

Techno-economic evaluation of butanol production via black liquor fractionation

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ABSTRACT

The hemicelluloses fraction of black liquor is an underutilized resource in many chemical pulp mills. It is possible to extract and separate the lignin and hemicellulose from the black liquor and use the hemicellulose for biochemical conversion into biofuels and chemicals. Precipitation of the lignin from the black liquor would consequently decrease the load on the heat recovery boiler, which might be a bottleneck for increased pulp production. Fractionation of black liquor therefore represents an interesting business opportunity for pulp mills. The main objective of this work has been to techno-economically evaluate an integrated process for black liquor fractionation and the subsequent processing and recovery of the hemicelluloses and lignin-derived products. The considered final products are sodium-free lignin as a solid fuel and butanol to be used as fossil gasoline replacement in Otto engines. The hydrolysis and fermentation processes are modeled in Aspen Plus to analyze energy and material balances. A mathematical process integration model of an existing pulp and paper mill is used to analyze the effects on the energy performance of the mill subprocesses as well as to evaluate the plant economics. Based on the composition and amount of the extracted stream and the model developed in this work, about 13.8 ktonne-lignin/year (on dry basis) and about 1 ktonne-butanol/year are produced from the integrated process. In addition, about 0.5 and 0.02 ktonne/year of acetone and ethanol are co-produced, respectively. Under the assumed economy, the cost of production of n-butanol is estimated to be kUSD 3.95/tonne-butanol and this corresponds to kUSD 2.5/tonne-ABE on ABE (acetone-butanol-ethanol) basis. An assessment on the impact of the extracted hemicelluloses and lignin on the recovery boiler has resulted in about 30% reduction in the thermal energy output of the unit.

KEYWORDS: Black liquor, Fractionation, Butanol production, Techno-economic analysis

1 INTRODUCTION

Sweden has a large pulp and paper industry, presently about 8 Mtonnes of chemical pulp is produced with sulphate method giving approximately the same amount of black liquor (BL) as a byproduct [1]. Currently, the BL is used as a fuel in the recovery boiler (RB). The RB is an important part of chemical pulp mills as it provides the thermal energy and power demand of the mill while also playing a key role in the recovery process of the pulping chemicals, which is very important for the overall economy of the Kraft process. The BL contains the pulping chemicals as well as the lignin and degraded hemicellulose. The hemicellulose fraction of the BL is an underutilized resource in many chemical pulp mills. Extracting that fraction could be one way to generate a sugar feedstock amenable to biochemical conversion to fuels and chemical intermediates, such as ethanol, butanol, succinic acid and lactic acid. Hemicellulose have a low heating value (13.6 MJ/kg) compared to lignin (27 MJ/kg) [2] and therefore recovery of hemicelluloses from lignocellulosic material followed by biochemical conversion into value-added products may bring a better process economy of the plant. The highest content of hemicellulose is found in hard wood, for instance, birch wood is composed of 40% cellulose, 37% hemicellulose, 20% lignin and 3% extractives [3]. During the chemical pulping of birch wood about 50% of the organic content (the cellulose and part of the hemicellulose) is converted into pulp and the remaining part ends up in the BL. The figures confirm that the hemicellulose is an underutilized resource. The general idea of this work is to precipitate the lignin and hemicellulose together by decreasing the pH of the liquor. Then the hemicellulose can be extracted from that precipitate through hydrolysis at a further decreased pH. It has been also considered important to minimize the effect of the degradation of hemicellulose in the digester. The hemicellulose can then be used as a raw material to produce valuable products, e.g. succinic acid, butanol etc. An extension of the boundary of the lignin separation process is to include a biochemical/thermochemical transformation pathway that produce green chemicals and biofuels that can boost the product portfolio and the incentive.

In some cases the RB can be a bottleneck towards increased pulp production [3,4]. The integration of lignin separation can help debottlenecking in those situations. The benefits of separating lignin from the BL of pulp and paper mills to increase pulp production have been discussed by several authors in the literature (see e.g. [3,5,6]). The advantage is twofold: it opens the opportunity for increased pulp production without altering the ordinary pulping and chemical recovery processes, and lignin can be sold as a fuel by itself thereby increasing the products.

The focus of this study is the recovery of hemicellulose from the BL and the subsequent production of butanol from hemicellulose via fermentation. Butanol can play an important role in alleviating the dependence on fossil derivatives for transportation fuel. N-butanol with molecular formula C_4H_9OH (MW 74.12) and boiling point of 118 °C has energy density about three-fourth of gasoline. This makes it superior to ethanol as a biofuel, and more importantly it can be produced from more sustainable feedstock, than bio-diesel for instance [7,8]. In addition, butanol can surpass the blending limit of ethanol with gasoline (which is usually less than 10%) without inducing significant impact on the Otto engine performance. The production butanol from BL is not mentioned in the literature; however, commercial production of bio-butanol through fermentation of sugars has been used previously. See e.g., [9].

The main issue that poses problems with fermentative biobutanol using *Clostridial* cultures is the toxicity of butanol to the culture, which makes the production to slow down with increased concentration of butanol until it finally stops at a certain critical concentration (maximum concentration tolerable, 10-12 g/l butanol or a corresponding 20g/l total ABE (acetone-butanol-ethanol), see e.g., [10-15]). Other issues are low yield and the production of considerable amounts of other solvents along the side of n-butanol such as acetone (C₃H₅OH) and ethanol (C₂H₅OH). In addition acetic and butyric acids are also present in the fermentation broth. Obvious solution to inhibition would be to continuously remove solvents from the broth, or to engineer *Clostridia* strains with high tolerance to the fermentation solvents. Recent reports on fermentative bio-butanol production from cellulosic feedstock have indicated considerable improvements both from yield and solvent recovery point of views, see e.g., [10-15]. Several plausible solvent recovery technologies have also been reported in the literature, among others, gas stripping [13,16], pervaporation [10], liquid-liquid extraction [17], and adsorption [18] can be listed. Further details on the different recovery technologies can be found in [19-21]. Of all the techniques, gas stripping has been reported as one of the promising in situ recovery technologies both from operability and economic point of views [11-13,16,20]. There have been several reports on the fermentation of starchy feedstock (rich in sugar content, such as corn, starch and molasses) into biobutanol using *Clostridial* cultures. The fermentation process largely depends on the sugar content of the feedstock, pre-treatment process by which fermentable sugars are liberated, and the *Clostridia* strain used.

