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

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Title: Techno-Economic Comparison of Acetone-Butanol-Ethanol Fermentation Using Various Extractants

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Lay abstract

The rapid depletion of fossil fuels and increased concern surrounding greenhouse gas emissions and global warming have led to increased research in biofuels. Bio-butanol is an attractive biofuel as it has higher energy density and better compatibility with current fuel infrastructures than both bio-ethanol and bio-diesel. Bio-butanol is traditionally produced via Acetone-Butanol-Ethanol (ABE) fermentation. The major drawbacks of ABE fermentation are low product concentrations which in turn makes recovery of these products quite expensive. One technique to combat this is liquid-liquid-extraction. This involves contacting the fermentation broth with another chemical to extract acetone, butanol and ethanol from the fermentation broth. This can be performed directly in ABE fermenters with biocompatible extractants, (known as in-situ extraction) or outside of fermentation with toxic extractants. Non-toxic extractants have the added benefit of increasing fermentation yields, while toxic extractants have better physical properties. Thus trade-offs exist between the different chemicals. This work compares a set of candidate ABE extraction chemical based on their minimum butanol selling price and on their environmental impact through the cost of CO_2 emissions avoided by bio-butanol compared to conventional gasoline. This study found the best extractant to be 2-ethyl-1-hexanol with a minimum selling price of \$1.58/L and a cost of avoided CO_2 of \$471.57/tonne CO_2 equivalent emissions avoided.

Abstract

This work seeks to compare various Acetone-Butanol-Ethanol (ABE) fermentation extraction chemicals on an economic and environmental basis. The chemicals considered are: decane, a decane/oleyl alcohol blend, decanol, a decanol/oleyl alcohol blend, 2-ethyl-hexanol, hexanol, mesitylene, and oleyl alcohol. To facilitate comparison a pure-distillation base case was also considered. The aforementioned extractants are a mix of both toxic and non-toxic extractants. Non-toxic extractants can be used directly in fermentation reactors, improving overall fermentation yield by removal of toxic butanol. The extractants were modelled in Aspen Plus V8.8 and separation trains were designed to take advantage of extractant properties. The separation section of the plant was then integrated with upstream and downstream units to determine the Minimum Butanol Selling Prices (MBSP) for second generation extractive ABE fermentation. Upstream processes include biomass (switchgrass) solids processing, biomass pre-treatment/saccharification and fermentation while downstream processes include utility generation and wastewater treatment. The cost of CO_2 equivalent emissions avoided (CCA) was used as a metric to compare environmental impact of each process as compared to gasoline. The economic best and environmental best extractant is shown to be 2-ethyl-hexanol with a MBSP of \$1.58/L and a CCA of \$471.57/tonne CO_2 equivalent emissions avoided. Wastewater treatment, which is often ignored in other works, was found to makeup over 30% of total installed capital cost for all extractants.

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Abbreviations

ABE	Acetone-butanol-ethanol
LLE	Liquid-liquid-equilibrium
VLE	Vapour-liquid-equilibrium
VLLE	Vapour-liquid-liquid-equilibrium
MBSP	Minimum butanol selling price
CCA	Cost CO_2 avoided
NPV	Net present Value

Symbols

X	Mass fraction
Z	Cell concentration (g/L)
S	Substrate concentration (g/L)
P_i	Product concentration component i in fermentation broth (g/L)
P_{im}	Inhibition concentration component i (g/L)
P_i^*	Product concentration component i in extractant (g/L)
V	Volume of broth
V^*	Volume of fermentation broth
J_i	Average concentration component i between the broth and extractant phase
Y_s	Substrate yield coefficient
Y_i	Yield coefficient component i
μ_m	Bacteria specific growth rate
K_s	Saturation constant (g/L)
n_i	Extent of components i inhibition effect
m_i	Extractant distribution coefficient for component i

Declaration of academic achievement

All work presented in this thesis, including model development, data collection, techno-economic analyses, and environmental analyses were performed by myself. Guidance and advice on research direction was provided by Dr. Thomas Adams II of the Chemical Engineering Department. Contents of this work have been prepared for publication in peer reviewed journals.

Chapter 1: Introduction

1.1. Motivation

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 only to 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 additions of greenhouse gases into the atmosphere throughout their life cycle. Agricultural based alternative fuels (biofuels) meet this carbon neutral criteria and are being championed by policy makers as a key strategy for greenhouse gas emission reduction. The biofuel market in Canada was estimated to be worth over CAD$2 billion in 2012 [2].

Biofuels can be divided into three "generations" based on the type of biomass from which they are derived. First generation biofuels are produced primarily from food crops such as cereals, sugar crops and oil seeds. These were the first crops considered for biofuels due to the ease of extraction of their sugars and oils, which can be converted into usable fuels. First generation biofuels are well studied and accounted for approximately 3.4% of global road transportation fuel requirements in 2012. The most common first generation biofuel feedstock is corn, with approximately 60 billion litres of corn-derived bio-ethanol being produced worldwide in 2012 [3]. Despite the fact that first generation biofuels have been commercialised at a large scale, their sustainability has been questioned. First generation biofuels compete directly with food production for arable land use and concerns have been raised over their water-intensive and expensive production [3].

Second generation biofuels seek to address the limitations of first generation biofuels by using non-food biomass, known as lingo-cellulosic biomass. Such ligno-cellulosic feedstock materials include food crop by-products (cereal straw) as well as dedicated energy feedstocks (purpose-grown vegetative grasses, short rotation forests). These crops can be produced on land that cannot be effectively used for food production (unless they are a food by-product) and tend to be more energy-dense than their first generation counterparts. It is predicted that second generation biofuel production will surpass first generation production in the United States by 2022 [2].

Second generation biofuels are poised to take a noteworthy share of the biofuel market in Canada and the United States. This is exemplified by the opening of several pilot and demonstration-scale second generation biofuel plants across Canada [4]. Furthermore, the United States Renewable Fuel Standard regulatory body mandate for a minimum production of 16 billion gallons (60 billion litres) per year of cellulosic biofuels by 2022 [5]. In order to meet these targets and reduce the government subsidies required to make second generation biofuels economically viable, technological improvements to the biomass to biofuel conversion process are needed.

Lastly, third generation biofuels are produced from algae. Algae are aquatic microorganisms that grow rapidly on saline water, coastal seawater, wastewater, or land unsuitable for agricultural farming. Despite these advantages, third generation biofuel production is in its technical infancy and requires technological improvements over its entire supply chain before it can economically compete with first and second generation biofuels [6].

Over the past few decades several biofuels have been investigated that can either completely replace, or can be safely blended with, petroleum derived fuels without requiring specially designed vehicle engines. One such biofuel is bio-butanol. The interest in bio-butanol stems from its potential to substitute for both gasoline and diesel [7] [8]. Moreover, bio-butanol has a higher energy content and lower affinity for water (does not separate in the presence of moisture) when compared to the more-studied ethanol. In addition, bio-butanol is more compatible with current automobile engines and gasoline pipeline networks than both ethanol and biodiesel [7]. Table 1 gives a comparison of some of the properties of *n*-butanol, ethanol, biodiesel and gasoline.

Table 1: Comparison of properties of different liquid fuels *[7, 8, 9, 10, 11]*

Fuel	**Density 20°C (g/cm^3)**	**Research Octane Number**	**Cetane Number**	**Energy Density (MJ/L)**	**Water Solubility (wt%)**	**Air:fuel Ratio**
Gasoline	0.791	91-99	-	32	-	14.6
Ethanol	0.794	129	-	19.6	100	9.0
***n*-Butanol**	0.810	96	17	29.2	7.7	11.2
Biodiesel	0.875-0.885	-	48-65	31-33	2-4	12.5

There are two major production routes for second generation bio-butanol: biochemical and thermochemical. A typical thermochemical bio-butanol production process proceeds as follows: The biomass feedstock is gasified into a synthesis gas (syngas) consisting of carbon monoxide (CO) and hydrogen (H_2). The syngas is then cleaned of impurities (e.g. Cl_2, S, Hg, SO_2) before being converted to butanol and other alcohols over a mixed alcohol synthesis inorganic catalyst. Lastly, the products are separated using conventional distillation. A significant advantage of the thermochemical route is its ability to easily handle a wide range of feedstock qualities, including woody biomass, as the gasification process efficiently converts lignin into syngas. Another advantage is that the product recovery and separation stage is relatively simple as the butanol is present in the mixed alcohols at a high concentration. Disadvantages of the thermochemical process include: low catalyst CO conversion (necessitating larger reactors and higher residence times), high process temperature and pressure requirements (which prove difficult to control and may cause safety concerns), and capital-intensive equipment [12].

Bio-butanol can also be produced biochemically by various forms of *Clostridia* bacteria in a process known as Acetone-Butanol-Ethanol (ABE) fermentation. The ABE process was first developed in the early 20th century as a way to produce acetone for use in munitions during the First and Second World Wars. Later, butanol became the major product of interest and was produced this way until the 1950s when the fermentative production process of bio-butanol could no longer economically compete with petro-chemically derived competitors. The *Clostridia* bacteria naturally metabolize sugars into acetone, butanol and ethanol in a 3:6:1 ratio with combined product yields peaking at around 20 g/L. Products are then typically recovered through conventional distillation methods [13]. The key challenges of ABE fermentation are well documented and include: difficulty in handling second generation biofuel feedstocks, low fermentation productivity, high water usage and effluent treatment cost, and difficulty of product removal from the dilute fermentation broth [14, 15].

Fermentation feedstock (also known as the fermentation substrate) and consequently substrate price, are important factors influencing the cost of bio-butanol production regardless of the route chosen [13, 16, 17]. The ability to use cheaper second generation feedstocks would be an asset to fermentative production, however *Clostridia* bacteria cannot metabolize crystalline cellulose or lignocellulosic biomass directly. Instead, these carbon sources must first be degraded to simpler sugars before they can be converted into butanol by the bacteria. Few studies exist that analyze the impact of second generation biofuel feedstocks on ABE economics and no studies utilize state-of-the-art technologies or modelling and simulation techniques in their analyses [17]. One of the primary thrusts of this thesis is to study the economics of second generation ABE fermentation in greater detail and to utilize newer, more efficient technologies than previously considered.

