Process for producing acetic acid in hardwood kraft pulp mills

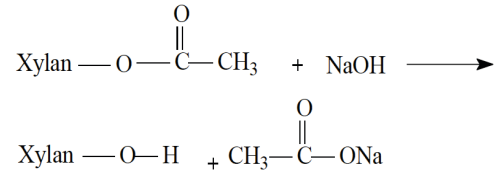
RAVIKANT PATIL, JOSEPH GENCO, HEMANT PENDSE, AND ADRIAAN VAN HEININGEN

ABSTRACT: To determine the economic feasibility of producing acetic acid from commercial hardwood chips in kraft pulp mills, laboratory experiments were conducted to obtain sufficient data to perform a preliminary economic analysis for a proposed acetic acid recovery process. The acetyl groups in northeast hardwood were hydrolyzed from the xylan polymers in the wood to obtain sodium acetate. The extraction experiments were performed by using 4%–6% sodium hydroxide at low temperature (50°C–80°C). Sodium acetate from the extract was concentrated and then converted into acetic acid and sodium hydroxide by salt splitting using bipolar membrane electrodialysis (BPMED). Flow diagrams were prepared and cost estimates made for the capital and operating costs for the proposed acetic acid recovery process. The discounted cash flow rate of return on investment was estimated for pulp mills in the range of 1000–2000 tons/day. A preliminary economic analysis showed that the discounted cash flow rate of return on investment is primarily a function of (1) the plant size, (2) the selling price of acetic acid, and (3) the content of acetyl groups present in wood species. The income for the process and thus the rate of return on investment increases with increasing acetyl content in the wood and selling price of the acetic acid. When food grade acetic acid is produced, for example, the rate of return varies between 9% and 16% depending upon the size of the pulp mill, assuming the wood contains 3.5% acetyl groups on a dry basis and the selling price of acetic acid is US$900/ton.

Application: A process to recover acetic acid or acetate salt as a byproduct of kraft pulp mills will be useful to scientists and engineers who are developing the biorefinery concept.

Technical grade acetic acid is widely used in the manufacture of vinyl acetate monomer; polyethylene terephthalate; and a host of other industrial chemicals including ethyl and butyl acetate esters, monochloroacetic acid, ketene and diketene derivatives, pharmaceuticals, and dyestuffs. The worldwide market for technical grade acetic acid was about 11.9 million metric tons in 2012 and is expected to grow to 15 million metric tons by 2022 [1]. The global market for food grade acetic acid and other organic acids (citric, lactic, and malic acids) grows at about 7% annually. The market for organic acids for use in foodstuffs is expected to reach US$5.2 billion by 2018 [2]. Paper companies can increase their revenue by producing acetic acid in addition to conventional pulp and paper products. Because the market for acetic acid is large and growing, production of acetic acid at kraft mills would be small relative to the total market and would not be disruptive.

Hardwoods contain approximately 3%–4% acetyl (CH_3CO-) groups on a dry weight basis. The acetyl groups are located in hemicelluloses, primarily the glucuronoxylan polymer [3]. In a conventional hardwood kraft pulp mill, the acetyl groups end up as sodium acetate in the black liquor and are burned for recovery of the sodium content and energy in the recovery boiler. Recent work by Patil [4] has shown that acetyl groups in wood hemicelluloses can be readily hydrolyzed by using dilute alkali at low temperature (50°C) before the pulping process to produce an aqueous solution containing approximately 15 g/L of sodium acetate [5], as in Eq. (1):



(1)

The results of semi-batch feed and bleed mode experiments performed using model sodium acetate solution have shown that up to 170 g/L of acetic acid and 30 g/L of sodium hydroxide can readily be produced using bipolar membrane electrodialysis (BPMED) [6]. Although higher concentrations of sodium hydroxide can be produced using BPMED, 30 g/L concentration of sodium hydroxide is an appropriate target for caustic recycle back to the extraction step for the deacetylation reaction to occur. The feed and bleed mode experiments also showed that the efficiency of the BPMED process can be improved if the sodium acetate in the raw wood extract and the accompanying chip wash liquid were concentrated to about 85 g/L.

Acetic acid is an attractive chemical for recovery at kraft mills for the following reasons. First, a significantly higher selling price for acetic acid can be achieved if acetic acid is

concentrated to about 99% by weight or converted into food grade reagent. A liquid-liquid extraction plant to produce food grade acetic acid from an effluent stream at a sulfite pulp mill is operated by A.G. Lenzing in Austria [7]. Second, depending upon the amount of sodium acetate removed from the wood, the use of BPMED allows recovery of most of the sodium hydroxide used in the extraction process at little additional cost. It has been shown that up to 90% of the acetyl groups present in the raw wood can be recovered by washing the extracted chips before adding effective alkali (EA) and completing the kraft pulping process. Finally, the proposed process can be fully integrated into an existing kraft mill. It has been shown that pulp obtained from the two-stage process has the same yield and physical properties as conventional kraft hardwood pulps provided white liquor is used in both the extraction and pulping stages [8].

The objectives of our work were to (1) demonstrate splitting of sodium acetate from hardwood caustic extract using BPMED and (2) present the results of a preliminary economic analysis for production of acetic acid in a two-stage kraft pulping process. In the present study, acetyl groups were extracted in the form of sodium acetate before pulping and subsequently converted into acetic acid and sodium hydroxide using BPMED. The preliminary economic analysis was performed using the data from the laboratory study.

BACKGROUND

Retsina and coworkers evaporated the acetic acid in wood hydrolysate and neutralized the condensate to form acetate salts that were subsequently separated using reverse osmosis [9]. Tertiary amine-type ion exchange resin was evaluated for separating acetic acid from activated charcoal–treated prehydrolysis liquor in kraft pulp mills [10]. The results showed that about 66%–84% of acetic acid could be recovered using this method. Reactive extraction using trioctylamine/octanol was also evaluated for separating acetic acid from kraft prehydrolysis liquor [11]. About 10%–15% acetic acid solution was produced when the ratio of masses of organic to aqueous phase was 40 and an equimolar amount of caustic was used to regenerate the solvent.

Kassotis and coworkers describe converting 6% solution of sodium acetate into 35% acetic acid and about 8% sodium hydroxide using a three-compartment BPMED cell at a current density of 109 mA/cm^2 [12]. In another laboratory-scale study using a three-compartment cell, 4%–12% solutions of sodium acetate were converted into 8%–12% acetic acid solution [13]. The membranes used in this study were synthesized using ion exchange resins. Eurodia Industry, Germany, commissioned a two-compartment pilot-scale BPMED unit that converted a byproduct stream of 22% sodium acetate into 18% acetic acid and 6% sodium hydroxide. The current efficiency was optimum and the payback period was less than two years [14]. Yu and coworkers used a two-compartment BPMED system to concentrate a dilute 0.2% solution of acetic acid in wastewater to as much as 70% [15].

BPMED technology has been previously applied to kraft mills. To overcome the high capital cost of the kraft recovery system for small pulp mills, BPMED was studied for recovering organic and inorganic salts from spent liquor [16]. A similar process has been developed for use in soda-anthraquinone pulping where lignin in the spent liquor was precipitated by the addition of acid; sugars were separated using ultrafiltration and sodium acetate was crystallized and converted into acetic acid and caustic using BPMED [17]. BPMED has been used to selectively remove chloride ion from the kraft recovery cycle to prevent corrosion problems [18]. Paleologou and Davis applied a BPMED process to split sodium sulfate originating from the chlorine dioxide generation system into caustic and sulfuric acid for internal use in the mill [19–21]. An economic analysis of this process showed the rate of return on investment was 24.6% when economic credit was given for both the sulfuric acid and caustic [22].