In the current work a mathematical model for a lignin separation and fermentative production of ABE solvents from Birchwood Black Liquor (BBL) has been developed. The new process is assumed to be integrated in an existing pulp and paper mill. The model has then been used to evaluate the energy and material balances of the system for different process conditions. An economic evaluation of the new process has been made based on published price data.

2 MATERIAL AND METHOD

The fractionation plant considered in this work produces butanol from BBL hydrolzate via the conventional ABE fermentation process, while lignin is separated as an intermediate product. A model is developed in Aspen Plus in which material and energy balances are obtained. The input data to the lignin extraction and hydrolysate preparation processes are based on the experimental data carried out in an existing pulp and paper mill. The input data to the ABE fermentation and downstream processes are based on the literature. The plant is assumed to run 8000 hrs/year and the butanol production capacity is fixed by the amount of hydrolysate feed. The final product purity specifications were set as follows: n-butanol 99.9 wt. %, acetone 99.9 wt. %, and lignin 65 % DM.

2.1 Process Description

In order to extract lignin carbohydrate complexes (LCC) for the production of biofuels (or green chemicals) via hydrolysis and fermentation pathway, a Birch Black Liquor (BBL) stream at about 12-15% Dry Matter (DM) is rerouted from the digester of a pulp and paper mill. The extracted stream is composed of organic and inorganic (mainly alkali) substances. The organic content in the extracted stream is equivalent to about 10% of the total pulp production of the mill and the inorganic matter is about 10% of the total cooking chemicals charged, both on dry matter basis.

The diverted stream is then sent to a flash tank, or to one of the multiple effect evaporator units of the pulp and paper mill, to increase its solid content up to 25-30% DM before its pH is lowered by injecting CO₂, which causes the LCC in the diverted stream to precipitate. The precipitate, which accounts for about 30% of the total dry solids extracted from the digester, is then filtered to separate it from the alkali rich solution that comes along with the diverted stream from the digester. The alkali rich solution is returned back to the chemical recovery cycle of the pulp and paper mill, whereas the LCC stream with about 50% DM undergo the hydrolysis and fermentation pathway to produce n-butanol and alkali free lignin as main products, and acetone and ethanol as co-products. The hydrolysis is carried out using diluted sulfuric acid in agitated reactor which is maintained at about 100°C for one hour. Alkali free lignin, at about 65% DM, is filtered out of the stream exiting the hydrolysis reactor and the rest of stream is let into the downstream processes. The pH of the hydrolysate is increased from about 1, in the hydrolysis reactor, to about 5 prior to its admission into the fermenter by dissolving lime mud (CaCO₃) which is freely available in the pulp and paper mill. Overview of the process is shown in Fig. 1.

The hydrolysate stream is the feed stream to the ABE fermentation process which is developed based on two experimental data: ABE from hexose sugars substrate reported in [11,15,16] via butanol producing strain *C. beijerinckii* BA101 and ABE from agricultural residues substrate (mainly pentose sugars) reported in [14,22,23] using strain *C. beijerinckii* P260. Moreover, the yield of butanol from hexose and pentose sugars has been reported to be in a similar range, see e.g., [11,23,24]. The reactor is assumed to be operated on a fed-batch mode and the conditions are maintained at a temperature of 35°C and a pressure of 1atm.

The ABE process solvent recovery system is based on gas stripping technique. Gas stripping is a simple technique of recovering solvents from the fermentation broth using inert gases, such as N₂ or CO₂, as stripping medium. The inert gas is sparged through the broth so that volatile solvents are removed continuously. Gas stripping can be applied to reactors operated on batch, fed-batch or continuous basis. It is favorable since it does not remove reaction intermediates from the fermentation broth [16]. The main disadvantage of gas stripping is that it disfavors butanol due to the fact that butanol has the highest boiling point compared to the other solvents present in the fermentation broth [16]. The selectivity of the stripping process for a specific compound is calculated according to Eq (1).

$$Selectivity = \frac{[y/(1-y)]}{[x/(1-x)]} \quad (1)$$

Where:

y- The concentration of a compound in the product condensate (wt. %)

x- The concentration of that compound in the fermentation broth (wt. %)

