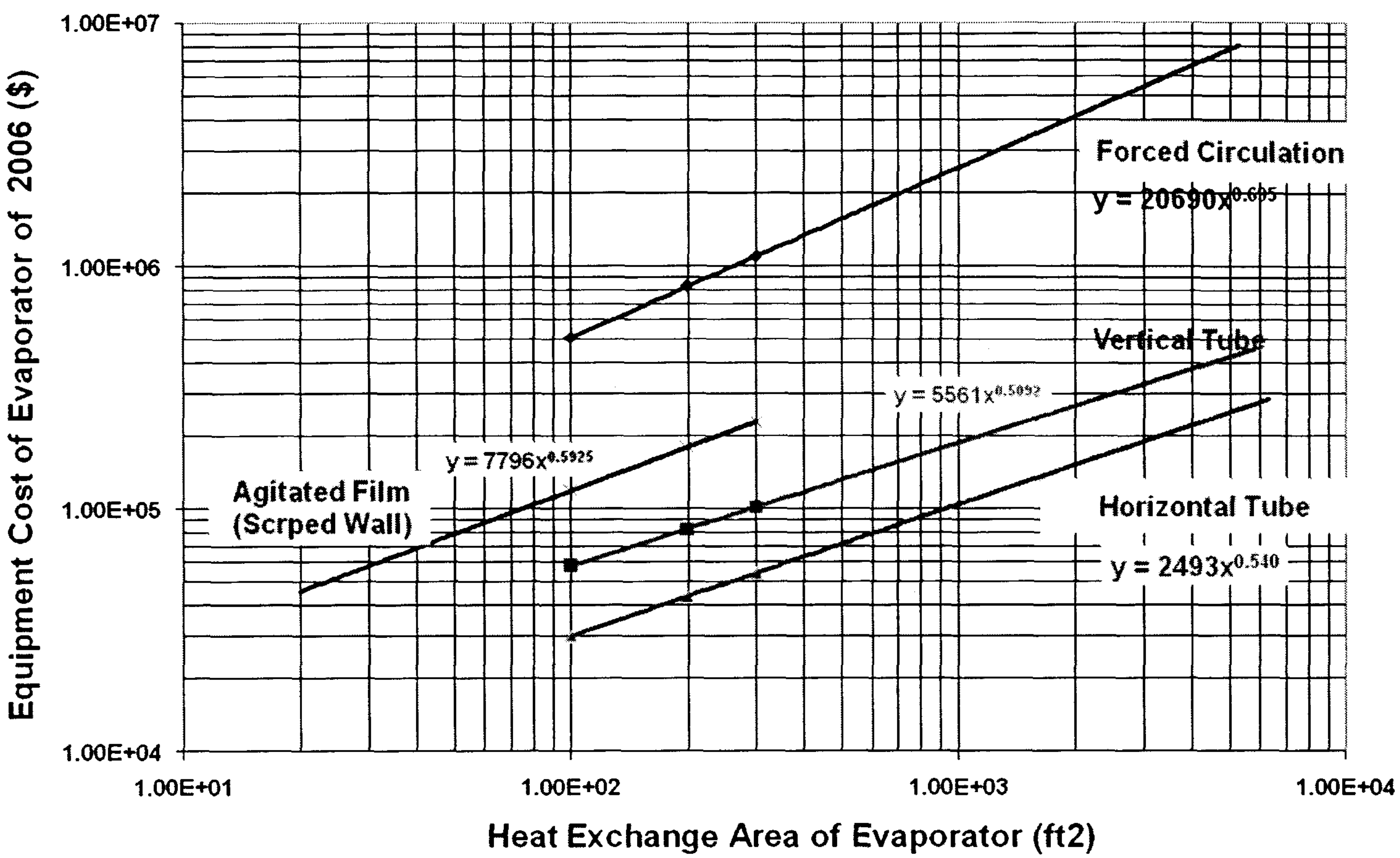


Figure 4.4 Capital Cost of Evaporator Equipment vs. Heat Exchanged Area [Peters and Timerhaus, 1991]

Table 4.3 Total Installed Equipment Cost of Different Sections for 1000 tonne/day with a New Extraction Vessel Case

Plant Section	Plant Size	CEPCI 2005	Equation of 2005 Installed Equipment Cost ($)	Installation factor^2	CEPCI 2006	Equation of 2006 installed equipment cost	2006 Total Installation Cost ($)
A100 Extraction Vessel	1000 MT/day Pulp	468.2	$CAA100 = 161572\ (P_{Pulp})^{0.650}$	1.0	499.6	$CA_{A100} = 161{,}572\ (P_{Pulp})^{0.650}$	14,318,000
A200 Evaporation	Ethanol 4.62 MG/year	468.2	$CA_{A200} = 876{,}371(P_{EtOH})^{0.3565}$	1.5	499.6	$CA_{A200} = 1{,}402{,}718(P_{EtOH})^{0.36}$	2,418,000
A300 Acid Hydrolysis	Ethanol 4.62 MG/year	468.2	$CA_{A300}+CA_{A400}= 1{,}453{,}100\ (P_{EtOH})^{0.6929}$	1.473	499.6	$CA_{A300}+CA_{A400} = 2{,}283{,}964\ (P_{EtOH})^{0.683}$	6,495,000
A400 Separation	Ethanol 4.62 MG/year	468.2					
A500 Fermentation	Ethanol 4.62 MG/year	468.2	$CA_{A500} = 285{,}906\ (P_{EtOH})^{0.9568}$	1.294	499.6	$CA_{A500} = 394{,}774\ (P_{EtOH})^{0.965}$	1,728,000
A600 Distillation	Ethanol 4.62 MG/year	468.2	$CA_{A600} = 670{,}763\ (P_{EtOH})^{0.7068}$	1.811	499.6	$CA_{A600} = 1{,}296{,}220\ (P_{EtOH})^{0.707}$	3,823,000
A700 Storage	Ethanol 4.62 MG/year	468.2	$CA_{A700} = 119{,}319\ (P_{EtOH})^{0.6610}$	1.538	499.6	$CA_{A700} = 195{,}820\ (P_{EtOH})^{0626}$	510,000
A800 Waste Treatment	Ethanol 4.62 MG/year	468.2	$CA_{A800} = 946{,}720\ (P_{EtOH})^{0.5963}$	1.237	499.6	$CA_{A800} = 1{,}286{,}000\ (P_{EtOH})^{0.593}$	3,187,000
A900 Utilities	Ethanol 4.62 MG/year	468.2	$CA_{A900} = 224{,}863\ (P_{EtOH})^{0.7568}$	1.472	499.6	$CA_{A900} = 353{,}197\ (P_{EtOH})^{0.747}$	1,108,000
Equipment Cost Contingency	15% of total installed equipment cost						5,038,000
Total Installed Equipment Cost (TC)							38,627,000

Note: Installation factors for areas A200 is picked up from Peters [Peters, 1999]. A300 ~A900 are calculated from Mitchell [2006].

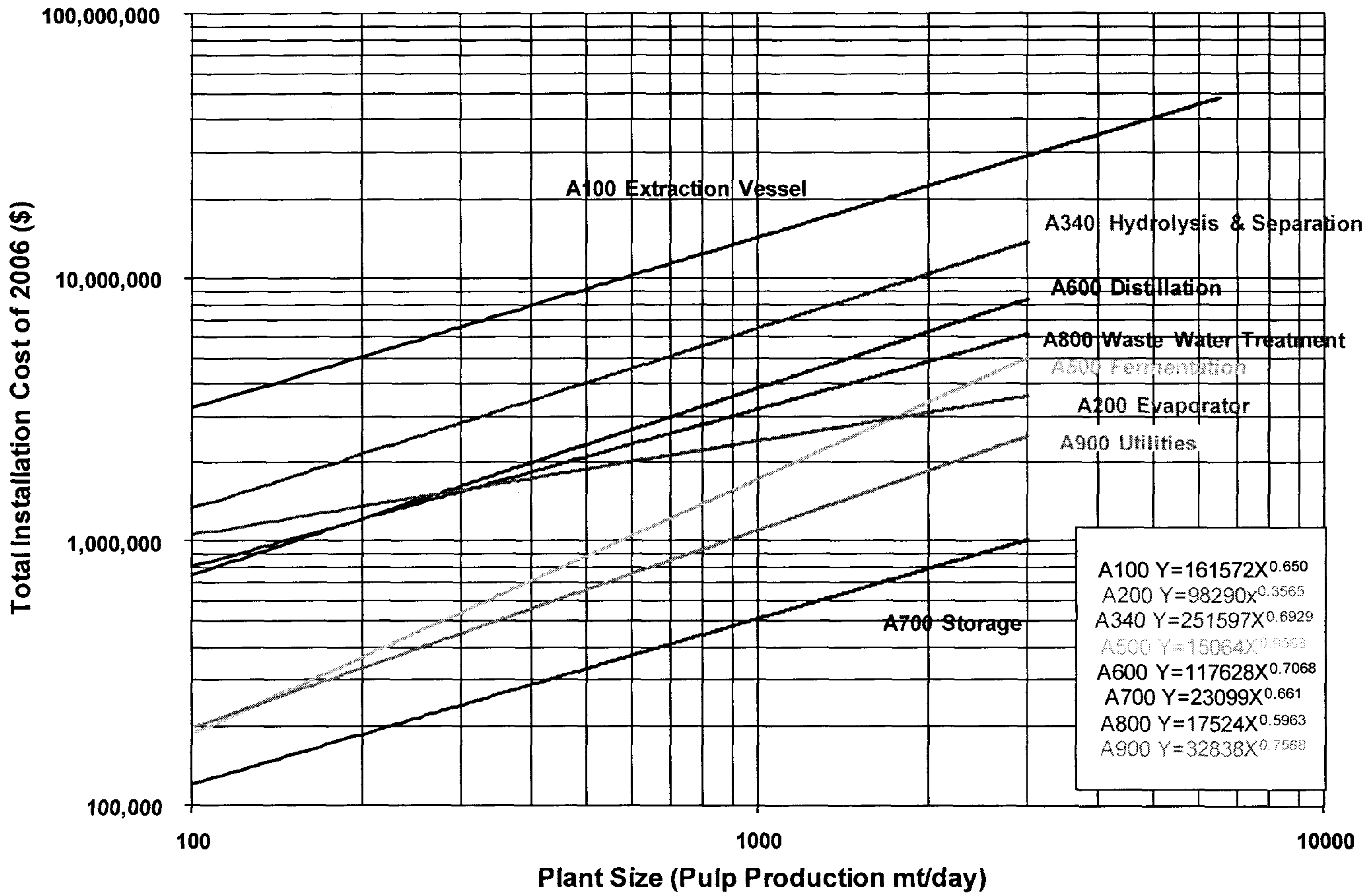


Figure 4.5 Installed Capital Cost of Different Plant Area of Modified Kraft pulp Mill vs. Pulp Production Rate

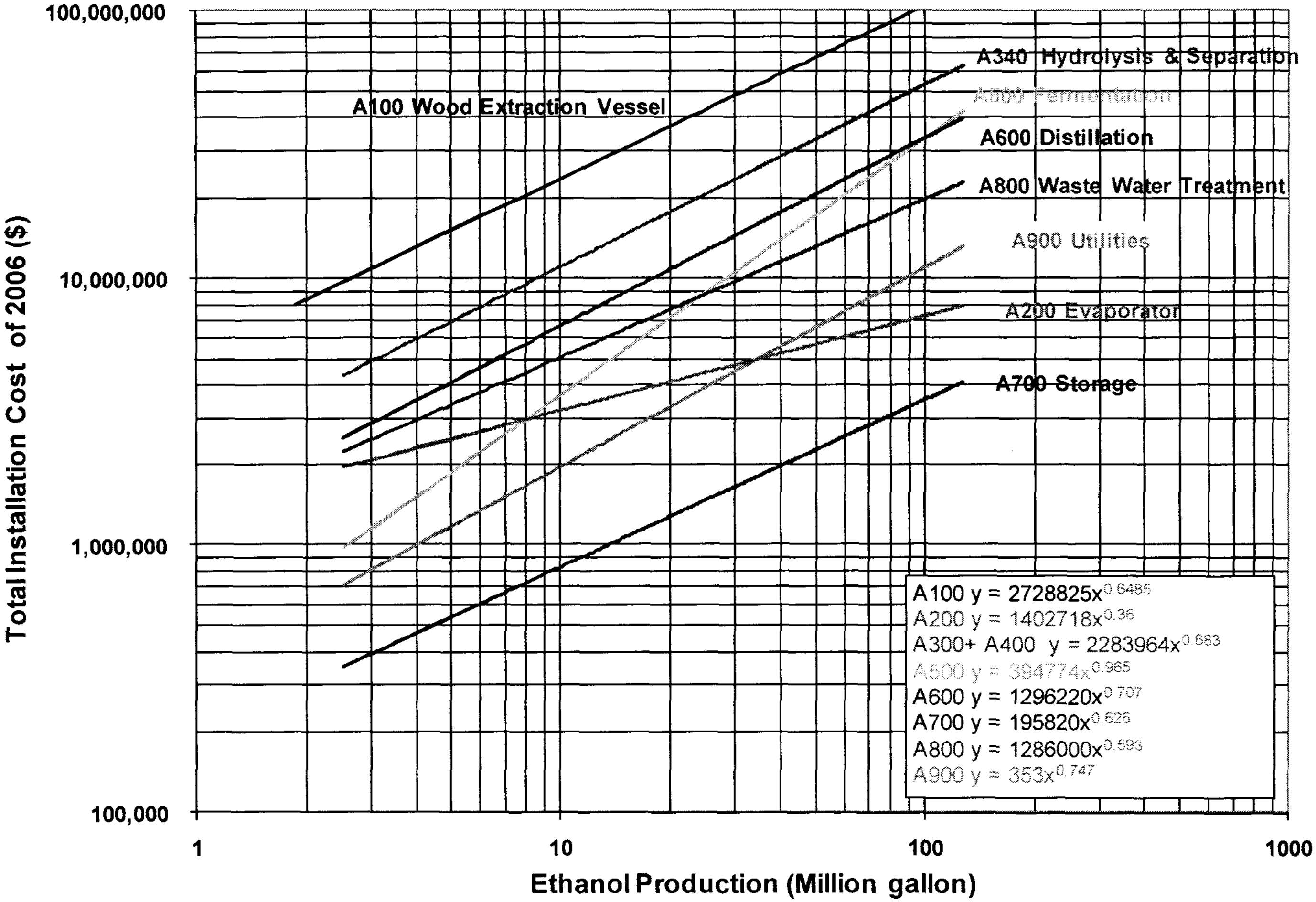


Figure 4.6 Installed Equipment Cost of Different Area of Modified Kraft Pulp Mill vs. Ethanol Production Rate