The problems of product separation and low fermentation yields are strongly intertwined. The fermentation can only achieve relatively low yields because butanol is toxic to the bacteria. As butanol accumulates in the fermentation broth, it dissolves the cellular membrane of the bacteria, limiting yields to the aforementioned 20 g/L, at which point the bio-butanol producing bacteria are killed off. As a result of the low product concentration, product separation can be very energy intensive, requiring 20 tonnes of steam per tonne of butanol produced [16]. Separation is further complicated by the presence of a butanol-water heteroazeotrope. A potential solution to these problems is the use of alternative product removal techniques. These can either occur directly in the fermentation tanks, known as *in-situ* separation, or downstream from the fermenters. The main advantage of *in-situ* product removal is that toxic butanol is separated from the bacteria, allowing fermentation to continue past its natural limits. On the other hand, downstream product removal does not need to consider the health of the bacteria, and can accommodate harsher, but more effective, separation options. There are four main advanced product recovery methods: gas stripping, pervaporation, adsorption, and liquid-liquid extraction [7].

Gas stripping is an *in-situ* technique that removes products from the fermentation broth as a vapour and recovers them through condensation. The quality of the separation is governed by the vapour-liquid equilibrium between the phases. The primary benefit of this method is that it is relatively simple and that no supplementary stripping gas is needed to remove the solvents as all gases used are produced by the fermentation process itself [7].

Pervaporation involves contacting a membrane that is selectively permeable to the products with the fermentation broth. Acetone, butanol and ethanol get solubilized into the membrane, diffuse through it, and evaporate on the other side. The vapours can then be recovered by condensing them, or collecting them using a sweep gas. Pervaporation can be used both *in-situ* and downstream. Membrane fouling by bacteria is a major drawback to this method [7].

The use of adsorbents that have high affinity for the fermentation products is also a viable method. Solid-phase adsorbents are generally non-toxic to the bacteria and the ABE products are easy to recover from the adsorbent (e.g. by heat treating the adsorbent). The downsides to this method are adsorbent cost and fouling of the adsorbent surface [7].

Lastly, liquid-liquid extraction can be used to separate products from the broth. Candidate extractants for this process are defined by three major properties: the butanol distribution coefficient, selectivity, and toxicity. The butanol distribution coefficient defines the affinity of butanol for the extractant over the affinity for the fermentation broth. Selectivity defines the quantity of water taken up by the extractant relative to the quantity of butanol. These equations can be viewed in Equations 1 and 2, respectively. The toxicity of the solvent falls into two sub-categories: Non-toxic solvents are harmless to the bacteria and can thus be used directly in the fermentation broth to improve yields (*in-situ* applications), but generally do not have as good extraction properties as their toxic counterparts, which cannot be used *in-situ*. Thus, there are several trade-offs between the extractants that should be considered before making a decision. For example, a toxic extractant may be able to remove butanol from the fermentation broth efficiently enough to avoid the butanol-water azeotrope (thereby significantly reducing the costs of separation), while a non-toxic extractant may improve the yield of the fermentation but still encounter the azeotrope during downstream product separation. These extractants have been extensively studied at the lab scale. A list of common extractants and their toxicities can be viewed in Table 2.

$$DC_i = \frac{mass\ fraction\ component\ i\ in\ extractant\ phase}{mass\ fraction\ component\ i\ in\ aqueous\ phase} \tag{1}$$

$$Selectivity = \frac{DC_{butanol}}{DC_{water}} \tag{2}$$

Table 2: List of common extractants and their toxicities *[18]*, *[19]*, *[20]*

Solvent Name	**Toxicity**
Decanol	Toxic
Hexanol	Toxic
Mesitylene	Toxic
Decanol	Toxic
Decane	Non-Toxic
Oleyl Alcohol	Non-Toxic
2-Ethyl-1-Hexanol	Non-Toxic

1.2. Thesis objectives and outline

Motivated by the discussion above, this work addresses the trade-offs between different extraction chemicals by systematically comparing optimal separation trains for the solvents listed in Table 2 using updated physical property parameters. To the best of the author's knowledge, an in-depth systems level comparison of different extractants has not yet been completed. In addition, these separation trains will be integrated with upstream and downstream units to determine the minimum butanol selling price (MBSP) for second generation extractive bio-butanol production, and be used to determine the economically optimal extractant. These will also be compared to an optimized pure-distillation separation base-case, which is the currently employed industrial standard. In addition, the cost of CO_2 equivalent emissions avoided (CCA) will be used as a metric to quantify the potential environmental impact reduction of the optimal plant configuration for each extractant. The rest of the thesis is organized as follows:

Chapter 2 performs an in-depth literature search of the ABE fermentation area look at pre-treatment of second generation biomass, fermentation methods and systems level studies of the ABE fermentation area. Chapter 3 covers the methodology of the study, gives a detailed plant overview, covers physical property modelling, separation pathways considered and gives parameters for the economic and CCA analysis. Chapter 4 presents final separation train configurations, economic and environmental results and sensitivities analyses on key parameters. Chapter 5 summarizes major conclusions of the thesis and discusses future research directions.

Chapter 2: Literature review

The ABE fermentation system has been around for nearly 100 years and has thus been the subject of many scientific studies. This chapter will review some of the key studies for this process, the majority of which originate from the microbiology community, and give more insight into the novelties of this work.

The metabolic pathway of bio-butanol production is well studied and understood. The bacteria go through two main production phases: acidogenesis and solventogensis. During acidogensis, the pH of the fermentation broth drops from a starting level of 6.8-7.0 to 4.5-5.0. This phase is associated with the rapid growth of cells and the production of carboxylic acids, acetate and butyrate. The second phase of the process converts sugars and the aforementioned acidogenesis products into acetone, butanol and ethanol through two primary pathways (1) pentose sugars, like xylose, are converted to pyruvate via the Pentose Phosphate Pathway, while (2) hexose sugars, like glucose and fructose, are converted to pyruvate via the Embden-Meyerhoff pathway. The pyruvate is then converted to acetone, butanol and ethanol by various enzymes [21]. Fermentation ends when the total product concentration (the sum of all acetone, butanol and ethanol) reaches approximately 20 g/L. At this point, butanol destabilizes the bacterial cell membranes, killing the cells and ceasing further fermentation. Potential solutions to this problem include the continuous removal of products from the fermentation broth, or the development of more resilient bacteria [7, 21, 22].

There are many species of butanol-producing bacteria, all of which belong to the *Clostridia* genus and the selection of which is primarily based on type of feedstock, targeted productivity and butanol tolerance [7]. *C. acetobutylicum* was the first microorganism that was employed in industrial fermentation. It was originally believed that this was the only species capable of ABE fermentation; however, three more species were later identified to also be capable of producing ABE: *C. beijerinckii, C. saccharoperbutylacetonicum, C. saccharabutylicum* [7]. Several studies exist comparing the efficacy of various butanol producing bacteria, based on their utilization of raw materials and ratio of product production [23, 24]. A summary table some bacterial species and their total product yields can be seen in Table 3. With the objective of increasing the bacteria production of butanol, a hyper-producing mutant strain of *C. beijerinckii* bacteria called *C. beijerinckii BA101* has been cultivated by Quereshi *et al*. that has reportedly higher butanol yields (18.6 g/L), with approximately the same product mass ratio (3:6:1 for A:B:E) as *C. acetobutylicum* (with a comparably lower butanol yield of 9.2 g/L). Bacterial co-cultures have also been investigated with the aim of improving product yield. Li *et al*. used *C. tyrobutyricum* in combination with *C. beijerinckii* and reported higher productivity and yield of butanol than single bacteria cultures (12.1 g/L for the co-culture versus 8.8 g/L for *C. beijerinckii* alone) [25]. Tran *et al*. investigated co-culturing *Bacillus subtilis* with *C. butylicum* and reported substantial enhancements of butanol production (7.5 g/L versus 1.13 g/L for single cultures) [26].

Unfortunately, infection of these species by bacteriophages is a major drawback to co-culturing methods [7].

Table 3: Comparative analysis of four Clostridia species; adapted from Ranjan and Moholkar [7]

Microbial Strain	Total Product Concentration (g/L)	ABE Solvent Yield (g product/ g sugar)
C. acetobutylicum NCIMB 619	19.6	24.5
C. saccharobutylicum NCP P262	11.3	14.1
C. saccharoperbutylacetonicum N1-4	14.2	17.8
C. beijerinckii NRRL B592	16.2	20.8

As previously mentioned, the selection and therefore cost of the fermentation feedstock (which provides the sugary substrates to be consumed by the bacteria) are key drivers for the economic feasibility of fermentation-based biochemical processes. Since ABE fermentation has such a long history, first-generation biofuel feedstocks have been greatly studied in the context of ABE fermentation. Second-generation biofuel feedstocks such as lignocellulosic biomass have been studied less but show encouraging results. One significant difference between first- and second-generation feedstocks is the necessity for pre-treatment processing of the lignocellulosic biomass, which is discussed below [27].

The goal of biomass pre-treatment (specifically hydrolysis) is to efficiently de-polymerize hemi-cellulose and break up the crystalline cellulose matrix while minimizing the addition of inhibitory compounds to the fermentation broth (various acids, dissolved lignin, and salts) [28]. One common pre-treatment method is called steam explosion, which involves sealing lingo-cellulosic biomass into a reactor with high-temperature and high-pressure steam. After a few minutes, the pressure in the vessel is relaxed, which causes steam to expand within the biomass breaking up the ligocellulosic matrix [28, 29]. Steam explosion is relatively cheap, however it also has relatively low hemicellulose conversion and is currently not commercialized [28]. Another hydrolysis option is the ammonia fiber/freeze explosion (AFEX). AFEX is similar to steam explosion, but with the addition of liquid ammonia to the pressure vessel. The residence time for explosion methods is short, however they do not directly liberate any sugars. Instead, these methods break up the cellulosic polymers, thereby increasing the effectiveness of downstream saccharification [28, 29]. Comparatively, dilute acid pre-treatment involves the addition of an acid (e.g. sulfuric acid) to a heated biomass slurry ($\approx 140°C$). The acid breaks apart the cellulose crystals in the biomass while simultaneously converting hemi-cellulose into soluble sugars. Dilute acid pre-treatment has high hemi-cellulose conversion and integrates well with saccharification downstream. On the other hand, dilute acid pre-treatment requires a larger capital investment owing to the corrosive properties of the acid [30]. Lastly, alkaline pre-treatment is similar to dilute acid pre-treatment but involves the addition of a caustic chemical (e.g. sodium hydroxide). Alkaline treatment causes lignocellulosic biomass to swell, decreasing the degree of crystallinity and disrupting the lignin structure. Alkaline pre-treatment can occur at ambient temperatures (an advantage over the other two hydrolysis methods), however it is more expensive due to the use of alkaline species, and has lower yields than dilute-acid pre-treatment. Another concern surrounding alkaline pre-treatment is the formation of irrecoverable salts that causes excessive scaling of this option and also raises concern around downstream operations and inhibits downstream fermentation [28, 29, 27].