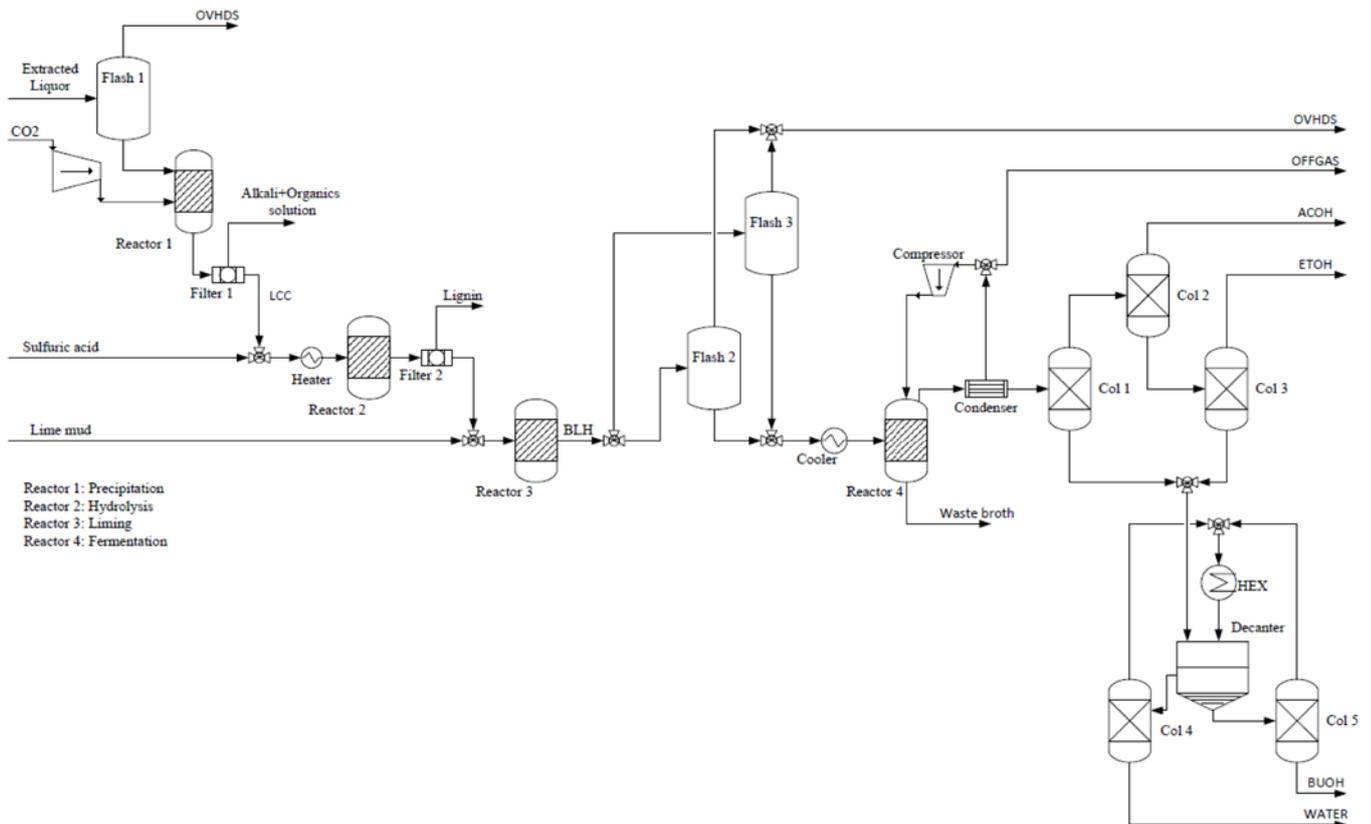


Fig. 1: Process flow diagram

ABE is selectively removed during the fermentation process. In the fed-batch fermentation (20–200 h), butanol selectivities were reported in the range of 10–22. Acetone and ethanol selectivities ranged over 6.69–12.72 and 4.45– 11.16, respectively [11]. Furthermore, the results did not show any direct relationship between the ABE concentration in the fermentation broth and each component's respective selectivity. The solvents are recovered by condensing the gases flowing out of the fermenter to a temperature of 2°C in a refrigeration unit.

Table 1 summarizes reports on experimental results of biobutanol production via fermentation of starchy substrates with in situ gas stripping. The composition of the product condensate i.e. concentration fractions of acetone, butanol and ethanol to the total ABE in all the reports fairly agree, see Fig. 2.

Table 1: Fermentation with in-situ gas stripping

Operation mode		ABE fermentation of different substrates					
		Fed-batch			Batch		
Substrate		Glucose	Cassava	starch	Glucose	WSH+Glucose	Corn
Fermentation Time	hrs	201	169	263	127	132	66
Glucose initial	g/l	100.00					
Glucose final	g/l	26.10					
Glucose utilized	g/l	500.10	244.60	336.60	161.49	128.65	64.63
Total ABE	g/l	232.80	90.31	108.51	75.90	47.60	26.50
Productivity	g/l/h	1.16	0.53	0.41	0.60	0.36	0.40
Yield	g/g	0.47	0.37	0.32	0.47	0.37	0.41
Acetone	g/l	77.70	25.72	26.98	24.70		8.30
Butanol	g/l	151.70	59.81	76.44	46.40		17.60
Ethanol	g/l	3.40	4.78	5.09	4.80		0.60
Butyric acid	g/l	4.20	3.82	1.97			
Acetic acid	g/l	4.30	4.29	5.24			
Gas flowrate	l/min/l	3.00	1.25	1.25			
References		[11]	[12]	[15]	[19]	[14]	[15]



Fig. 2: Fraction of solvent concentration in product condensate (A-acetone; B-butanol; E-ethanol)

2.2 The Aspen Model

The Aspen model is a steady-state flowsheet based on a stoichiometric reactor approach. The total fermentation time is 200 hrs and stripping starts after 20 hrs. In order to render a continuous process, the overall productivity in the model is maintained using average mass flow rates over the total fermentation time. Thus, the mass flow rate of products from the fermenter is 0.625%, (=1/160, the stripping process is operated for 160 hrs), of the fermentation broth. For the same reason, the substrate intermittently added during the fed-batch fermentation process is simulated as a continuous addition using averaged mass flow rates over the entire fermentation period.

The BBL hydrolysate stream (pre-fermentation) contains about 38.51 g/l xylose, 3.4 g/l acetic acid, 0.06 g/l furfural, 0.53 g/l hydroxymethylfurfural (HMF), 3.79 g/l phenolic (acid soluble lignin (ASL)) and 2.07 g/l formic acid. In addition about 65 g/l of gypsum is present in the hydrolysate. Moreover, evaporators are required to concentrate the BBL hydrolysate up to 100 g/l sugar concentration for the main feed stream and up to 500 g/l of sugar concentration for the intermittent feed stream. The fractional conversion of the sugars in the BBL hydrolysate to ABE solvents is based on experimental data reported in [11] and fermentation stoichiometry as summarized in Table 2. The precipitation, hydrolysis and liming processes have also been modeled based on experiments conducted in a real pulp and paper mill.

Table 2: Fermentation stoichiometry (Stoichiometry this work and yield [11,24])

Product	Stoichiometric reaction	Fractional conversion	Yield g/g sugar
Acetone	$C_5H_{10}O_5 \rightarrow C_3H_6O + 2CO_2 + 2H_2$	0.343	0.148
N-butanol	$C_5H_{10}O_5 \rightarrow C_4H_{10}O + CO_2$	0.524	0.288
Ethanol	$3C_5H_{10}O_5 \rightarrow 5C_2H_6O + 5CO_2$	0.011	0.006
Butyric acid	$C_5H_{10}O_5 \rightarrow C_4H_8O_2 + CO_2 + H_2O$	0.012	0.008
Acetic acid	$C_5H_{10}O_5 + H_2O \rightarrow 2C_2H_4O_2 + CO_2 + 2H_2$	0.009	0.008

The stoichiometry is rather a qualitative representation of the conversion process and the solvents yield are controlled by the literature data. It should be noted that the conversion stoichiometry of pentose sugars to butanol is only balanced for the carbon atom. The substrate utilization rate for hexose sugars is set to 95.1% and that of pentose sugars is set to 90% [24]. According to the model 63 vol. % of the carbon in the pentose sugars of the substrate is converted to ABE, 25 vol. % to CO₂ and the rest into acids.