4.2.2 Estimation of Ancillary Costs

Besides the capital cost of the installed equipments, there are a variety of additional charge in a real chemical plant. Commonly additional cost can be separated into additional direct cost and additional indirect cost. Additional direct cost includes a Warehouse (W) and Site Development (SD). Additional indirect cost includes Pro-ratable Cost (PC), Field Expenses (FE), Home Office and Construction (HOC), Project Contingency (P_{contin}) and Other Cost (OC). Table 4.4 lists the detailed description and calculation method of additional direct costs and additional indirect costs. [Mitchell, 2006]

Table 4.4

Additional Direct and Indirect Cost

Item	**Description**	**Amount**
Additional direct costs		
Warehouse(W)	Storage warehouse	1.5% of total installed equipment cost
Site Development (SD)	Site development: includes fencing, curbing, parking lot, roads, well drainage, rail system, soil borings and general paving. This factor allows for minimum site development assuming a clear site, with no unusual problems such as right-of-way, difficult land clearing, or unusual environmental problems. 9% of the installed cost of process equipment.	9% of the installed equipment cost (A100~A700)
Additional indirect costs		
Pro-ratable	This includes fringe benefits, burdens and	10% of total

Table 4.4 continued

Cost(PC)	insurance of the construction contractor.	installed cost
Field Expense (FE)	Consumables, small tool equipment rental, field services, temporary construction facilities and field construction supervision.	10% of total installed cost
Home Office and Construction(HOC)	Engineering plus incidentals, purchasing and construction.	25% of total installed cost
Project Contingency(P_{contin})	Small because of the detail included in the process design.	3% of total installed cost
Other Cost(OC)	Start-up a commissioning costs. Land, right-of-way, permits, survey and other fees. Piling, soil compaction/dewatering, unusual foundations. Sales, use and other taxes. Freight, insurance in transit and import duties on equipment, piping, steel instrumentation, etc. Overtime pay during construction. Field insurance, project team. Transportation equipment, bulk shipment, containers, plant vehicles, etc. escalation or inflation of costs over time. Interests on construction loan.	10% of total capital investment

4.2.3 Estimation of Total Project Investment

The Total Direct Cost (TDC) is composed of total installed equipment Cost (TC) and additional direct cost which includes a Warehouse (W) cost and Site Development (SD) cost.

$$Total Direct Cost = TDC(2007) = TC(2007) + W + SD \tag{4.18}$$

Total Indirect Cost (TIC) includes Pro-ratable Cost (PC), Field Expenses (FE), Home Office and Construction (HOC), Project Contingency (P_{contin}) and Other Cost (OC) (Equation 4.19).

$$Total\ Indirect\ Cost = TIC(2007) = PC + FE + HOC + P_{contin} + \mathrm{OC} \tag{4.19}$$

The Total Project Investment (TPI) equals the summary of Total Direct (TDC) and Total Indirect (TIC) Costs.

$$Total\ Project Investment = TPI(2007) = TDC(2007) + TIC(2007) \tag{4.20}$$

For the 1,000 tonne per day full scale case, the Total Project Investment is summarized in Table 4.5.

Table 4.5

Total Project Investment (TPI) for 1000 tonne/day Full Scaled Case –

New Extraction Vessel

Item	Value
Total installed equipment cost (See Table 4.3)	\$38,627,000
Warehouse(W)	\$579,400
Site development (SD)	\$2,636,000
Total Installed Cost	\$41,842,000
Indirect costs	
Pro-ratable cost(PC)	\$4,184,000
Field Expense (FE)	\$4,184,000
Home Office and Construction(HOC)	\$10,460,000
Project Contingency(P_{contin})	\$1,255,000
Total capital investment	\$61,926,000
Other Cost(OC)	\$6,192,000
Total Project Investment (TPI)	\$68,119,672

4.3 Estimation of Operation Cost

Operation cost includes both variable and fixed operating costs. Variable operating costs included the costs for Raw Material (RM), Energy such as electricity and steam (PE), and Waste Disposal charges (WD). Variable operating costs are incurred only when the plant is operating and depend upon the production rate. Fixed operating cost include Labor Cost (LS), Overhead for Maintenance (OM), Maintenance per se (M) and Taxes and Insurance (TI).

4.3.1 Variable Operating Cost

The raw materials used for the mill operation and waste material produced were determined from the WinGEMS computer simulation model. Table 4.6 summarizes the variable operating cost for 1,000 tonne per day pulp mill case.

Table 4.6

Variable Operation Cost for 1000 tonne/day Case – New Extraction Vessel

Raw Materials	**Amount used (tonnes/day)**	**Unit Cost (dollars/tonne)**	**Total Cost (dollars/yr)**
Sulfuric Acid (H_2SO_4)	74.8	110.23	2,885,200
Anthraquinone (AQ)	1.09	3306.9	1,225,800
Lime	53.21	148.8	2,771,400
Gypsum Disposal	161.8	20	1,132,600
Cooling Water	3341	0.26	308,700
Ash Disposal	0.12	20	800
Steam Consumption for Distillation	114.5	7.00	280,427
Fermentation Cost@			692,486
Total Variable Operation Cost			9,327,000
@ The operation cost for ethanol Fermentation is estimated based on the ethanol production rate of Wooley's report [1999].			

It should mention that the cost of feedstock– hardwood is not included in the modified Kraft pulp mill using the hemicellulose extraction process. This was done because of experimental work performed by Van Heiningen [2006]. Consequently, it was assumed that there is no additional wood required for keeping the market pulp production rate.

4.3.2 Fixed Operating Cost

Fixed operating cost is estimated based on Wooley's report [1999] which described the fixed operating cost of a similar ethanol plant. Commonly the labor cost will vary slightly with the plant size. In currently research the labor cost were treated as a fixed expense. Table 4.7 summarizes the labor cost for the 1,000 tonne per day medium sized Kraft Pulp mill.

Table 4.7

Cost of Labor and Supervision of the Ethanol Process for the Modified Kraft Pulp Mill

Job Description	**Salary**	**Labor Number From Wooley's Report**	**Cost of 1998**	**No.**	**Cost of 2007**
General Manger	100,000	1	100,000	0	0
Plant Manager	80,000	1	80,000	0	0
Plant Engineer	65,000	1	65,000	1	78,780
Maintenance Supervisor	60,000	1	60,000	0	0
Lab Manager	50,000	1	50,000	1	60,600
Shift Supervisor	37,000	2	74,000	2	89,700
Lab Technician	25,000	2	50,000	2	60,600
Maintenance Technician	28,000	8	224,000	0	0
Clerk & Secretaries	20,000	5	100,000	0	0
Shift Operators	25,000	20	500,000	20	606,000
Yard Employee	20,000	8	160,000	0	0
Total	510,000	50	1,463,000	26	895,700
Note: the Labor Index for1998 and 2006 is 17.17 and 20.81 respectively.					

The fixed operation cost includes Overhead Maintenance (OM), Maintenance per se (M), and Taxes & Insurance (TI). The fixed operation cost and capital recovery are listed in Table 4.8.

Capital Recovery (R_C). Capital Recovery is the yearly cost of borrowing money and repaying the borrowed capital (FCI, dollars) in the form of an annuity over n-years at interest rate (i).

$$R_C = FCI \times \left[\frac{i\,(1+i)^n}{(1+1)^n - 1} \right] = FCI \times CRF \tag{4.21}$$

The capital recovery factor (CRF) is given as by the factor $[i(1+i)^n]/[(1+i)^n-1]$.

A capital recovery factor (CRF) of 16.5% was used in the current analysis. The yearly charge for capital was calculated using Equation 4.21. The capital recovery factor was obtained by assuming that 100% of the capital was borrowed at a 10% rate of interest (i) over a ten (10) year period (n). The capital recovery factor was applied to the fixed capital exclusive of the value of the land (FCI_L).

$$R_C = CRF \times [FCI_L] \tag{4.22}$$

Table 4.8

Fixed Operating Cost and Capital Recovery

Cost Item	**Calculated Approach**
Fixed Operation Cost	Overhead Maintenance (OM) = 0% of Total Salaries
	Maintenance per se (M) = 2% of Total Installed Equipment Cost
	Taxes and Insurance (TI) = 1.5% of Total Installed Cost
Capital Recovery	Year of Money Borrow = 10 Years
	Interest Rate on Borrowed Capital = 10%
	Capital Recovery Factor = $\frac{10\%\times(1+10\%)^{10}}{(1+10\%)^{10}-1} = 16.3\%$

4.3.3 Operation Cost and Unit Production Cost

Table 4.9 summarizes the Variable and Fixed Operating Costs for the 1,000 tonne per day full scaled case.

Table 4.9

Operation Cost of Modified Kraft pulp Process for 1000 tonne/day

Full Scaled Case – New Extraction Vessel

Item	Value
Variable Operating Cost	$9,327,400
Fixed Operating Cost	
Labor cost	$895,600
Over Maintenance	$0
Maintenance per se (M)	$772,000
Taxes and Insurance (TI)	$672,000
Capital Recovery Cost	10,919,000
Total Operation Cost	$22,543,000

The total operation cost was split into costs associated with the production of ethanol and acetic acid. This was done by allocating the total operating cost according to the mass production ratio of the ethanol and acetic acid. The unit production cost of ethanol and acetic acid are listed in Table 4.10 for 1,000 tonne per day full-scaled case with a new extraction vessel installed.

Table 4.10

Unit Production Cost of Full Scaled 1000 tonne/day Case – New Extraction Vessel

Pulp Mill Size (tonne/day)	Ethanol (dollars/gallon)	Acetic Acid (dollars/gallon)
1000	2.28	3.02

4.4 Revenue

The main products of the modified Kraft pulp mill using the hemicellulose extraction process are market pulp, ethanol and acetic acid. Additional by-products are methanol, furfural, carbon dioxide and gypsum. The market pulp was considered as the primary product of the existing Kraft pulp mill and its production rate remains unchanged. Consequently the value of the market Kraft pulp was not included in the revenue stream for the modified Kraft pulp mill. Also, it was assumed that no revenue was obtained from methanol, furfural and carbon dioxide. These products were assumed to be discharged at no cost in the case of the CO_2 or incinerated in the case of methanol and furfural and appropriate charges incurred. The gypsum was assumed to be discharged as a waste product and 20 dollars per tonne disposal fee against the process. A summary of the revenue stream associated with the hemicellulose extraction process are listed in Table 4.11.

Table 4.11

Revenue of Modified Kraft Pulp Mill for 1000 tonne per day Full Scaled Case

Item	**Unit Price**	**Production Rate**	**Revenue per Year**
Ethanol	$2/gallon($669/tonne)	39.47 tonne/day	9,239,000
Acetic Acid	$4 /gallon($1047/tonne)	45.09 tonne/day	16,511,000
#6 Oil saving in Lime Kiln	$2.2/ gallon ($557/tonne)	9.93 tonne/day	1,935,000
Electricity power (KW)	$0.041/KWH	8800 kW	-2,962,000
Total			24,723,000
Note: The oil saving was discussed in Chapter 3.3. The modified kraft mill will produced less electricity power when compared with the case of the existing Kraft pulp mill.			

4.5 Profitability Analysis

There are a variety of methods used as economic barometers for determining profitability of potential engineering projects. Three common methods for estimating profitability are the Net Present Value (NPV), Discounted Payback Period (DPBP) and Discounted Cash Flow Rate of Return (DCFROR) respectively [Richard Turton, 2003, Peters and Timmerhaus, 1991]. All of these methods take into account the time value of money. In the current investigation, the discounted cash flow rate of return on investment was used as the economic indicator in evaluating the profitability of the hemicellulose extraction process. This was done by using the estimates for the Total Project Investment (TPI), Total Operation Costs and the anticipated revenue for the process and calculating the net profit and cash flows over the life of the plant.

