TECHNO-ECONOMIC COMPARISON OF ACETONE-BUTANOL-ETHANOL FERMENTATION USING VARIOUS EXTRACTANTS

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ABSTRACT:

This work compares various chemicals for use as extractants in second-generation Acetone-Butanol-Ethanol fermentation on economic and environmental bases. Both non-toxic and toxic extractants are considered in this study. The combinative extractive-distillation separation process was modelled using a combination of Microsoft Excel 2013, MATLAB 2015 and Aspen Plus v8.8. Separation trains were designed and optimized for each extractant to best take advantage of extractant properties. Upstream units considered in this analysis include: biomass (switchgrass) solids processing, biomass pre-treatment and saccharification, and fermentation. Downstream processes considered include utility generation and wastewater treatment. The cost of CO_2 equivalent emissions avoided (CCA) was used as the metric to compare the environmental impact of each process as compared to conventional petroleum-based gasoline. The economic and environmental best extractant is shown to be 2-ethyl-hexanol with a minimum butanol selling price of $1.58/L and a CCA of $471.57/tonne CO_2 equivalent emissions avoided.

KEYWORDS:

Extraction

Acetone-Butanol-Ethanol (ABE) fermentation

Bio-butanol

Techno-economic analysis

Cost of CO_2 equivalent emissions avoided

INTRODUCTION:

The rapid depletion of fossil fuels, combined with increased concern surrounding greenhouse gas emissions and global warming has made the quest for alternative fuels a high priority. In Canada, the transportation sector accounted for 23% of greenhouse gas emissions in 2014, second in emissions to only the oil and gas sector [1]. These large contributions precipitate a motivation for alternative transportation fuels that should ideally be carbon-neutral, with minimal net addition of greenhouse gases into the atmosphere throughout their life cycle. Along these lines, agricultural based alternative fuels (biofuels) are being championed by policy makers as a key strategy for greenhouse gas emission reduction. The 2012 biofuel market in Canada was estimated to have an aggregate positive impact of 2 billion CAD on the economy annually [2].

Biobutanol is a candidate biofuel that has the potential to reduce the life-cycle emissions of the transportation and fuels industries. The interest in biobutanol stems from its potential to act as a substitute for both gasoline and diesel, though it is more commonly used as a gasoline substitute [3, 4]. Moreover, biobutanol has a higher energy content and lower affinity for water when compared to the more studied bioethanol. In addition, biobutanol is more compatible with current automobile engines and gasoline pipelines than ethanol [3].

Biobutanol can be produced biochemically from various forms of *Clostridia* bacteria in a process known as Acetone-Butanol-Ethanol (ABE) fermentation. During ABE fermentation, acetone-butanol and ethanol are produced in an approximate 3:6:1 ratio with total product yields typically peaking at around 20 g/L [5]. Product yields are limited to this concentration because butanol is toxic to the bacteria causing them to die off as butanol accumulates in the fermentation broth [3].

ABE fermentation has historically been a first-generation biofuel process. First-generation biofuel feedstocks consist primarily of food crops such as cereals, oil seeds and sugar crops such as corn or sugarcane. The choice of feedstock (and consequently feedstock price) have been shown to be important factors to influence the cost of biobutanol. In particular, first-generation feedstocks, which generally have high prices, make the production of butanol economically unfavourable [5, 6, 7].

An alternative to the above substrates are the so-called second-generation substrates. Second-generation biofuels seek to address the limitations of first generation biofuels by using non-food-competitive biomass such as lignocellulosic biomass. These crops are either food by-products or can be produced on land that cannot be effectively used for food production, such as corn stover or dedicated energy feedstocks such as grasses. The downside to fermenting second-generation biomass is that pre-treatment of the biomass is necessary to break up the polymeric sugar chains o that fermentation can occur [8]. Steam explosion, acid pre-treatment, enzyme assisted hydrolysis and alkaline pre-treatment methods are all methods that may be used to this effect. [8, 9, 10, 11]. With proper biomass pre-treatment, ABE fermentation has been shown to be compatible with barley straw [12], corn stover [13], distillers' dry grains and solubles (DDGS) [14], switch grass [13], and wheat straw [15].

1.1 PRODUCT REMOVAL IN DOWNSTREAM PROCESSING

Due to low product yields, product recovery from the dilute fermentation broth also hinders industrial production of bio-butanol. Product recovery, typically accomplished using pure distillation, is quite energy intensive, requiring 13-25 tonnes of steam per tonne of butanol produced [6]. To bring down the cost of separation, many alternative separation methods have been proposed including: gas stripping [16, 17, 18, 19], pervaporation [20, 21, 22], adsorption [23], and liquid-liquid extraction [24, 25, 26, 27]. Of these options Groot *et al.* indicated that hybrid processes with pervaporation or extraction are most attractive for product removal due to high selectivities and operational advantages including technology maturity and maintenance [28]. Qureshi *et al.*, suggested that adsorption or extraction are the most energy-efficient product removal alternatives [23]. Liu *et al.*, generated a superstructure for downstream ABE processing that compared conventional distillation, gas stripping and extraction. The optimal configuration they identified considered liquid-liquid extraction combined with distillation [29]. It is for these reasons that this work further explores the use of liquid-liquid extraction to reduce the cost of biochemical biobutanol production.

1.2 LIQUID-LIQUID EXTRACTION

Candidate extractants for butanol liquid-liquid extraction can be defined by three major properties: their distribution coefficient for each of the products (especially butanol), selectivity and toxicity. The distribution coefficient defines the affinity of the product for the extractant over the affinity of the product for the fermentation broth. Selectivity is the ratio of water taken up by the extractant relative the quantity of butanol. The toxicity of an extractant falls into two sub-categories: non-toxic extractants are harmless to the bacteria and thus can be used directly in the fermentation broth to improve yields by removing toxic compounds from the fermentation broth (*in-situ* applications). The downside to non-toxic solvents is that they have inferior extraction properties compared to their toxic counterparts, which in contrary to non-toxic options cannot be used *in-situ* [3].

Many extractants have been extensively studied at the lab scale; Groot *et al.* examined the properties of 36 different chemicals including both toxic and non-toxic compounds. The parameters that define the efficacy of a solvent are the butanol distribution coefficient (mass fraction of butanol in the extractant phase over mass fraction of butanol in the aqueous phase) and selectivity (distribution coefficient of butanol over the distribution coefficient of water). In general they found that extractants with higher butanol distribution coefficients (this study considers a range of products with butanol distribution coefficients between 0.3-12) had lower selectivities (from 160-4300) and vice-versa [24]. Other popular extractants include oleyl alcohol and 2-ethyl-1-hexanol. Both of these compounds are non-toxic and have moderately high distribution coefficients of 3.8 for oleyl alcohol and 6.9 for 2-ethyl-hexanol [25]. It is also possible to blend toxic solvents with non-toxic solvents to produce a non-toxic mixture with better extractive properties than the non-toxic extractant could achieve on its own, while still remaining non-toxic. An example of this type of extractant is 20 wt% decanol (toxic) mixed with oleyl alcohol (non-toxic) [30]. Kraemer *et al.* used computer-aided molecular design to screen thousands of chemicals for their potential use as ABE extractants. The best chemical they identified was mesitylene. Mesitylene is toxic to butanol-producing bacteria, however it boasts excellent mechanical properties and a distribution coefficient of 2.2 and a selectivity of 1970 [26]. The use of ionic liquids for extraction has also been proposed. The proposed extractants are biocompatible, however they report low selectivities (2.6 – 132.4) and butanol distribution coefficients (0.8 – 2.3) [27].

The use of non-toxic extractants directly in fermentation reactors has also been studied to determine the effect of in-situ extraction on fermentation yield. Roffler *et al.*, studied the effects of various extractants on batch fermentation using *C. Acetobutylicum* and found that butanol yield improved with all non-toxic extractants [31]. Following up on this work, Roffler *et al.* also studied extractive fed-batch fermentation with oleyl alcohol as the extractant. This resulted in a final butanol concentration of 125 g/L [32]. Bankar *et al.* compared two stage continuous extractive fermentation (using a decanol/oleyl alcohol blend) to single stage continuous fermentation and found that ABE product concentration increased by nearly 60% [33].