Process description

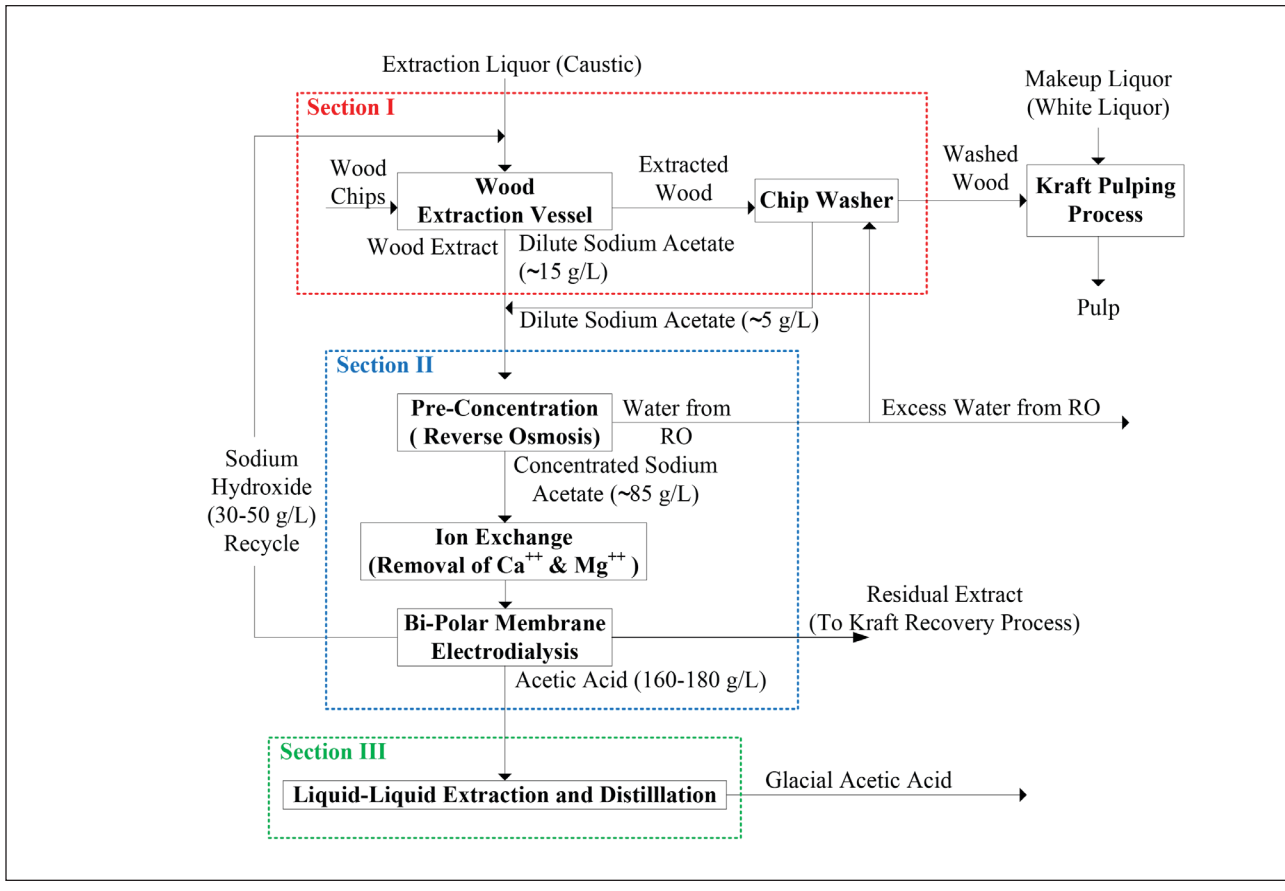
Figure 1 shows a block flow diagram of the overall process that consists of three sections; extraction and chip washing (section I), preconcentration and BPMED (section II), and product recovery by liquid/liquid extraction and distillation (section III). A detailed description of the important unit processes follows.

Sodium acetate extraction

Wood chips are presteamed in a steaming vessel for 15 min and conveyed to the extraction vessel where they are extracted using dilute sodium hydroxide solution for 2 h at low temperature. The extraction step is conducted at 50°C (6% EA) or 80°C (4% EA) at a liquid-to-wood (L/W) ratio of 3.5. The extraction can be performed in an atmospheric vessel because the extraction temperature is below 100°C. The extraction liquor is then drained from the partially macerated wood chips following the extraction step and the extracted wood chips are washed using warm recycled water in a chip washer. The chips are washed with sufficient water to remove approximately 85%–90% of the sodium acetate that was formed in the deacetylation reaction; the dilution factor is about 1. The dilute extract is sent for processing into acetic acid and caustic while the partially macerated wood chips are sent to the kraft digester for processing into brownstock pulp.

Kraft pulping

In the second stage of the kraft pulping process, the white liquor charge would be adjusted to maintain the pulp yield and properties equal to those in a conventional one-stage kraft pulping process. For pulping mixed northeast hardwoods, for example, the total alkali applied in the two-stage pulping process would be 14.9% EA white liquor (on a sodium oxide basis) at a L/W ratio of 3.5. The top temperature would be set at 160°C to give an H-factor of 780 h. The difference is simply that the alkali would be split between the two stages. For example, because 4% or 6% EA (sodium hydroxide) was applied in the



1. Modified kraft pulp mill for the production of acetic acid using bipolar membrane electrodialysis (BPMED).

extraction step, 8.9%–10.9% EA would be applied in the second stage. Thus, the total alkali applied would be the same in the two-stage process that would equal that in a conventional one-stage process. Using this strategy, Patil [8] has shown that brownstock pulp with equivalent properties can be obtained.

Converting sodium acetate into acetic acid and caustic

The combined drained extract and wash liquor are preconcentrated using reverse osmosis. The concentrated sodium acetate solution is then passed through an ion exchange column to remove multivalent ions. The resultant solution is then processed in the BPMED cells to produce acetic acid and sodium hydroxide, which is recycled back to the extraction process. The concentrated acetic acid is sent to liquid-liquid extraction and a series of distillation columns to produce glacial acetic acid. The concentrated acetic acid is converted into food grade acetic acid to achieve a higher selling price [7].

Purification of acetic acid

Acetic acid can be recovered using a combination of liquid-liquid extraction and fractional distillation [23]. A variety of solvents can be used for extracting acetic acid from water; notable among them are ethyl acetate, isopropyl acetate, and methyl tertiary butyl ether (MTBE) [24]. Reactive extraction using trioctylamine/octanol has also been proposed [11]. Special techniques are sometimes employed because acetic acid forms an azeotrope with water. Commercial acetic acid separation processes consist of (1) an extraction tower for removing acetic acid from the water phase, (2) a rectification tower for purification of the acetic acid and for recovery of the extraction agent, and (3) a water-stripping tower for removal of water and reclaiming residual solvent. Depending on the number of equilibrium stages in the extraction tower, the residual concentrations of acetic acid can be reduced to between 0.1% and 0.5 wt% acetic acid in the extraction tower. Because the aqueous phase leaving the extraction tower is simultaneously saturated with the extraction agent, the residual solvent is recovered in the downstream stripping tower, which can be operated either as a conventional distillation tower or as a steam stripper by the injection of live steam.

Bipolar membrane electrodialysis

Sodium acetate can be readily split into acetic acid and sodium hydroxide by application of an electrical field in a BPMED cell (Eq. [2]):

$$NaAc + H_2O + Energy_{Electrical} \rightarrow HAc + NaOH \quad (2)$$

Detailed information regarding the basic principles and general process guidelines for BPMED are available in the lit-

erature [25-27]. The current efficiency (η) for splitting or transferring a given mass of sodium acetate (W) is the ratio of the theoretical ($C_{Theoretical}$) to the actual (C_{Actual}) charge required to transform the sodium acetate into the corresponding acetic acid and sodium hydroxide (Eq. [3]):

$$\eta = \frac{C_{Theoretical}}{C_{Actual}} = \frac{W \cdot F}{E \cdot N \cdot C_{Actual}} \cdot 100 \quad (3)$$

where E = equivalent or molecular weight of sodium acetate (gm/equivalent), N = number of cell pairs, and F = Faraday's constant (96,485 coulombs/equivalent).

The actual charge (C_{Actual}) is simply the integral of the current (i) over the time that the voltage is applied across the cell pairs (Eq. [4]):

$$C_{Actual} = \int_0^t i \cdot dt \quad (4)$$

where i = current (A) and t = time (s).

The electric energy (E_{Elec}) is calculated by integrating the product of voltage (V) and current (i) with respect to time (t). E_{elec} is the sum of the energies required for transferring ions from one compartment to another and decomposing water molecules in the bipolar membranes (Eq. [5]):

$$E_{Elec} = \int_0^t V \cdot i \cdot dt \quad (5)$$

The degree to which a desired ion is selectively removed from the feed solution is a measure of the efficiency of the electrodialysis system. Conventional selectivity (S) is defined as the ratio of molar flow rate of the desired product (acetic acid) to that of an undesired product. However, conventional selectivity is not useful for characterizing efficiency when a reaction system leads to the formation of more than one undesired product. In such cases, the relative number of moles of each species transported (or split) is more useful. It is defined as the ratio of the number of moles of a given salt transported across the membranes to the total moles of all salts transported in the same direction (Eq. [6]):