Net Profit. The net profit (NP) for any year "i" is defined as the revenue stream obtained from selling the products (R_i) minus the cost of manufacturing $(COM)_i$ minus the depreciation (d_i) multiplied by one minus the tax rate (t).

$$NP_i = [R - COM - d]_i \times (1-t) \tag{4.23}$$

In the present analysis the tax rate was assumed to be 39% or t = 0.39; which is the same as used by Mitchell [2006]. The selling prices for ethanol and acetic acid were estimated to be $2.00 per gallon and $4.00 per gallon respectively.

Depreciation. The depreciation is the fraction of the capital investment that the government allows companies to charge as a yearly operating expense in order to make up for the decrease in plant value over time [Turton, 2003].

A straight line method of depreciation was used in the current economic analysis with a depreciation period (N_d) of 10 year.

$$d_i = \frac{FCI_L}{N_D} \tag{4.24}$$

Cash Flow. The cash flow (CF_i) for any given year is defined as the net profit $(NP)_i$ plus the depreciation (d_i).

$$CF_i = [R - COM - d]_i \times (1 - t) + d_i \tag{4.25}$$

The cash flow can be either positive or negative depending upon the cost of manufacturing and the depreciation. The depreciation invariably results in a tax credit $(d_i \times t)$.

$$CF_i = [R - COM]_i \times (1 - t) + d_i \times t \tag{4.26}$$

Negative cash flows occur in the early years when the land is purchased, the plant is constructed and the working capital is installed. Cash flow diagrams were constructed using methods described by Turton [Turton, 2003]. These diagrams show both negative and positive cash flows for the project. Negative cash flows result from the capital investment while positive cash flows occur when the revenue stream is greater than the cost of manufacturing and depreciation as given by Equation (4.26).

Net Present Value (NPV). The net present value (NPV) takes into account the time value of money and discounts capital investments and future cash flows from anticipated revenues to a constant value.

The yearly discounted cash flows were calculated by using appropriate discount factors. For example the discounted cash flow for the kth year would be given by the Equation 4.27 [Turton, 2003].

$$\mathrm{DCF_k} = \frac{\mathrm{C\,F_k}}{(1+\mathrm{i})^{\mathrm{k}}} = \textit{Discounted Cash Flow for } k^{th} \textit{ year} \tag{4.27}$$

The net present value at the end of the project (NPV) was determined by taking the sum of all negative and positive discounted cash flows for the entire 12 year project life.

$$NPV(i) = \sum_{k=0}^{k=N} \left[\frac{CF_k}{(1+i)^k} \right] \tag{4.28}$$

When applied to the Hemicellulose extraction process, Equation (4.28) becomes

$$\begin{aligned} NPV(i) = -\left[\frac{L}{(1+i)^0}\right] - \left[\frac{FCI_1}{(1+i)^1}\right] - \left[\frac{FCI_2}{(1+i)^2}\right] \\ - \left[\frac{WC}{(1+i)^2}\right] + \sum_{k=3}^{k=12}\left[\frac{CF_k}{(1+i)^k}\right] + \left[\frac{(WC+L)}{(1+i)^{12}}\right] \end{aligned} \tag{4.29}$$

Discounted Cash Flow Rate of Return on Investment. The discounted cash flow rate of return on investment (DCFROR) is the discount rate at which the net present value (NPV) given by Equations (4.28) and (4.29) at the end of the project go to zero [Turton, 2003]. 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. The DCFROR method of judging projects involves a trial and error solution.

The discount rate (i) is varied until the net present value (NPV) became zero. Table 4.12 lists the basis for the discount cash flow analysis.

$$NPV(i) = \sum_{k=0}^{k=N=Termination} \left[\frac{CF_k}{(1+i)^k} \right] = 0 \qquad (4.30)$$

Table 4.12

Discounted Cash Flow Parameters

Item	**Basis**	**Value**
Land Value	1.5% of Total Capital Investment	$\$31,601,000 \times 1.5\% =$ \$474,000
Construction Period and Capital Distribution	2 years	60% in year 1 and 40% in year 2
Working Capital	5% of Total Project Investment	$\$31,601,000 \times 5\% =$ \$1,580,000
Federal Tax Rate	39% of Gross Profit	39%
Depreciation	10 Year straight line depreciation method	
Project Life	12 Years from purchase of land or 10 years after startup	12 year
Recovery of Land and Working Capital	Fully recovery in year 12	Year 12

In the discounted cash flow rate of return a project is judged to be good, neutral or bad 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%.

$$\text{Case 1. } i >> i_C = 10\% \text{ Very Good Project Investment} \tag{4.31}$$

$$\text{Case 2. } i = i_C = 10\% \quad \text{Project Investment is Neutral} \tag{4.32}$$

$$\text{Case 3. } i << i_C = 10\% \quad \text{Poor Project Investment} \tag{4.33}$$

Sample Calculation. Sample calculation is presented for the discounted cash flow analysis for the 1,000 tonne per day pulp mill case where an extraction vessel is available and sufficient utilities and wastewater facilities are available so that upgrading is not necessary. Table 4.13 lists the facts for the sample case. Details of this analysis are listed in Table 4.14.

Table 4.13

Facts for the 1000 tonne per day Modified Pulp Mill Sample

(Extraction vessel is available and no utilities and waste water facilities upgrading)

Pulp Production Rate	1000 tonne per day
Total Installed Capital Cost (dollars)[@]	17,755,00
Total Project Cost(dollars)	31,601,000
Annual Operation Cost(dollars)	16,162,000
Revenue(dollars)	24,720,000
@ The extraction vessel is charged as 20% modification fee and no utilities and waste water facilities upgrading.	

Table 4.14 Non-discounted and Discounted after-Tax Cash Flow for 1000 tonne/day Full Scaled Modified Kraft Pulp Process (all number is in \$ 10^6).

End of Year	Investment	dk	FCI-dk	R	Operation Cost (OC)	(R-Com-dk)*(1-t)+dk	Cash Flow (No Discount)	Cumulative Cash Flow (No Discount)	Discounted Cash Flow	Cumulative Discounted Cash Flow
0	(0.47)		31.13				(0.47)	(0.47)	(0.47)	(0.47)
1	(19.91)		31.13				(19.91)	(20.38)	(17.70)	(18.17)
2	(13.27)		31.13				(13.27)	(33.66)	(10.49)	(28.66)
3		3.11	28.02	24.72	16.16	6.43	6.43	(27.22)	4.52	(24.14)
4		3.11	24.90	24.72	16.16	6.43	6.43	(20.79)	4.02	(20.12)
5		3.11	21.79	24.72	16.16	6.43	6.43	(14.35)	3.57	(16.55)
6		3.11	18.68	24.72	16.16	6.43	6.43	(7.92)	3.18	(13.38)
7		3.11	15.56	24.72	16.16	6.43	6.43	(1.48)	2.82	(10.55)
8		3.11	12.45	24.72	16.16	6.43	6.43	4.95	2.51	(8.04)
9		3.11	9.34	24.72	16.16	6.43	6.43	11.38	2.23	(5.81)
10		3.11	6.23	24.72	16.16	6.43	6.43	17.82	1.98	(3.83)
11		3.11	3.11	24.72	16.16	6.43	6.43	24.25	1.76	(2.07)
12	2.05	3.11	-	24.72	16.16	6.43	8.49	32.74	2.07	0.00

Note: All number in parentheses () are negative cash flows.

Fixed capital Investment Excluding Land FCI_L = TPI (2007) – Land =31,601,000-474,000 = \$31,127,000.

Figure 4.7 illustrates the discount cash flow diagram by year over the entire life of the project for the 1,000 tonne per day case (medium size pulp mill). It is assumed that the new land is purchased at the first year (year 0), and the construction of plant is taken two years to finished. In the third year the plant begins to operate, and the finished products will be sold in the market. The net revenue of each year becomes positive which equals the revenue after tax subtracting operation cost. After ten years operation, the plant was assumed to be shut down and land value and working capital recovered. Notice in Figure 4.7, the present value at the end of the life of the project is equal to zero.

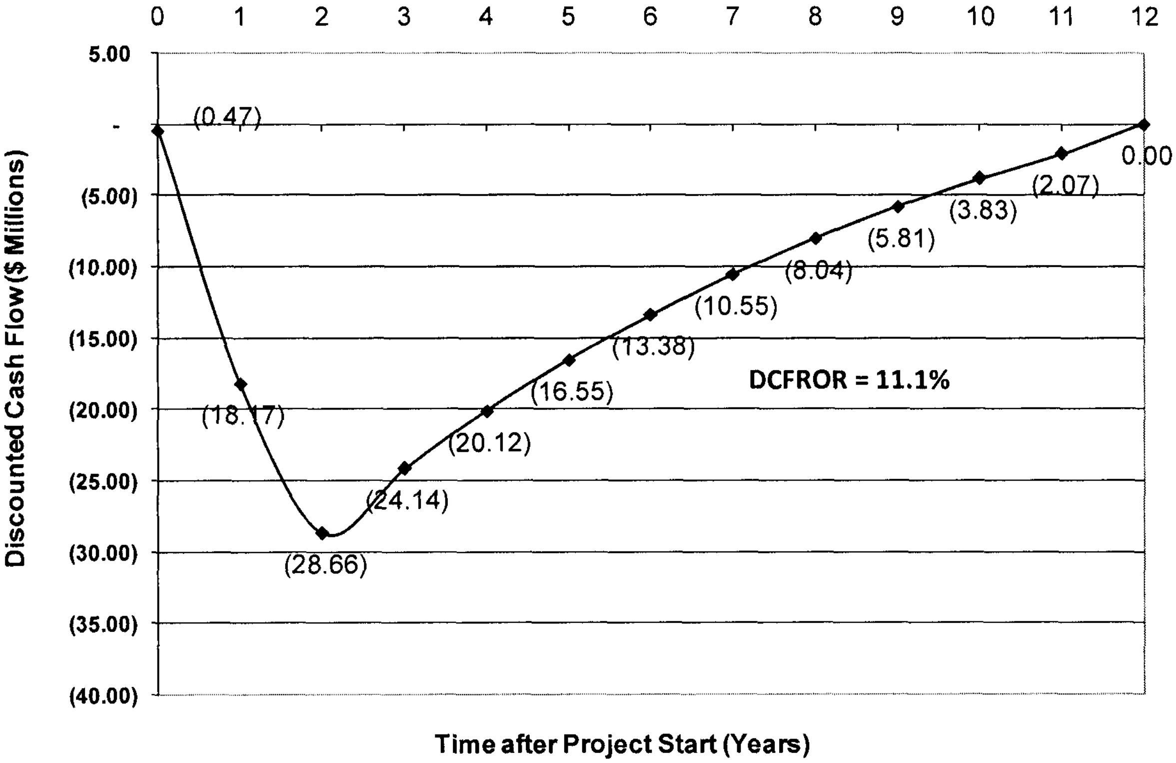


Figure 4.7 Discount Cash Flow Rate of Return on Investment for the 1000 tonne/day Full Scale Case with Extraction Vessel Available and no Utility Upgrading Required

For the case where the hemicellulose extraction process is installed with extraction vessel available at a 1,000 tonne per day pulp mill, the discounted cash flow rate of return was equal to 11.1%, and the net present value after ten year's operation is zero.

$$DCFROR = 11.1\% > 10\% \tag{4.34}$$

4.6 Evaporation of Extract

A major design variable that affects the economics is whether evaporation is required for the extract leaving the extraction vessel to be concentrated. Since the solids content in the extract coming from the flash tank is only 8.5%, two cases were considered. One case is to raise the solids content of the organic portion of the extract by evaporation. This can be done by re-using the flash steam and by adding a thermo-compressor to raise the pressure of the flash steam to a pressure suitable for use in the evaporator [Smook, 2002]. Two solids levels were considered (20% and 30%) after evaporation. Another case is no evaporator and the extract would be sent into hydrolysis reactor directly.

4.6.1 Evaporator

Cases IA and IB. Concentrating Extract Prior to Hydrolysis. In this case the extracted liquor would be removed from the extraction vessel and flashed to 20psig and then concentrate to 20% solids (1A) or 30% solids (1B). These cases are illustrated in Figure 4.8.

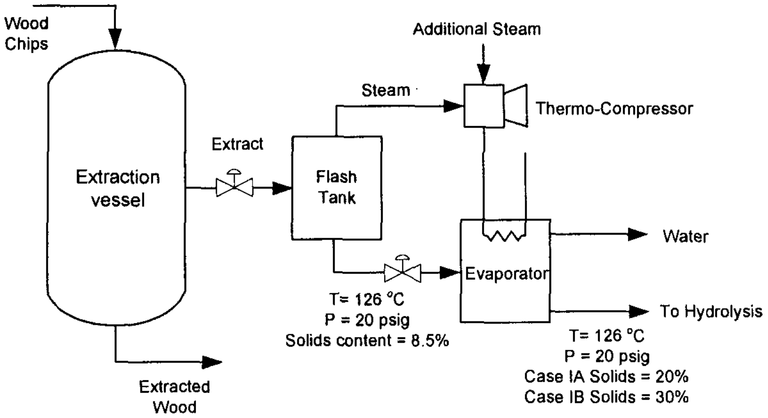


Figure 4.8 Concentrating Extracted Liquor Prior to Hydrolysis

Case II. Using Extract Directly. In the alternative case, the extracted liquor would be removed from the extraction vessel and flashed to 20 psig. The extract would be used directly without concentration (see Figure 4.9).