Systems-level comparisons of alternate product recovery techniques can also be found in literature. Liu *et al*. generated a superstructure for downstream ABE processing that compared conventional distillation, gas stripping and liquid-liquid extraction using 2-ethyl-1-hexanol. Processes were modelled using short-cut distillation methods. The optimal solution, which minimized the annualized cost of the separation over a three year timespan, identified extraction as the optimal solution. In fact, each of the top ten configurations involved extraction [29]. As previously mentioned, Kraemer *et al.* studied the use of the extractant mesitylene. They compared the energy requirements of product separation using pure-distillation, oleyl alcohol, and mesitylene for continuous ABE fermentation. Assuming ideal vapour-liquid equilibrium (VLE) they determined that Mesitylene had the lowest energy demand per kilogram of butanol produced (4.8 MJ/kg) followed by oleyl alcohol (18.5 MJ/kg) and lastly the traditional distillation method (25.6 MJ/kg) [26]. van der Merwe *et al.* compared the energy requirements of several separation trains. Once again, liquid-liquid extraction (coupled with gas stripping) featured in the best scenario with an energy input of 1.72 MJ/kg of butanol. The extractant in this case was 2-ethyl-1-hexanol. The simulations in this study are thermodynamically robust, however the authors note uncertainty in liquid-liquid equilibrium predictions and remarked that “improved physical property methods should be used for more accurate simulation of the complicated system.” [34]

For biobutanol to be a viable diesel or gasoline substitute, the economics of ABE fermentation need to be assessed. Recent economic analyses include that by Qureshi *et al.*, who investigated the economics of second-generation ABE fermentation using wheat straw as the fermentation substrate. Their work used a combination of pervaporation, distillation and membrane separation to recover the products. The final minimum butanol selling price (MBSP; butanol selling price which results in an NPV of zero over the plant lifetime) in this study was $1.05/kg for a production rate of 150,000 tonnes per year [35]. Kumar *et al*. compared the economics of ABE fermentation using various substrates including: corn, corn stover, bagasse, wheat straw and switchgrass. The plant was designed to produce 10,000 tonnes of butanol per year with an assumed mass yield of 39% total ABE products per unit of sugars and an assumed recovery of 99%. They determined that the cheapest option was corn stover or bagasse with a butanol sales price of $0.59/kg followed by switchgrass ($0.6294/kg), wheat straw ($0.6856/kg) and corn ($1.2953/kg) [36]. However, this study did not perform rigorous simulations of the plant (especially the separation section in particular), did not account for the significant cost of wastewater treatment, and did not consider alternative technologies (such as liquid-liquid extraction) for product separation. Therefore, the estimates presented in that work have a high uncertainty.

This study seeks to compare various proposed ABE extraction chemicals at a plant-wide level on both environmental and economic bases. Products are recovered to their ASTM standard specifications [37, 38, 39] and product separation is modelled considering the azeotropic butanol-water vapour-liquid-liquid equilibrium (VLLE). Some questions that are addressed by this work are: (1) which extractant results in the lowest MBSP when the full VLLE for the butanol-water system is considered? (2) Which extractant has the lowest cost of CO_2 equivalent emissions when compared to conventional gasoline? (3) How does downstream broth wastewater treatment affect the MBSP?

METHODS

The design for this process was inspired by a design proposed by the National Renewable Energy Laboratory (NREL) for a biochemical biomass-to-ethanol process [40], with major modifications made to the fermentation and separation sections of the plant to account for production of biobutanol. Figure 1 displays a block flow diagram of the major sections of the plant for the conversion of switchgrass to biobutanol. The fermentation was modelled in MATLAB 2015, while product separation was modelled in Aspen Plus v8.8. The remainder of the plant was modelled by performing mass and energy balances in Microsoft Excel. All plants considered in this study were sized for an annual butanol production rate of 80,000 metric tonnes/yr.

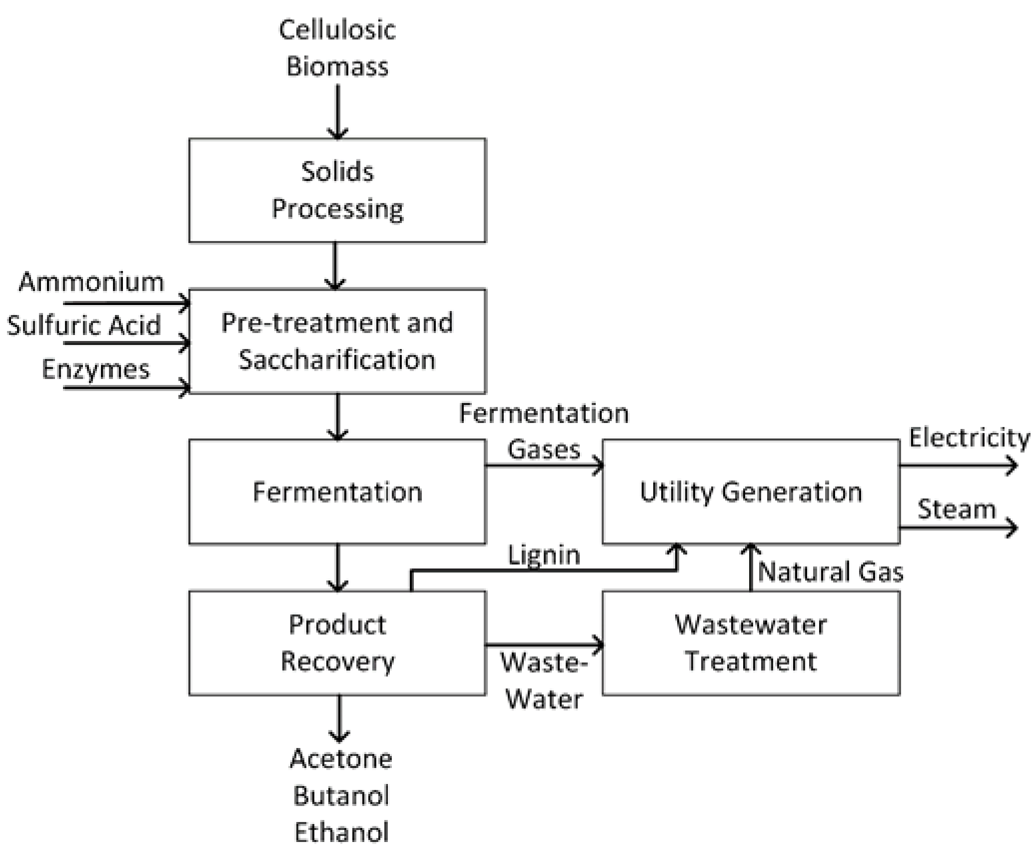

Figure 1: Process flow diagram for the second generation biochemical butanol plant considered

2.1 SWITCHGRASS STORAGE AND SOLIDS PROCESSING

Switchgrass is assumed to be delivered to the plant by truck, with properties given in Table 1, where it is stored for up to three days in an external silo. The switchgrass is transported to the plant via conveyors at which point it is ground into finer particles by a hammer mill. Electrical requirements for the mill were assumed to be 90kWh/tonne biomass processed [41]. From there the biomass is slurried using water and sent to biomass pre-treatment. This work takes into consideration the capital costs for each of the aforementioned units, as well as their electricity and water consumption requirements.

Table 1: Analysis of switchgrass feedstock (with references in square brackets)

Component	Content	Unit
C	46.68 [42]	wt%
H	5.82 [42]	wt%
N	0.98 [42]	wt%
S	0.13 [42]	wt%
O	47.2 [42]	wt%
Cellulose	37 [36]	wt%
Hemicellulose	29 [36]	wt%
Lignin	19 [36]	wt%
Density	85 (8% moisture) [43]	kg/m^3
HHV	17.06 [42]	MJ/kg

2.2 PRE-TREATMENT AND SACCHARIFICATION

The goal of biomass pre-treatment and saccharification is to break down polymeric sugars such as cellulose and hemicellulose into monomeric sugars that are more readily fermented by butanol-producing bacteria. This study considers the use of dilute sulfuric acid, coupled with enzymatic hydrolysis to accomplish this. These methods were chosen for their technical maturity [11] and for the fact that they were shown to achieve high sugar conversion with relatively low cost [10].

Slurried biomass from the solids processing area of the plant is first treated with 1wt% sulfuric acid at 140°C and 5.6 bar [10]. The residence time for this reactor is five minutes [40]. Most of the heating is performed by waste heat from the separation with steam making up the remainder of the required energy. The dilute acid pre-treatment serves two purposes: it converts the majority of hemicellulose into pentose sugars [3] (for this study it is assumed that hemicellulose is broken down exclusively into xylose) and breaks apart the cellulosic matrix into enabling more efficiency downstream enzymatic hydrolysis [11].

Before enzymatic hydrolysis of the mixture can occur, the pH of the mixture needs to be raised so as not to denature the cellulase enzymes. Traditionally this is accomplished by the addition of lime which precipitates out the sulfuric acid as gypsum. However, this method has been linked to the loss of up to 12% of the viable sugars. A proposed method to avoid this deficiency is pH balancing via the addition of ammonia, which results in negligible sugar loss [44]. The NREL carried out experiments and determined that the addition of 4.8 g/L of ammonia was sufficient for hydrolyzate conditioning [40]. This neutralization reaction occurs at atmospheric pressure. Therefore, we chose this approach for our study.

Following pH balancing, the hydrolyzate is cooled to 48°C and sent to enzymatic hydrolysis. The cellulase enzyme loading rate is 58mg protein per g of cellulose [10] and the reactor is assumed to have a 72-hour residence time [40]. After pre-treatment and saccharification, it is assumed that 85.1% of the cellulose present in the biomass has been broken down into glucose and that 95.6% of the hemicellulose has been broken down into xylose [10]. A flow diagram outlining the major operations of the pre-treatment section can be seen in Figure 2. Operating costs considered in the economic analysis for this section of the plant are the costs of heating and cooling (through the use of steam and cooling water), electricity for pumping, as well as the cost of sulfuric acid, ammonia, and the enzymes.