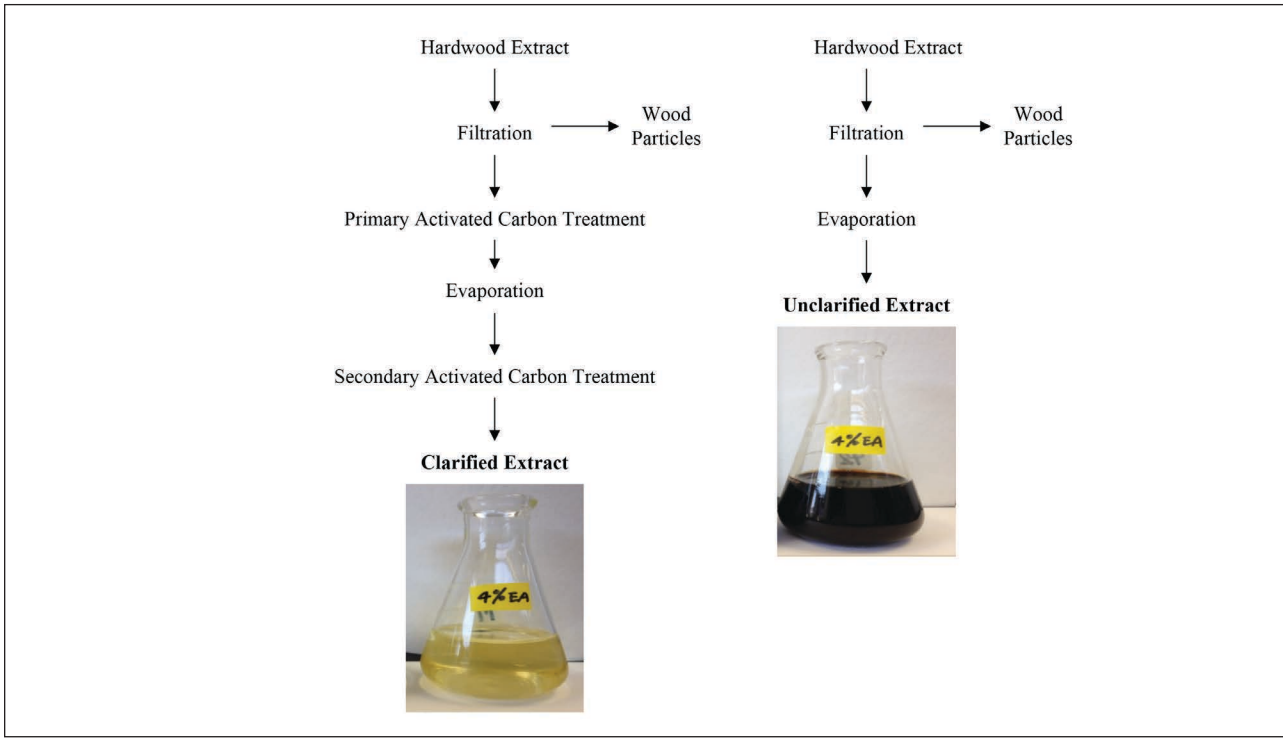
$$RM_i = \frac{V_F(0) \cdot C_{F,i}(0) - V_F(t) \cdot C_{F,i}(t)}{V_F(0) \cdot C_F(0) - V_F(t) \cdot C_F(t)} \quad (6)$$

where RM_i = relative number of moles of a given salt (sodium acetate) transported across membranes or split, V_F = volume of feed solution (m^3), $C_{F,i}$ = concentration of an ion in feed solution ($mol \cdot m^{-3}$) at time 0 and (t), and C_F = total concentration of all ions present in feed solution ($mol \cdot m^{-3}$) at time 0 and (t).

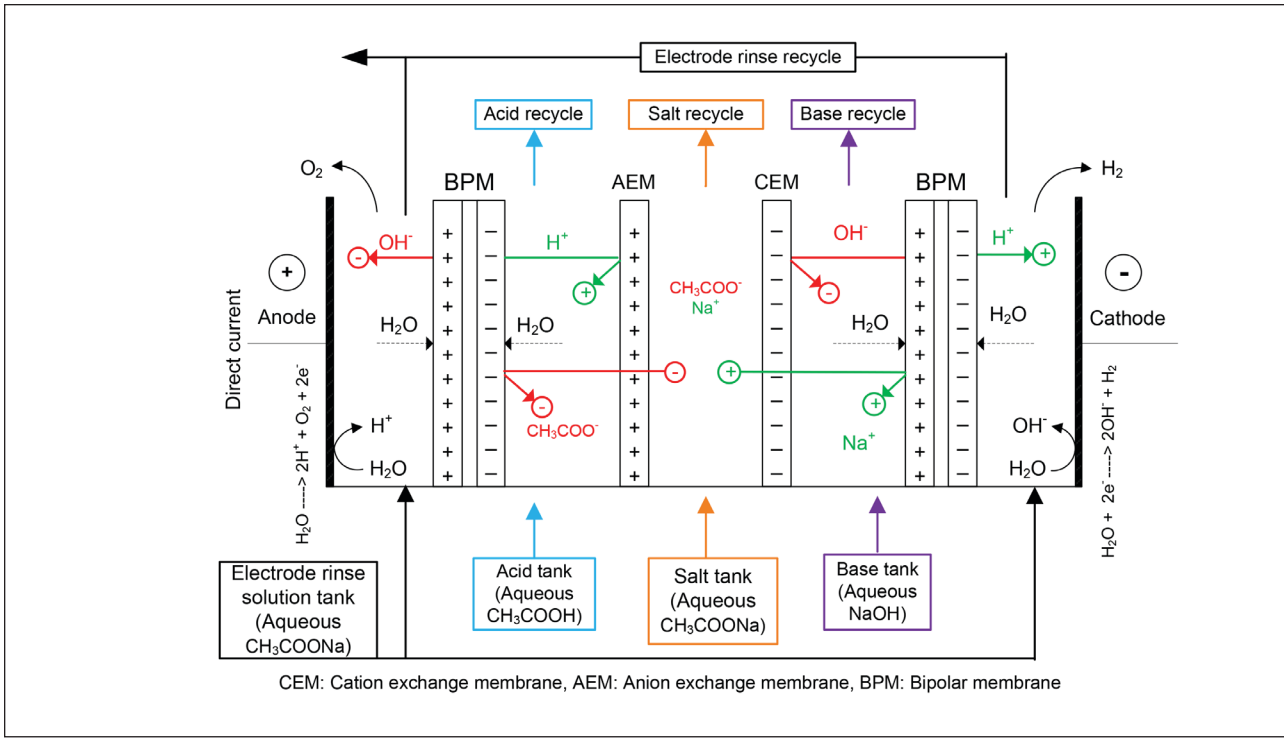
EXPERIMENTAL METHODS

Pretreatment of hardwood extract

Figure 2 illustrates the procedure used to prepare the pretreated hardwood extracts. Although reverse osmosis is the proposed method for the preconcentration of wood extract, evaporation was used in the present study to simplify the laboratory work. The concentration of sodium acetate in the pretreated extracts following evaporation was maintained at



2. Pretreatment of hardwood extract before use in the electrodialysis.



3. Arrangement of ion-exchange membranes in the BPMED cell.

47–57 g/L so that these solutions could be processed at a middle-level current density of about 40 mA/cm². The use of clarified solution allows the exclusive understanding of the effect of different salts present in the extract on the splitting of sodium acetate and protects ion exchange membranes from possible fouling due to the lignin. However, because the activated charcoal is not easily regenerated, such type of pretreatment is expensive and thus will adversely affect the economic viability of the process. Therefore, additional experiments were performed to demonstrate the processing of unclarified extract in BPMED. For practical applications, the effect of lignin on ion exchange membranes can be determined by performing long-term stability studies.

Detailed information about the equipment used in this study and the experimental procedure is given by Patil [8].

Experimental apparatus

The experimental BPMED cell was manufactured by PCCell/PCA GmbH, Heusweiler, Germany. **Figure 3** shows the arrangement of membranes for the unit cell pair of a three-compartment BPMED cell. The experimental cell consisted of five cell pairs of cation, anion exchange, and bi-polar membranes (Neosepta CMB/AHA/BP-1, Tokuyama America; Arlington Heights, IL, USA). The surface area of each membrane was 64 cm². Spacers were placed between adjacent membranes, which allowed the flow of solutions between the membranes. The maximum allowed voltage drop for the BPMED cell used in this study was 16.4 V. The equipment also consisted of a heat exchanger, which maintained the temperatures of all solutions below 25°C.

Experimental procedure

The BPMED process was operated at constant current mode. All experiments were conducted in the batch recycle mode. The feed solution was recirculated at a flow rate of about 550 mL/min, which corresponded to a superficial velocity of 5.1 cm/s. It is necessary to maintain the applied current density below its limiting value to avoid the loss of electric energy resulting from the decomposition of water at overlimiting currents. The limiting current density data for use with the equipment has been reported previously [6]. In the BPMED experiments, the initial liquid placed in the acid-receiving vessel was one liter of 17 g/L sodium acetate. The initial liquid placed in the base-receiving vessel and the liquid used as the electrode rinse solution consisted of one liter each of 6 g/L and 40 g/L of sodium hydroxide, respectively. Approximately the same amounts of electric energy and charge were applied in the BPMED experiments using pretreated extracts.