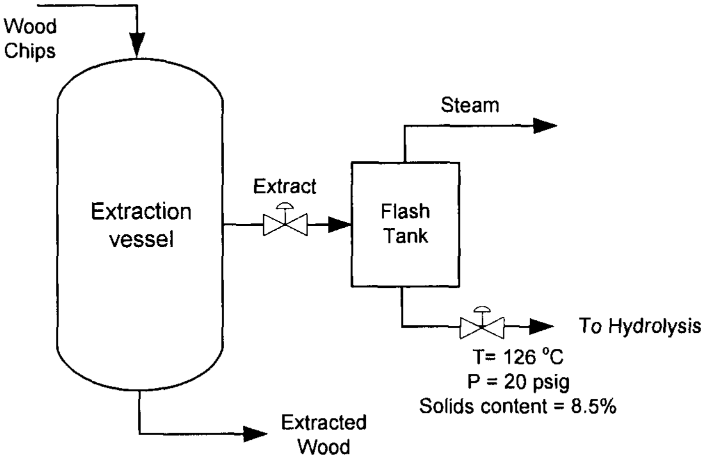


Figure 4.9 Using Extract Directly

As the solids content of the extract is raised, the downstream processing equipment will become smaller and thus will reduce the total equipment cost of downstream process. This will also reduce the cost of the sulfuric acid used in the hydrolysis process as well as the waste disposal for the gypsums, thus the operating cost. But in this scenario there will be additional equipment cost for the purchase of evaporator and thermo-compressor as well as for the motive steam to the thermo-compressor. The alternative to Cases 1A and 1B which involve evaporation is to process the liquor from the flash tank directly at the low concentration (8.5%). From the flash tank, the extracted liquor then goes to the hydrolysis reactor.

4.6.2 Hydrolysis of the Extract

The hydrolysis reactors are illustrated schematically in Chapter 3 Figure 3.6. The hydrolysis can be conducted at a variety of solids contents as previously discussed and sulfuric acid concentrations. In the current study the concentration of sulfuric acid going to the hydrolysis reactors was assume to vary between 0.5% and 4% and the operating cost determined. In the case of 0.5% sulfuric acid concentration the pH of the hydrolyzate would equal approximately 1. Figure 4.10 illustrated the relationship between annual variable operation cost and hydrolysis condition. The lowest operating cost occurs at a sulfuric acid concentration of 0.5% and when the inlet solids concentration is equal to 8.5% that is the case where no-evaporator is used. Under this condition the variable cost is $9.33 million dollar per year (see Figure 4.10). In Chapter 3 it was mentioned that the concentration of sulfuric acid recommended for the hydrolysis condition is 0.5%. Table 4.15 summarized the project cost, operation cost and economy performance for the three different solid content cases.

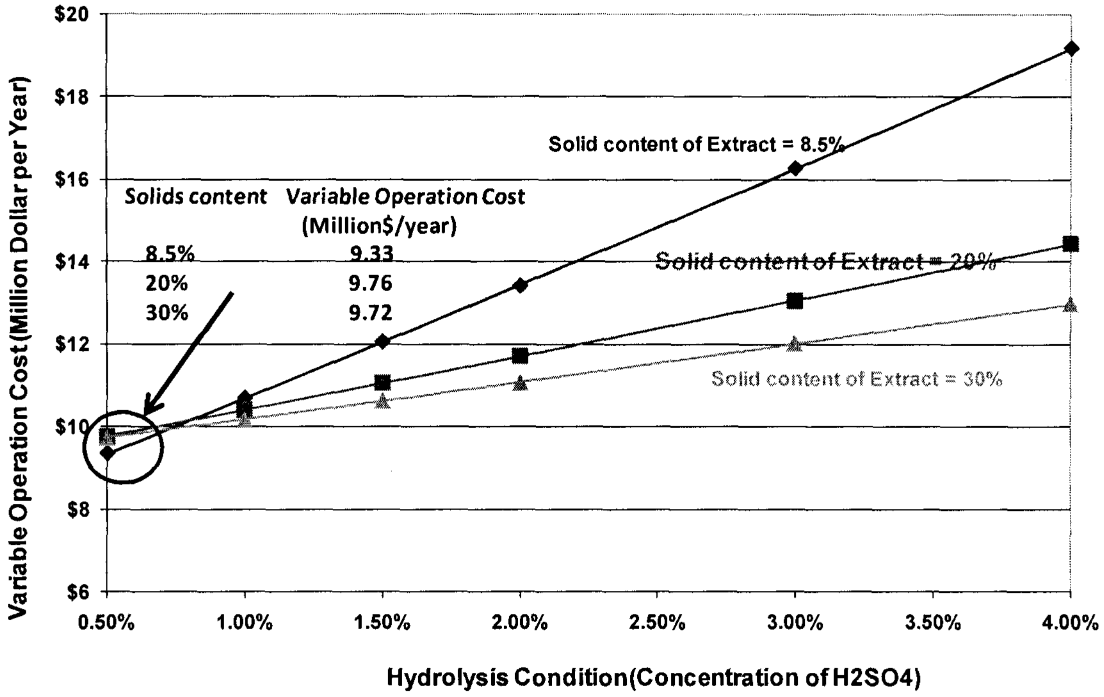


Figure 4.10 Annual Variable Operation Cost verse hydrolysis condition

Table 4.15

Summary of Process Economics Assuming Different Solid Contents of the Extract Going to the Hydrolysis Reactor

Different Solid Contents of the Extract	Case IA (20% Solids)	Case IB (30% Solids)	Case II (8.50% Solids)
Total Project Cost	$68,119,000	$68,119,000	$63,169,000
Steam Consumed by evaporator (tonne/day)	463	528	0
Operational Cost	$22,712,000	$22,500,000	$21,648,000
Revenue	$24,723,000	$24,723,000	$24,723,000
Discount Cash Flow Rate Of Return	-7.1%	-7%	-5.1%
Note: In Case I and Case II, a new extraction vessel is purchased and utilities and waste water facilities need to be upgraded.			

From Table 4.15, it is clear that the case without evaporator is less costly than the cases where the extract is evaporated prior to going to the hydrolysis reactor. Including an evaporator system did not improve the process economics of the hemicellulose extraction process. Consequently use of an evaporator was not included in the final process design.

4.7 Process Analysis

In previous section, sample calculations were shown for installation of the hemicellulose extraction process at a pulp mill having a production rate 1,000 tonne per day market pulp where a new extraction vessel had to be purchased. A process was performed to look at the affects of plant size and for cases where an extraction vessel is available at the mill site. This available extraction vessel could be an unused continuous digester resulting from a fiber line being shut down or also involving the conversion of an impregnation vessel into an extraction vessel by adding addition heat exchange equipments. Another case considered dealt with the availability of utilities and a waste water treatment being available with suitable capacity for the process addition.

Affect of Pulp Mill Size. The affect of pulp mill size on the process economics was determined by considering three plant sizes. Plant sizes considered were a small plant producing 750 tonne per day of market Kraft pulp, an intermediate plant producing 1,000 tonne per day and a large pulp mill producing 1,500 tonne per day of market Kraft pulp.

Extraction Vessel Availability. A second situation arises where assessing the full cost of a new extraction vessel is unrealistic. In some Kraft pulp mills, because of recent shut downs of a fiber line a continuous digester may be idle that could be modified into an extraction vessel. Another perhaps more likely situation is that an impregnation vessel already existed at the mill site and this vessel could be converted into an extraction vessel. In both situations there would be no need to purchase a new extraction vessel. In this situation 20% of the cost of a new extraction vessel was applied to the project for modification of the existing vessel to the hemicelluloses extraction process.

Upgrading Utilities and Waste Water Treatment Systems. Another common situation relates to the availability of utilities at the site and the impact of the new process on the fresh water treatment plant, steam generation and waste water treatment systems. In some Kraft pulp mills the waste water treatment and utilities system may be sufficient to accommodate the new process and there is no need for a capital expenditure to upgrade the utility systems. For such situation the capital cost of waste water treatment and utilities system are not included in the project cost. In other situations the opposite may be true and the utilities need to be upgraded. The various cases considered in the process analysis are listed in Table 4.16.

Table 4.16

Case Number Assigned for Different Scenarios

Pulp Mill Production Rate	Utilities and Waste Water system Extraction Vessel		Utilities and Waste Water Treatment System	
			Upgrading	No Upgrading
			A	B
750 tonne/day	Extraction vessel Modification	1	1A-750	1B-750
	Extraction vessel Purchased	2	2A-750	2B-750
1000 tonne/day	Extraction vessel Modification	1	1A-1000	1B-1000
	Extraction vessel Purchased	2	2A-1000	2B-1000
1500 tonne/day	Extraction vessel Modification	1	1A-1500	1B-1500
	Extraction vessel Purchased	2	2A-1500	2B-1500

4.7.1 Capital Cost for Different Cases Investigated

The total estimated project costs for the twelve (12) different cases considered in this analysis are summarized in Figure 4.11. This figure gives the capital investment as a function of plant size and whether an extraction vessel is available or not and whether the utilities need to be upgraded or are sufficient for the new process.

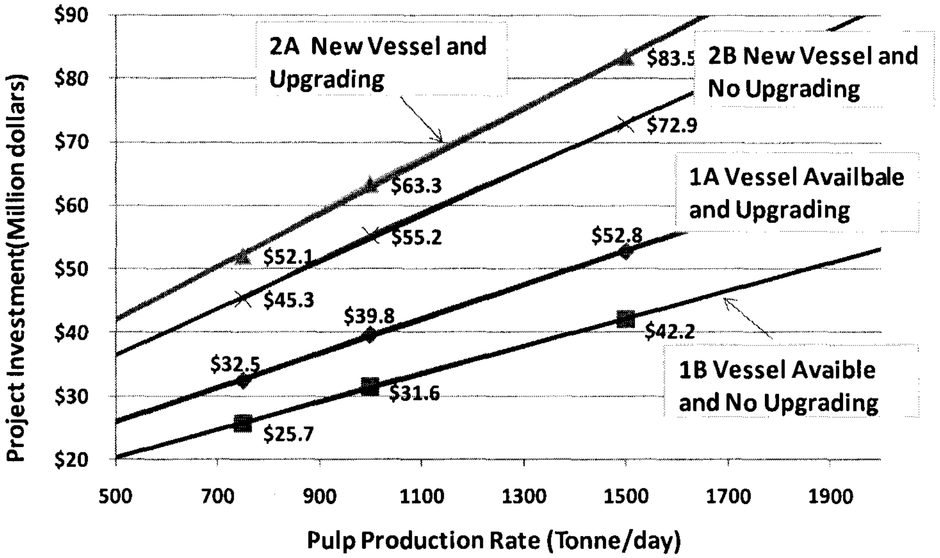


Figure 4.11 Total Project Investment for Cases Investigated

From Figure 4.11, 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.

4.7.2 Annual Operation Cost for Different Cases Investigated

The annual operation cost for the twelve (12) different scenarios are illustrated in Figure 4.12. Comparing Figures 4.11 and 4.12, it is clear that the project with the high capital investment invariable lead to high annual operating cost; and results from the application of the capital recovery factor to the total capital investment. Projects with high capital investment lead result in high annual charges for repaying the capital investment. The unit production costs for the twelve different cases considered are listed in Table 4.17.

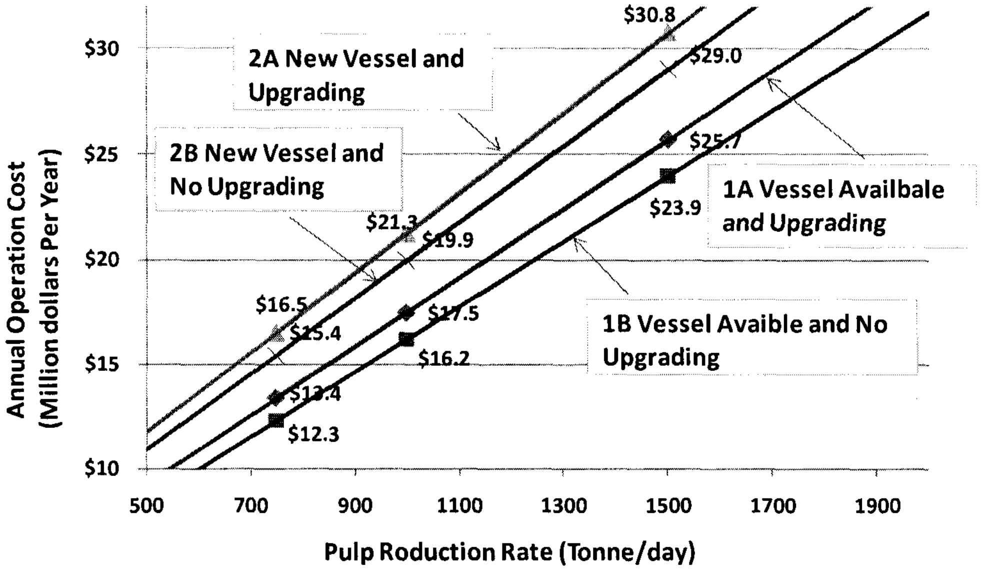


Figure 4.12 Annual Operation Cost for Different Cases

Table 4.17

Unit Production Cost for Different Cases

Pulp Mill Size (tonne/day)	Case Number	Ethanol (dollars/gallon)	Acetic Acid (dollars/gallon)
750	1A - 750	1.80	2.39
	1B -750	1.65	2.20
	2A - 750	2.22	2.95
	2B -750	2.08	2.76
1000	1A - 1000	1.77	2.34
	1B -1000	1.63	2.17
	2A - 1000	2.15	2.85
	2B -1000	2.02	2.68
1500	1A - 1500	1.73	2.30
	1B -1500	1.61	2.14
	2A - 1500	2.07	2.75
	2B -1500	1.95	2.59

4.7.3 Production Rate and Total Revenue for Cases Investigated

The production rates for the ethanol, acetic acid and furfural for the small, medium and large pulp mill plants are illustrated in Figure 3.12. This figure is repeated here as Figure 4.13. For the different plant size, the corresponding revenues are listed in Table 4.16. No credit was taken for the production of furfural, gypsum or carbon dioxide.