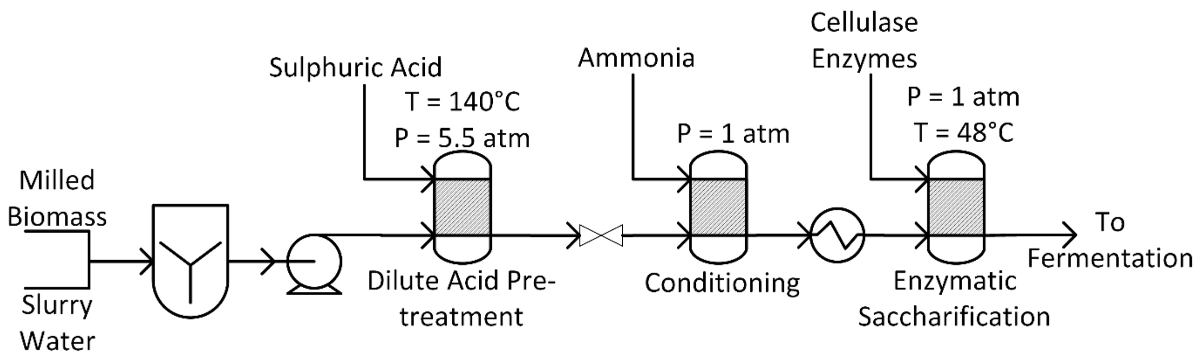

Figure 2: Process flow diagram for the pre-treatment section of the plant

2.3 FERMENTATION

Once the biomass has been treated it proceeds to fermentation. In our analysis, batch fermentation is carried out by *C. Acetobutylicum*, and was assumed to reach final concentrations of 13.2 g/L of butanol, 6.3 g/L of acetone and 0.8 g/L of ethanol [18] after 60 hours. *In-situ* extraction extends the duration of fermentation by removing toxic butanol from the broth containing active cells, thereby delaying end-product inhibition. In order to determine the benefit of in-situ extraction on batch fermentation yields, the model of Honda *et al* [45] was used in combination with butanol inhibition effects from Yang and Tsao [46]. The model consists of ordinary differential equations of the mass and energy balances, reaction rates, and includes the Monod equation under the effects of end-product inhibition and the effect of product removal from the broth by the extractants.

For each extractant, the ratio of solvent to broth volume was varied in to maximize the total profit from the fermentation section of the plant. This includes revenue from the products, cost of the fermentation tanks and cost of the extractant itself. The model was solved using the MATLAB ODE solver `ode45`. The fermentation model was run in such a way that the fermentation was limited by product accumulation in the broth, and not due to substrate limitations. The output of the model was the average value of the concentration of the butanol in the broth and the extractant. This value represents the concentration of butanol in the fermentation broth entering the separation section of the plant. The fermentation extractant was assumed to be recycled for the next batch with a small loss.

The concentration of acetone and ethanol in the broth was determined from the 3:6:1 bacteria production ratio. Extractant blends were considered to be a single component in this model. The extractants considered in this study, their properties, and their fermentation yields can be viewed in Table 2. The distribution coefficients for acetone and ethanol for some of the extractants considered have not yet been reported in literature. If the distribution coefficient value for either acetone or ethanol does not appear in Table 2 it is assumed to be the same as that of oleyl alcohol (0.34 and 0.28 for acetone and ethanol respectively). All distribution coefficients reported were measured at fermentation temperature (35°C) unless otherwise noted.

Table 2: List of extractants considered and their associated physical and fermentative properties (with references in square brackets)

Extractant Name (Toxicity)	Distribution Coefficients [kg/kg]	Selectivity	Yield A:B:E (g/L)	Solvent : broth fermentation ratio	Reason for Selection
2-Ethyl-1-Hexanol (Non-Toxic)	Butanol: 6.09 Acetone: 0.58 Ethanol: 0.47	276.7	17.46 : 34.92 : 5.82	0.5867	High butanol distribution coefficient; Considered in many other works [25] [29] [34]
Decane (Non-Toxic)	Butanol: 0.3	4300	7.524 : 15.05 : 2.51	3.1287	Highest selectivity of simple alkanes; used in solvent blends [24]
Decanol (Toxic)	Butanol: 6.2	200	6.3 : 13.2 : 0.8	N/A	Highest selectivity of simple alcohols; Used in blends [24]
Hexanol (Toxic)	Butanol: 12	160	6.3 : 13.2 : 0.8	N/A	Highest butanol distribution coefficient for straight chained alcohols [24]
Mesitylene† (Toxic)	Butanol: 2.2 Acetone: 0.83 Ethanol: 0.1	1970	6.3 : 13.2 : 0.8	N/A	UNIFAC predicted best solvent [26]
Oleyl Alcohol (Non-Toxic)	Butanol: 3.8 Acetone: 0.34	330	14.24 : 28.483 : 4.75	0.9322	Considered in many other works; used

	Ethanol: 0.28				in blends [26] [31] [32]
Blend 1: 50wt% Decane 50wt% Olely Alcohol (Non-Toxic)	Butanol: 2.05	2315	10.27 : 20.54 : 3.42	1.8708	Considered in other economic analyses; good blend potential [47]
Blend 2: 20wt% Decanol 80wt% Olely Alcohol (Non-Toxic)	Butanol: 4.28	304	14.98 : 29.96 : 5.00	0.9322	Good balance between selectivity and distribution coefficient [30]

†Mesistylene's properties are measured at 80°C

Fermentation tanks were sized to provide six hours of feed to the separation section. For in-situ extraction the volume of the extractant was also considered when sizing the tank. Fermentation time, including tank turnover, was assumed to be 72 hours (60 hours for fermentation, plus 6 hours of feed provided to the separation section, plus 6 hours for tank turnover). As a result, 12 fermentation tanks are required. During fermentation, hydrogen gas and carbon dioxide are produced. It is assumed that 0.067g of hydrogen gas is produced per gram of butanol during fermentation [48]. *C. Acetobutylicum* has been shown to consume 100% of glucose and 71% of xylose during fermentation with a similar cellulosic feedstock [14] and has also been shown to have a butanol yield of 0.18 g of butanol produced per gram of sugar consumed [31]. Two parallel seed trains were used to grow the bacteria. Corn steep liquor (CSL) has been shown to be an appropriate nutrient supplement for other butanol-producing bacteria and is assumed to be appropriate for *C. Acetobutylicum* as well. CSL and was fed to the bacteria at a loading rate of 0.5 wt% [49].

2.4 PRODUCT SEPARATION

The goal of the separation section is recover acetone, butanol and ethanol from the fermentation broth. This is most-commonly performed via distillation. Products are recovered to their ASTM standard purities. Chemical grade acetone is recovered at 99.5% by mass [37] while ethanol and butanol are recovered at fuel grade specifications: 92.1% [39] and 96% [38] by volume, respectively. Extractants are recovered to minimum 99.5 wt% before being considered eligible for recycle.

The separation section of the plant was modelled using Aspen Plus V8.8. The only products considered in the fermentation broth were acetone, butanol, ethanol and water. Intermediate fermentation components such as butyric acid were assumed to only be present in negligible amounts. The default UNIFAC and NRTL parameters in Aspen Properties, normally considered to be suitable for mixtures such as this [34], are actually quite inadequate at predicting the LLE between butanol and water (see Figure 3 and Figure 4). This can occur on individual distillation column trays and in an atmospheric decanter, which can be used to further aid in separation. As such, updated properties were needed to improve the accuracy of this study. Kosuge and Iwakabe proposed updated NRTL parameters to predict the butanol-water VLLE as calculated from experimental data [50]. These new parameters were found to predict the butanol-water LLE much better than Aspen’s default parameters (again see Figure 3 and Figure 4).

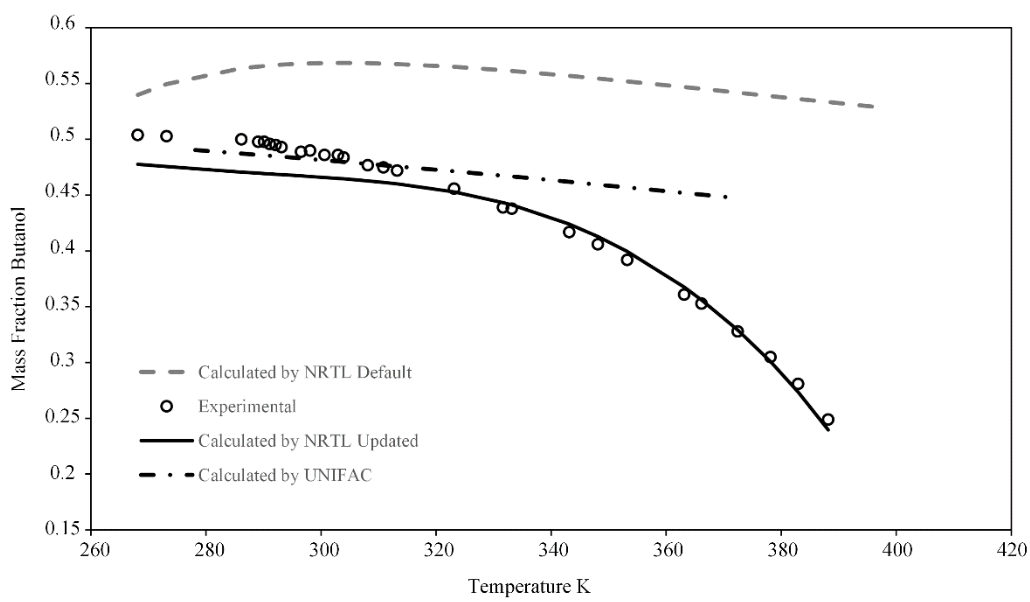

Figure 3: Comparison of models which predict butanol-rich liquid phase butanol mass fraction