Small quantities of sodium formate, sodium lactate, and sodium glycolate would be expected to be present in the extract under alkaline conditions. The formate, lactate, and glycolate ions are byproducts of the extraction process resulting from alkaline peeling and stopping reactions that occur simultaneously with the alkaline cleavage of the acetyl groups from the xylan hemicellulose polymers [28]. The concentrations of sodium acetate, sodium formate, sodium lactate, and sodium glycolate were measured at the conclusion of each experiment following conversion to their corresponding acid forms using high performance liquid chromatography (HPLC). Thus, the total concentration of all acids present in the final acid solution was separately determined by titration with base. This inde-

Parameter	Value
Acetic acid selling price (reagent and food grade)	US$600–900/ton
Pulp mill size	500–2000 tons/day
Acetyl group content in wood	3%–4% (on dry basis)
Fractional recovery of acetic acid	90% (with chip washing)
Project life	10 years
Startup period	18 months
Operating factor	95%
Tax rate	35%
Working capital	5% of fixed capital investment
Depreciation	Modified accelerated cost recovery system
Financing	100% equity, no loan

I. Assumptions used in the economic analysis.

pendent check was thought necessary because HPLC measurements might not identify all the component acids present in the acid solution. Sodium hydroxide was analyzed by titrating a sample of synthetic extract with 0.1 N hydrochloric acid.

METHODOLOGY FOR PRELIMINARY ECONOMIC ANALYSIS

The economic analysis was performed by estimating the capital investment and operating cost using standard methods described by Turton and coworkers [29]. The viability of the project was determined by estimating the discounted cash flow rate of return and payback period for the process. **Table I** shows the major assumptions made in this analysis. It was also assumed that mills would have sufficient utilities (waste treatment and steam generating capacity) to accommodate the new acetic acid process and no new capital would be incurred for upgrading these facilities. Only costs associated with tying the new process into the mill utility system were included in the analysis. The size of the kraft pulp mill was considered a parameter in the economic analysis. The analysis was performed for four plant sizes: a small plant (500 tons/day), a medium size plant (1000 tons/day), and two large (1500 and 2000 tons/day) kraft pulp mills.

RESULTS AND DISCUSSION

Composition of extract

Table II summarizes the composition and volumes of the pretreated (feed) solutions used in the BPMED experiments, as well as the concentration of the raw hardwood extract. A variety of sodium compounds are present in the extract in addition to sodium acetate, even at the low temperature used in the extraction experiments (80°C). Notably among these lesser compounds found in the raw extract are sodium formate, sodium lactate, and sodium glycolate, as well as lignin and component sugars. Because sodium formate and sodium lactate were also present in the extracts, it was expected that smaller quantities of formic and lactic acids would be present in the acid compartment in addition to the desired acetic acid product. For the extraction experiments conducted at 50°C, a similar concentration of sodium acetate was obtained, but lesser quantities of sodium formate, sodium lactate, and sodium glycolate were present in the extract [8].

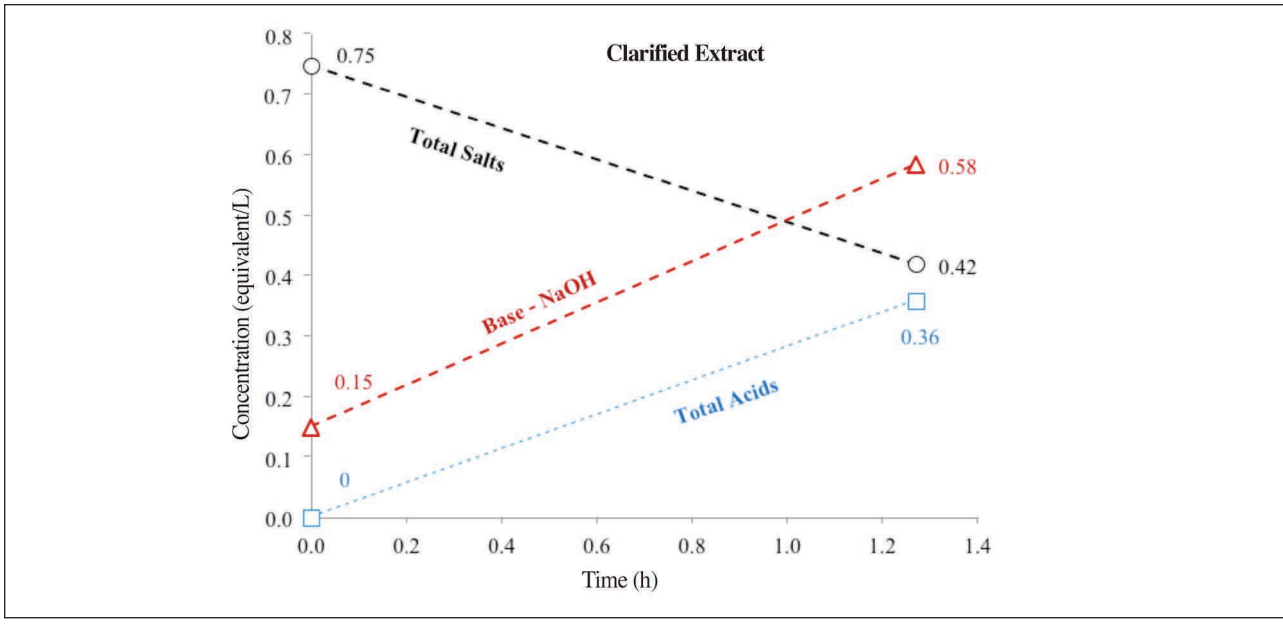
Salt splitting experiments using pretreated and concentrated extracts

Figures 4 and **5** show the variation in the concentrations of the salt feed solution and the acid and base product solutions for the BPMED experiments using the clarified and unclarified extracts, respectively. Only the initial and final concentration points were sampled and thus appear on the graphs. By comparing these figures, it can be seen that approximately the same amounts of salts were decomposed in both experiments. The total concentration of all acids present in the final acid solution from each experiment was about 0.36–0.38 equivalent/L. Similarly, the final base solutions contained about 0.56–0.58 equivalent/L of caustic.

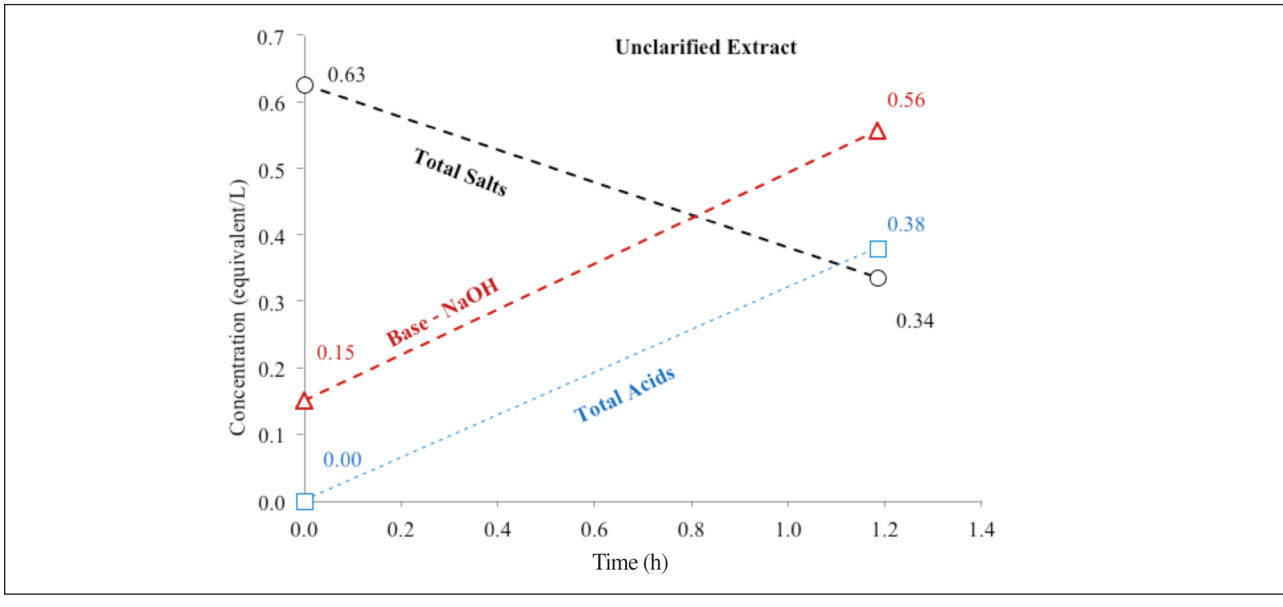
Tables III, **IV**, **V**, and **VI** summarize the composition data obtained in the BPMED experiments. Because both the clarified and unclarified feed solutions contained small amounts of sodium formate and sodium lactate, these salts were subsequently converted into the corresponding acids and sodium hydroxide in the BPMED electrochemical reactor. However, the total sugars and the lignin were predominately retained in the feed solutions and did not penetrate the membranes. The small amounts of sugars transferred from the salt to the acid and base solutions are thought to occur by diffusion because the component sugars are not charged. For the BPMED experiment performed using the clarified extract, the

Extract Type	Concentration, g/L						pH	Volume, L
	Sodium Acetate	Sodium Formate	Sodium Lactate	Sodium Glycolate	Total Lignin	Total Sugars		
Raw extract (dilute)	14.60	1.55	0.28	0.69	4.52	0.76	12.2	---
Concentrated unclarified extract	46.20	3.24	1.72	1.93	12.07	2.11	10.2	1.74
Concentrated clarified extract	56.50	3.28	1.18	1.09	0.62	0.25	10.5	1.64

II. Composition of pretreated hardwood extract (4% effective alkali [EA], 0% sulfidity, and 80°C; liquor-to-wood ratio [L/W] = 4).