In the model, the gas stripper is represented as a separator with butanol selectivity set to 20 [11,16]. The selectivity of n-butanol is set as a design specification according to Eq. (1). In addition, no selectivities has been assigned to the butyric and acetic acids since the presence of both is not reported in the condensate [7,11]. The selectivities for acetone and ethanol are set in the separator as split fraction such that their amounts in the condensate correspond to the reported values. The stripper gas is composed of the fermentation process byproduct gases, CO₂ (97 wt. %) and H₂. The gas recycle rate is set to 3 l/min per liter of fermentation broth [11]. According to the model, the fermentation gas produced is more than that of required for the gas stripping process and therefore part of it is bled-off.

The product separation process is composed of five distillation columns, all based on RadFrac unit operation of Aspen Plus, and a triple phase flash decanter. The product condensate from the refrigeration unit is fed to the first column where the light components, acetone and ethanol, are separated as overheads and the heavy ones, butanol and water, as bottoms. The overhead stream from the first column is fed into a second column where acetone is separated as overhead with a purity of 99.9 wt. % and hydrous-ethanol as bottoms. The hydrous-ethanol is fed to a third column where it is fractionated into 94 wt. % ethanol as overhead and n-butanol/water azeotrope as bottoms. The bottoms from the third column are mixed with the bottoms from the first column, which is also an n-butanol/water azeotrope. Consequently, a triple phase flash decanter and two distillation columns arrangement,

as reported in [25], is used to separate the azeotropic mixture. The azeotropic solution is a heterogeneous one, which means that it is split into aqueous and organic streams in the decanter. The aqueous solution is fed into a water stripping column and the organic solution is fed into an n-butanol stripper, where n-butanol with a purity of 99.9 wt. % is separated as bottoms.

2.3 Economic Evaluation

The study estimates method together with the Hand method as well as Aspen Icarus has been implemented in the estimation of the investment cost. The pre-requisite for using the study estimates method (that is a flowsheet diagram of the process) has been fulfilled. Accordingly, the sets of equipment which are required by the process have been sized based on the mass and energy balance flowsheet developed in Aspen Plus. The evaluation of the equipment cost is performed by estimating the purchase cost of unit operations, based on published data as well as in-house database information, and by multiplying them with their respective Hand factor for the equipment type to account for piping, insurances, installations etc. Moreover, since the fermentation process is operated on a fed-batch mode a schedule for rendering continuous operation has been assumed and evaluated during the economic assessment. The capital cost is estimated according to Eq. (2).

$$\text{Capital cost} = \sum \left[(\text{Equipment purchase cost} \times h_f \times f_m) \right] \times f_i \times f_b \times f_p \quad (2)$$

Where:

h_f - Hand factor, f_m - material factor, f_i - instrumentation factor, f_b - building factor and f_p - place factor.

The cost of equipment for the unit operations involved in the process are initially estimated using correlations and data available in literature [26]. The initial estimates have been corrected to match the pressure and material requirement of the current process using factors reported on the same literature. The estimated costs are based on the chemical engineering plant cost index (CEPCI) 460 (year 2005) and are adjusted for inflation and are reported for the year 2011 (CEPCI 586).

3 RESULTS AND DISCUSSION

3.1 Material and Energy Balances

This section presents the input-output structure of the model developed. The composition of the extracted stream is used as the basis for determining carbon dioxide, sulfuric acid and lime mud demand of the precipitation, hydrolysis and liming processes, respectively. In addition, water is added to dilute the sulfuric acid, initially at 72% H_2SO_4 , to 4% H_2SO_4 concentration in the hydrolysis reactor.

Alkali free lignin as a biomass fuel and butanol as an alternative transport fuel are the main products considered. However, acetone and ethanol are also produced along with butanol as co-products. The material balance of the integrated model is presented in Table 3.

Table 3: Material balance of the model

Input	Tonne/hr	Output	Tonne/hr
Organics (13% DM)*	6.75	Alkali & organics solution	24.01
Inorganics (alkali) (13% DM)*	1.88	Lignin (65% DM)*	1.72
Carbon dioxide	0.56	N-butanol	0.13
Sulfuric acid 72%	0.91	Acetone	0.06
Lime mud	0.55	Ethanol	0.003
Process water	10.89	Water	0.18
		Off-Gas (CO_2 (97 wt. %) & H_2)	0.27
		Flash overheads	45.87
		Waste broth (21% DM)*	1.26

*dry basis, Streams are as depicted in Fig. 1

3.2 Process Utility Requirement

The hydrolysis and butanol plant utility requirement can be classified into heating (using MP (medium pressure) steam), cooling (using water) and electricity. The steam is mainly required by the re-boilers of the distillation columns, heaters, and flash evaporators. For the cold utility, water is assumed to be the cooling medium which is mainly required by the coolers as well as the condensers of the distillation columns. The steam, cooling water and electricity demand of the process are evaluated in Aspen Plus and are used as the basis for the evaluation of the cost of utility during the economic assessment. The utility requirement of the plant is summarized in Table 4.

Table 4: Process utility requirement

Utility requirement		
Steam MP	30	tonne/tonne-butanol
Cooling water	417	tonne/tonne-butanol
Power	1480	KWh/tonne-butanol

3.3 Butanol Production Cost

Since the integrated process has multiple products, the cost of production of butanol is chosen to be the basis for the economic analysis while the price of lignin is kept fixed, at least for the case where the lignin price is set to USD 20/MWh. The reason for this is that, the price of lignin is available in the in-house data base as well as in the open literature in a fairly similar range. That is not the case with the prices of butanol. Nonetheless, the selling price of lignin has been a subject of a sensitivity analysis in the next section. The cost of production of butanol via BBL fractionation accounts mainly for the costs incurred by the investment, the purchase of raw materials, the utilities (MP steam, water, electricity, refrigeration etc.), and the labor.