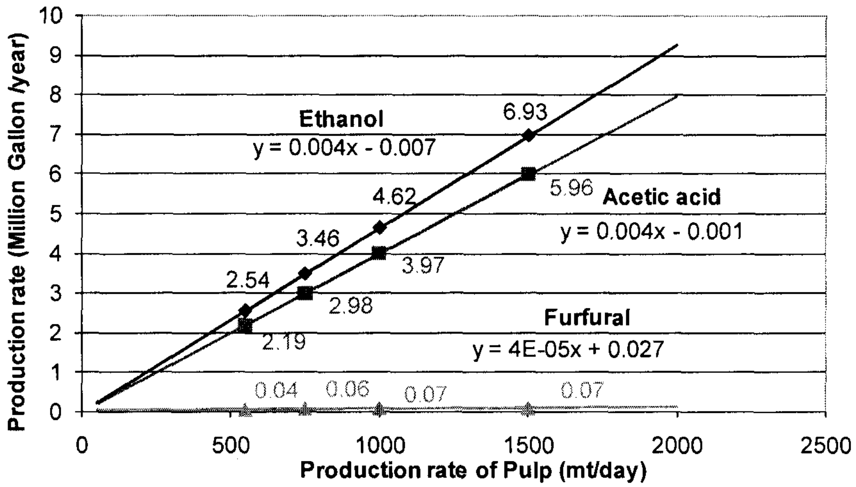


Figure 4.13 Production Rate of Ethanol, Acetic acid and Furfural

Table 4.18

Total Revenue for Different Plant Size

Plant Size (Pulp Production rate)	**750 tonne/day**	**1000 tonne/day**	**1500 tonne/day**
Revenue From Ethanol(M$)	6.92	9.23	13.86
Revenue From Acetic acid (M$)	12.38	16.51	24.77
Revenue From Oil Saving(M$)	1.45	1.93	2.90
Revenue From Energy (M$)	-2.48	-2.96	-5.34
Total Revenue (M$)	18.27	24.72	36.12

A comparison of the revenue streams for the acetic acid and the ethanol show that approximately 67 percent is derived from acetic acid. Considering the processing required producing acetic acid relative to ethanol and the size of the revenue stream, it raises the question regarding the feasibility of maximizing the production of acetic acid. A major advantage in producing ethanol is the very large size of the market and producing ethanol is a national goal [White House News Release, 2007].

4.7.4 Profitability Analysis for Different Case

As previously mentioned profitability analysis was performed using the Discounted Cash Flow Rate of Return (DCFROR) for the twelve (12) different cases. The results of this analysis are listed in Table 4.19 and repeatedly shown in Figure 4.14. It is clear from the Table 4.19, that the larger the plant size, the more profitable the investment. The condition leading to the highest discounted cash flow rate of return is for the case where the extraction vessel is available and no upgrading is required for the utilities and waste water treatment systems. In those Kraft pulp mills where these conditions are fulfilled, the rate of return can be as high as 9.9% for the small pulp mill (750 metric tonne per day) and 11.7% and 14.0% for the medium (1,000 tonne per day) and large (1,500 tonne per day) pulp mills respectively. 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, no matter what the reason, the discounted cash flow rate of return decreased.

Table 4.19

Discounted Cash Flow Rate of Return for Different Cases

	Utilities and waste water system upgrading	DCFROR	No Utilities and waste water treatment system upgrading	DCFROR
Extraction Vessel Modification	1A -750	4.0%	1B -750	9.9%
	1A -1000	5.8%	1B -1000	11.7%
	1A -1500	7.8%	1B -1500	14.0%
New Purchased extraction vessel	2A -750	-7.2%	2B -750	-3.9%
	2A -1000	-5.1%	2B -1000	-1.9%
	2A -1500	-3.0%	2B -1500	0.4%

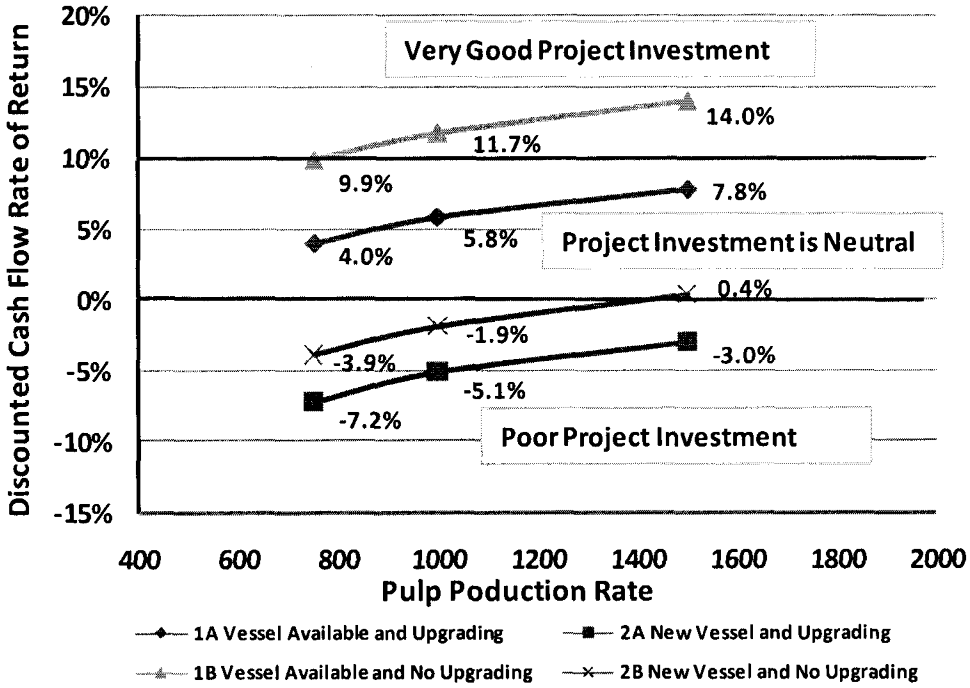


Figure 4.14 Discount Cash Flow Rate of Return for Different Case

Chapter 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

Contrast to the NREL Process. This thesis summarizes a technical economic evaluation that was performed for the "near-neutral" hemicellulose extraction process. In the hemicellulose extraction process acetic acid and ethanol are produced as co-products in addition to bleached hardwood Kraft pulp. This work complements the work of Mitchell [2006] who studied the NREL process for producing ethanol from hardwood. In the NREL process, the entire carbohydrate proportion of the wood is used to produce ethanol and the lignin fraction is burned to produce green power. The NREL process differs from the current work reported in that the main product from the mill is still hardwood Kraft pulp and the extracted materials are converted to ethanol and acetic acid. In the hemicellulose extraction process the acetyl groups on the hemicelluloses are hydrolyzed to sodium acetate during the extraction process and subsequently converted to acetic acid in the acid hydrolysis step in the process. By contrast in the NREL process the acetyl groups in the wood would either be burned or sent to the waste treatment plant.

Simulation Packages. The heat and material balance for the hemicellulose extraction process was initially performed using MathCAD computer package and then later using the WinGEMS simulation package. The MathCAD program proved to be ill suited for the simulation; which had very long run time and hard to debug. The WinGEMS program was found to be well suited to the simulation except for its lack of physical properties that pertained to the ethanol and acetic acid separation processes. Consequently the ASPEN plus computer package was used to simulate both the Lenzing and ethanol distillation processes. Although the ASPEN plus computer program is very powerful and has a very comprehensive thermodynamic library, the solids handling proved to be very complicated and extremely time consuming.

Process Advantages. There are several important advantages associated with the "near- neutral" hemicellulose extraction process. Firstly, the quantity and quality of the pulp is unchanged compared to pulp obtained from a conventional Kraft process. This point has been amply illustrated by the data presented by Van Heiningen [2007]. Secondly, the physical properties of pulp produced by the hemicellulose extraction process pulp are as good as or slightly better than that of the Kraft pulp produced using conventional methods. A third advantage of the "near-neutral" extraction process is that the recovery cycle is off-loaded because the amount of organic matter in the black liquor is reduced and less white liquor is needed for pulping. This change in operation would potentially allow a Kraft pulp mill to significantly increase its pulp production rate if the recovery cycle is the bottleneck in the plant. In addition the hemicellulose extraction process has several potential environmental advantages. In the hemicellulose extraction process the methanol content of the black liquor is thought to be reduced by about 40%, while the TRS content is also diminished. These advantages result because of the lower white liquor charge and shorter pulping time during the modified Kraft cook. Finally, a new feed stock stream of sugars is produced which may be used for the production of biofuels and renewable chemicals.

Process Disadvantages. There are several disadvantages to the hemicellulose extraction process. A major disadvantage of the process is that the production rates for the two co-products, ethanol and acetic acid, is low when compared to corn to ethanol processes. A second major disadvantage to the process is that organic matter in the wood chips is extracted, and hence less steam is produced in the recovery boiler; and additional steam must be supplied from a biomass boiler or by burning fossil fuels such as natural gas, coal or fuel oil. Lastly the near neutral extraction process is capital intensive unless an extraction vessel is available for use.

Technical Economics. A detailed technical economy analysis was performed for the hemicellulose extraction process. Products from the process include market pulp which remained unchanged over the base case, ethanol and acetic acid. No credit was taken for the production of furfural, carbon dioxide and gypsum which were treated as waste products that needed to be treated. It is clear from the economic analysis that the hemicellulose extraction process is more profitable as the pulp mill size increases. Increasing the size of the plant lowers the unit production cost of the products produced from the extraction process. The effect of adding an evaporator to concentrate the extract to a solids content greater than that which is obtained from the flash tanks could not be economically justified.

A variety of cases were considered that relate to conditions prevailing at the host site. These cases considered both modifications and/or purchased of the extraction vessel and cases where the pulp mill had sufficient utilities and waste water treatment facilities to accommodate the new process. The best economic cases occur where the capital investment at the plant is minimized. This occurs for those cases where the extraction vessel is available or an existing digester can be modified and where the utilities and waste water treatment facilities are sufficient to handle the new process. The highest discount cash flow rate of return on investment 14% occurred for the 1,500 tonne per day pulp production rate case. Sequentially lower rates of return occur for the 1,000 and 750 tonne per day pulp mill cases; 11.7% and 9.9% respectively. The process is not economically justified for the case where a new extraction vessel must be purchased, regardless whether the utilities and waste water treatment are sufficient to handle the new process.

5.2 Recommendations

Pulp Yield and Physical Properties. Experimental work should be performed to confirm the data on pulp yield and physical properties provided by Van Heiningen and co-workers. It was assumed in this analysis that the yield was the same as the base case where conventional pulping was done. This leads to the assumption that no additional wood is required in the hemicellulose extraction process.

Chip Washing Study. It is highly recommended that a chip washing study be performed. In the present analysis, it was assumed that the washing time in the bottom of the digester was 30 minutes and that this lead to a Norden efficiency factor of three (3). Experimental data are necessary to confirm this assumption and determine the amount of sugar polymers that can be washed from the extracted chips as a function of the washing time and temperature in the extraction vessel.

Acid Hydrolysis Model. Further experimental work should be done to confirm the acid hydrolysis model of Garrote, et al. [Garrote, 2001]. Garrote and co-workers used Kraft Eucalyptus pulp in their work. They propose that the sulfuric acid concentration can be reduced significantly by raising the hydrolysis temperature. This assumption has a marked affect on the sulfuric acid consumption, gypsum produced and gypsum disposal, and thus on the process economics.

Acetic Acid and Furfural Separation. Experimental work needs to be done to confirm the effectiveness of liquid-liquid extraction process for the separation of acetic acid and furfural from the hydrolyzate. Although the Lenzing process is commercial for the separation of acetic acid and furfural from evaporator condensate in sulfite mills, this process has never been tried commercially for separating acetic acid and furfural from mixed sugars in hydrolyzate. Particular attention need to be paid to selection of an appropriate solvent.

Process Economics. Vender quotations are needed to confirm the cost of important process equipment used in the capital cost analysis. The cost equations used in the current work were scaled from the data of Wooley [1999] and Mitchell [2006] which were developed for the NREL process. In the current business climate it was very difficult to obtain vender quotations. It is especially important to verify the cost of a new extraction vessel and the cost for tying two digesters together. The capital cost estimation for the new extraction vessel presented in this work was obtained from one vender and should be confirmed.

Sensitivity Analysis. Lastly it is recommended that a sensitivity analysis be perform for the economic analysis. It is especially important to consider price fluctuations of the ethanol and acetic acid products.