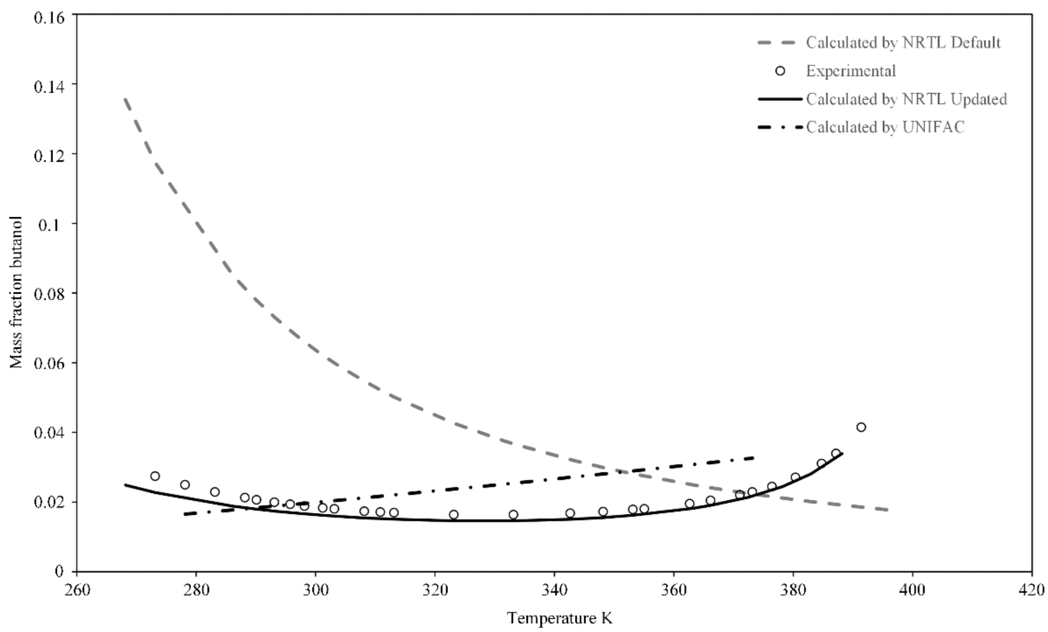

Figure 4: Comparison of models which predict water-rich phase butanol mass fraction

In addition, previous work in literature has noted uncertainty in the modelling of the liquid-liquid equilibrium between extractants and the fermentation broth. Again, property methods such as UNIFAC and NRTL, normally considered suitable for such mixtures have been shown to be poor predictors of solvent properties [26, 34]. This work addresses those concerns by calculating the LLE between the broth and solvent phases based on the experimentally calculated distribution coefficients.

The first step in the separation train is to remove solids (such as lignin and cell mass) from the fermentation broth using a filter-press unit. It is assumed that 100% of the lignin and cell mass is removed from the broth and sent to the utility generation section of the plant. Other studies have looked at selling the remainder of the feedstock and cell mass as cattle feed, however with second-generation feedstocks these by-products are less nutritionally valuable and cannot be used as cattle feed [10].

Following the removal of solids the next step is the extraction of ABE from the fermentation broth via the addition of solvent. This is followed by a sequence of distillation columns to recover the extractant for recycle and to separate the acetone, butanol and ethanol from each other and any residual water. To fairly compare the extractants, the remainder of their separation trains need to be configured to best suit the extractant properties. This results in two possible sets of separation trains that are distinguished from one another based on whether or not the butanol-water heteroazeotrope is encountered during separation.

If the heteroazeotrope is encountered during separation it must be broken at the end of the separation train in order to separate the butanol and the water. Thus, the first separation-related decisions are centered on the best methods to recover acetone and ethanol (if it is economically favourable to do so). This recovery can occur in two possible ways: (1) acetone and ethanol are removed sequentially in a direct sequence, or (2) acetone and ethanol are removed together and then separated from each other in a second column. Following the removal of the acetone and ethanol, the butanol-water heteroazeotrope can be also broken in two ways: (1) the full heteroazeotropic distillation method involves purifying both water and butanol with two distillation columns integrated with a decanter, noting that a small purge is needed on the recycled water to prevent buildup of acetone and ethanol, and (2) the half-heteroazeotropic method in which the butanol is purified but the water is not. This involves a single column and decanter. A superstructure diagram for the case where the heteroazeotrope is encountered during separation can be viewed in Figure 5.

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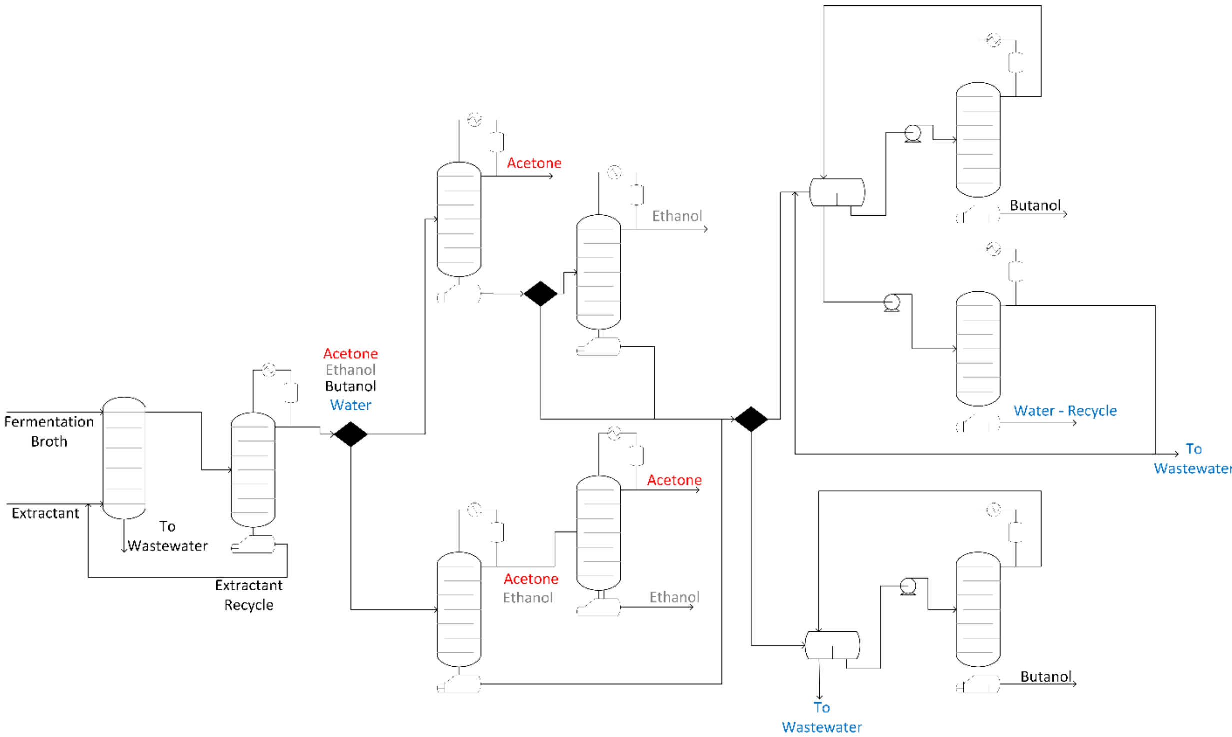

Figure 5: Superstructure considered for the case where the butanol-water heteroazeotrope is encountered during separation. Diamonds are decisions points of the process superstructure: a stream will either go one way or another.

There is more variation in the possible separation train configurations if the azeotrope is avoided. Possible separation sequences include the direct sequence (acetone removal followed by ethanol and lastly butanol). Alternatively, butanol can be removed before ethanol. A modification of the reverse direct sequence can also be used, involving the removal of butanol followed by acetone and lastly ethanol. The superstructure diagram for the separation train avoids the heteroazeotrope can be viewed below in Figure 6.

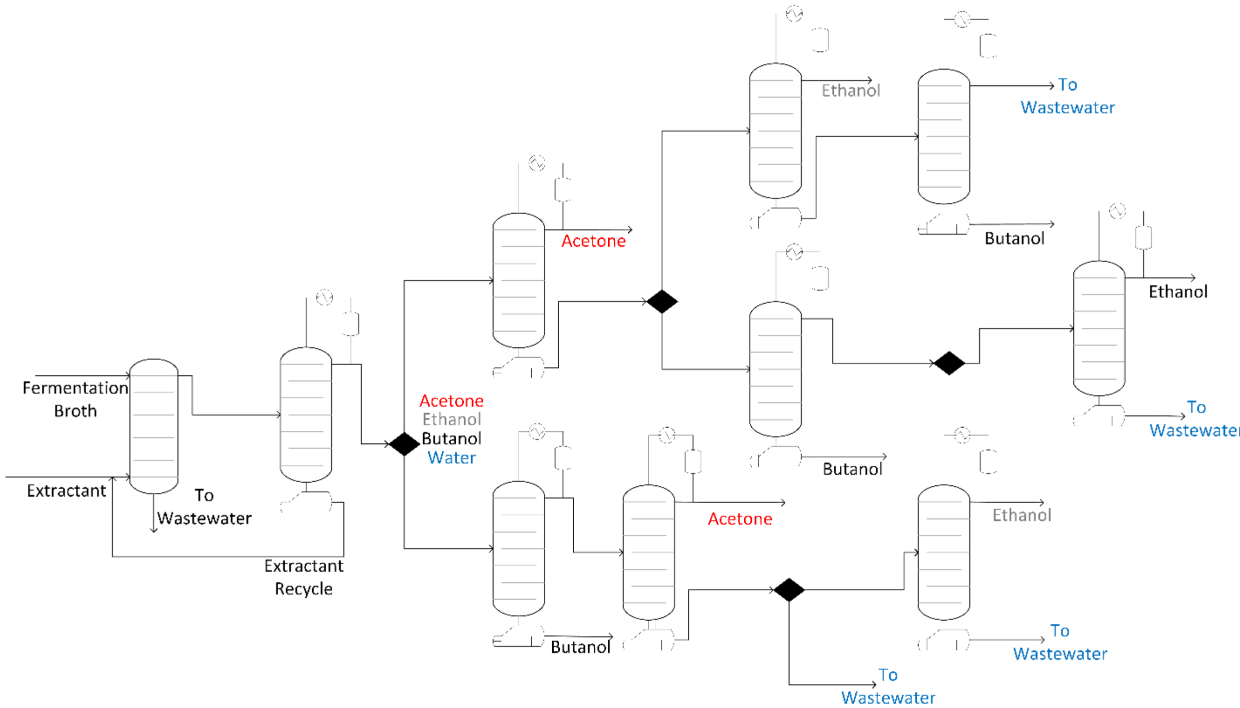

Figure 6: Separation train considered when the butanol-water heteroazeotrope is avoided. Diamonds are decisions points of the process superstructure: a stream will either go one way or another.