The capital cost is estimated according to Eq. (2) and is accounted in the analysis using the annuity method, assuming 15 years plant life time and 13 % interest rate. The Hand factors used in the analysis are as follows: for the compressors 2.5, reactors 4, pumps 4, heat exchangers 3.5, pressure vessels 4 and fractionation columns 4. Moreover, the instrumentation factor is set to be 1.55 (that is for central control and computerization), and the building factor is set to be 1.11 (that is for new solid-fluid processing unit at an existing site). Accordingly, the total initial capital cost, as a function of lignin production rate, is estimated to be about $23.6 \cdot \dot{L}^{0.65}$ [MUSD], where \dot{L} is the separated lignin mass flow rate in [kg/s, dry basis].

The required number of personnel has been estimated using the data available in literature [26] where fractions are assigned for personnel per unit operation per shift. These fractions are multiplied with the number of unit operations of each type and with the number shifts and summed up to obtain the total number of persons needed. The fractions used in the analysis are as follows: for the compressors (0.09 persons/shift/unit), for the reactors (0.25 persons/shift /unit), for the distillation towers (0.25 persons/shift /unit), for the heat exchangers (0.05 persons/shift /unit), for the centrifugal separators and filters (0.12 persons/shift/unit) and for the evaporators (0.15 persons/shift /unit). Assuming 5 shifts, about 15 personnel are required. This has been accounted in the production cost estimation by assigning kUSD 71.5 per person per year. This resulted in a labor cost, again as a function of separated lignin mass flow rate, of about $1.7 \cdot \dot{L}^{0.65}$ [MUSD/year].

In regards to the cost of the feed stream to the lignin separation and butanol production plant, that is the stream extracted from the digester, it is fair to assume that the cost of the extracted stream can be excluded from the economic evaluation since the organic content of the extracted stream is only 10% of the total charge of organic substance and the cost of woodchips has already been accounted with the pulping process. In such case the digester would be providing a pretreated feed stream to the lignin separation and butanol production plant free of charge, meaning that the cost of pretreatment is assumed to be accounted with the pulping process. In fact, the celluloses and part of the hemicelluloses in the wood are converted into pulp, and therefore the pulping is not impacted by the extracted stream. The evaporation unit and the recovery boiler are the only subprocesses of the pulp and paper mill which are affected by the BBL fractionation plant.

Table 5 summarizes the utilities and raw material prices associated with the fractionation and butanol production plant. It is worth mentioning that part of the cooking chemicals in the extracted stream is lost in the downstream processing. During the economic evaluation a NaOH make-up stream that accounts for the loss is evaluated. According to Olsson M.R. et al. [5], the amount of the cooking chemicals lost in the process is estimated to be about 5% of the total amount of cooking chemicals in the extracted stream.

Table 5: Chemicals and utility prices used in the analysis

Utility and material usage	Tonne/tonne-lignin ¹	Price (USD/tonne)
MP steam	1.62	50
Water	37.13	0.2
Carbon dioxide	0.32	52*
Sulfuric acid	0.53	71*
Make-up sodium hydroxide	0.06	280*
	KWh/tonne-lignin ¹	(USD/KWh)
Power consumption	109	0.045*

¹Lignin on dry matter basis. *Prices adapted from Olsson M.R. et al. and Axelsson E. et al.[5,6]. The prices are reported here after being adjusted for inflation using CPI (consumer price index) to the USD value of 1Q2011 (the first quarter of the year 2011).

For the economic conditions described above and a lignin selling price of USD 20/MWh, the butanol production cost is estimated to be kUSD 3.95/tonne-butanol. The production cost is reduced to kUSD 2.5/tonne-ABE, if acetone and ethanol are included in the product stream. The major contributors to the production cost are the capital cost of the integrated process (about 40% of the production cost) followed by the labor cost and utility steam, with about 20% of the production cost each.

3.4 Sensitivity Analysis

Sensitivity analysis of some influential parameters towards the production cost of n-butanol, such as the prices of lignin, CO₂ and H₂SO₄, has been carried out and the results are presented in this section.

Lignin is the major product with respect to the quantity produced and this makes it an important parameter to the economy of the integrated process. In fact, a huge part of the earning from the integrated process is expected to come from the selling of lignin. Olsson M.R. and his co-workers reported that the lignin price has to be above EURO 20/MWh in order to achieve a pay back time of 4 years [5]. In their case the integrated system was only a lignin separation plant and the investment was assumed to be a long term one meaning that an interest rate of 5% and 14 years plant life was used. A EURO 20/MWh corresponds to USD 32/MWh after being adjusted for inflation to the 1Q2011 and this figure alone would reduce the butanol production cost by about 35% compared to the butanol production cost corresponding to a lignin price of USD 20/MWh and if an interest rate of 5% is used instead of 13%, the production cost is reduced by a further 24%.

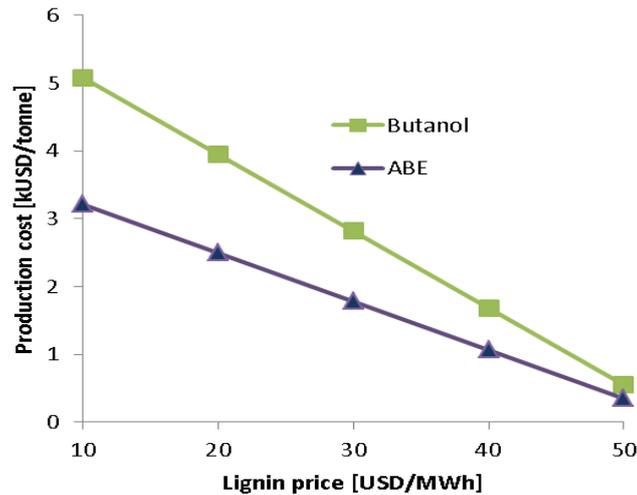


Fig. 3. Production cost sensibility towards the price of lignin

According to the assumed economic condition, butanol can be produced in the cost range of kUSD/tonne-butanol 3.95 to 2.25 for a lignin selling price in the range USD 20 to 35/MWh. Should acetone and ethanol be included in the product stream, the production cost reduces to the cost range of kUSD 2.50 to 1.42/tonne-ABE, for the same lignin selling price range. These figures can be readily perceived from Fig. 3. Hereafter, the selling price of lignin is fixed at USD 20/MWh unless specified otherwise.