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Appendix A

MathCAD Model of Xylooligomer Acid Hydrolysis

Definitation

$KJ := 1000J \qquad \rho := 1.07994 \cdot 1000 \frac{gm}{L} = 1.08 \times 10^3 \frac{kg}{m^3}$ density of hydrolysis liquor

$MW_{H2SO4} := 98 \frac{gm}{mole}$ molecular weight of sulfuric aicd

$MW_{CaSO4} := 136 \frac{gm}{mole}$ Molecular weight of $CaSO_4$

In Garrotes's Model, Xylooligomers are first hydrolyzed into xylose, and then xylose is further decomposed into furfural and a variety of degradation products. Lastly, acetyl groups in the extract are converted into acetic acid. In the following equations, K1, k2, k3 and ka are the corresponding reaction rate coefficients.

(A.1) Xylooligomers ---^{k1}---> Xylose ---^{k2}---> Furfural ---^{k3}---> Degradtion Product

(A.2) Acetyl group ---^{ka}--->Acetic acid

Corresponding to Equation A.1 and A.2, the concentration of Xylooligomers (XO) , Xylose (X), Furfural (F) and Degradation products (DP) are:

$$XO(t) := XO_0 \cdot \exp(-k1 \cdot t \cdot hr) \cdot \frac{L}{gm} \qquad \text{(Xylooligomers)}$$

$$X(t) := \left(C_1 \cdot \exp(-k1 \cdot t \cdot hr) + C_2 \cdot \exp(-k2 \cdot t \cdot hr)\right) \cdot \frac{L}{gm} \qquad \text{(Xylose)}$$

$$F(t) := \left(C_3 \cdot \exp(-k1 \cdot t \cdot hr) + C_4 \cdot \exp(-k2 \cdot t \cdot hr) + C_5 \cdot \exp(-k3 \cdot t \cdot hr)\right) \cdot \frac{L}{gm} \qquad \text{(Furfural)}$$

$$DP(t) := \left(XO_0 + \frac{150}{96} \cdot F_0\right) \cdot \frac{L}{gm} - \left(XO(t) + X(t) + \frac{150}{96} \cdot F(t)\right) \qquad \text{(Degradation Products)}$$

Where XO correspond to the initial concentration of xylooligomers. C1, C2, C3,C4 and C5 are constants that used in the concentration equation

1. hydrolysis of xylooligomers

1.1 Find the reaction rate coefficient (k1). The reaction rate coefficient follows an Arrhenius Equation

(A.3)

$$\boxed{\ln(k1) = a1 + n1\cdot\ln(C) - \frac{Ea1}{R\cdot T}}$$

(C) is the concentration of sulfuric acid
(T) is reaction temperature (K)

k1 is known from Garrote Work. Garrotes's values for a1, n1 and Ea1 are:

$\boxed{a1 := 36.66}$ $\boxed{n1 := 1}$ $\boxed{Ea1 := 108}$

Result (A.4)

$$\boxed{\ln(k1) = 36.66 + \ln\left(\frac{Con}{\frac{mole}{L}}\right) - \frac{108.0\cdot\frac{KJ}{mole}}{8.314\cdot\frac{J}{mole\cdot K}\cdot Temp}}$$

1.2 Find the reaction rate coefficient (k2):

(From Garrote's data, different value for the temperatures and acid concentrations were selected, and the reaction rate constants (a2,n2 and Ea2) were calculated for reaction rate coefficient k2)

(A.5)

$$\boxed{\ln(k2) = a2 + n2\cdot\ln(C) - \frac{Ea2}{R\cdot T}}$$

(C) is the concentration of sulfuric acid
(T) is reaction temperature (K)

Value of Temperature selected:

$Temp := (100.5\ \ 100.5\ \ 100.5\ \ 100.5\ \ 115\ \ 115\ \ 115\ \ 115\ \ 125\ \ 125\ \ 125\ \ 125\ \ 135$

Value of Concentration of the acid selected:

$Con := (0.5\ \ 1\ \ 1.5\ \ 2\ \ 0.5\ \ 1\ \ 1.5\ \ 2\ \ 0.5\ \ 1\ \ 1.5\ \ 2\ \ 0.5\ \ 1\ \ 1.5\ \ 2)^T\,\%$

Reaction rate corresponding to the temperatures and acid concentration selected from Garrote's work

$k2 := (0.000\ \ 0.000\ \ 0.004\ \ 0.006\ \ 0.029\ \ 0.046\ \ 0.024\ \ 0.030\ \ 0.027\ \ 0.041\ \ 0.059\ \ 0.071$

The Minerr function in MathCAD was used to calculated the constants (a2,n2 and Ea2) shown in Equation A.5

Guess $a2 := 31$ $n2 := 0.72$ $Ea2 := 109$

(A.6)
$$kk2(Con, Temp, a2, n2, Ea2) := \exp\left(a2 + n2 \cdot \ln\left(\frac{\frac{Con \cdot \rho}{MW_{H2SO4}}}{\frac{mole}{L}}\right) - \frac{Ea2 \cdot \frac{KJ}{mole}}{8.314 \cdot \frac{J}{mole \cdot K} \cdot Temp}\right)$$

Given
$$0 = \sum (k2 - kk2(Con, Temp, a2, n2, Ea2))^2$$

$$Minerr(a2, n2, Ea2) = \begin{pmatrix} 31.507 \\ 0.716 \\ 109.021 \end{pmatrix}$$

Result (A.7)
$$\boxed{\ln(k2) = 31.510 + 0.716 \ln\left(\frac{Con}{\frac{mole}{L}}\right) - \frac{109.031 \cdot \frac{KJ}{mole}}{8.314 \cdot \frac{J}{mole \cdot K} \cdot Temp}}$$

$\boxed{a2 := 31.51}$ $\boxed{n2 := 0.716}$ $\boxed{Ea2 := 109.031}$

1.3 Find the reaction rate coefficient (k3):

(From Garrote's data, different value for the temperatures and acid concentrations were selected, and the reaction rate constants (a3,n3 and Ea3) were calculated for reaction rate coefficient k3)

(A.8)
$$\boxed{\ln(k3) = a3 + n3 \cdot \ln(C) - \frac{Ea3}{R \cdot T}}$$

(C) is the concentration of sulfuric acid
(T) is reaction temperature (K)

Value of Temperature selected:

$Temp^T = (100.5\ \ 100.5\ \ 100.5\ \ 100.5\ \ 115\ \ 115\ \ 115\ \ 115\ \ 125\ \ 125\ \ 125\ \ 125\ \ 135\ \ 135$

Value of Concentration of acid selected:

$$Con^T = (5 \times 10^{-3} \;\; 0.01 \;\; 0.02 \;\; 0.02 \;\; 5 \times 10^{-3} \;\; 0.01 \;\; 0.02 \;\; 0.02 \;\; 5 \times 10^{-3} \;\; 0.01 \;\; 0.02 \;\; 0.02$$

Reaction rate corresponding to the temperatures and acid concentration selected from Garrote's work

$$K3 := (0.029 \;\; 0.003 \;\; 0.109 \;\; 0.115 \;\; 0.091 \;\; 0.360 \;\; 0.144 \;\; 0.207 \;\; 0.050 \;\; 0.204 \;\; 0.251 \;\; 0.268$$

The Minerr function in MathCAD was used to calculated the constants (a2,n2 and Ea2) *shown in* Equation A.8

Guess $a3 := 20.689 \quad n3 := 0.342 \quad Ea3 := 70.509$

$$KK3(Con, Temp, a3, n3, Ea3) := \exp\left[a3 + n3 \cdot \ln\left(\frac{\frac{Con \cdot \rho}{MW_{H2SO4}}}{\frac{mole}{L}}\right) - \frac{Ea3 \cdot \frac{KJ}{mole}}{8.314 \cdot \frac{J}{mole \cdot K} \cdot Temp}\right]$$

Given $0 = \sum (K3 - KK3(Con, Temp, a3, n3, Ea3))^2$

$$Minerr(a3, n3, Ea3) = \begin{pmatrix} 20.79 \\ 0.34 \\ 70.88 \end{pmatrix}$$

result(A.9)

$$\boxed{\ln(k3) = 20.789 + 0.343 \ln\left(\frac{Con}{\frac{mole}{L}}\right) - \frac{70.875 \cdot \frac{KJ}{mole}}{8.314 \cdot \frac{J}{mole \cdot K} \cdot Temp}}$$

$\boxed{a3 := 20.789} \quad \boxed{n3 := 0.343} \quad \boxed{Ea3 := 70.875}$

1.4 Input desired hydrolysis condition and calculated the concentration of different components changed with the reaction time

Temperature of Hydrolysis $\boxed{T := 126\,°C}$

Concentration of sulfuric acid (wt/wt) $\boxed{C := 0.5\%}$

Reaction time

$$Time := 2hr$$

Iniatial concentration of different components

$$XO_0 := 17.7418\frac{gm}{L} \qquad F_0 := 0\frac{gm}{L} \qquad X_{opt} := XO_0\frac{gm}{L} \qquad X_0 := 0\frac{gm}{L}$$

XO is the concentration of xylooligomers (g/L), X and F are the concentrations of xylose and furfural (g/L), DP is the concentration of degradation products in xylose equivalent (g/L) and t is the reaction time (hour).

Rewrite the reaction rate coefficients for k1, k2 and k3

$$k1 := \exp\left(a1 + n1\cdot\ln\left(\frac{\frac{C\cdot\rho}{MW_{H2SO4}}}{\frac{mole}{L}}\right) - \frac{Ea1\cdot\frac{KJ}{mole}}{8.314\cdot\frac{J}{mole\cdot K}\cdot T}\right)\cdot hr^{-1}$$

$$k2 := \exp\left(a2 + n2\ln\left(\frac{\frac{C\cdot\rho}{MW_{H2SO4}}}{\frac{mole}{L}}\right) - \frac{Ea2\cdot\frac{KJ}{mole}}{8.314\cdot\frac{J}{mole\cdot K}\cdot T}\right)\cdot hr^{-1}$$

$$k3 := \exp\left(a3 + n3\ln\left(\frac{\frac{C\cdot\rho}{MW_{H2SO4}}}{\frac{mole}{L}}\right) - \frac{Ea3\cdot\frac{KJ}{mole}}{8.314\cdot\frac{J}{mole\cdot K}\cdot T}\right)\cdot hr^{-1}$$

The Constants used in the concentration equations are:

$$C_1 := \frac{k1\cdot XO_0}{k2 - k1} \qquad C_2 := X_0 - C_1 \qquad C_3 := \frac{96}{150}\cdot\frac{k2\cdot C_1}{k3 - k1}$$

$$C_4 := \frac{96}{150}\cdot\frac{k2\cdot C_2}{k3 - k2} \qquad C_5 := F_0 - C_3 - C_4$$

Xylooligomers's concentration equation is:

$$XO(t) := XO_0\cdot\exp(-k1\cdot t\cdot hr)\cdot\frac{L}{gm}$$

xylose's concentration equation is:

$$X(t) := \left(C_1\cdot\exp(-k1\cdot t\cdot hr) + C_2\cdot\exp(-k2\cdot t\cdot hr)\right)\cdot\frac{L}{gm}$$

Furfural's concentration equation is:

$$F(t) := \left(C_3 \cdot \exp(-k1 \cdot t \cdot hr) + C_4 \cdot \exp(-k2 \cdot t \cdot hr) + C_5 \cdot \exp(-k3 \cdot t \cdot hr)\right) \cdot \frac{L}{gm}$$

Degradation products's concentration equation is:

$$DP(t) := \left(XO_0 + \frac{150}{96} \cdot F_0\right) \cdot \frac{L}{gm} - \left(XO(t) + X(t) + \frac{150}{96} \cdot F(t)\right)$$

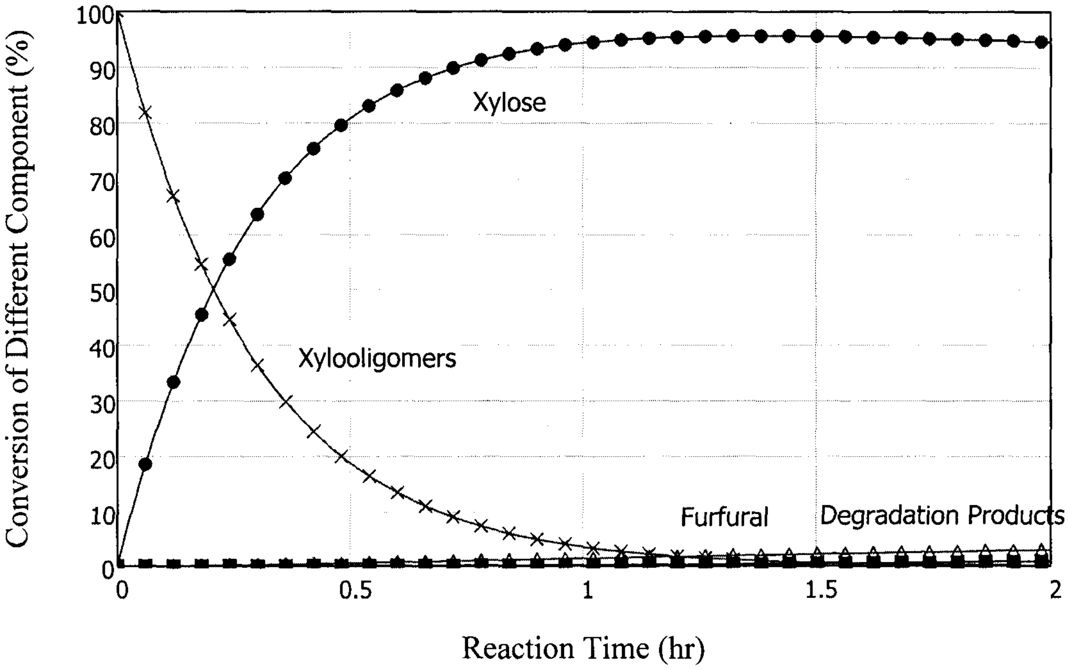

Figure A.1 Hydrolysis Reaction of Xylooligomers

2.1 Calculate the maximum concentration of Xylose in the given hydrolysis condition shown in section 1.4

Guess $tt := 0$

Given $\frac{d}{dtt} X(tt) = 0$

Find the time for the maximum concentration of xylose

$tt := \text{Find}(tt) = 1.3868$ hr

The maximum concentration of xylose is : $X(tt) = 16.96\ \frac{gm}{L}$

The ratio of Furfural to Xylose is: $\frac{F(tt)}{X(tt)} = 2.08 \cdot \%$

At the same time the concentration of furfural is: $F(tt) = 0.35\ \frac{gm}{L}$

2.3 Time calculated for achieve the maximum xylose concentration for different hydrolysis condition (different sulfuric acid concentration and reaction temperature)