Lastly, to facilitate comparison, a pure-distillation base case (the current standard) is also considered. In this case, a distillation column is used to remove water from the broth (dehydration column) in place of the extraction column and stripper. The remaining steps follow a similar path to the extractant case where the heteroazeotrope is encountered. Operating costs for this section of the plant include heating and cooling requirements, electricity required for pumping, and make-up extractant costs.

2.4 PRODUCT SEPARATION – MODELING AND OPTIMIZATION

Each of the feasible separation pathways for a particular extractant were modeled in Aspen Plus v.8.8. Optimization using the particle swarm optimization (PSO) algorithm was then performed on each pathway to ensure they were compared on a fair basis [51]. The PSO algorithm was coded in Visual Basic and was integrated with Aspen Plus via the Aspen Simulation Workbook. The objective function considered was to maximize the NPV of the separation section of the plant. This includes capital cost of the equipment, side product revenues for acetone and ethanol and operating costs. A more detailed description of the economic modeling of the plant will be discussed later in this paper. Decision variables of the optimization consisted of the major distillation column design decisions (number of stages and feed locations), as well as operating conditions (pressure and product-to-feed ratios). Column boilup and reflux ratios were constrained by product purity requirements. For the extraction column, the extractant flow rate and number of contact stages were varied. Stage efficiency for all distillation column stages was assumed to be 80% and the pressure drop across each stage was assumed to be 0.1 psi.

2.5. WASTEWATER TREATMENT

The butanol process generates a number of wastewater streams that must be treated before recycle to the process. Such streams include water from the dehydration column and extraction columns. These streams cannot be directly recycled or disposed of as they contain high levels of organic salts (formed during pre-treatment and conditioning), fermentation nutrients not consumed by the bacteria, soluble inorganic compounds from the biomass, and residual acetone, butanol, and ethanol. Since the cellulosic bio-butanol plant is quite similar to the cellulosic bioethanol plant designed by the NREL [40], the wastewater treatment required is assumed to be similar and detailed modeling is not considered. For economic analysis the capital cost of the wastewater treatment plant is based on a power-law scaling factor of 0.6 applied to the NREL design [52]. A brief description of their process follows.

The first step in the waste treatment process is anaerobic digestion. Anaerobic digestion uses bacteria to breakdown residual acetone, butanol, and ethanol in the water. In anaerobic digestion, it is assumed that 91% of each organic compound is destroyed. During anaerobic digestion, methane and CO_2 are produced according to the following reaction [53]:

$$C_nH_aO_b + \left(n - \frac{a}{4} - \frac{b}{2}\right) H_2O \rightarrow \left(\frac{n}{2} - \frac{a}{8} + \frac{b}{4}\right) CO_2 + \left(\frac{n}{2} + \frac{a}{4} - \frac{b}{4}\right) CH_4. \tag{1}$$

It is assumed that all methane produced during digestion is collected and combusted in the utility generation section of the plant.

Anaerobic digestion follows aerobic digestion to further remove remaining organic compounds. During anaerobic digestion, nitrifying bacteria lower the pH of the anaerobic digestion lagoons, requiring a caustic species to be added for neutralization purposes [40]. The cost of the caustic is considered in the economic analysis of the wastewater treatment section of the plant.

The fully digested material is pumped to a membrane bioreactor for clarification in which any residual organic compounds are removed. Biomass sludge from the aerobic lagoons are removed using filtration. Contrary to the NREL analysis, the sludge is assumed to be recycled in this work. In actuality, a small portion of this would not be recycled and would be sent to the utility generation section of the plant for combustion.

The last step in wastewater treatment is salt removal. This is accomplished via reverse osmosis (RO). The RO effluent is assumed to be pure water and eligible for recycle to the process. It is assumed that non-cellulose, hemicellulose, or lignin in the biomass is disposed in this manner. Following wastewater treatment, the water is assumed fit for recycle to the process. A simple block-flow diagram for the wastewater section of the plant can be viewed in Figure 7.

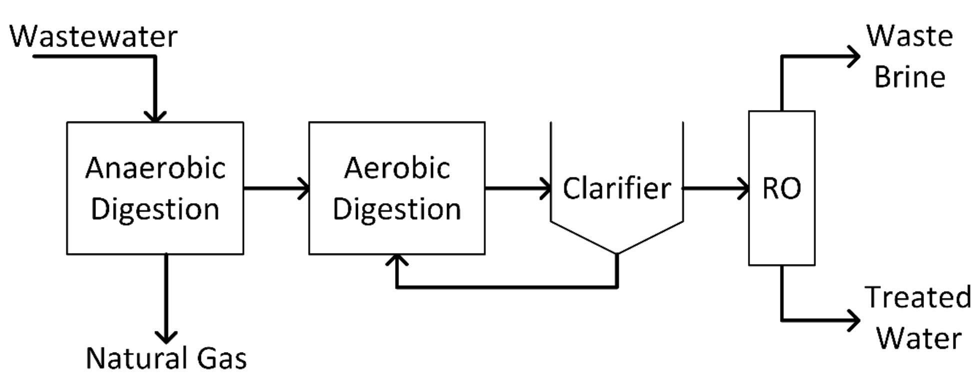

Figure 7: Block flow diagram for the wastewater treatment section of the plant

2.6 UTILITY GENERATION

The purpose of this section is to burn various organic by-product streams to produce steam and electricity. Combustible by-products include all of the lignin in the feedstock (the LHV of lignin is 20.92 MJ/kg), hydrogen gas produced during fermentation, and methanol produced during anaerobic digestion. The streams are fed to a combustor capable of handling the wet solids. The combustor/boiler system is assumed to generate high-pressure steam (HPS) with 80% efficiency. A multistage steam turbine attached to a generator is used to generate electricity from the HPS. CO_2 produced in this section is emitted to the atmosphere.

2.7 ECONOMIC ANALYSIS

The economics of this process were determined based on the "nth-plant assumption." This means that the learning curve associated with building new plants of this type have been surmounted and that costs are for mature technologies. A discounted cash flow rate of return (DCFRR) analysis is used to determine the minimum butanol selling price (MBSP – selling price of butanol such that the NPV of the plant is zero over the project lifetime). Capital cost estimates and economic parameters were based on a combination of literature data, particularly from the NREL [40] and Seider *et al.* [52]. The cost of the separation section was determined by using Aspen Capital Cost Estimator. Values from literature were scaled using power law expressions with exponents ranging from 0.5 to 0.8 depending on the type of equipment [40, 52] and adjusted to 2015 United States Dollars using the Chemical Engineering Plant Cost Index. The plant is financed using an equity to debt ratio of 60%/40% where the debt is financed over 10 years at an interest rate of 8%. The plant is assumed to operate for 30 years preceded by a three year construction period with a discount rate of 10% per year calculated after a 35% tax is deducted. 8% of total construction cost is incurred in the first year, 60% in the second and 32% in the third. Land costs and royalties were each assumed to be 2% of total depreciable capital (T_{dep}), working capital was assumed to be 5% of T_{dep}. Other costs include additional direct costs (site preparation, warehouses, additional piping, etc.) which is assumed to be 17.5% of total direct costs (TDC) and indirect costs (field expenses, contingency, home office and construction), which is assumed to be 60% of TDC. Depreciation is calculated over seven years using a 200% declining balance method with a plant salvage value of zero. Normal plant operation is 350 days per year (8400 hours) and plants were sized to ensure an annual butanol production rate of 80,000 tonnes. The plant start-up period is assumed to be three months during which 50% of normal revenue is received. During this period 100% of fixed operating costs and 75% of variable costs are incurred. Fixed operating costs are calculated using correlations from Seider *et al.* and includes items such as labour-related operations, maintenance, operating overhead, property tax and insurance [52].

Variable costs and side product revenues are presented below in Table 3.