The other uncertainties are related to the costs of chemicals such as carbon dioxide and sulfuric acid. A sensitivity analysis towards the cost of carbon dioxide and sulfuric acid is presented in Fig. 4, for a CO₂ and H₂SO₄ prices in the range of USD/tonne 50 to 150. The range for CO₂ is chosen based on literature data [5]. The CO₂ cost range resulted in a production cost of butanol in the range kUSD/tonne-butanol 3.94 to 4.45, and the corresponding production cost range on ABE basis is kUSD/tonne-ABE 2.5 to 2.8. And the H₂SO₄ cost range resulted in a production cost of butanol in the range kUSD/tonne-butanol 3.9 to 4.6 and the corresponding production cost on ABE basis is kUSD/tonne-ABE 2.4 to 2.9. The price of CO₂ is kept fixed at the value presented in Table 5 during the assessment of the production cost against the prices of H₂SO₄, and vice versa.

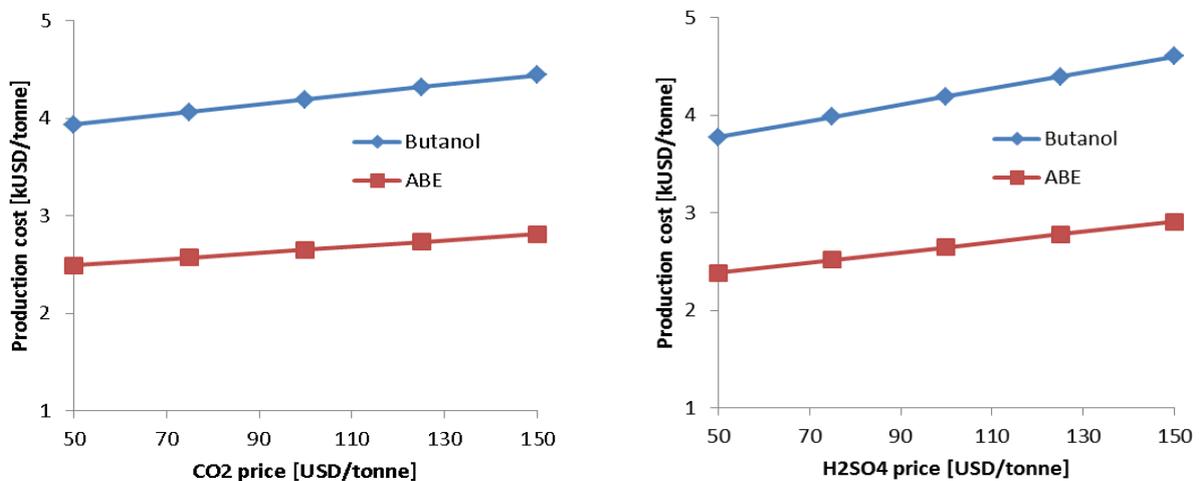


Fig. 4. Production cost sensibility towards the price of CO₂(left) and towards the price of H₂SO₄ (right)

The economy of biobutanol production through fermentation is largely affected by the capital costs which are mainly incurred due to the large volumes of fermenters required as a result of the long holding time. However, there are several reports for batch fermentation which require shorter fermentation time than used in the current work. A sensitivity analysis has also been performed to emphasize on the effect of the fermentation time on the production costs (see Fig. 5).

Should the fermentation time be reduced to 80 hrs, the production cost of butanol would reduce from kUSD 3.95 to 2.95/tonne-butanol and the production cost on ABE would reduce from kUSD 2.50 to 1.90/tonne-ABE. In all the cases, 20hrs is assumed for cleaning, refilling and inoculation and another 20 hrs before gas stripping is commenced. Furthermore, the productivity is assumed to remain the same during the sensitivity analysis.

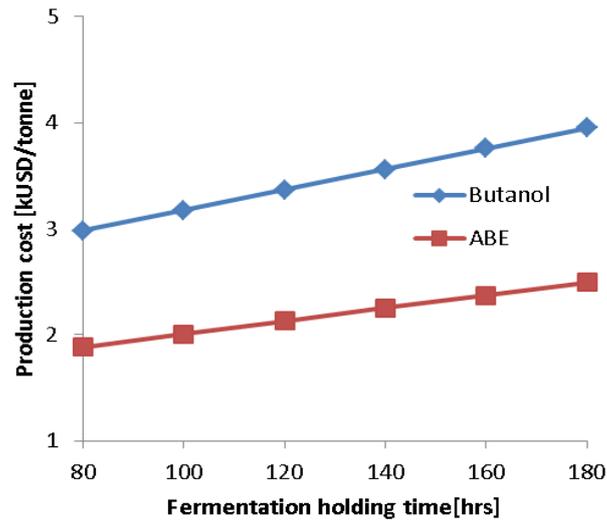


Fig. 5. Production cost sensibility towards the fermentation holding time

3.5 Impact of the Hemicellulose and Lignin extracted on the Evaporation unit and RB

The removal of hemicellulose and lignin from the extracted stream will afterward change the organics composition of the BL stream when it comes to the evaporation plant and later to the RB. The inorganics composition on the other hand does not change as much, except for the part that is filtered out with the LCC stream which is then directed to the lignin separation plant and later to the butanol production plant. In addition to the composition, the physical properties of the black liquor are expected to change. In this work, the physical properties of BL, such as viscosity and boiling point elevation (BPE), after the lignin removal are assumed to remain the same. Moosavifar A. et al. reported that the viscosity and BPE change are insignificant compared to an ordinary BL [27]. However, the composition and heating value have been recalculated based on data reported by Vakkilainen E. and Välimäki E., in [3]. In fact the same results, as reported in their work, have been achieved by recalculating the composition of BL by assuming the organics removed to be shared according to the ratio of carbon to hydrogen in ordinary BL. Ordinary black liquor is roughly composed of about one-third of organics, one-third inorganics and the remaining one-third water.

According to the experimental results, up on which the model is based, about 30 wt. % (dry basis) of the extracted stream is separated as filter-cake after the CO₂-precipitation. The rest of the stream is assumed to be recycled and mixed with the black liquor stream that comes from the digester before entering the evaporation unit. In addition the extracted stream is concentrated to about 25-30% DM in one the evaporator units after being mixed with a recirculated hemicellulose stream with about 60-70% DM content.