Every pre-treatment option produces some products that inhibit fermentation. As a result, a detoxification step is needed after pre-treatment to remove these inhibitory compounds [29]. Detoxification methods are primarily dependent on the upstream pre-processing step and include: electrodialysis, activated carbon adsorption, and overliming [27]. Electrodialysis can be used to remove salt ions produced during alkaline pre-treatment [31]. Activated carbon adsorption, which proceeds steam explosion pre-treatment, uses a carbon adsorbent to remove soluble lignin compounds. Unfortunately, a significant portion of sugar ($\approx 20\%$) is also lost to the carbon matrix [32]. Overliming, used following acid hydrolysis, involves the addition of lime ($Ca(OH)_2$) to the hydrolysate. This causes the SO_2 formed during acid pre-treatment to precipitate into calcium sulfite and sulfate ($CaSO_3$ and $CaSO_4$) which in turn can bind to soluble lignin and precipitate as a lignin calcium compound or as gypsum. Detoxification of dilute acid lignocellulosic hydrolyzates using liming has been frequently studied with both bioethanol fermentation and ABE fermentation [27]. The downside to overliming is that downstream separation of calcium-based solids results in the loss of approximately 12% of monomeric sugars, which are the primary energy source for fermentation. In order to combat this problem, Jennings and Schell proposed the addition of ammonium hydroxide instead of lime. They found that the addition of ammonium hydroxide has comparable inhibitory product removal rates as liming and results in two- to four-fold less sugar loss [33].

After pre-treatment and detoxification, the hemicellulose once present in the biomass has been broken down into smaller sugars and the cellulose matrix has been broken apart and may now be further processed into simple sugars via saccharification. There are two main methods of saccharification, acid saccharification and enzymatic saccharification. Acid saccharification involves the addition of dilute sulfuric acid to the pre-treated biomass slurry at higher concentrations than the dilute-acid pre-treatment. These harsher conditions are necessary to recover the six carbon sugars from the cellulose. The benefits of acid saccharification is the fast rate of reaction, which facilitates continuous processing. The downside is that glucose yields are limited to approximately 50% of those available in the cellulose. Enzymatic saccharification degrades cellulose into glucose using naturally occurring plant proteins as catalysts. Enzymatic saccharification occurs at relatively mild conditions (pH $\approx 4.8, T \approx 320\ K$) and has much better yields than acid-catalyzed saccharification. The downside to this method is that enzymes tend to be quite expensive and the rate of reaction drops rapidly during the process [28]. Enzymatic saccharification can occur separately from, or simultaneously with, fermentation. The advantage to performing saccharification and fermentation separately are that saccharification and fermentation can both occur at their respective optimal conditions. The drawback to this method is that cellulolytic enzymes are end-product inhibited such that the rate of hydrolysis is reduced as more glucose is produced. Conversely, simultaneous saccharification and fermentation does not encounter end-product inhibition of enzymatic saccharification but, must occur in the same vessel and at the same operating conditions [28].

The effects of pre-treatment and hydrolysis methods on lingocellulosic biomass and its relation to ABE fermentation has been extensively studied. Several pre-treatment options were compared using rice straw as a feedstock by Ranjan and Moholkar [34]. They found that acid pre-treatment followed by enzymatic hydrolysis resulted in better downstream fermentation than steam explosion. Acid pre-treatment followed by enzymatic hydrolysis has also been studied with other feedstocks including: wheat [35], barley straw [36], corn stover [37], switchgrass [37] and woody biomass [38], all of which were feasible to ferment after biomass treatment.

2.1. Fermentation methods

Batch fermentation is the simplest fermentation mode. To begin, the substrate and supplementary nutrition are charged into a reaction vessel. Next, the fermentation vessel is autoclaved at approximately 120°C to ensure sterility. The vessel is then cooled to the optimal fermentation temperature of 35°C and is inoculated with bacteria. Typical fermentation batch times are 48-72 hours and product yields peak at the aforementioned 20 g/L [7].

Fed-batch fermentation is similar to batch fermentation. To begin, the reactor is initiated similarly to the batch mode reactor with the fermentation broth occupying around half the vessel's volume. Later, as substrate is consumed by the bacteria culture, additional substrate is added at a slow rate. This serves a two-fold purpose: (1) it keeps the substrate concentration at sufficiently high level to encourage fermentation, and (2) keeps butanol concentration below a certain threshold, increasing the longevity of the active bacteria. The yields and conditions of fed-batch fermentation are similar to those of batch fermentation unless coupled with an *in-situ* product recovery technique [7].

Continuous fermentation is meant to increase the productivity of the fermentation reactor by eliminating batch turnover time. The downside of continuous fermentation is that product concentration is lower than batch fermentation and the ratio of acetone, butanol and ethanol produced by the bacteria may not be constant over time [7]. There are two main methods of continuous fermentation: free cell continuous and immobilized cell continuous. In free cell fermentation, cells are able to move within the fermentation broth due to mechanical agitation, promoting mass transfer between the substrate and the bacteria. Conversely, immobilized cell fermentation allows for longer cell survival time (due to the lack of mechanical agitation) and promotes easy separation of cells from the fermentation broth [22]. While both methods of continuous fermentation have been shown to work at a lab scale [39], they have not been demonstrated at an industrial scale as they pose significant operational challenges including butanol productivity fluctuations over extended operation times [7, 13]. In addition, the bacteria are biphasic, and maintaining the bacteria in just the solventogenic phase is difficult [13].

2.2. Combined fermentation and product recovery

As noted previously, the formation of ABE in the fermentation broth leads to the inhibition of fermentation. In Chapter 1, alternate product separation techniques were introduced. This section reviews literature surrounding ABE fermentation combined with these *in-situ* product recovery techniques. It is worth noting that this review presents only key studies. It is outside the scope of this work to provide a complete review of all *in-situ* ABE fermentative studies.

Gas stripping coupled with ABE fermentation was determined to be feasible by Ennis *et al.* in 1987 [40]. In this batch experiment, reactor productivity was increased by 41% and a final ABE product concentration of 75.9 g/L was achieved. Gas stripping has also been studied with fed-batch fermentation [41] and continuous fermentation [42] resulting in final product concentrations of 26.7 and 53.7 g/L respectively and yield increases of about 20% versus fermentation without *in-situ* product recovery [43].

Research on pervaporation-integrated ABE fermentation started in the 1980s when Groot and Luyben demonstrated the feasibility of silicone tubing membranes for *in-situ* butanol product removal [44]. Flux through their membrane was reported to be 12.9-19.5 $g/m^2 \cdot h$ with a selectivity of 45-57 [7] [44]. Since then many other membranes have been studied including liquid membranes [45] and polypropylene membranes [46] with selectivities ranging from 3 to 180. These high-selectivity membranes yielded butanol concentrations of up to 700g/L in the permeate [7].

The most popular alcohol-selective adsorbents are activated carbon, silicalite, polymeric adsorbents, cross-linked resins, zeolites and molecular sieves. Qureshi *et al*. have performed a comparative assessment of various adsorbents including: silicalite, various resins, activated charcoal and more [47]. Silicalite adsorbents appeared to be the most attractive as they were able to concentrate butanol solutions from 5 to approximately 800 g/L. It is worth noting that these experiments were performed in model butanol mixtures, and not directly in fermentation tanks. Energy requirements for adsorption were shown to be about 41% less than pervaporation, 66% less than gas stripping and 8% less than liquid-liquid extraction [47]. The downside to adsorption is that fouling of the adsorbent surface by the cells occurs quickly and the adsorbents often remove intermediate chemicals such as butyric and acetic acids from the broth [7].

The properties of butanol extraction chemicals for use in ABE fermentation has been studied extensively. Groot *et al*. examined the properties of 36 different extraction chemicals in batch fermentation with *C. beijerinckii* [18]. These 36 extractants consisted of both toxic and non-toxic extractants, with butanol distribution coefficients ranging from 0.3 to 12 and selectivities ranging from 2 to 4100. In general, extractants with a high butanol distribution coefficients had low selectivities and vice-versa. Kraemer *et al*. used computer-aided molecular design to screen thousands of chemicals for their potential use as ABE extractants [20]. The best chemical they identified was mesitylene. Mesitylene is toxic to *Clostridia* bacteria. However it boasts a moderate distribution coefficient and high selectivity of 2.2 and 1970 respectively. Other popular extractants include oleyl alcohol and 2-ethyl-1-hexanol. Both of these compounds are non-toxic and have high distribution coefficients of 3.8 and 6.9 respectively [19] [20]. It is also possible to blend toxic solvents with non-toxic solvents to produce a non-toxic mixture with a higher distribution coefficient and selectivity than the non-toxic solvent could manage on its own. An example of this type of extractant is 20 wt% decanol (toxic) mixed with oleyl alcohol (non-toxic) [48].

The use of ionic liquids for extraction has also been proposed. The proposed extractants are biocompatible, however they report low to moderate selectivities (2.6 – 132.4) and butanol distribution coefficients (0.8 – 2.3) [49].

The use of non-toxic extractants directly in fermentation reactors has also been studied to determine the effect of *in-situ* extraction on 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 [50]. Maximum butanol yield for each extractant was not determined as the fermentations were limited by lack of the glucose present in the broth. Ishizaki *et al*. compared batch fermentation with extractive batch fermentation using oleyl alcohol and crude palm oil as extractants using *C. saccharoperbutylacetonicum*

[51]. They found that batch fermentation with oleyl alcohol increased butanol yield by 21% while using palm oil increased yields by 32%. The increased yield from palm oil was partially due to the fact that some of the oil was consumed as a secondary substrate by the bacteria. Roffer *et al.* also studied extractive fed-batch fermentation with oleyl alcohol as the extractant [52]. In this experiment, fed-batch extractive fermentation produced a butanol concentration of 125 g/L, indicating a 400% increase in glucose consumption and butanol productivity. 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% [53].