4. Concentration profiles for the BPMED experiment performed using clarified extract.



5. Concentration profiles for the BPMED experiment performed using unclarified extract.

Concentrations, equivalents/L					Total Lignin, g/L	Total Sugars, g/L	pH	Volume, L
Solution	Sodium Acetate	Sodium Formate	Sodium Lactate	Sodium Hydroxide				
Initial salt	0.69	0.05	0.0105	0	0.62	0.25	10.5	1.64
Final salt	0.40	0.01	0.0060	0	0.48	0.23	11.5	1.54
Initial base	0	0	0	0.15	0	0	---	1.00
Final base	0.0012	0	0	0.58	0.0036	0.0040	---	1.11

III. Composition of salt and base solutions for the BPMED experiment performed using clarified extract (4% EA, 0% S, and 80°C; L/W = 4).

Solution	Concentrations, equivalents/L						Total Lignin, g/L	Total Sugars, g/L	Volume, L
	Sodium Acetate	Formic Acid	Lactic Acid	Acetic Acid	Total Acids, by HPLC*	Total Acids, by Titration			
Initial acid	0.21	0	0	0	0	0	0	0	1.00
Final acid	0.18	0.0450	0.0056	0.3075	0.3581	0.4040	0.26	0.043	1.16
Composition of Final Acid Solution, g/L									
	Formic Acid		Lactic Acid		Acetic Acid				
Final acid	2.1		0.5		18.5				
* HPLC = high performance liquid chromatography									

IV. Composition of acid solution for the BPMED experiment performed using clarified extract (4% EA, 0% S, and 80°C; L/W = 4).

Solution	Concentrations, equivalents/L				Total Lignin, g/L	Total Sugars, g/L	pH	Volume, L
	Sodium Acetate	Sodium Formate	Sodium Lactate	Sodium Hydroxide				
Initial salt	0.56	0.05	0.0154	0	12.07	2.11	10.2	1.74
Final salt	0.32	0.01	0.0078	0	11.65	2.11	10.8	1.67
Initial base	0	0	0	0.15	0	0	--	1.00
Final base	0.0021	0	0	0.56	0.0034	0.004	--	1.11

V. Composition of salt and base solutions for the BPMED experiment performed using unclarified extract (4% EA, 0% S, and 80°C; L/W = 4).

Solution	Concentrations, equivalents/L						Total Lignin, g/L	Total Sugars, g/L	Volume, L
	Sodium Acetate	Formic Acid	Lactic Acid	Acetic Acid	Total Acids, by HPLC*	Total Acids, by Titration			
Initial acid	0.21	0	0	0	0	0	0	0	1.00
Final acid	0.18	0.0537	0.0113	0.3150	0.3800	0.3860	0.24	0.003	1.16
Composition of Final Acid Solution, g/L									
	Formic Acid		Lactic Acid		Acetic Acid				
Final acid	2.5		1.0		18.9				
* HPLC = high performance liquid chromatography									

VI. Composition of acid solution for the BPMED experiment performed using unclarified extract (4% EA, 0% S, and 80°C; L/W = 4).

total acid concentration determined using titration was about 10% higher than the HPLC measurement whereas, for the experiment with the unclarified extract, both values were almost equal.

Table VII shows the current efficiencies, the specific electric energy, the selectivity, and the relative number of moles of each species split in the BPMED experiments performed using pretreated extracts with compositions of about 45 g/L of sodium acetate in the feed. The current efficiencies and specific energies for the experiments performed with the pretreated extracts were similar to those of the experiments performed using model sodium acetate solution. The relative number of moles of each species split also indicates the fraction of the total useful electric energy spent for splitting the given salt molecule. Because the model sodium acetate solution contained only sodium acetate along with water, all of the useful electric energy was spent for splitting only sodium acetate. The pretreated extract contained additional salts such

Parameters	Type of Feed Solution*		
	Synthetic Sodium Acetate Solution	Clarified Extract	Unclarified Extract
Current efficiency for total acids (per HPLC** data), %	76	68	76
Current efficiency for base, %	80	81	81
Specific electric energy, kJ/equivalent of acid formed	382	424	411
Relative number of moles of each species split, %			
Sodium acetate	100	87.4	84.3
Sodium formate	------	11.1	12.9
Sodium lactate	------	1.5	2.8
Selectivity, moles of each acid formed per unit mole of formic and lactic acids formed			
Acetic acid	------	5.87	6.83
Formic acid	------	1.00	1.00
Lactic acid	------	0.21	0.12

* The concentrations of the sodium salts in the feed solutions are summarized in Tables III and V.

** HPLC = high performance liquid chromatography.

VII. Summary of the BPMED experiments performed using pretreated extracts (4% EA, 0% S, and 80°C; L/W = 4).

as sodium formate, sodium lactate, and sodium glycolate, which were also split along with sodium acetate. Hence, about 13%–15% of the useful electric energy was lost in splitting these additional salts.

Selectivity values shown in Table VII were calculated using Eq. (6). Selectivity data show that about 5–6 moles of acetic acid were formed for every mole of undesired product.

These experiments suggest that BPMED can be used to obtain a clear solution of concentrated acetic acid together with smaller quantities of formic acid and lactic acid, provided that the presence of lignin in the feed-salt solution does not lead to appreciable fouling of the membranes over extended run times. The mass balances for the major components of the extracts, such as sodium acetate, sodium formate, and lignin, could be close to 90%–100% depending upon the species.

Results of economic analysis

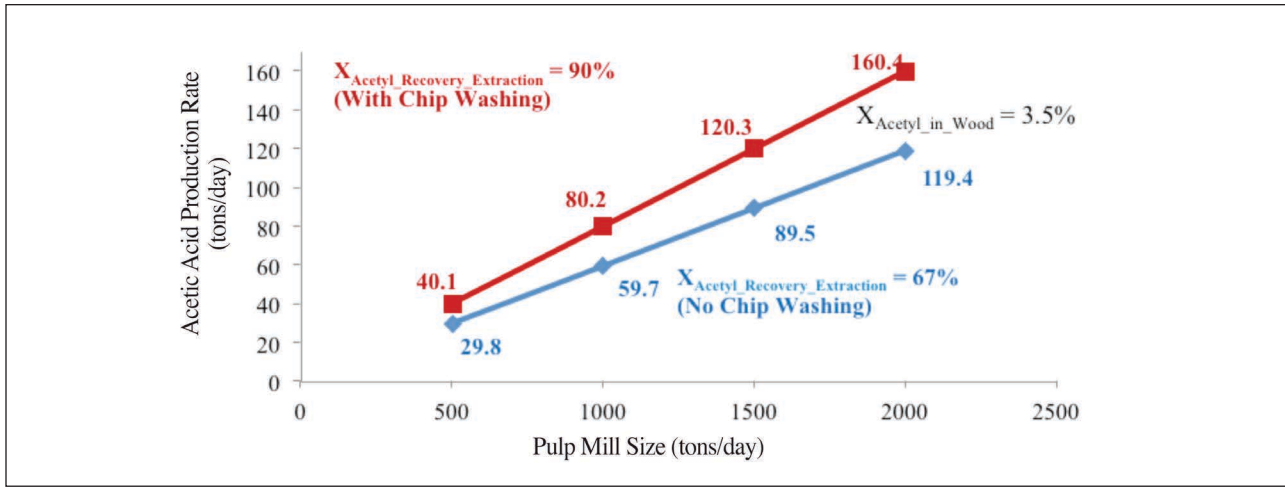
Acetic acid production rates

Figure 6 shows the rate of production of acetic acid as a function of pulp mill size. When chip washing is included in the process, about 40–160 tons/day of acetic acid can be produced depending upon the size of the pulp mill. If the extract is simply drained from the chips and no washing is performed, then only about 75% of these values can be obtained.