The effect of hemicellulose and lignin separation on the pulp and paper mill has been carried-out on a mathematical model of an existing pulp and paper mill with emphasis on the effect of the lignin separation in regard to the energy performance of the evaporation unit and recovery boiler. A full detail of the mathematical model mill is reported in [28]. Hereafter, the basecase refers to the ordinary pulp and paper mill process and the new case refers to the pulp and paper mill process with the integrated lignin separation and butanol production plant. The evaporation unit with the new configuration is presented in Fig. 6. The impact of the new evaporation unit configuration on the live steam demand has been evaluated over a range of the dry content of the recycled alkali stream and the temperature of the stream entering effect 3 (E-3, see Fig 6). The stream entering E-3 is the mixture of the extracted stream and the organics recirculation, see Fig 6. The mass flow rate of the recirculated organic stream is also influenced by the dry content of the recycled alkali stream and the temperature of the mixed organics stream. See Fig. 7.

In the basecase evaporator operation the live steam demand is calculated to be around 6.75 kg/s and is represented in Fig. 7 by the broken line for comparison purpose. It should be noted that the basecase pressure level of the evaporator effects are kept constant during the analysis and no attempt has been made to optimize the system in anyway. In addition, the BL coming from the digester (BL, thin at 14.4% DM) has to be mixed with a recirculated BL from effect 2 (E-2) to achieve a target dry matter of 21% before it enters effect 4 (E-4). This is done in order to avoid foaming inside the effects [29]. The target dry content (DM_{mix_1}, as depicted in Fig. 6) is kept as a technical constraint in the new configuration as well. The results presented in Fig. 7 show that the live steam consumption of the evaporator and the organics recirculation mass flow rate dependence on the dry content of the recycled alkali stream and the temperature of the mixed organics stream (T_{mix_2}, as depicted in Fig. 6).