According to Groot *et al,* hybrid processes with pervaporation or extraction are most attractive for product removal due to high selectivities and operational advantages including maturity of technology and maintenance concerns (e.g. no need to clean membranes) [44]. Qureshi *et al.* suggested that adsorption or extraction are the most energy-efficient product removal alternatives [47].

2.3. Systems level studies and economic analyses

For bio-butanol to be a viable diesel or gasoline substitute, the economics of ABE fermentation need to be assessed. Initial economic analyses were published in the 1980s including those by Marlatt and Datta [54], Roffler *et al.* [55] and Dadgar and Foutch [56]. Notable among these studies are the latter two analyses. Roffler *et al.* compared conventional first-generation ABE fermentation, where products were recovered through pure-distillation, to an extractive-distillation separation method using an oleyl alcohol/decanol blend. The processes were modelled using the UNIFAC activity coefficient method to model the vapor-liquid equilibrium in the recovery section of the process. They found that extractive separation resulted in a 21% lower minimum butanol selling price (\$0.489/L) when compared to conventional distillation (\$0.617/L) [55]. The analysis by Dadgar and Foutch also found that extractive product separation, this time using 2-ethyl-1-hexanol, was less expensive than product recovery by conventional distillation resulting in a minimum butanol selling price of \$0.26/L [56].

More recent economic analyses include those by Qureshi and Blaschek, who assessed the economics of corn based bio-butanol using a hyper-butanol producing strain of *C. beijerinckii BA101* [57]. In this study hexane was used as an extractant and distillation columns were assumed to recover 98% of acetone, butanol and ethanol at 99% purity. They reported a minimum butanol selling price of \$0.55/kg. Continuing in the area, Qureshi *et al*. assessed the economics of second-generation ABE fermentation using wheat straw as the fermentation substrate [58]. They assumed a 20% (by mass) yield of butanol to sugars and used membranes to break the butanol-water and ethanol-water azeotropes. No modelling simulations or wastewater treatment was considered in this study. The final required butanol selling price in this study was \$1.05/kg for a production rate of 150,000 tonnes per year. Kumar *et al*. compared the economics of ABE fermentation using various substrates including: corn, corn stover, bagasse, wheat straw and switchgrass [17]. 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 prices of $0.59/kg followed by switchgrass ($0.6294/kg), wheat straw ($0.6856/kg) and corn ($1.2953/kg). Tao and Aden investigated the economics of corn-ethanol, soybean-diesel and corn-butanol among others. Product separation in this study were modelled in Aspen Plus using the Non-Random-Two-Liquid (NRTL) property and economics considered annualized cost of production. They determined that the gasoline energy equivalent bio-butanol cost ($2.28) was lower than both bioethanol ($2.33) and biodiesel ($2.48). They also note the potential for cellulosic feedstocks to lower butanol production costs and call for more cost data for cellulosic production [59].

The economics of thermochemical bio-butanol has also been investigated. Okoli and Adams determined the MBSP of thermochemical bio-butanol to be $0.83/L ($1.02/kg). This work used woody biomass as a feedstock and assumed a futuristic 40% butanol yield from the mixed alcohol synthesis catalyst. Products were recovered to chemical grade of 99.5% [12].

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 extraction using 2-ethyl-1-hexanol [60]. 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, the top 10 best configurations all involved extraction. As previously mentioned, Kraemer *et al*. studied the use of the extractant mesitylene [20]. They compared the energy requirements of product separation using pure-distillation, oleyl alcohol and mesitylene. They assumed an acetone to butanol mass ratio of 1:2 during fermentation and a butanol yield of 8 g/L. They also assumed ideal vapor-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). A.B. van der Merwe *et al*. compared the energy requirements of several separation trains [61]. Once again, liquid-liquid extraction (coupled with gas stripping) featured in the best scenario with an energy input of 1.39 MJ/L 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." [61]

2.4. Main contribution of current work

With this outlook in mind, this work presents a systematic and consistent comparison of ABE fermentation for fuel production using a variety of extractants for product separation using economic and environmental metrics. The separation train modelling is the most detailed to date and includes updated physical properties on the ternary vapour-liquid-liquid equilibrium (VLLE) between butanol and water in addition to experimentally validated liquid-liquid equilibrium between the extraction chemicals and the ABE fermentation broth as called for in literature [61]. Products are recovered to their ASTM standard specifications. In addition, the separation train is integrated with downstream and upstream units, including fermentation tanks, to take advantage of the *in-situ* properties of some extractants. Wastewater treatment will also be considered, which although often neglected, plays a major role in the economics of the process since wastewater needs vary greatly from solvent to solvent. Some questions that are addressed by this work include the following: (1) which extractant results in the lowest minimum butanol selling price? (2) Which extractant has the lowest CCA when compared to petrochemical butanol? (3) How does the valuation of co-products affect the butanol selling price?

Chapter 3: Process design and methodology

The design of the plant is broken into sections as follows: feedstock storage and solids processing, pre-treatment and saccharification, fermentation, product separation/recovery, utility generation and wastewater treatment. Figure 1 shows the major plant sections and their connectivity. The following subsections will be used to describe the proposed design and analysis in the following order:

3.1. Product separation
3.2. Fermentation modelling
3.3. Solids processing
3.4. Pre-treatment and saccharification
3.5. Fermentation revisited
3.6. Product separation revisited
3.7. Wastewater treatment
3.8. Utility generation
3.9. Economic analysis
3.10. Cost of carbon avoided

The separation section model will be described first. This is done for two reasons: (1) it will introduce the extractants considered, giving details into how they will be compared, and (2) the plant was sized for a butanol production rate of 80,000 tonnes per year exiting the separation section, from which the remainder of the plant was sized. Following the separation model, the fermentation model will be described. The upstream and downstream plant sections, (revisiting fermentation and separation to describe their connectivity to other plant sections), will be discussed following the separation and fermentation modelling sections. The design is inspired by the National Renewable Energy Laboratory (NREL) proposed biochemical biomass-to-ethanol process [62], with major changes made to the fermentation and separation sections to account for the production of butanol and for the comparative analysis of different extraction chemicals. A detailed simulation of the process was completed using a combination of Microsoft Excel 2013, MathWorks MATLAB 2014a, and Aspen Plus V8.8. More details about the model, and modelling assumptions will be given for each of the proceeding sections.

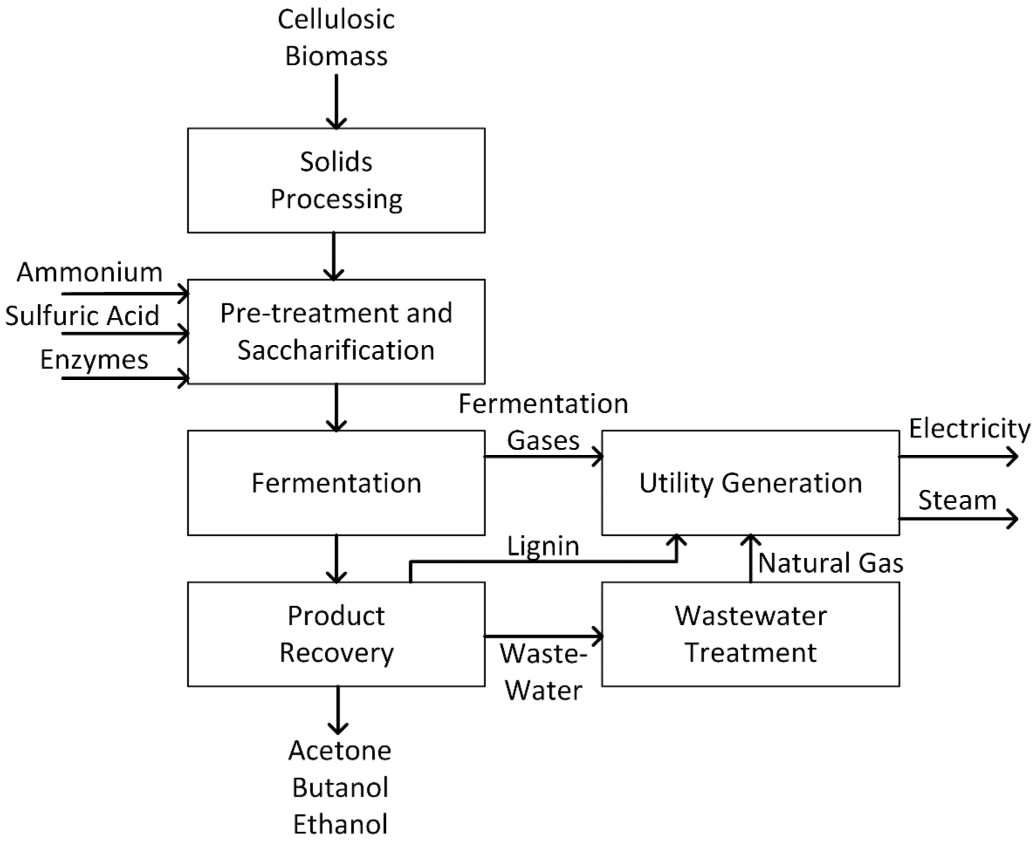

Figure 1: Process flow diagram for second generation biochemical butanol production

3.1. 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 [63] while ethanol and butanol are recovered at fuel grade specifications: 92.1% [64] and 96% [65] by volume, respectively. Extractants are recovered to minimum 99.5% by mass before being considered eligible for recycle.

Traditionally, conventional distillation was used to recover the target products from the broth. Liquid-liquid extraction, followed by distillation, has been identified as a way to reduce separation cost [47]. Dozens of extractants have been studied at the lab-scale and at the systems level [18, 19, 20, 60, 61]. Two main groups of solvents have been identified: straight-chain alcohols, which have a large butanol distribution coefficient but low selectivity, and alkanes, with high selectivities but low butanol distribution coefficients. Many authors have also looked at more complex alcohols, oleyl alcohol and 2-ethyl-1-hexanol, as extracting agents due to their high butanol distribution coefficients and non-toxicity toward the microorganisms that promote fermentation. In addition, extractant blends have been investigated combining oleyl alcohol with other alcohols or alkanes. This work seeks to compare a set of extractants, narrowed down by heuristics, to determine the best overall extractant. Table 4 below shows the list of extractants considered and their reason for inclusion in this work.