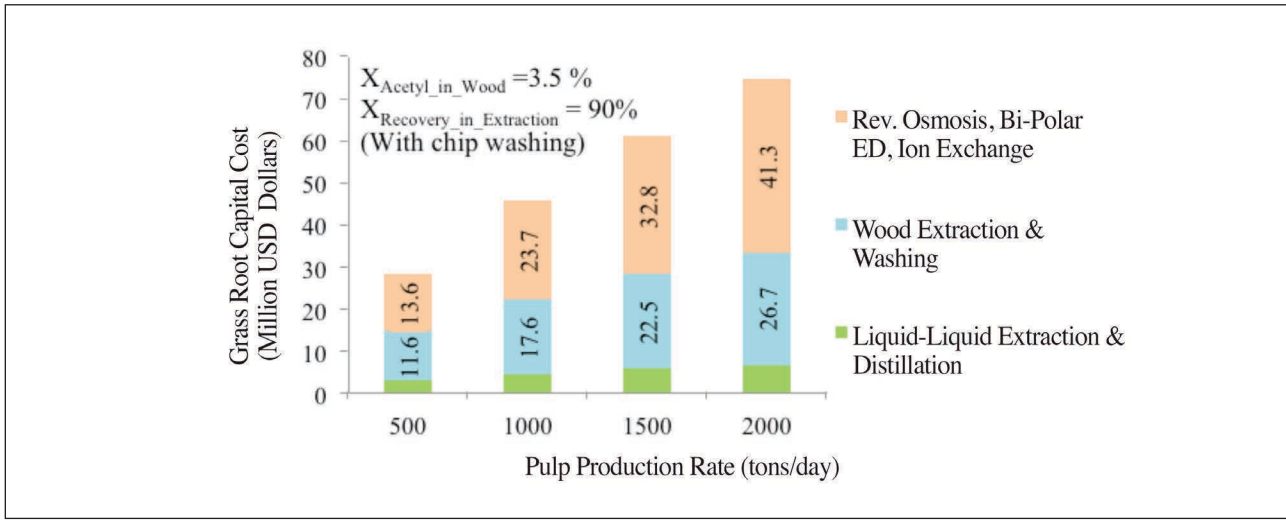
Estimation of capital cost

The capital cost for the process was estimated by using a combination of vendor estimates for the major pieces of equipment and estimates obtained from the CAPCOST cost estimating program for the less important equipment in the process [29]. CAPCOST presents a series of tables and graphs for estimating the capital cost of various pieces of process equipment in terms of what is called the bare module cost. The bare module cost program represents the sum of the direct and indirect costs associated with each piece of equipment. The direct costs involve the equipment FOB cost, as well as materials and labor for installation. The indirect costs involve freight charges, insurance, taxes, construction overhead, and contractor engineering expenses. The grassroots capital costs include the bare module cost plus all direct and indirect costs, contingency fees, and auxiliary cost for site development.

An estimate of the total bare module cost for the extraction vessel and chip washing system was obtained from Andritz Inc. (Alpharetta, GA, USA). The extraction reaction was assumed to be conducted in chip bins because the extraction temperature is below 100°C. To achieve a 2-h time, the chip flow was split between two chip bins operating in parallel. The total bare module cost for the reverse osmosis, ion exchange, and bipolar membrane electrodialysis equipment was obtained from the Ameridia Division of Eurodia Industrie (Somerset, NJ, USA). About half of the cost estimate from Ameridia is associated with the membranes used in BPMED cells. The cost estimates obtained from the vendors for both sections I and II were obtained for a 1000 tons/day and



6. Rate of production of acetic acid in kraft pulp mill using BPMED.



7. Grassroot capital cost as function of pulp mill size.

1500 tons/day pulp mill, respectively. These values were scaled to the other mill sizes using the power law scaling rule [29], as in Eq. (7):

$$C_A = C_A\left(\frac{P_A}{P_B}\right)^n \quad (7)$$

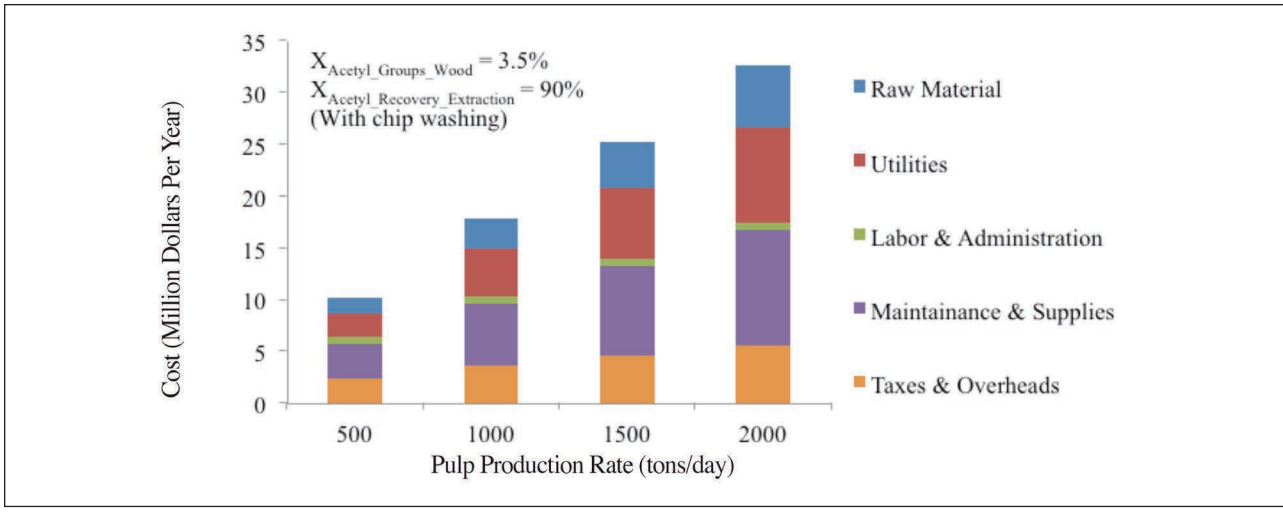
where P_A and P_B = size of pulp mills A and B; C_A and C_B = capital cost of process for mills A and B; and n = scaling cost exponent.

The scaling exponent (n) for section II (reverse osmosis, ion exchange, and BPMED) was taken to be 0.8 because the surface area of membranes increases linearly with increase in acetic acid production rate. The scaling factor for the remaining equipment in sections I and III of the process was scaled by using a scaling factor of 0.6. MTBE was used as the solvent in the liquid-liquid extraction process. The capital costs for the liquid-liquid extraction tower for removal of acetic acid from the solvent, the rectification tower for purification of acetic acid and solvent recovery, and the stripping tower for scalping residual solvent were obtained using CAPCOST.

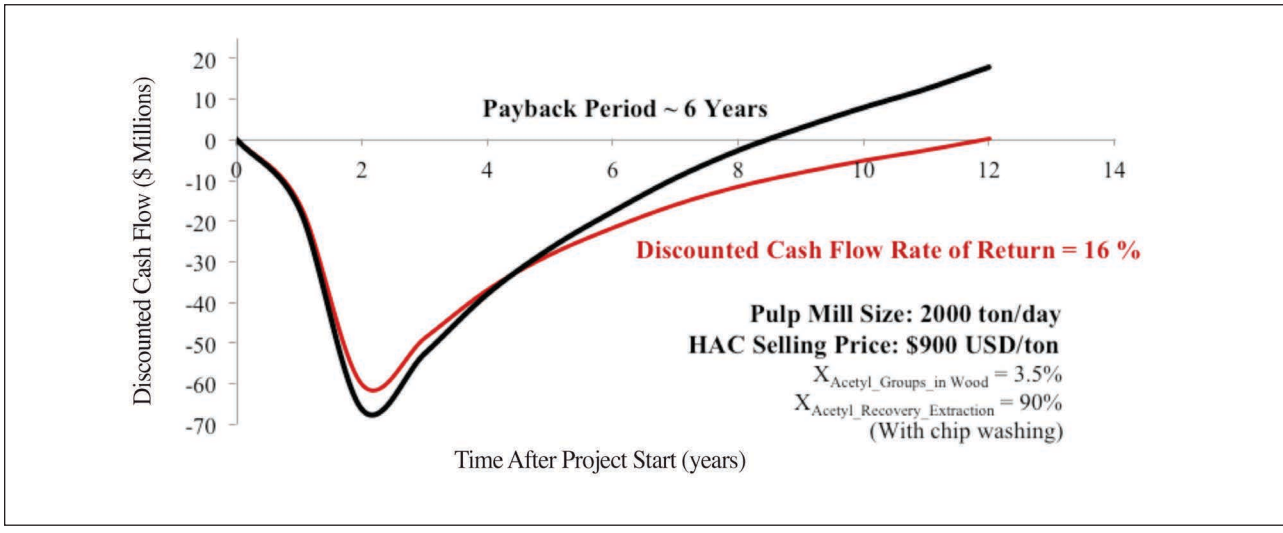
A contingency factor of 18% was applied to the total bare module cost (C_{BM}) when estimating the grassroot capital cost (C_{GR}) for the process. Another 20% of the total bare module cost was included for site development, auxiliary buildings, and utility connections. Thus, the grassroots cost for the process was assumed to be 38% greater than the total bare module or installed equipment cost (Eq. [8]):

$$C_{GR} = 1.38 \cdot \sum_{i=1}^{N} C_{BM,i} \quad (8)$$

Figure 7 shows the total grassroot capital cost for the acetic acid process. The project cost was estimated to be between US$28 million and US$75 million depending upon the size of the pulp mill (500–2000 tons/day).