Table 3: Variable costs and side product revenues

Component	Price
Switchgrass Cost [54]	$67.64/dry tonne
Natural Gas [55]	$2.88/GJ
Solid Disposal (wastewater salts) [52]	$36/tonne
Sulfuric Acid [40],	$87.78/tonne
Ammonia [40],	$406.96/tonne
Caustic for wastewater [40],	$149.16/tonne
Enzyme cost [40],	$4,240/tonne
Electricity [52]	$0.06/kWh
Decane [56]	$500/tonne
Decanol† [56]	$903/tonne
2-Ethyl-1-Hexanol [56]	$690/tonne
Hexanol [56]	$473/tonne
Mesitylene [56]	$789/tonne
Oleyl Alcohol‡ [56]	$982/tonne
Acetone [56]	$1100/tonne
Ethanol [56]	$900/tonne

2.8 COST OF CO_2 AVOIDED

The reduction of greenhouse gas emissions in the transportation sector is one of the major objectives driving policy for the use of biofuels as a replacement for fossil-derived fuels in vehicles. However, there is a cost associated with reducing greenhouse gas emissions that must be considered. This cost can be computed using a metric known as the cost of CO_2 avoided (CCA) [57]. The CCA is the extra cost spent on biofuel production (relative to the cost of gasoline), divided by the amount of CO_2 equivalent emissions avoided by using a biofuel instead of gasoline. The lower the CCA, the more cost-effective the biofuel is for reducing net greenhouse gas emissions to the environment. The CCA is a fair way to compare biofuel processes because it factors in both cost and life cycle impacts. The CCA is computed using conventional gasoline as a baseline and is computed as follows:

$$CCA = \frac{Biobutanol\ marginal\ cost}{CO_2\ emissions\ avoided} = \frac{MBSP - WGP}{CIG - CIB}, \quad (2)$$

where MBSP is the minimum butanol selling price (\$/GJ), WGP is the wholesale gasoline price (\$/GJ), CIG is the carbon intensity of gasoline (tonne CO_2 equivalent emissions per GJ), and CIB is the carbon intensity of bio-butanol (tonne CO_2 equivalent emissions per GJ). The carbon intensity of gasoline (CIG) is defined as its total wells-to-wheels life cycle emissions per unit energy. It encompasses the emissions of its entire supply chain including drilling, production, refining, distribution, and combustion in a vehicle. The carbon intensity of bio-butanol is similarly defined, and encompasses biomass production and harvesting, direct emissions from the plant and combustion in a vehicle. Note that it is assumed that all carbon in the biomass originated from atmospheric CO_2. Additionally, to separate the butanol portion of the emissions from the emissions associated with the production of co-products acetone and ethanol, an energy-basis allocation factor is used. Specifically, the well-to-gate-exit lifecycle emissions are divided among the three products based on their HHV content. For this analysis, all greenhouse gas related chemicals are considered and expressed in terms of CO_2-equivalent (CO_2e) using the IPCC 100-year metric [58]. It is assumed that all carbon consumed by the bacteria exits as CO_2 unless it exits in the products. It is further assumed that biobutanol combusts perfectly in a vehicle resulting in 100% conversion of carbon atoms to CO_2, and no NOx is formed. A summary of all direct and indirect CO_2-equivalent emissions along the wells-to-wheels life cycle considered in this work are in Table 4 for a plant based in the United States.

Table 4: Breakdown of greenhouse gas emissions data used in this study. All units are grams CO_2 equivalent per GJ of butanol produced (by HHV).

Description	
Feedstock production and harvesting [59]	18,550
Land use changes, cultivation [59]	N/A
Feedstock transportation [59]	2,000
Feedstock preprocessing [59]	22,000
Well-to-gate greenhouse gas emissions for switchgrass	42,550
Butanol dispensing [60]	179
Butanol distribution and storage [60]	1,458
Butanol combustion in a vehicle (this work)	63,430
Gate-to-wheel greenhouse gas emissions for bio-butanol (this work)	65,057
Feedstock extraction [60]	8,495
Feedstock transportation [60]	935
Land use changes, cultivation [60]	2
Fuel production [60]	12,968
Gas leaks and flares [60]	2,643
Fuel dispensing [60]	138
Fuel distribution and storage [60]	575
Gasoline combustion in a vehicle [61]	67,870
Well-to-wheel greenhouse gas emissions for gasoline	93,626
Well-to-gate greenhouse gas emissions for natural gas [62]	8,400
Well-to-gate greenhouse gas emissions for electricity [63]	21,260

3. RESULTS AND DISCUSSION

The pure-distillation base case resulted in a MBSP of $2.15/L of butanol produced. Four of the tested extractants had a lower MBSP than this: 2-ethyl-hexanol ($1.57/L), Blend 2: 20wt% decanol 80wt% oleyl alcohol ($1.89/L), oleyl alcohol ($1.97/L) and mesitylene ($2.13/L). The extractants that performed worse than the base case were: Blend 1: 50wt% decane/oleyl alcohol ($2.18/L), decanol ($2.36/L); and lastly decane and hexanol (both at 2.41/L). A visualization of the MBSP of the various extractants and their toxicities can be viewed in Figure 8. Sensitivity analyses on key parameters including acetone selling price, ethanol selling price, and natural gas price shows no change in the relative ordering of extractants that performed better than the base case and thus are omitted. A detailed cost breakdown for each of the cases can be viewed in Table 5.

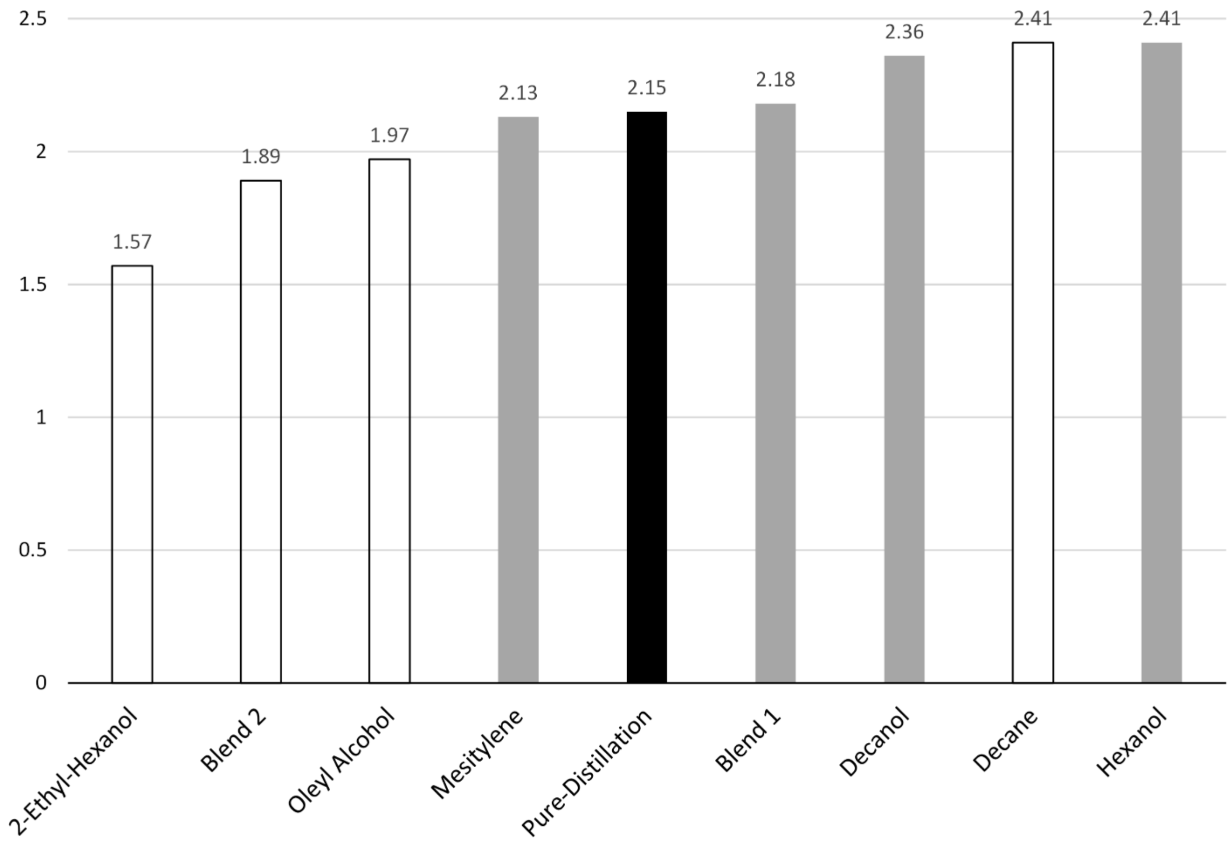

Figure 8: MBSP for each of the cases considered. The black bar represents the base case, gray bars represent toxic extractants and the white bars represent non-toxic extractants

Table 5: Summary of economic results and key model results for each of the cases considered.