Table 4: List of extractants considered. Distribution coefficients and selectivities were measured at 35°C unless otherwise noted

Extractant Name (Toxicity)	**Distribution Coefficients [kg/kg]**	**Selectivity**	**Reason for Selection**	**References**
2-Ethyl-1-Hexanol (Non-Toxic)	Butanol: 6.09 Acetone: 0.58 Ethanol: 0.47	276.7	High butanol distribution coefficient; Considered in many other works	[60, 61, 19]
Decane (Non-Toxic)	Butanol: 0.3	4300	Highest selectivity of simple alkanes; used in solvent blends	[18]
Decanol (Toxic)	Butanol: 6.2	200	Highest selectivity of simple alcohols; Used in blends	[18]
Hexanol (Toxic)	Butanol: 12	160	Highest butanol distribution coefficient for straight chained alcohols	[18]
Mesitylene† (Toxic)	Butanol: 2.2 Acetone: 0.83 Ethanol: 0.1	1970	UNIFAC predicted best solvent	[20]
Oleyl Alcohol (Non-Toxic)	Butanol: 3.8 Acetone: 0.34 Ethanol: 0.28	330	Considered in many other works; used in blends	[50, 52, 20]
Blend 1: 50wt% Decane 50wt% Olely Alcohol (Non-Toxic)	Butanol: 2.05	2315	Considered in other economic analyses; good blend potential	[55]
Blend 2: 20wt% Decanol 80wt% Olely Alcohol (Non-Toxic)	Butanol: 4.28	304	Good balance between selectivity and distribution coefficient	[48]

†Mesistylene's properties are measured at 80°C

Another goal of this study is to analyze the valuation of the fermentation co-products acetone and ethanol on the MBSP. The distribution coefficients for acetone and ethanol of some of the extractants have not been reported in literature, which complicates this issue. If the distribution coefficient value has not been reported in Table 4 it is assumed to be the same as that of oleyl alcohol (0.34 and

0.28 for acetone and ethanol respectively). Sensitivity analyses will be performed on the unknown distribution coefficients to determine their effect on the MBSP.

3.1.1. Updated physical property models

Previous work in literature has noted uncertainty in ABE separation modelling, specifically surround the liquid-liquid equilibrium between extractants and the fermentation broth, as well as in the complex VLLE between butanol and water [61]. Other works have shown that UNIFAC, which is commonly used in studies of this system, is a poor predictor of solvent properties [20]. This work seeks to address those concerns by using updated physical property parameters when modelling product separation.

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, are actually quite inadequate at predicting the LLE between butanol and water (see Figure 2 and Figure 3). This can occur on individual distillation column trays, and also in an atmospheric decanter, which can 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 [66]. These new parameters were found to predict the butanol-water LLE much better than Aspen's default parameters (again see Figure 2 and Figure 3). Table 5 shows the values of the default NRTL parameters and compares them to the updated versions as calculated by Kosuge and Iwakabe [66]. A butanol-water VLE validation is presented in Figure 4 to show that the updated parameters can accurately predict this as well.

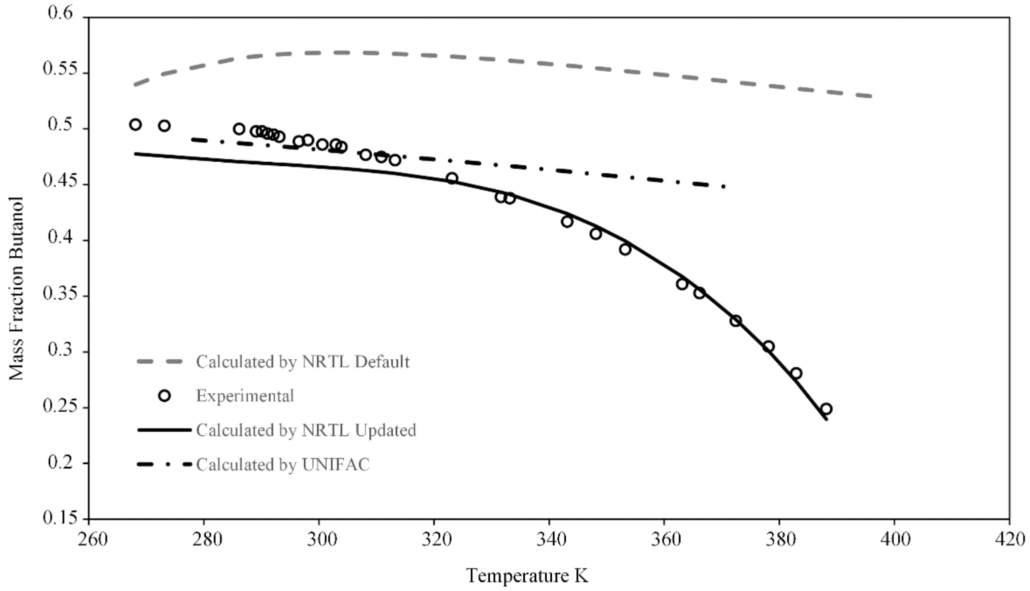

Figure 2: Comparison of models which predict butanol-rich liquid phase butanol mass fraction

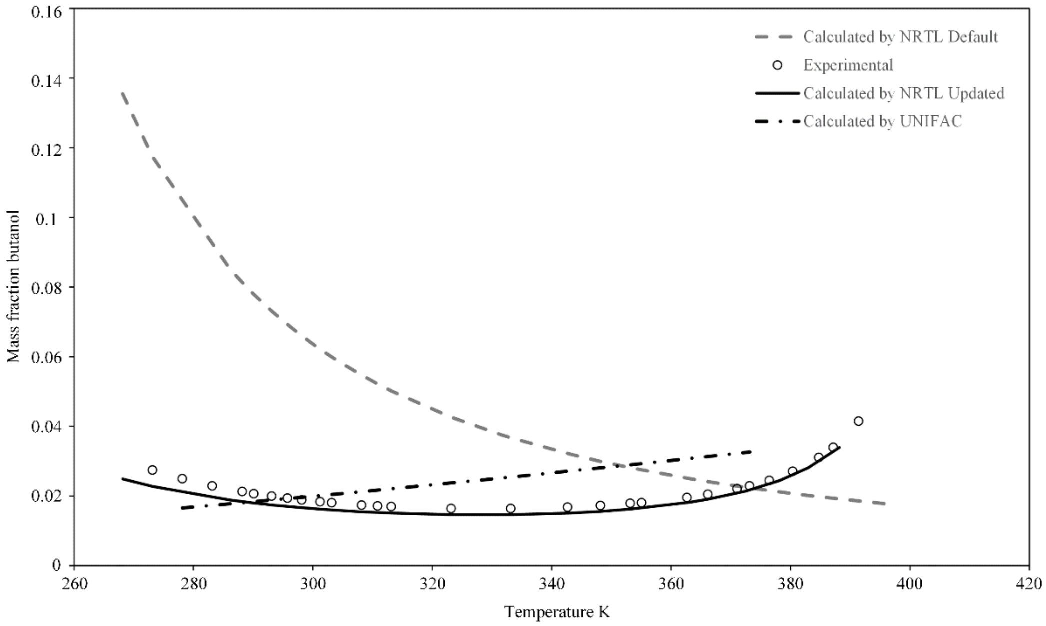

Figure 3: Comparison of models which predict water-rich phase butanol mass fraction

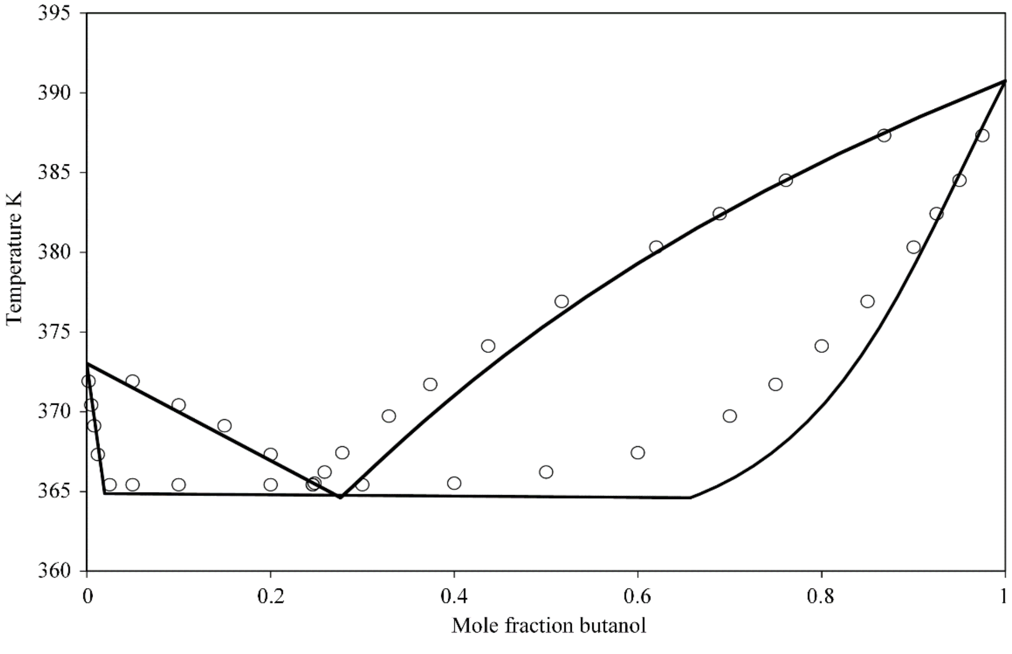

Figure 4: Comparison of models which predict butanol-water vapour-liquid equilibrium; updated NTRL parameter predicted value (solid line), experimental value (circles)

Table 5: Aspen Plus default and updated NRTL parameters

Parameter	Default NRTL	Updated NRTL [66]
A_{ij}	7.6531	19.4473
A_{ji}	-1.2367	30.3193
B_{ij}	-1422.31	-2610.15
B_{ji}	470.834	-3884.3
F_{ij}	19.14	-0.023704
F_{ji}	0	-0.0527519
α	0.3	0.45

Since lab-scale extraction studies calculate the distribution coefficients at a single temperature, and no information is available concerning how the extractants distribution coefficients change with temperature, all of the designs in this work used extraction only at the temperature for which data were available.