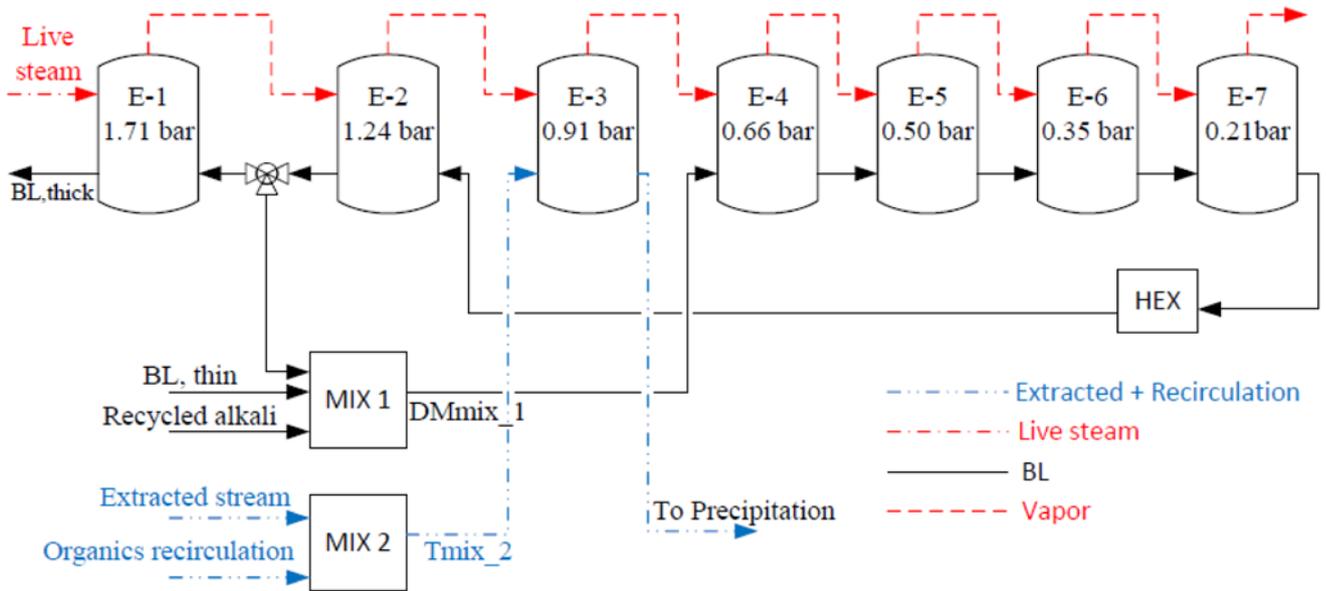


Fig. 6. Evaporation unit with the new configuration

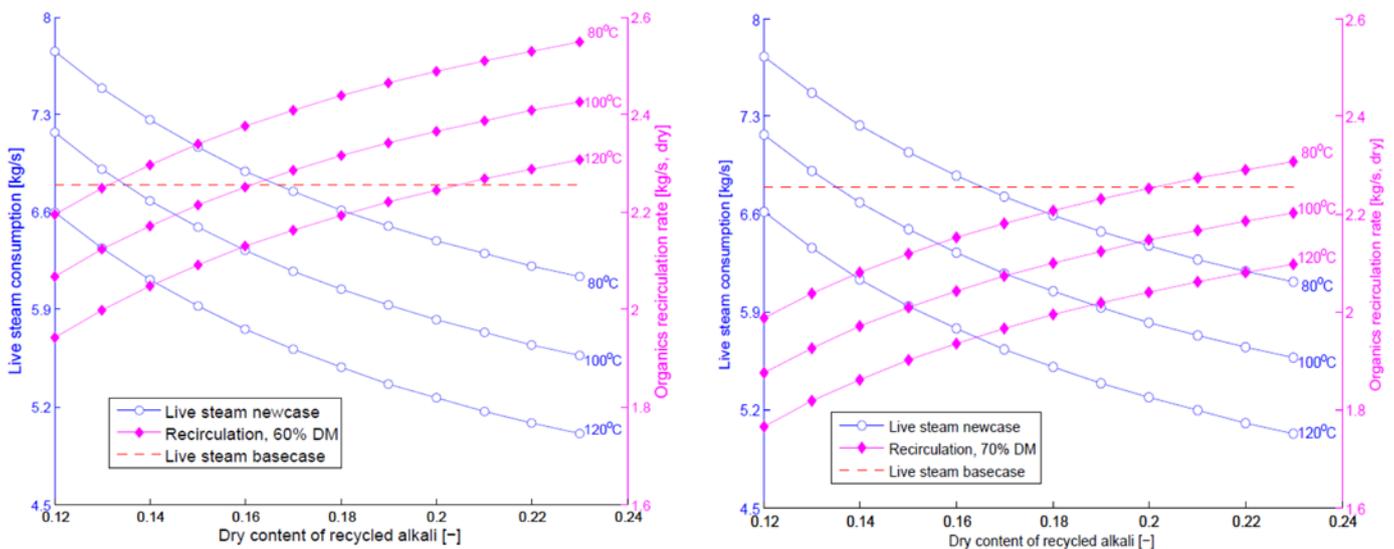


Fig. 7. The live steam consumption of the evaporation unit with the new configuration versus the dry content of the recycled alkali stream for different temperatures of the mixed organics stream (T_{mix_2}). The mass flow rate of the organics recirculation versus the dry content of the recycled alkali stream for different temperatures of the mixed organic stream. Left (organics recirculation at 60% DM), Right (organics recirculation at 70% DM). Note the Y-axes scale difference

All the thermal energy output of the RB comes from the combustion of the organic part of the BL. Therefore, altering the organic composition of the BL would have a direct consequence on the thermal energy output of the RB. The impact of extracting organics has been evaluated against the thermal energy output as well as against the exhaust gases mass flowrate. The results are presented in Fig. 8. It should be noted that, in all the cases, the BL is concentrated to 71 % DM and fed to the RB at a temperature of 129°C. Moreover, the excess combustion air is kept constant at 5% during the assessment.

The fuel balance of the RB puts a limitation on the amount of organics that can be extracted for the integrated process. A 28% extraction of the organics in the woodchips, which is the case in this work, has resulted in about 30% reduction in thermal energy output of the RB. The thermal energy output refers to the useful energy left for steam generation after the subtraction of the energy requirement of the endothermic reduction reaction (the reduction of Na_2SO_4 to Na_2S) which takes place inside the RB. The corresponding amount of lignin separated, shown in Fig. 8 on the top X-axis scale, is about 36% of the total lignin charged with the woodchips.

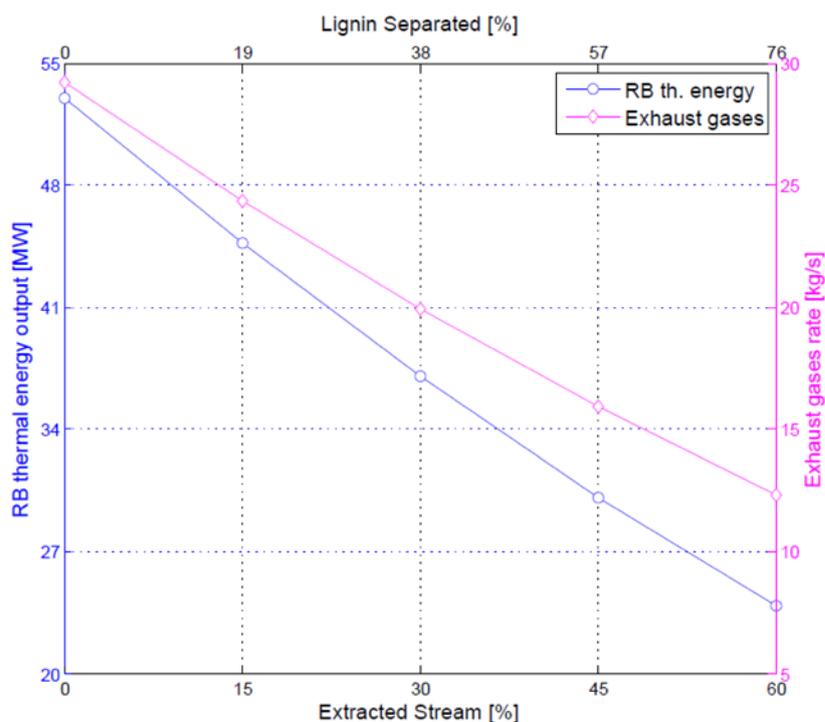


Fig. 8. Recovery boiler thermal energy output and the exhaust gases mass flow rate as a function of the organics in the extracted stream expressed as percentage of the total organics charged. The top X-axis scale represents the corresponding amount separated lignin expressed as percentage of the total lignin charged.

The exhaust gases mass flow rate has also been reported in Fig. 8 as a function the organics extraction rate expressed as percentage of the total organics charged. It is meant to give an idea of the change in the composition of the BL. The combustion air flow is proportional to the amount of carbon and hydrogen present in the BL and so is the resulting exhaust gases flow. For the current work, that is a 28% extraction of organics, the exhaust gases mass flow rate has reduced by 32%.

4 CONCLUSIONS

An Aspen model for the production of alkali free lignin and biobutanol from the underutilized organic part of woodchips used in chemical pulping process has been developed and evaluated from techno-economic point of view. A mathematical model of an existing pulp and paper mill has been used to assess the impact of the integrated process on the energy performance of the evaporation unit and RB.

The energy and material balances of the units and the total system have been evaluated for the main case. The balances include some local limitations, e.g. the fuel balance of the RB. The effect of some parameters on the subsystems of the pulp and paper mill namely the evaporator and the RB has been analyzed. The calculated balances and available data on prices have been used for a preliminary economic analysis. Published price data have been used whenever available. The economy of the integrated process has shown a strong dependence on the selling price of lignin. This is because of the much higher production rate of lignin compared to butanol.

The impact of the hemicellulose and lignin extraction on the live steam consumption of the evaporation unit, according to the new configuration evaluated in this work, has been demonstrated as a function of the dry content of the recycled alkali stream and the temperature of the mixed organics stream (T_{mix_2} , in Fig. 6). The amount of recirculated organics stream, which is mixed with the extracted stream prior to the evaporation unit, has also been demonstrated over a range of dry content of the recycled alkali stream as well as the temperature of the mixed organics stream. The overall impact of the new process to the RB boiler is as a result of the reduction in the organic composition of BL and consequently, the reduction in its heating value.

In order to ensure complete integration of the new process with the exiting pulp and paper mill, evaluation of the potential for energy/ resources saving using innovative process integration techniques is necessary. Hence, future work will see the current model used as a base to develop an exhaustive energy integration analysis that accounts all the thermal and power loads of the new process as well as that of the pulp and paper mill.

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