8. Operating costs as a function of pulp mill size.



9. Example of discounted cash flow diagram (HAC = acetic acid).

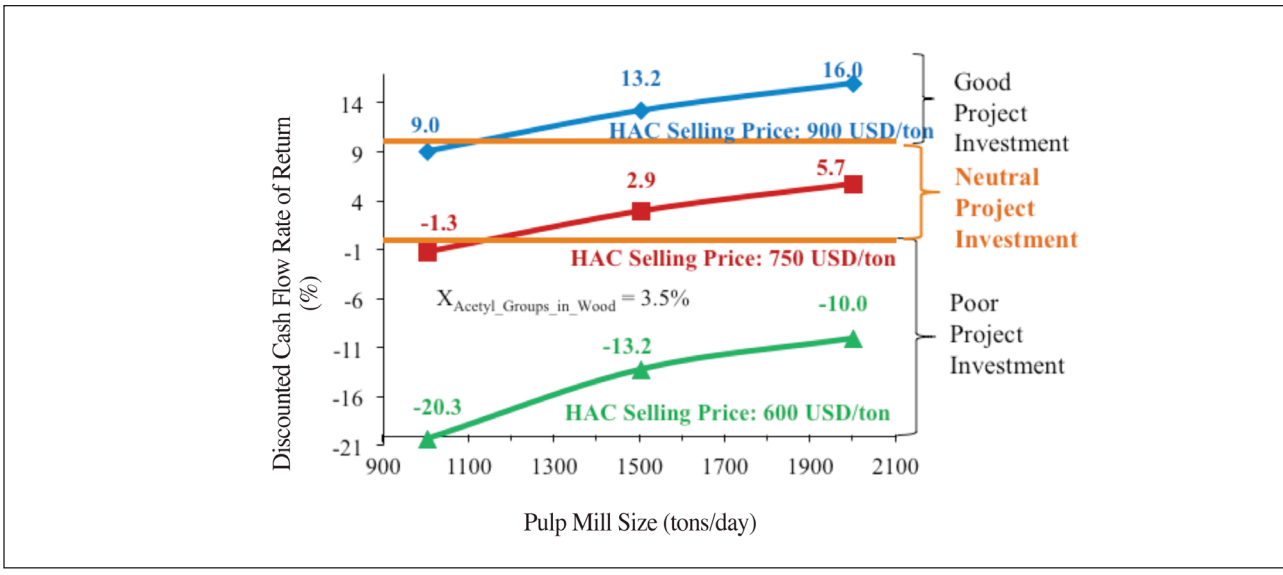
Estimation of operating costs

Because only 90% of the caustic used in the extraction process is recovered, the remaining 10% of the caustic requirements necessary for the extraction need to be purchased at a cost of US$530/ton. Because the BPMED process produces caustic, this is equivalent to extending the chemical recovery process. Utilities required by the process are water and electricity costs for the BPMED process. The number of operators required for this process was calculated by following the method described by Turton and coworkers [29]. It was assumed that this plant will have one shift supervisor, one laboratory technician, and 13 process operators. The major maintenance and supplies cost is due to the replacement of the membranes used in BPMED processes. The other maintenance costs, taxes, and overhead were calculated using the multiplication factors given by Turton and coworkers [29]. **Figure 8** shows the operating costs as a function of pulp mill size. The total operating cost varied from US$10 million to US$33 million per year, depending upon the pulp mill size.

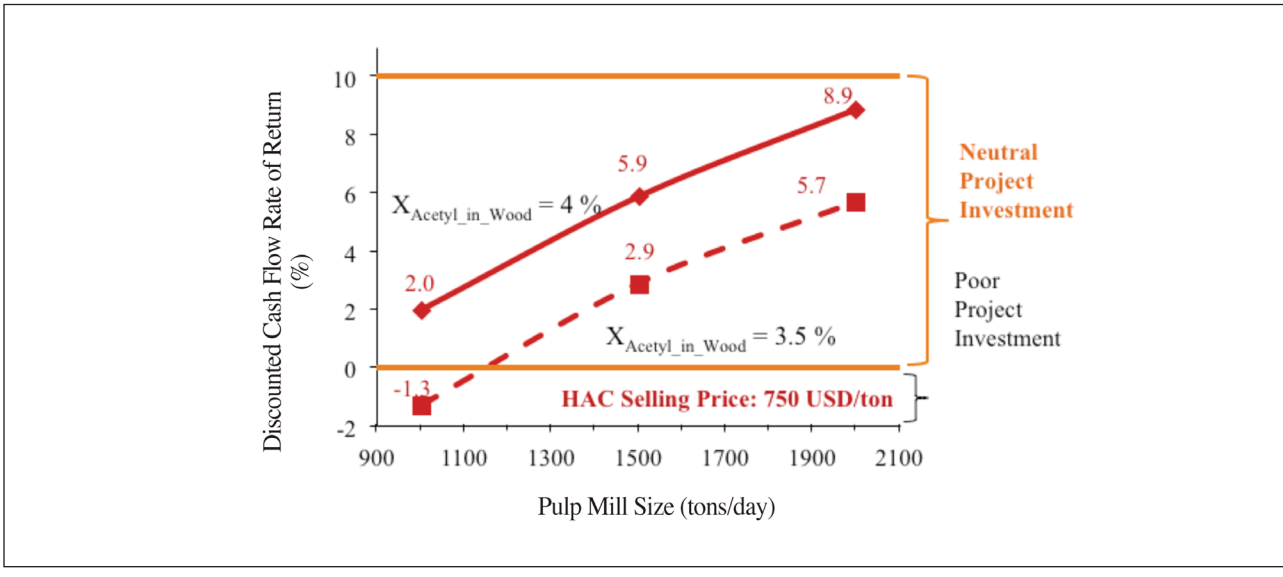
Discounted cash flow rate of return

In the discounted cash flow rate of return (DCFROR) method, the economic feasibility of a project is determined by comparing the calculated discounted rate of return with the cost of capital, which is considered to be the minimum acceptable rate of return. An example of the discounted cash flow diagram is illustrated in **Fig. 9** for the case of a 2000 tons/day pulp mill producing food grade acetic acid as a byproduct. In this analysis, the selling price for food grade acetic acid was assumed to be US$900/ton, and the rate of return on investment was estimated to be 16%. The payback period was estimated to be 6 years. This case was one of the best evaluated because of the large plant size and high selling price. **Figure 10** summarizes the results of the economic analysis for all of the cases evaluated.

As the pulp mill size increases, DCFROR increases because additional product is produced and the operating cost per unit of product is reduced. The highest DCFROR was 16%, which was



10. Discounted cash flow rate of return on investment (HAC = acetic acid).



11. Effect of acetyl group content on rate of return (HAC = acetic acid).

obtained for the case with the highest acetic acid selling price (US$900/ton) and for a large pulp mill size (2000 tons/day). However, the process did not prove it was profitable to install the acetic acid process if the selling price of acetic acid was below US$900/ton. Thus, food grade acetic acid must be produced for the process to be profitable.

Effect of acetyl group content on rate of return

The process becomes more profitable as the amount of acetyl groups in wood increases (**Fig. 11**). This figure shows the economic analysis when the selling price is US$750/ton for technical grade acetic acid. DCFROR increases for the 4.0% acetyl group case compared with the 3.5% case results from the increase in the rate of production of acetic acid, which in turn lowers the unit cost of production. White birch (4.4%), eucalyptus (3.9%), white elm (3.9%), beech (3.9%), and red maple (3.9%) contain high amount of acetyl groups [28,30]. The acetyl groups measured in this study using commercial mixed northeast hardwoods contain about 3.5% acetyl groups on a dry mass basis; therefore, some improvement in process economics is possible if wood with higher acetyl content is used.

Process uncertainties

Several uncertainties exist in the present analysis that warrant further investigation. First, the increase in manufacturing cost for producing food grade rather than technical grade acetic acid is associated with increased costs for product purification. These costs arise from the increase in steam and process water required in the distillation processes to meet

the higher purity requirements for the food grade acetic acid. No costs other than those associated with distillation were considered for removing formic, lactic, and glycolic acids. This is justified by conducting the extraction reaction at 50°C rather than 80°C, where experimentally it is seen that little if any sodium formate, sodium lactate, and sodium glycolate are formed. No credit was taken for any potential cost savings associated with the kraft process. Second, because caustic is being generated electrochemically in the BPMED unit, this could conceivably lead to cost reductions associated with the lime cycle and causticization process. Lastly, it should be possible to supply 85%–95% of the caustic requirements in the extraction step from the caustic recovered from the salt splitting process. The required L/W ratio in the extraction vessel to meet the concentration requirements to drive the deacetylation reaction would be satisfied by recycling extract back to the vessel, much like what is done with dilute black liquor in the kraft process.