3.1.2. Separation train synthesis

The first step in the separation train is extraction of ABE via the solvent from the fermentation broth. This is followed by a sequence of distillation columns in order to recover the extractant for recycle and to separate the acetone, butanol and ethanol from each other and any residual water. In order to fairly compare the extractants, the remainder of their separation trains need to be configured to best suit the extractant properties. For example: Kraemer et al. compared mesitylene to oleyl alcohol and determined that the water-butanol separation when oleyl alcohol was the extractant benefitted from a decanter while mesitylene’s downstream processing did not. Other points that need to be investigated include whether or not it is economically advantageous to recover ethanol (as opposed to allowing it to leave with the wastewater). Separation trains were only considered for each extraction if at least 98% of butanol present in the broth could be recovered from that distillation sequence. 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. These distillation sequences can be viewed below in Figure 5 and Figure 6. To facilitate a comparison, an optimized pure-distillation base case (the current standard) is also determined. In this case, a distillation column is used to remove water from the broth (dehydration column), followed by the recovery of the main fermentation products. The separation pathway considered for this case can be viewed in Figure 7.

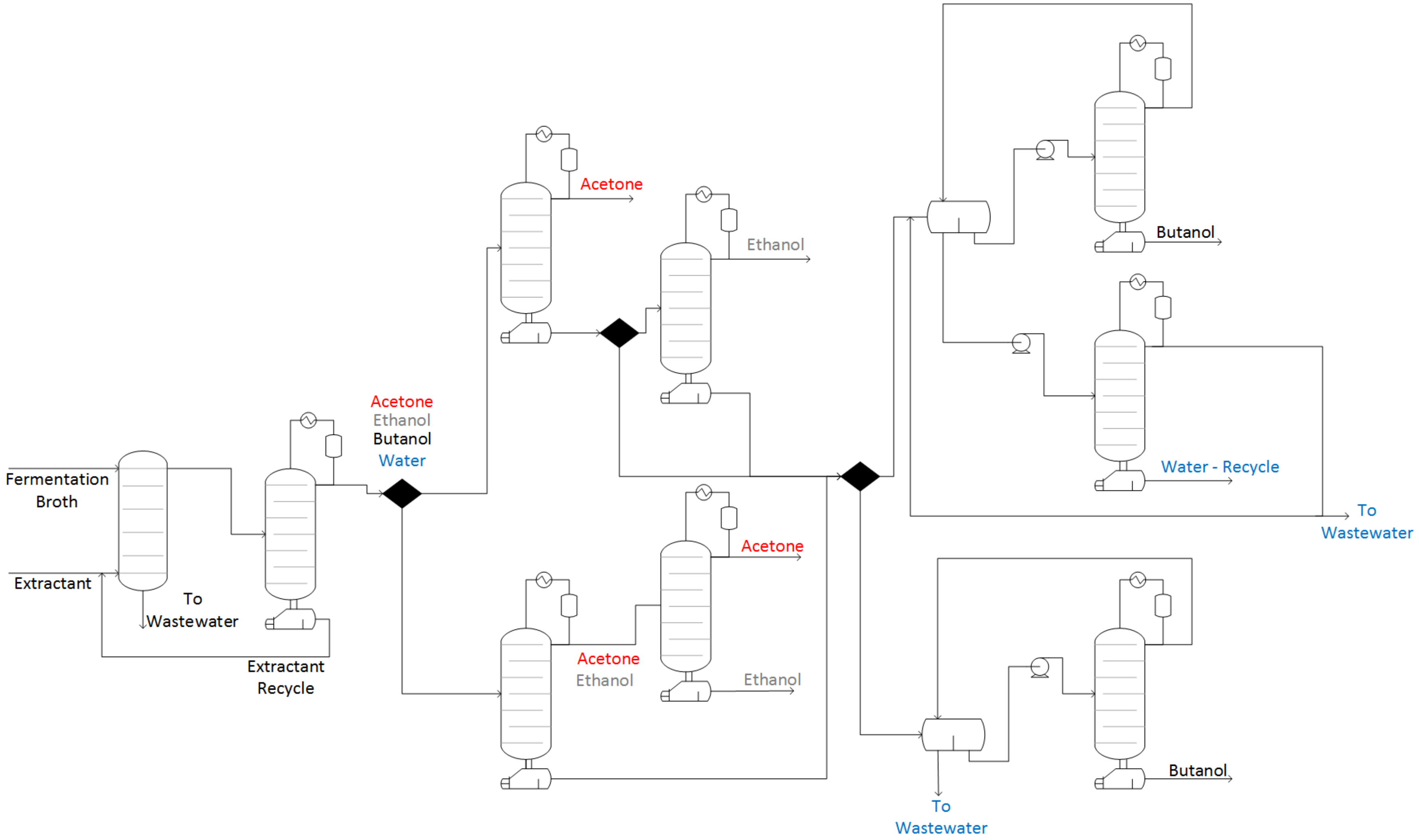

Figure 5: Possible Separation train configurations if the butanol-water heteroazeotrope is encountered. Diamonds represent XOR decisions in the separation sequence

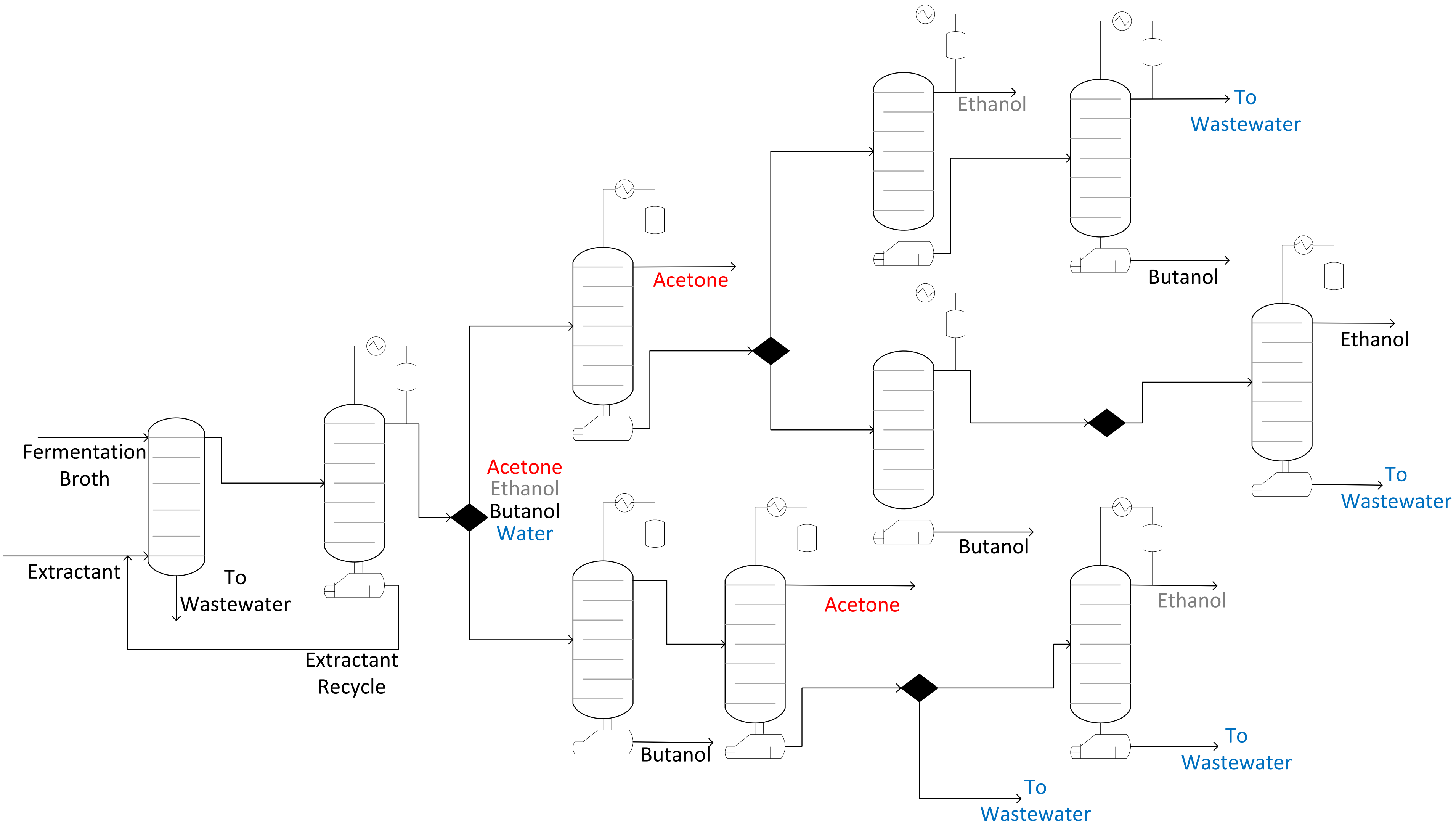

Figure 6: Possible separation train configurations if the butanol-water heteroazeotrope is not encountered. Diamonds represent XOR decisions in the separation sequence