	Base case	Decane	Blend 1	Decanol	Blend 2	2-Ethyl-Hexanol	Hexanol	Mesitylene	Oleyl Alcohol
Capital Investment ($1000s)									
Solids Processing	3,261	3,265	3,264	3,259	3,267	3,261	3,263	3,276	3,274
Pre-treatment and Saccharification	46,915	46,264	44,645	46,893	43,144	42,554	46,949	47,147	43,456
Fermentation	22,690	46,804	31,171	22,692	18,871	15,795	22,717	22,811	20,343
Separation	12,618	10,906	12,115	10,990	7,616	10,302	15,342	14,371	9,157
Wastewater	73,009	68,426	56,232	73,594	44,025	38,995	73,364	73,981	45,817
Utility Generation	17,175	17,385	27,089	26,470	28,002	18,733	26,795	18,752	27,470
Total installed equipment cost	175,668	193,049	174,516	183,899	144,945	129,639	188,431	180,338	149,517
Additional Direct Costs	14,960	18,766	15,959	14,671	12,757	12,585	15,447	15,331	13,341
Indirect Costs and non-depreciable capital	141,826	157,591	132,714	147,737	117,315	105,814	151,685	145,579	121,165
Total Capital Investment	332,454	369,407	332,190	346,307	274,997	248,038	355,563	341,248	284,024
Operating Costs ($1000s)									
Solids Processing	4,663	4,667	4,654	4,658	4,667	4,663	4,668	4,701	4,695
Pre-treatment and saccharification	26,674	24,270	19,041	26,671	14,554	13,127	26,721	26,907	15,210
Fermentation	1,535	1,360	981	1,535	655	552	1,538	1,549	701
Biomass Cost	58,869	58,987	58,952	58,810	59,047	58,869	58,928	59,345	59,267
Separation	27,082	52,168	11,863	7,680	5,132	21,499	7,939	16,096	11,166
Wastewater	6,794	6,589	6,061	6,817	5,615	5,436	6,815	6,878	5,695
Total Variable Operating Costs	125,616	148,045	101,567	106,172	89,679	104,147	106,610	115,476	96,732
Total Fixed Operating Costs	60,030	64,652	60,004	61,763	52,844	49,472	62,920	61,130	53,973
Total Operating Cost	185,639	212,670	161,571	167,95	142,522	153,620	169,530	176,606	150,705
Side-Product Revenue($1000s)									
Revenue Acetone	40,186	42,789	8,288	2,575	4,052	38,956	1,326	38,518	6,956
Revenue Ethanol	4,466	11,940	1,982	0	975	9,374	0	452	1,681
Utility Generation	6,857	7,003	14,806	14,158	15,614	7,971	14,448	7,944	15,117
Total Side-Product revenue	51,509	61,731	25,077	16,733	20,640	56,302	15,775	46,914	23,753
MBSP									
$/kg	2.66	2.98	2.69	2.91	2.34	1.95	2.97	2.63	2.43
$/L	2.15	2.41	2.18	2.36	1.89	1.58	2.41	2.13	1.97
$/gal	8.15	9.13	8.24	8.93	7.16	5.97	9.11	8.05	7344
$/Lge	2.47	2.76	2.49	2.70	2.17	1.81	2.76	2.44	2.25
Separation Features									
Extractant Toxicity	N/A	Non-toxic	Non-toxic	Toxic	Non-toxic	Non-toxic	Toxic	Toxic	Non-toxic
Product concentration (g/L) A:B:E	6.3:13.2:0.8	7.524:15.05:2.51	10.27:20.54:3.42	6.3:13.2:0.8	14.98:29.96:5.00	17.46:34.92:5.82	6.3 13.2:0.8	6.3:13.2:0.8	14.24:28.483:4.75
Number of total distillation columns required	5	3	4	4	4	5	4	4	4
Method to break heteroazeotrope	Full	Not Encountered	Not Encountered	Full	Half	Full	Full	Not Encountered	Half
Acetone recovery (% of total produced)	99.9	99.9	19.4	7	10	92.4	4	94.6	16.2
Butanol recovery (% of total produced)	99.8	99.6	99.7	99.9	99.5	99.8	99.7	99.0	99.1
Ethanol recovery (% of total produced)	97	93.8	15.6	Not Recovered	8	74	Not Recovered	10	13

All extractants that performed better than the base case did so with considerably lower separation costs. It is interesting to note that mesitylene is the only toxic solvent that avoids the heteroazeotrope and it is also the only toxic extractant that performed better than the base case.

The three non-toxic extractants that performed better than the base case greatly benefitted from higher product broth concentrations. The benefits of the higher concentration start in the pre-treatment section where units could be smaller and operating costs were lower. The difference in operating costs stems from the fact that a higher concentration of sugar could be fermented in the extractive fermentation cases than could be in the pure batch fermentation processes. This also enabled smaller fermentation units being required for the extractive cases further reducing the capital cost relative to the base case. Along the same theme, the higher product concentration in the fermentation broth also enabled less expensive more compact product separation than the base case.

The effect of increased product concentration is also evident in wastewater treatment costs. In the base case wastewater treatment accounts for 41.6% of the total installed equipment cost (TIEC), while for the three non-toxic extractants with lower MBSP it only made up about 30% of the TIEC. This large contribution of wastewater treatment to capital and operating costs indicated that it is an important consideration when calculating the economics of ABE fermentation, and can result in an overly optimistic MBSP if it is ignored, as is often the case in other works. For example, the MBSP of the base case considering wastewater treatment is \$2.15/L while omitting it results in an MBSP of \$1.61. In the case of 2-ethyl-hexanol, neglecting wastewater treatment results in an MBSP of \$1.28/L, which is 20% lower than the MBSP when wastewater is considered.

Mesitylene resulted in a lower MBSP than the base case as it had a much lower cost of separation; operating costs of the separation section of the plant is approximately 60% lower for mesitylene than for the base case. Unlike the non-toxic extractants, mesitylene had the same batch yield as the base case and thus did not receive any benefits from product concentration. This is evident due to the similar capital costs for mesitylene and the pure-distillation case, especially in the similar costs of the wastewater treatment section.

From an economic perspective, it is evident that non-toxic solvents generally seem more promising than their toxic counterparts. Standing out from the non-toxic extractants is 2-ethyl-hexanol, which has the lowest MBSP by over $0.70/kg. A diagram of the results from the simulation of the separation section can be viewed below in Figure 9. The simulation results for the rest of the cases can be viewed in the supplementary material.

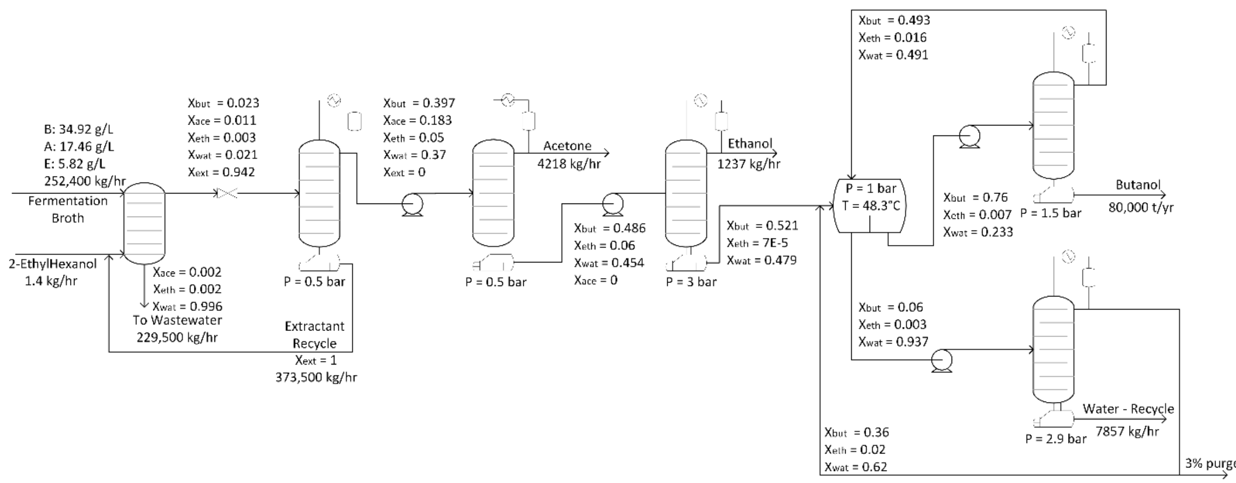

Figure 9: Simulation results from the 2-ethyl-hexanol case

As previously mentioned, this benefit stems mainly from the increased product concentration achieved during batch-extractive fermentation; butanol concentration in this case was over 2.5 times that of the pure-batch case. This is exemplified in the separation section as neither the base case nor the 2-ethyl-hexanol case avoided the heteroazeotrope. However both the capital and operating cost of separation for the 2-ethyl-hexanol extractive case are much lower than for the base case. A summary table of some of the key operating costs between the two aforementioned cases can be viewed in Table 6. This table highlights the added benefit of the increased product concentration throughout the whole plant. For example, in the pre-treatment section, sulfuric acid costs for 2-ethyl-hexanol case were about 55% lower than the base case. Furthermore, heating and cooling costs were 26% and 52% lower. The benefits of the increased broth concentration also propagated to the wastewater treatment section. The operating costs of wastewater treatment are 25% lower for the 2-ethyl-hexanol case.

Table 6: Breakdown of key operating costs for the 2-ethyl-hexanol extractive case and for the pure-distillation base case

Operating Cost	2-Ethyl-Hexanol		Pure-distillation Base case	
	Annual Amount	Annual Cost ($M)	Annual Amount	Annual Cost ($M)
Switchgrass	869,907 t	58.869	869,906 t	58.869
Sulfuric Acid	138,480 t	2.512	310,067 t	5.623
Net Water	70,891 t	4.750	73,643 t	4.934
Enzymes	1,121 t	4.749	1,121 t	4.749
Ammonia	9,752 t	3.970	27,118 t	11.025
Total Heating	2,682,457 GJ	22.533	3,625,572 GJ	30.455
Total Cooling	1,886,640 GJ	0.668	3,971,300 GJ	1.406
Total Electricity	76,998,611 kWh	4.657	80,012,222 kWh	4.840
Wastewater	N/A	5.4	N/A	7.158

In order to determine the effects of fermentation broth concentration on MBSP, a sensitivity analysis was run on fermentation yields of 2-ethyl-hexanol. The results shown in Figure 10 indicated that the MBSP is strongly tied to the product broth concentration as expected. The results also show that even with a 33% reduction in broth concentration 2-ethyl-hexanol still outperforms product recovery via the pure-distillation route.