CONCLUSIONS

The results of the BPMED experiments performed using pretreated extracts were similar to those obtained using model sodium acetate solution previously reported [6]. However, an increase of about 15% in the consumption of electric energy occurred when the real extract was used. This loss is caused by the transport of additional sodium salts present in the extract originating from sodium formate, sodium lactate, and sodium glycolate. The loss is expected to be smaller when extraction is performed at 50°C rather than at 80°C. Lignin and sugars were retained in the feed solution and the acetic acid recovered was not discolored. Hence, it was concluded that BPMPED can be used to obtain a clear solution of concentrated acetic acid, provided the presence of lignin in the feed solution does not lead to membrane fouling when the apparatus is operated over extended periods. If fouling occurs, then membrane life would be shortened and operating cost would be increased.

Possibly, the formic and lactic acids in the acetic acid product could be recovered and sold as additional byproducts. However, their concentration in the acetic acid solution is low and thus most likely not practical to separate and recover economically. In the present analysis, it was assumed that any formic, lactic, and glycolic acids were not recovered and hence no credit was taken as possible byproducts.

The rate of return on investment for the acetic acid process is a function of plant size, selling price of acetic acid, and amount of acetyl groups in the wood. The economic analysis showed that the acetic acid process is profitable for the large plants when food grade acetic acid is recovered and the wood contains appreciable quantities of acetic acid. The rate of return varies between 9% and 16% depending upon the size of the pulp mill (1000–2000 tons/day) for the case where the selling price of acetic acid is US$900/ton and the acetyl contained in the wood chips is 3.5% on dry weight basis. Although the rate of production of wood-based acetic acid is much smaller than in modern acetic acid plants, the process discussed here, if implemented, could lead to positive revenue for some hardwood kraft pulp mills. **TJ**

ACKNOWLEDGEMENTS

The authors acknowledge funding from the Forest Bio-Products Research Institute's NSF-SEP grant No. CHE-1230908 and are thankful to Brad Cort of Andritz Pulp & Paper and Daniel Bar of Ameridia, Division of Eurodia Industrie, for their assistance.

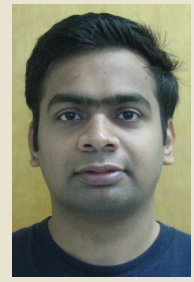
LITERATURE CITED

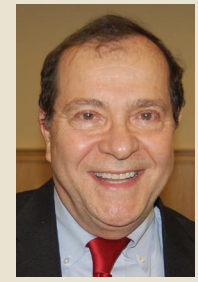
1. Grand View Research, "Acetic Acid Market Analysis by Application (VAM, Acetic Anhydride, Acetate Esters, PTA) and Segment Forecasts to 2022," Market Research Report, Grand View Research, San Francisco, CA, USA, July 2015. Available [Online] http://www.grandviewresearch.com/industry-analysis/acetic-acid-market <17May2017>.
2. Markets and Markets, "Acidity Regulators Market by Type (Acetic Acid, Citric Acid, Lactic Acid, Malic Acid, Phosphoric Acid), Application (Beverages, Sauces, Dressings and Condiments, Processed Foods, Bakery and Confectionery), and Geography—Global Trends and Forecasts to 2018," Market Report FB 1525, Markets and Markets Inc., Seattle, WA, USA, April 2013. Available [Online] http://www.marketsandmarkets.com/Market-Reports/food-acidulants-market-1072.html <17May2017>.
3. Sjöström, E., *Wood Chemistry—Fundamentals and Applications*, Academic Press, New York, 1993, pp. 62-65.
4. Patil, R., "Cleavage of acetyl groups for acetic acid production in kraft pulp mills," M.S. thesis, University of Maine, Orono, ME, USA, 2012.
5. Patil, R., Truong, C., Genco, J.M., et al., *TAPPI J.* 14(11): 695(2015).
6. Patil, R., Genco, J.M., Pendse, H., et al., *TAPPI J.* 15(3): 215(2016).
7. Sixta, H., "Zellstoffherstellung und Recycling von Rohund Hilfsstaffen nach dem Leninger Mg-Bisulfitverfahren," Lenzing AB, Lenzing, Austria, July 1986. Available [Online] https://www.lenzing.com/fileadmin/template/pdf/konzern/lenzinger_berichte/ausgabe_61_1986/LB_1986_01_Sixta.pdf <18May2017>.
8. Patil, R., "Production of acetic acid in kraft pulp mill biorefinery using bipolar membrane electrodialysis," Ph.D. thesis, University of Maine, Orono, 2016.
9. Retsina, T. and Pylkkanen, V., U.S. pat. 20110195468 (Aug. 11, 2011).
10. Ahsan, L., Jahan, M.S., Khan, M.I.H., et al., *BioResources* 9(1): 1588(2014).
11. Ahsan, L., Jahan, M.S., and Ni, Y., *Ind. Eng. Chem. Res.* 52(26): 9270(2013).
12. Kassotis, J., Harry, P., and Chlanda, F.P., *J. Electrochem. Soc.* 131(12): 2810(1984).
13. Trivedi, G.S., Shah, B.G., Adhikary, S.K., et al., *React. Funct. Polym.* 32(2): 209(1997).
14. Bar, D., "The 'Eurodia Industry' bipolar membrane electrodialysis unit for the conversion of sodium acetate into reusable acetic acid and caustic acid: More than five years of successful operation," *Membrane and Separation Technology News*, BCC Research, Wellesley, MA, USA, March 2006.
15. Yu, L., Guo, Q., Hao, J., et al., *Desalination* 129(3): 283(2000).

16. Mishra, A.K. and Bhattacharya, P.K., *J. Membr. Sci.* 33(1): 83(1987).
17. Gordon, O.W., Plattner, E., and Doppenberg, F., U.S. pat. 5,595,628 (Jan. 21, 1997).
18. Thompson, R., Paleologou, M., and Berry, R.M., *TAPPI J.* 80(6): 154(1997).
19. Paleologou, M., Wong, P.Y., and Berry, R.M., *J. Pulp Pap. Sci.* 18(4): J138(1992).
20. Paleologou, M., Thibault, A., Wong, P.Y., et al., *Sep. Purif. Technol.* 11(3): 159(1997).
21. Davis, S.M., "Electrochemical splitting of sodium sulfate," M.S. thesis, Georgia Institute of Technology, Atlanta, GA, USA, 2006.
22. Thompson, R., Paleologou, M., and Berry, R.M., *Tappi J.* 78(6): 127(1995).
23. Seader, J.D. and Henley, E.J., *Separation Process Principles*, John Wiley and Sons, Hoboken, NJ, USA, 2011.
24. DE Dietrich Process Systems, "Recovery of acetic acid by means of liquid-liquid extraction" Literature, DE Dietrich Process Systems GmbH, Mainz, Germany. Available [Online] http://www.dedietrich.com/en/recovery-acetic-acid-means-liquid-liquid-extraction<17May2017>.
25. Strathmann, H., in *Ullmann's Encyclopedia of Industrial Chemistry*, Vol. 21, Wiley-VCH, Weinheim, Germany, 2003, pp. 243-322.
26. Strathmann, H., in *Comprehensive Membrane Science and Engineering*, Vol. 2 (E. Drioli and G. Lidietta, Eds.), Elsevier Science, Oxford, UK, 2010, pp. 391-429.
27. Tanaka, Y., *Ion Exchange Membrane Electrodialysis*, Nova Science Publishers, New York, 2010.
28. Rydholm, S., *Pulping Processes*, Interscience Publishers, New York, 1965.
29. Turton, R., Bailie, R.C., Whiting, W.B., et al., *Analysis, Synthesis and Design of Chemical Processes*, Pearson Education, Upper Saddle River, NJ, USA 2012.
30. Inalbon, M.C., Mocchiutti, P., and Zanuttini, M., *BioResour. Technol.* 100(7): 2254(2009).

ABOUT THE AUTHORS

This work was an attempt to use the acetyl groups found in hardwoods. They are currently cleaved during the pulping process and are sent to the recovery boiler with the black liquor. Co-author Patil performed his doctoral research in this field. The current publication summarizes the basic data used in the process design for an acetic acid recovery process and summarizes the preliminary process economics.


Patil


Genco


Pendse


van Heiningen

The most difficult aspect of the research was coming up with realistic costs for the process. To address this challenge, we called vendors who helped us with estimates for the major equipment for a 1000 tons/day pulp mill. We then scaled the vendors' data to other pulp mill sizes.

An interesting aspect was minimizing the use of fresh caustic to the process. In theory, the process should not use any fresh caustic because the bipolar membrane process produces caustic in the same amounts that are used in cleaving the acetyl groups from the hemicelluloses in the wood.

Mills would benefit directly if management would make the capital investment and attempt to recover acetic acid for sale in the open market.

Patil is a postdoctoral student, Genco is a professor emeritus, Pendse is chair of the Chemical and Biological Engineering Department, and van Heiningen is a professor of Chemical Engineering at the University of Maine, Orono, ME, USA. Email Genco at JGenco@umche.maine.edu.