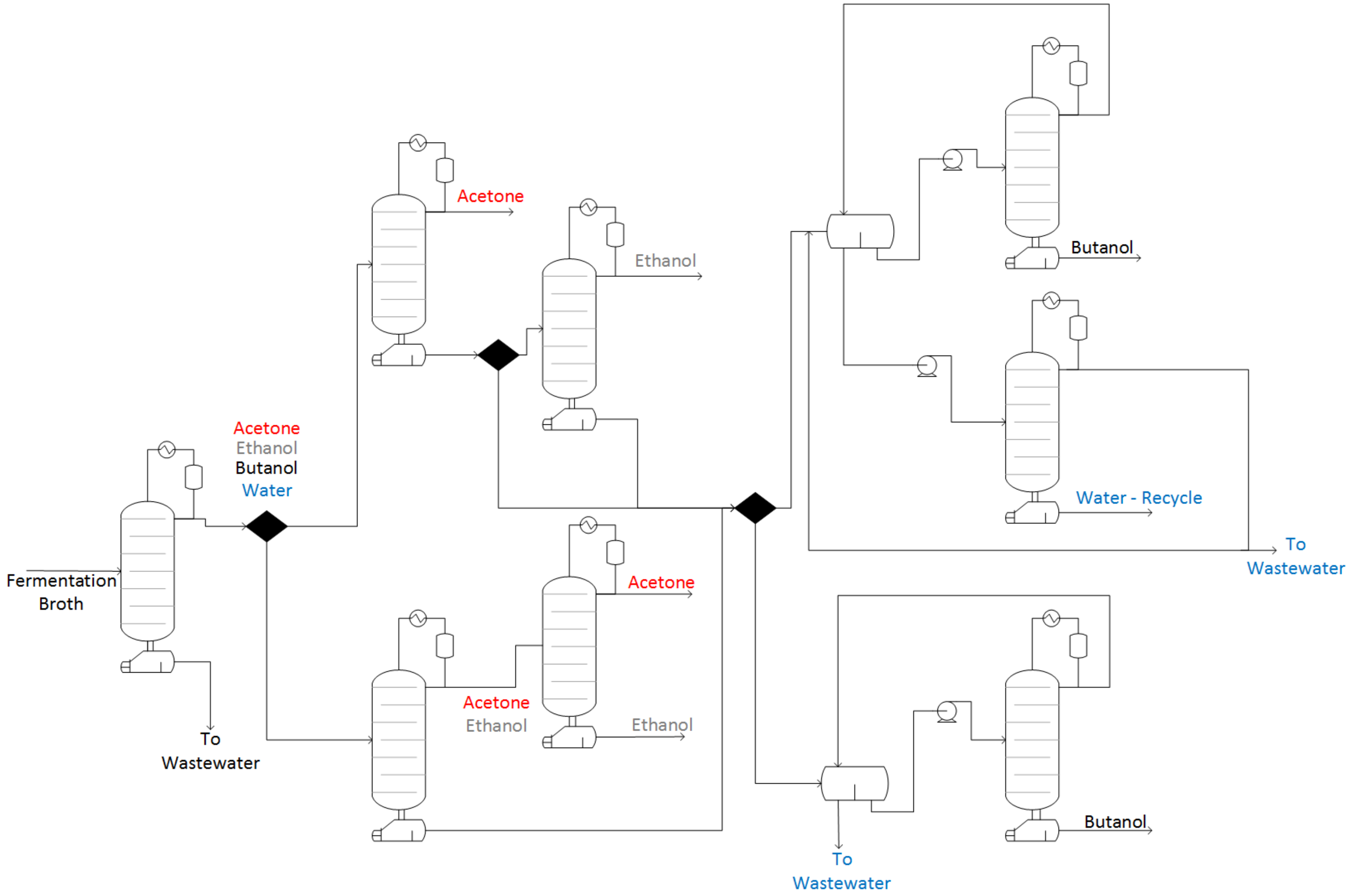

Figure 7: Separation pathways considered for the pure-distillation base case. Diamonds represent XOR decisions in the separation sequence

If the heteroazeotrope is encountered during separation (Figure 5), it must be broken at the end of the separation. Thus the first decisions in this set of separation trains 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 one after another 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.

There is more variation in the possible separation train configurations if the azeotrope is avoided (Figure 6). 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 potential separation configurations for the pure-distillation base case (Figure 7) are very similar to the extractive azeotrope case, however a dehydration column replaces the extraction column and stripper.

3.1.3. Process modeling and optimization

Each of the feasible separation pathways, for a particular extractant, were modelled in Aspen. Optimization using the particle swarm optimization (PSO) algorithm was then performed on each pathway to ensure that they were compared on a fair basis. 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 (see Section 3.9 for more info). This includes capital cost (using correlations from Sieder *et al.* [67] and Woods [68]), side product revenues for acetone and ethanol, and operating costs. Economic parameters can be viewed in Section 3.9. Decision variables of the optimization consisted of the major distillation column design decisions (number of stages and feed location) as well as process operating conditions (pressure and mole 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 pressure drop across each stage was assumed to be 0.1 psi.

3.2. Fermentation modelling

The concentration of ABE present in the fermentation broth entering the separation area of the plant is dependent on upstream fermentation. Batch fermentation by *C. acetobutylicum* was assumed to reach end product concentrations of 13.2 g/L of butanol, 6.3 g/L of acetone and 0.8 g/L of ethanol. This bacterial strain was chosen as it had the highest product yield and one of the highest utilizations of glucose and xylose when fermented with a lignocellulosic feedstock [24].

In-situ extraction involves the addition of an extraction chemical to the fermentation broth. This 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 benefits of *in-situ* extraction on batch fermentation, models were developed to predict butanol fermentation yield. This model is based on those proposed by Honda *et al.* [69] and Yang and Tsao [70]. The model formulation is presented below:

$$\frac{d(ZV)}{dt} = \mu(s, P_i)ZV, \tag{3}$$

$$\frac{d(SV)}{dt} = -\frac{\mu(S, P_i)ZY}{Y_s}, \tag{4}$$

$$\frac{d(P_iV + P_i^*V_i^*)}{dt} = \frac{\mu(S, P_1, P_2)ZV}{Y_i}, \tag{5}$$

$$\mu(S, P_i) = \left(\frac{u_m S}{K_s + S}\right)\prod_{i=1}^{2}(1 - P_i/\,P_{im})^{n_i}, \tag{6}$$

$$P_i^* = m_i P_i, \tag{7}$$

$$J_i = \frac{P_i(t)V + P_i^*(t)V^*}{V + V^*}, \tag{8}$$

where Z is the cell concentration (g/L), S is the substrate concentration (g/L), P is the product concentration in the broth (g/L), P_{im} is the inhibition concentration of component i (g/L), $P_i^*$is the product concentration in the extractant phase of component i, V and $V^*$are the volumes of the broth and the solvent respectively, J_i is the average concentration of component i in the broth and solvent phases, Y_s is the substrate yield coefficient, Y_i is the yield coefficient for component i, $\mu_m$is the bacteria specific growth rate, K_s is the saturation constant (g/L), n is a constant that represents the extent of a components' inhibition effects, and m_i is the extractant distribution coefficient of the extractant for component i. The fermentation was assumed to run for 60 hours, and a constant volume assumption was made. Equation 3 represents the cell growth rate over time. Equation 4 describes the concentration of substrate over time. Equation 5 represents the formation rate of product over time. Equation 6 is the Monod equation of the specific cell growth. Equation 7 equates the product in the broth to product in the extractant phase. Lastly, equation 8 represents the total products in the two phases at a given time. The model was solved using `ode45` in MATLAB A summary table of the parameters can be viewed in Table 6.

Table 6: Fermentation model parameters *[69, 70]*

Parameter	Physical Meaning	Value
$\boldsymbol{K_s}$	Saturation constant (g/L)	0.64
$\boldsymbol{\mu_m}$	Maximum specific growth rate (h^{-1})	0.58
$\boldsymbol{Y_s}$	Substrate yield coefficient	0.056
$\boldsymbol{Y_1}$	Butanol yield coefficient	0.347
$\boldsymbol{Y_2}$	Acetone yield coefficient	0.867
$\boldsymbol{P_{1m}}$	Butanol inhibition concentration (g/L)	13.2
$\boldsymbol{P_{2m}}$	Acetone inhibition concentration (g/L)	30
$\boldsymbol{n_1}$	Extent of butanol inhibition effects	2
$\boldsymbol{n_2}$	Extent of acetone inhibition effects	1

In order to determine the best solvent volume (V^*) to use in the fermentation, another optimization was performed. PSO was used again to vary the solvent to broth ratio (V^*/V) in order to maximize the total attainable profit of the fermentation section of the plant over a 30 year period (again see Section 3.9 for more info). This includes revenues from the products, cost of the fermentation tanks and the cost of the extractant itself. The model was run such that the fermentation was limited by product accumulation in the broth, and not due to substrate limitations. The model was used to determine the average butanol product coefficient in the broth and the extractant J_i. This value is important because this represents the concentration of butanol in the fermentation broth entering the separation section. In actuality, the butanol would be split between the extractant and broth phases and both would be sent to separation. To facilitate downstream separation modelling, the total yield of the two phases was used as the broth concentration entering the separation section. 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 distribution coefficients for the extractants can be found in Table 4. Product concentrations and fermentation solvent volumes determined from this model are presented in Table 7 below.

Table 7: Batch fermentation yields and solvent to broth ratios for each solvent considered

Extractant	V^*/V	Yield A:B:E (g/L)
Batch/Toxic Extraction Decanol Hexanol Mesitylene	N/A	6.3 : 13.2 : 0.8
2-Ethyl-1-Hexanol	0.5867	17.46 : 34.92 : 5.82
Decane	3.1287	7.524 : 15.05 : 2.51
Decane Oleyl Alcohol Blend	1.8708	10.27 : 20.54 : 3.42
Decanol Oleyl Alcohol Blend	0.8178	14.98 : 29.96 : 5.00
Oleyl Alcohol	0.9322	14.24 : 28.483 : 4.75

3.3. Solids processing

For this study, switchgrass was used as the feedstock. Switchgrass was chosen as it is not food-competitive and has been shown to be one of the least expensive second-generation feedstocks when coupled with ABE fermentation [17]. The switchgrass is assumed to be delivered to the plant gate with properties shown in Table 8 below.

Table 8: Analysis of switchgrass feedstock

Component	Content	Unit	Reference
C	46.68	wt%	[71]
H	5.82	wt%	[71]
N	0.98	wt%	[71]
S	0.13	wt%	[71]
O	47.2	wt%	[71]
Cellulose	37	wt%	[17]
Hemicellulose	29	wt%	[17]
Lignin	19	wt%	[17]
Density	85 (8% moisture)	kg/m^3	[72]
HHV	17.06	MJ/kg	[71]

The switchgrass is assumed to be dropped off in trucks. The contents of the truck are emptied via a truck tipper into biomass storage. The quantity of biomass utilized by the plant is dependent on the extraction chemical as plants were sized for an annual production of 80,000 tonnes butanol per year. On-site storage is sized for 72 hours in a cone-roof storage tank to allow for a weekend buffer. Biomass is moved from storage to the plant via belt conveyors. The conveyors are assumed to be 114.3 cm wide and 61 m long. Following transportation to the plant, the biomass is milled to 2-3 mm sized particles in a hammer mill. Electrical requirements for the mill were assumed to be 90 kWh/tonne biomass processed [73]. A schematic of the solids processing section can be viewed below in Figure 8.