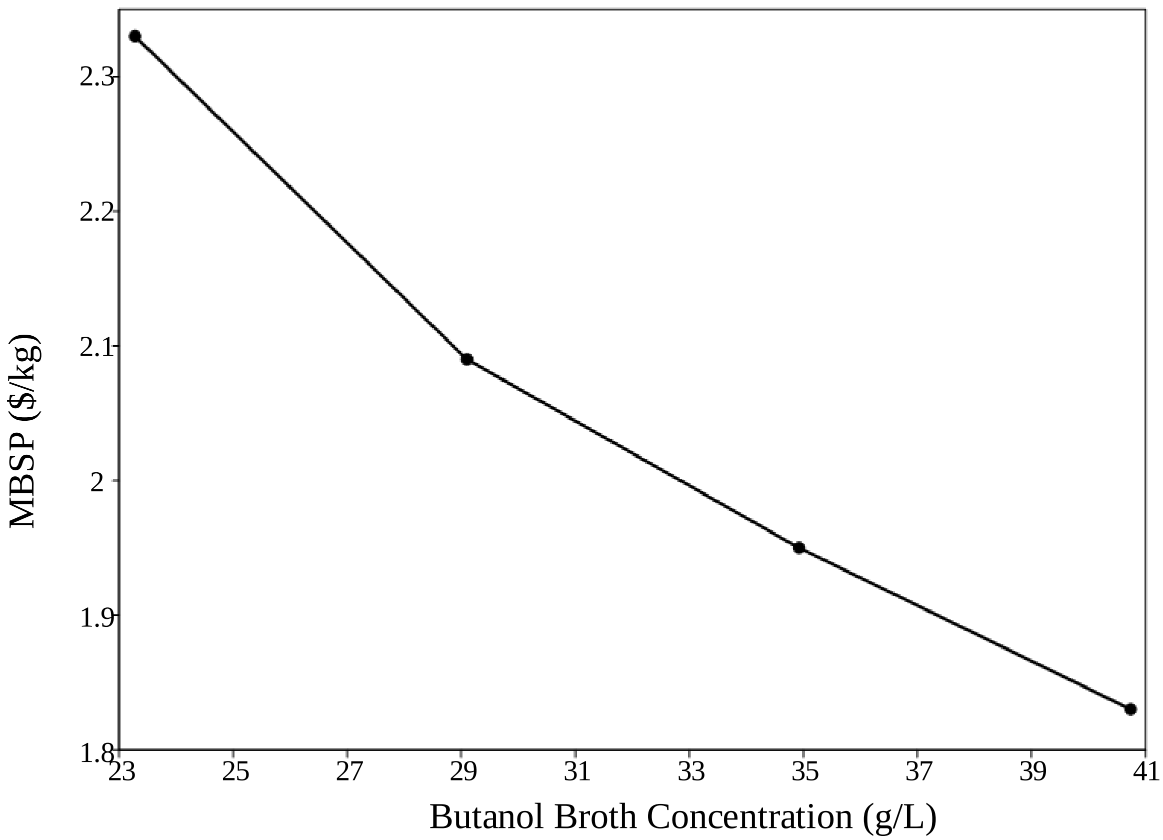

Figure 10: Sensitivity analysis of broth yield on MBSP for the 2-ethyl-hexanol extractive case

The CCA for biochemical bio-butanol ranged from $472 to $1314 per tonne CO_2e emissions avoided. A summary table of the environmental analysis for each of the cases can be viewed in Table 7.

Table 7: Summary of the economic analysis for each of the studied cases

Portion of Supply Chain	Base Case	Decane	Blend 1	Decanol	Blend 2	2-Ethyl-Hexanol	Hexanol	Mesitylene	Oleyl Alcohol
Biogenic CO_2 sequestered during biomass growth (calculated from ultimate analysis) ($kgCO_2$/dry tonne biomass)	-1690-	-1690	-1690	-1690	-1690	-1690	-1690	-1690	-1690
Wall-to-gate GHG emissions for switchgrass import ($kgCO_2$/dry tonne biomass)	729	729	729	729	729	729	729	729	729
Biomass to bio-butanol plant emissions (from simulation results) ($kgCO_2$/dry tonne biomass)	816.0	814	884	903	898	796	907	823	891
Well-to-gate GHG emissions for natural gas use ($kgCO_2$/dry tonne biomass)	27.5	56.3	0	0	0	14.2	0	11.0	0
Well-to-gate emissions for electricity import ($kgCO_2$/dry tonne biomass)	7.08	7.03	6.31	6.62	6.39	6.87	6.69	6.96	6.41
Well-to-gate exit emissions ($kgCO_2e$/dry tonne biomass)	-108.0	-81.5	-68.3	-49.2	-53.8	-142	-45.0	-117	-61.2
Well-to-gate exit emissions allocated to butanol ($kgCO_2$ e/GJ)	-20.6	-14.6	-16.8	-12.9	-13.9	-26.4	-12.0	-23.7	-15.4
Gate-to-wheel GHG emissions for bio-butanol ($kgCO_2e$/GJ)	65.1	65.1	65.1	65.1	65.1	65.1	65.1	65.1	65.1
Well-to-wheel emission for bio-butanol ($kgCO_2e$/GJ)	44.4	50.4	48.2	52.1	51.1	38.6	53.0	41.3	49.6
CO_2e emissions avoided ($kgCO_2e$/GJ)	49.2	43.2	45.4	41.5	42.5	55.0	40.6	52.3	44.1
MBSP ($/GJ)	71.2	79.7	72.0	78.0	62.6	52.2	79.6	70.4	65.0
Biofuel marginal cost ($/GJ)	44.9	53.5	45.7	51.8	36.3	25.9	53.3	44.1	38.7
CO_2e emissions avoided cost ($/tonne CO_2e)	913	1240	1006	1250	854	472	1310	843	879

As can be seen in Table 7, the lifecycle amount of CO_2e emissions is about half that of conventional gasoline (93.6 $kgCO_2e/GJ$) and is approximately the same for each of the cases, which arises from the fact that all plants considered in this study were based the same butanol production rate. It is interesting to note that the production of switchgrass accounted for nearly 50% of the lifetime CO_2e emissions for this process. The variation in the well-to-wheel emissions between the extractant cases themselves can be attributed to two main factors: the percent recovery of butanol and the percent recovery of the side products. The higher the percentage of butanol recovered, the less biomass was required by the plant, and thus emissions from biomass growth was lower. The percent recovery of the side products had a direct impact on the amount of power and natural gas import by the plant. In cases with low side-product recovery, the unrecovered acetone and ethanol was converted to methane in wastewater treatment, which in turn was used for heating and generation purposes. Some cases, such as the blended extractants, decanol, and hexanol recovered enough methane in this manner such that no natural gas import was required. The large difference in CCA for the cases stems mostly from the MBSP, thus the case with the best MBSP, 2-ethyl-hexanol also has the lowest CCA.

The CCA for European biofuels is put in the range of \$277-2,524\$/tonneCO_2e, putting fermentative biobutanol in the competitive range of values; however, the thermochemical biobutanol production route has been shown to have a CCA value of \$135 \$/tonneCO_2e [57]. The large difference between the two stems from the fact that the thermochemical biobutanol study used woody biomass, which requires only a very small amount of preprocessing, and from the fact that the MBSP for thermochemical butanol is lower (\$0.92/L) than that of biochemical biobutanol (\$1.58/L for 2-ethyl-hexanol). Furthermore, the target mark for CCA generally discussed by policy makers is \$50/tonne CO_2e emissions avoided [64]. Though all of the biochemical bio-butanol production routes studied here are much higher than this value, it is certainly plausible that this target can be achieved if improvements are made to the biomass supply chain. The largest sources of emissions for switchgrass growth are from fertilizer use and feedstock preprocessing. Utilizing a biomass that requires less fertilizers and less preprocessing (such as woody biomass) could greatly reduce the CCA for ABE fermentation, however fermentation yields for woody biomass fermentation need to improve before the process could compete economically.

4. CONCLUSIONS

This paper compared a variety of extractants for use in ABE fermentation on a plant-wide economic and environmental basis. The results show that four of the extractants resulted in a lower MBSP than the sequential pure-distillation base case and that three of these four extractants were non-toxic. The only toxic extractant that performed better than the base case was mesitylene. The economic benefits of mesitylene stem from the lower cost of separation compared to the base case, as it was able to avoid the water-butanol heteroazeotrope. The non-toxic extractants greatly benefitted from the increased product concentration achieved during batch-extractive fermentation compared to pure-batch fermentation. These benefits cascaded throughout the whole plant, from pre-treatment to final wastewater treatment. 2-ethyl-hexanol was shown to be the most economical with an ultimate MBSP of $1.58/L compared to $2.15/L for the base case.

Environmentally, the ABE process using switchgrass as a feedstock was shown to have approximately half the of lifecycle emissions when compared to conventional gasoline. The CCAs ranged from $472 to $1314 per tonne CO_2e emissions avoided. Since the lifecycle GHG emissions were approximately the same for all solvent types, the main factor affecting the CCA is the MBSP. Emissions from the growth and distribution of the switchgrass accounts for nearly half of the lifecycle CO_2e emissions.

5. FUNDING

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