$\begin{pmatrix} \text{Temp} \\ \text{OptTime} \end{pmatrix} :=$ **(Import File from Excel File)**

Worksheet

$Con_{0.5} := \text{submatrix}(OptTime, 1, 10, 1, 1)$

$Con_{1} := \text{submatrix}(OptTime, 1, 10, 2, 2)$

$Con_{1.5} := \text{submatrix}(OptTime, 1, 10, 3, 3)$

$Con_{2} := \text{submatrix}(OptTime, 1, 10, 4, 4)$

$Con_{2.5} := \text{submatrix}(OptTime, 1, 10, 5, 5)$

$Con_{3} := \text{submatrix}(OptTime, 1, 10, 6, 6)$

$Con_{3.5} := \text{submatrix}(OptTime, 1, 10, 7, 7)$

$Con_{4} := \text{submatrix}(OptTime, 1, 10, 8, 8)$

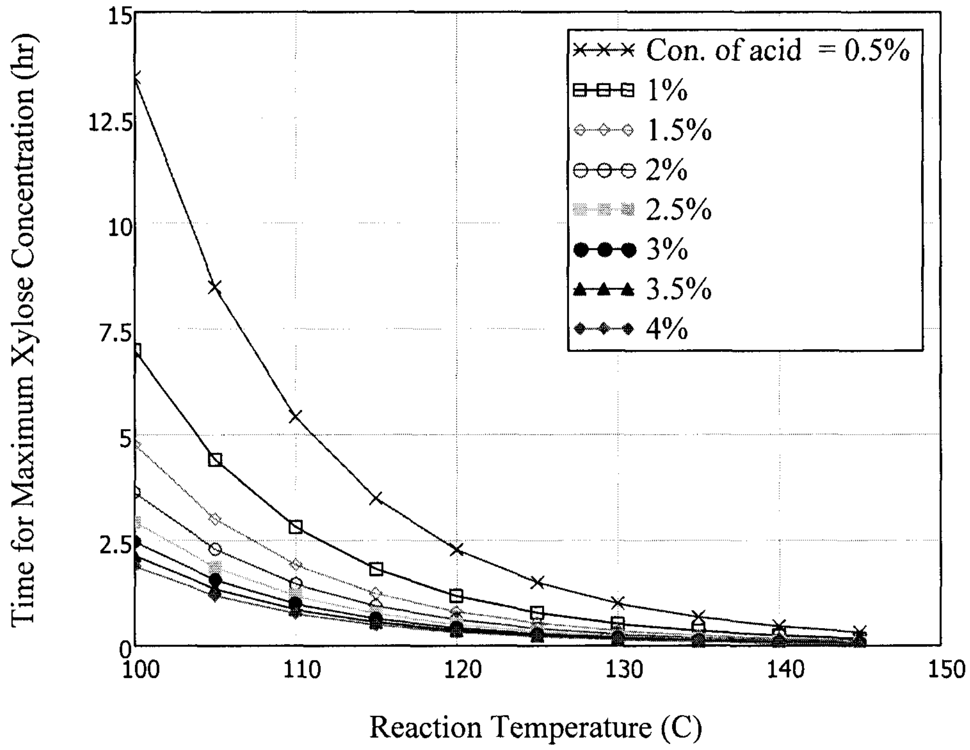

Figure A.2 Time for Maximum Xylose Concentration VS. Reaction Time

2.4 Calculated Relationship between the temperature, acid concentration and the amount of xylose and furfural generated

$$\begin{pmatrix} \text{Temp} \\ \text{Amount}_{\text{xylose}} \\ \text{Amount}_{\text{furfural}} \end{pmatrix} :=$$

(Import File from Excel File)

Worksheet

$\text{xylose}_{0.5} := \text{submatrix}(\text{Amount}_{\text{xylose}}, 1, 10, 1, 1)$

$\text{xylose}_{1} := \text{submatrix}(\text{Amount}_{\text{xylose}}, 1, 10, 2, 2)$

$\text{xylose}_{1.5} := \text{submatrix}(\text{Amount}_{\text{xylose}}, 1, 10, 3, 3)$

$\text{xylose}_{2} := \text{submatrix}(\text{Amount}_{\text{xylose}}, 1, 10, 4, 4)$

$\text{xylose}_{2.5} := \text{submatrix}(\text{Amount}_{\text{xylose}}, 1, 10, 5, 5)$

$\text{xylose}_{3} := \text{submatrix}(\text{Amount}_{\text{xylose}}, 1, 10, 6, 6)$

$\text{xylose}_{3.5} := \text{submatrix}(\text{Amount}_{\text{xylose}}, 1, 10, 7, 7)$

$\text{xylose}_{4} := \text{submatrix}(\text{Amount}_{\text{xylose}}, 1, 10, 8, 8)$

$\text{furfural}_{4} := \text{submatrix}(\text{Amount}_{\text{furfural}}, 1, 10, 8, 8)$

$\text{furfural}_{0.5} := \text{submatrix}(\text{Amount}_{\text{furfural}}, 1, 10, 1, 1)$

$\text{furfural}_{1} := \text{submatrix}(\text{Amount}_{\text{furfural}}, 1, 10, 2, 2)$

$\text{furfural}_{1.5} := \text{submatrix}(\text{Amount}_{\text{furfural}}, 1, 10, 3, 3)$

$\text{furfural}_{3.5} := \text{submatrix}(\text{Amount}_{\text{furfural}}, 1, 10, 7, 7)$

$\text{furfural}_{2} := \text{submatrix}(\text{Amount}_{\text{furfural}}, 1, 10, 4, 4)$

$\text{furfural}_{2.5} := \text{submatrix}(\text{Amount}_{\text{furfural}}, 1, 10, 5, 5)$

$\text{furfural}_{3} := \text{submatrix}(\text{Amount}_{\text{furfural}}, 1, 10, 6, 6)$

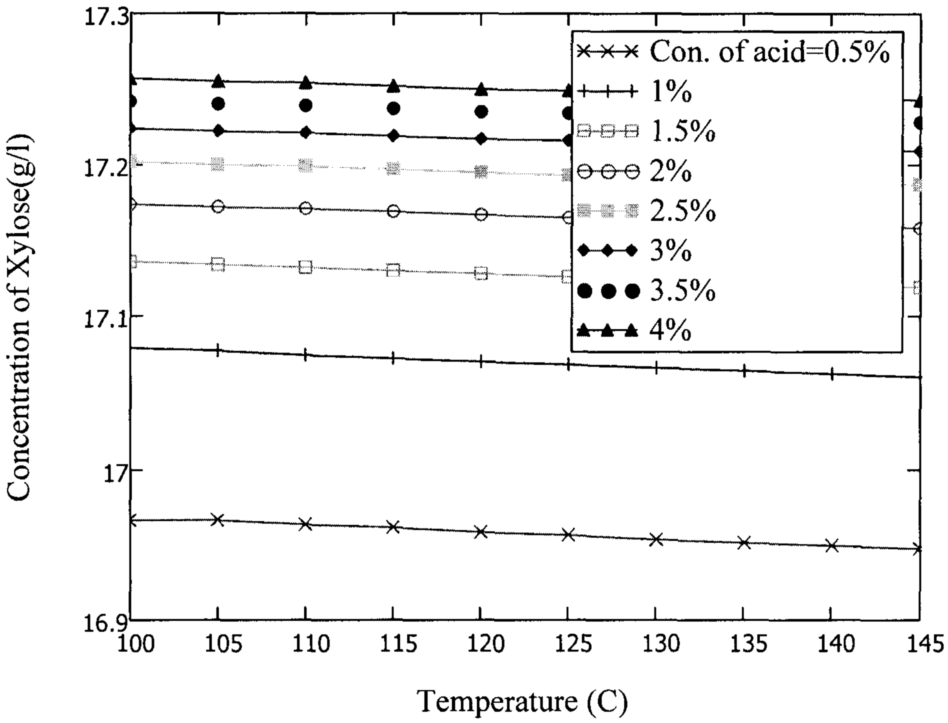

Figure A.3 Temperature of Reaction VS. Concentration of Xylose

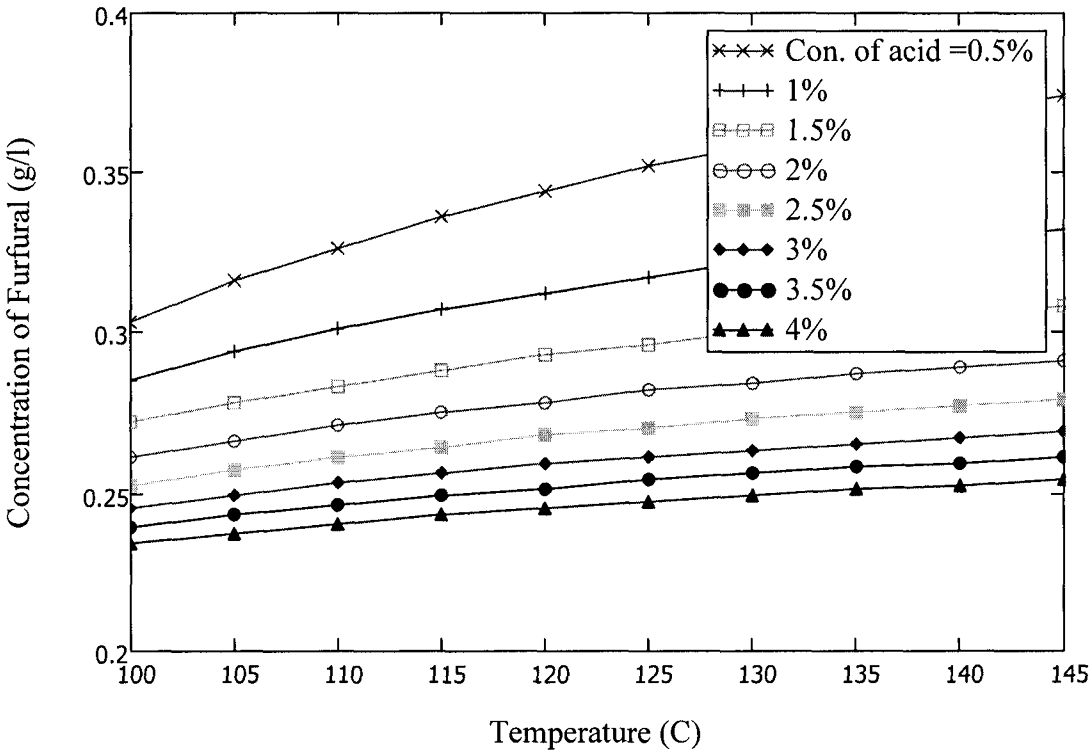

Figure A.4 Temperature of Reaction VS. Concentration of Furfural

Calculated Amount of $CaSO_4$ that will be generated in the liming process for different acid hydrolysis reaction condition (value for the acid concentration were varied and the amount of $CaSO_4$ were determinated. The calculation were based on 1 m^3 of Extract)

Concentration of acid applied $\text{Concentration} := (0.5\ \ 1\ \ 1.5\ \ 2\ \ 2.5\ \ 3\ \ 3.5\ \ 4)\%$

$$\text{Mass}_{CaSO4} := 1m^3 \cdot 20\frac{gm}{L}\cdot \text{Concentration}\cdot\frac{MW_{CaSO4}}{MW_{H2SO4}}$$

Gypsum will be generated are:

$$\text{Mass}_{CaSO4} = (0.14\ \ 0.28\ \ 0.42\ \ 0.56\ \ 0.69\ \ 0.83\ \ 0.97\ \ 1.11)\cdot kg$$

3 Hydrolysis of Acetate Group to Acetic Acid (HAC)

Acetate Group ---ka---> HAC

3.1 Find the reaction rate coefficient (ka)

$$\boxed{\ln(ka) = aa + na\ln(C) - \frac{Eaa}{R\cdot T}}$$

(C) is the concentration of sulfuric acid
(T) is reaction temperature (K)

Ka is known from Garrote Work. The Value of aa, na and Eaa are:

$\boxed{aa := 26.80}$ $\boxed{na := 1.18}$ $\boxed{Eaa := 73.37}$

(A.10)

$$\boxed{\ln(ka) = 26.80 + 1.18\ln\left(\frac{Con}{\frac{mole}{L}}\right) - \frac{73.37\cdot\frac{KJ}{mole}}{8.314\cdot\frac{J}{mole\cdot K}\cdot Temp}}$$

3.2 Input the desired hydrolysis condition and calculated how the concentration of acetic acid changes with the reaction time

Iniatial value of Acetate group	$AG_0 := 10.437\,\frac{gm}{L}$
Iniatial value of Acetic acid	$AcH_0 := 0\,\frac{gm}{L}$
Maximum value of acetic acid	$AcH_{max} := AG_0 = 10.44\,\frac{gm}{L}$
Temperature of Hydrolysis	$T := 115\,°C$
Concentration of sulfuric acid (wt/wt)	
Reaction time	$Time := 1hr$

$$ka(C) := \exp\left(aa + na\cdot\ln\left(\frac{\frac{C\cdot\rho}{MW_{H2SO4}}}{\frac{mole}{L}}\right) - \frac{Eaa\cdot\frac{KJ}{mole}}{8.314\cdot\frac{J}{mole\cdot K}\cdot T}\right)\cdot hr^{-1}$$

$$AG(C,t) := AG_0\cdot\exp(-ka(C)\,hr\cdot t)$$

$$AcH(C,t) := AcH_0 + \left(AcH_{max} - AcH_0\right)\cdot(1 - \exp(-ka(C)\cdot hr\,t))$$

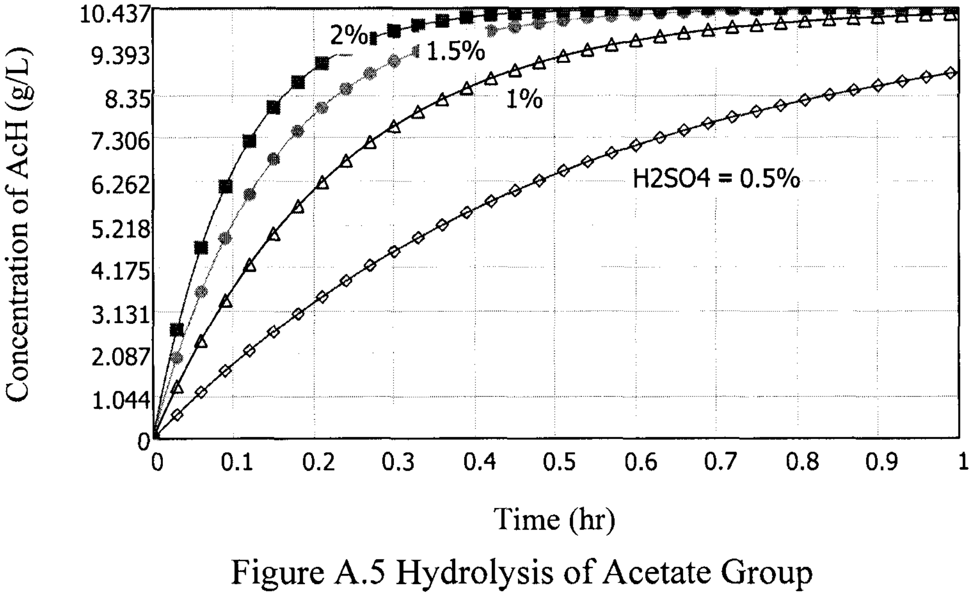

Figure A.5 Hydrolysis of Acetate Group

The maximum concentration of acetic acid at any given acid concentration and reaction temperature

Guess $tt2 := 1$

Given $\frac{d}{dtt2}AcH(2\%, tt2) = 0$

$Find(tt2) = 2.4$

$$\boxed{AcH(1.5\%, tt2) = 10.43\cdot\frac{gm}{L}}$$

Appendix B

Aspen Model of Liquid – Liquid Extraction Process

The objective of the liquid - liquid extraction process is to recovery acetic acid and furfural which are generated in the acid hydrolysis process. This is a variant of the Lenzing process [Lenzing Technology, 2006]. Acetic acid is also generated in glucuronic acid fermentation and must be recovered. Ethyl acetate was chosen as the solvent for the process. The boiling points of the various chemicals in the process are listed in Table 3.6. An Aspen Plus model of liquid- liquid extraction is illustrated in Figure B.1 and was used to perform a heat and material balance for the process. The unit operations comprising the process are:

- Three mixers designated (A,B and C), used for mixing solvent (Mixer A), streams high in acetic acid (Mixer B) and Mixer (C) used for mixing waste streams,
- Two liquid/liquid extraction columns, designated (F and E), used for the extraction of furfural and acetic acid,
- Solvent recovery column (G) used for separating the ethyl acetate solvent from acetic acid and furfural,
- Flash tank (H) for separating sodium sulfate from volatile acetic acid and furfural, and
- Acid column (I) for separating acetic acid from furfural.

Fresh ethyl acetate as the extraction solvent (Stream 1) is feed to process where it is mixed with recycle solvent (Stream 2) coming from the solvent recovery column (G). The mixed solvent is then sent to a splitter separator (D) where the mixed solvent is split into two streams, designated (4) and (5). Stream 5 coming from the separator/splitter (D) is high in ethyl acetate concentration and is sent to the main extraction column (F) where it is use to extract acetic acid and furfural from the component sugars coming from the liming and lignin filtration steps. Additional ethyl acetate in stream (4) coming from the splitter (D) goes to a second extraction column (E) for treatment of the bottoms product coming from the ethanol upgrading column. The primary extraction of acetic acid and furfural takes place in extraction tower (F) where the acetic acid and furfural are separated from sugar feed. Extraction column (E) is used to remove residual acetic acid from water. The acetic acid, furfural and ethyl acetate solvent leave in the extract (Stream 7) from extraction column (F) while residual sugars and water leave as the raffinate (Stream 18) off the bottom of the column. The raffinate leaving the liquid/liquid extraction column goes to the liming process and is very high in mixed sugars. The bottoms product from the ethanol upgrading column (stream 8) contains water and acetic acid. It is sent to extraction column (E) where it is extracted with recycle solvent (Stream 4) coming from the separator splitter (D). The extract stream (9) from extraction column (E) goes to a mixer (B) where it is mixed with extract (Stream 7) coming from the primary extraction vessel (F). After mixing the two extract streams (7 and 9), the mixed extract (Stream 11) is sent to solvent recovery column (G) where the ethyl acetate solvent is stripped out as the more volatile component (Stream 2) and sent back to mixer A. The bottoms product (Stream 12) from the solvent recovery column (G) is sent to flash tank (H) where the non-volatile sodium sulfate salts are removed as the bottoms product (Stream 14). The volatile component off the flash tank (Stream 13) is rich in acetic acid and furfural. Stream 13 is sent to the acid column (I) where acetic acid (Stream 15) is separated from the furfural (Stream 16) by distillation. The acetic acid (Stream 15) and furfural (Steam 16) would be sent to storage and then sold on the open market. The bottoms product stream (14) from the flash tank (H) is mixed with the raffinate from extraction vessel (E) in mixer (C). The mixture (Stream 17) is sent to the recovery boiler for recovery of sodium and sulfur.

The results of the simulation using the Aspen plus software are shown in Table B.1. The overall recovery efficiency for acetic acid was estimated to be approximately 90%.

$$Percent\ HAC\ Recovery = \frac{31.003\frac{kmole}{hr}}{\left(10.276\frac{kmole}{hr}+24.079\frac{kmoel}{hr}\right)} = 90\%\ .$$

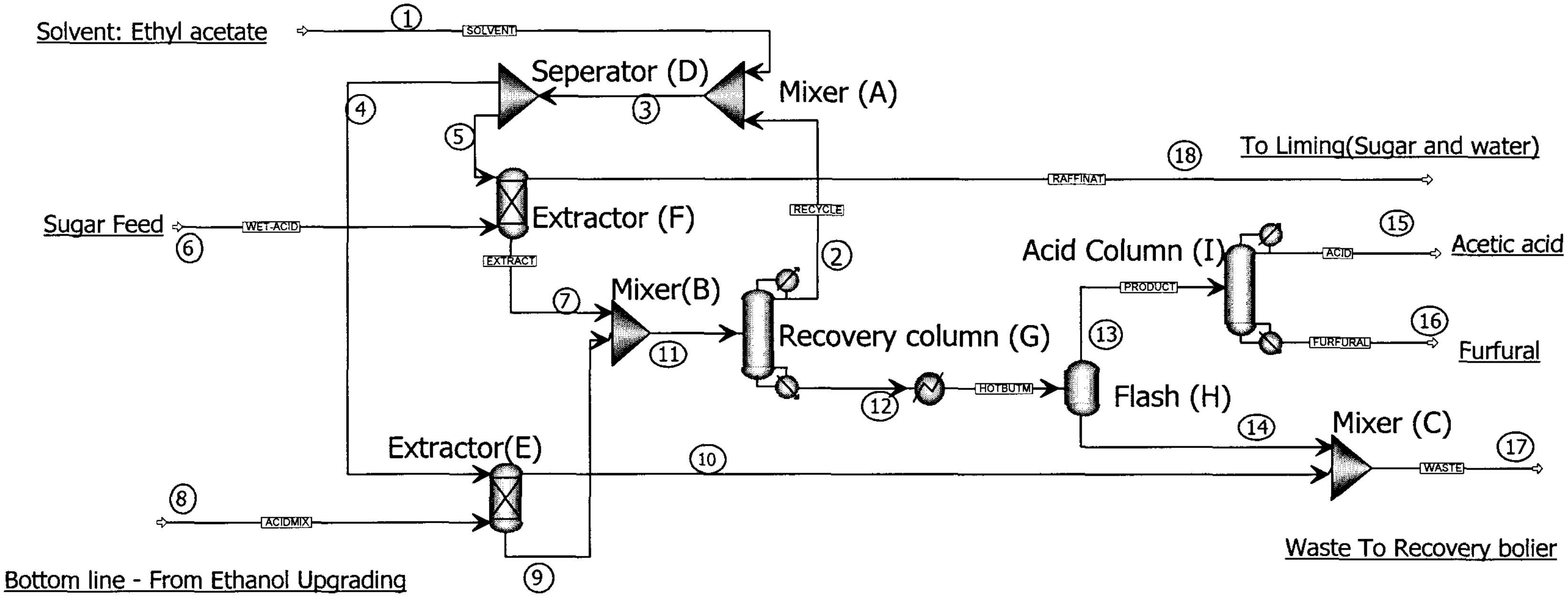

Figure B.1 Aspen Model of Liquid-Liquid Extraction Process

Table B.1 Simulation Result of Asepn Model of Liquid-Liquid Extraction Process

Acetci Acid Separation													
Stream ID		ACID	ACIDMIX	BOTTOM	EXTRACT	FURFURAL	HOTBUTM	PRODUCT	RAFFINAT	RECYCLE	SOLVENT	WASTE	WET-ACID
Temperature	C	97.7	100.0	109.7	101.5	156.9	662.2	305.3	101.0	59.9	20.0	101.2	100.0
Pressure	bar	1.000	10.000	1.000	10.000	1.000	0.500	1.000	10.000	1.000	10.000	1.000	10.000
Vapor Frac		0.000	0.000	0.000	0.000	0.000	0.700	1.000	0.000	0.000	0.000	0.001	0.000
Mole Flow	kmol/hr	41.336	6220.296	75.925	119.867	0.423	75.925	41.759	6852.264	88.860	10.000	6258.974	6922.701
Mass Flow	kg/hr	2737.368	112492.334	7125.612	8817.636	41.435	7125.612	2778.803	128207.120	4862.448	881.063	116540.433	134153.000
Volume Flow	cum/hr	3.114	117.357	10.618	12.466	0.040	8254.854	1995.694	132.181	5.582	0.973	283.322	141.329
Enthalpy	MMkcal/hr	-4.607	-416.680	-10.576	-13.954	-0.020	-8.532	-4.019	-457.620	-8.152	-1.149	-422.361	-466.923
Mole Flow	kmol/hr												
ACETI-01		31.003	10.276	31.519	22.922	0.031	31.519	31.035	1.680	1.046		1.640	24.079
WATER		0.496	6210.020	0.502	35.039	trace	0.502	0.496	6821.612	41.908		6223.609	6835.697
NA2CO3		trace		12.888	12.888	0.001	12.888	0.001	trace	trace		12.887	12.888
NA2SO4		trace		20.677	20.677	0.001	20.677	0.001	trace	trace		20.676	20.677
FURFURAL		< 0.001		0.385	0.385	0.369	0.385	0.369	< 0.001	< 0.001		0.015	0.385
ETHYL-01		9.835		9.881	27.883	trace	9.881	9.835	0.070	45.906	10.000	0.094	
DEXTR-01		trace		0.073	0.073	0.022	0.073	0.022	28.901	trace		0.052	28.975

BIOGRAPHY OF THE AUTHOR

Haibo Mao was born in Hunan, China on April 30, 1980. He graduated from high school in 1998 and enrolled in Nanjing University of Science and Technology where he received his Bachelor of Science in Chemical Engineering in 2002 and a Master of Science in Electronic Engineering in 2004. He is married to Jie Luo who also is a graduate student at the University of Maine.

After receiving his degree, Haibo hopes to work in Chemical Engineering field as an engineer. Haibo is a candidate for the Master of Science degree in Chemical Engineering from The University of Maine in December, 2007.