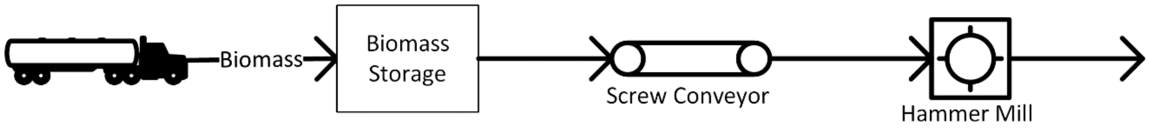

Figure 8: Schematic of the solids processing section

3.4. Pre-treatment and saccharification

After milling, the substrate enters the pre-treatment and saccharification section of the plant where it is slurried and treated with dilute (1 wt%) sulphuric acid at 140°C and 5.6 bar for five minutes [62, 30]. The majority of the heating is performed by waste heat from the separation section, with steam making up the remainder of the required energy. From here the pressure is relaxed to atmospheric and the hydrolyzate is sent to the conditioning tank. In the conditioning tank, 4.8 g of ammonia per L of hydrolyzate is added to the tank to balance the pH. The mixture is then cooled to 48°C and sent to enzymatic hydrolysis [62]. The cellulose enzyme loading rate is 58 mg protein per g of cellulose, and the reactor has a residence time of 72 hours [30, 62]. 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 [30]. It is also assumed that the relatively minor additions of sulphuric acid, ammonia and enzymes do not change the volume of the hydrolyzate. A diagram of the pre-treatment and saccharification section can be seen in Figure 9.

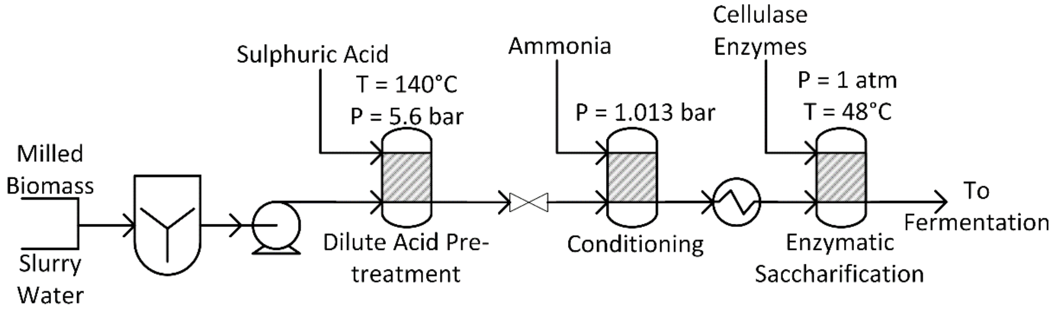

Figure 9: Schematic of the pre-treatment and saccharification plant section

3.5. Fermentation revisited

Now that the cellulose and hemicellulose have been broken down, fermentation can occur. *C. Acetobutylicum* has been shown to consume 100% of glucose and 71% of xylose during fermentation [24]. Butanol yield was assumed to be 0.18 g of butanol produced per g of sugar consumed [50]. 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 take 72 hours (60 hours 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 [57]. During fermentation, hydrogen gas and carbon dioxide are produced. It is assumed that 0.067g of hydrogen gas is produced per g of butanol during fermentation [74]. The hydrogen gas is collected from the fermenters and sent to the utility generation section of the plant. Two parallel seed trains were used to grow the bacteria. Corn steep liquor (CSL) has been shown to be an appropriate nutrient supplement for butanol producing bacteria and was fed to the bacteria at a loading rate of 0.5 wt% [62, 75].

3.6. Separation revisited

After fermentation, solids including cell mass and lignin were removed from the fermentation broth using a filter-press unit. It is assumed that 100% of lignin and cell mass was removed and sent to the utility generation section of the plant to be consumed by the boiler. Other studies have looked at selling the remainder of the feedstock and cell mass as cattle feed, however, with second-generation feedstocks this stream has limited feed value [30].

The modelling of the separation section was determined using the techniques described in Section 3.1. This section will describe the integration of the separation section with the rest of the plant. The section is run continuously, with feed constantly being provided by one of the 12 aforementioned fermentation tanks.

Water leaving the dehydration column or extraction column cannot be recycled back to the process as it will contain high level of organic salts (formed during pre-treatment and conditioning), fermentation nutrients not consumed by the organism, soluble inorganic compounds from the biomass and residual acetone, butanol and ethanol [62]. Thus, any water recovered in this manner will be directed to wastewater treatment. Water recovered from full heteroazeotrope separation is assumed to be recyclable. Waste heat from distillation columns is recovered and used to preheat the biomass slurry in the pre-treatment area.

3.7. Wastewater treatment

The butanol process generates a number of wastewater streams that must be treated before recycle to the process, all of which occur in the wastewater treatment section. All treated water is assumed fit for recycle to the process. Since the cellulosic bio-butanol plant is quite similar to the cellulosic bioethanol plant designed by the NREL [62], the wastewater treatment required is assumed to be similar for modelling purposes. For economic analysis the capital cost of wastewater treatment is based on a 6/10th rule of the NREL design [67]. The utility usage for the section is also calculated from their design. 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 [76]:

$$C_nH_aO_b + \left(n - \frac{a}{4} - \frac{b}{2}\right) H_2O \rightarrow \left(\frac{n}{2} - \frac{a}{8} + \frac{b}{4}\right) CO_2 + \left(\frac{n}{2} + \frac{a}{4} - \frac{b}{4}\right) CH_4 \qquad (9)$$

It is assumed that all the methane produced during digestion is collected and sent to the utility generation section of the plant. Hydrogen sulfide compounds produced during the digestion are ignored in this analysis.

Anaerobic digestion follows aerobic digestion to remove any remaining organic compounds. During anaerobic digestion, nitrifying bacteria lower the pH of the anaerobic digestion lagoons, thus a caustic must be added for neutralization purposes [62].

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, all the sludge is assumed to be recycled in this work. In actuality, a small portion of this would not be recycle and would be sent to the utility generation section of the plant for combustion [62].

The last step in wastewater treatment is salt removal. This is accomplished via reverse osmosis (RO). The RO effluent is assumed to be pure and eligible for recycle to the process. It is assumed that non cellulose, hemicellulose, or lignin in the biomass is disposed in this manner. A simplified schematic of the wastewater treatment section, adapted from the NREL bioethanol plant report, can be viewed in Figure 10.

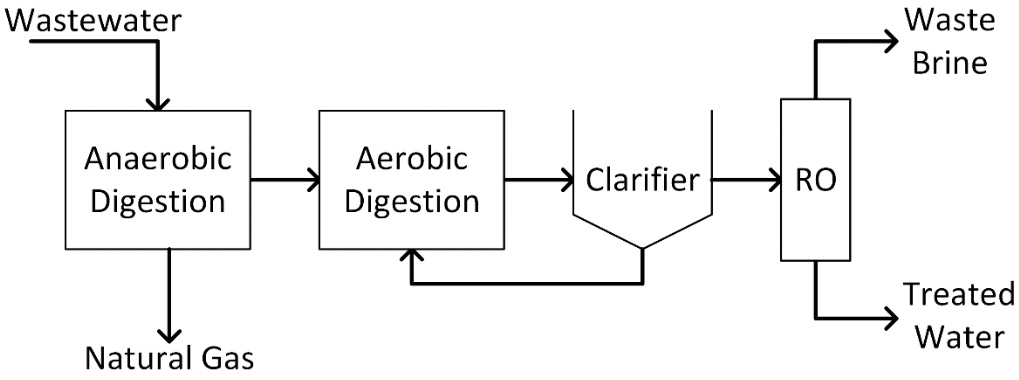

Figure 10: Simplified schematic of the wastewater treatment section of the plant. Adapted from Humbird *et al.* [62]

3.8. Utility generation

The purpose of this section is to burn various organic by-product streams to produce steam and electricity. The goal of this is to recover waste energy and to generate some value from otherwise waste streams. Combustible by-products include all of the lignin in the feedstock (the LHV of lignin is 20.92 MJ/kg [77]), hydrogen gas produced during fermentation, and methane 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.

3.9. 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. A discounted cash flow rate of return (DCFRR) analysis is used to determine the MBSP. Capital cost estimates were based on a combination of literature data, particularly from the NREL [62] and Seider *et al.* [67]. The separation section was costed using Aspen Capital Cost Estimator. Values from literature were scaled using power law expressions with exponents ranging from 0.5 to 0.8 and adjusted to 2015 United States Dollars using the Chemical Engineering Plant Cost Index. The Economic assumptions for this analysis are shown in Table 9.

Table 9: Economic parameters and indirect cost basis used in the analysis

Economic Parameter	**Value**
Cost year for analysis	2015
Plant financing by equity/debt	60%/40%
Discount rate	10% (after tax)
Debt financing	10 years at 8%
Plant life/analysis period	30 years
Depreciation method	200% declining balance for 7 years for general plant and utilities
Income tax rate	35%
Plant construction cost schedule [62]	3 years (8% year 1, 60% year 2, 32% year 3)
Plant salvage value	$0
Start-up period	3 months
Revenue and costs during start-up [62]	50% revenue 75% variable cost 100% fixed cost
Operating days per year	350 (8400 hours)
Land cost [67]	2% of total depreciable capital (Tdep)
Royalties [67]	2% of Tdep
Working capital [67]	5% of Tdep
Additional direct costs [62] (site prep, warehouses, additional piping)	17.5% of total direct cost (TDC)
Indirect Costs (field expenses, contingency, home office and construction) [62]	60% of TDC

Fixed operating costs are calculated using correlation from Seider *et al.* and include items such as labour-related operations, maintenance, operating overhead, property tax and insurance. Variable operating costs can be found below in Table 10.

Table 10: Variable operating cost parameters used in the analysis

Component	**Price**	**Reference**
Switchgrass Cost	$67.64/dry tonne	[78]
Natural Gas	$2.88/GJ	[79]
Solid Disposal (wastewater salts)	$36/tonne	[67]
Sulfuric Acid	$87.78/tonne	[62]
Ammonia	$406.96/tonne	[62]
Caustic for wastewater	$149.16/tonne	[62]
Enzyme cost	$4,240/tonne	[62]
Electricity	$0.06/kWh	[80]
Decane	$500/tonne	[81]
Decanol†	$903/tonne	[81]
2-Ethyl-1-Hexanol	$690/tonne	[81]
Hexanol	$473/tonne	[81]
Mesitylene	$789/tonne	[81]
Oleyl Alcohol‡	$982/tonne	[81]
Acetone	$1100/tonne	[81]
Ethanol	$900/tonne	[81]

† Estimated from the price of hexanol
‡ Estimated from the price of oleic acid

3.10. 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 has to be considered. This cost can be computed using a metric known as the cost of CO_2 avoided (CCA). The CCA is the 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:

$$CCA = \frac{Biobutanol\ marginal\ cost}{CO_2\ emissions\ avoided} = \frac{MBSP - WGP}{CIG - CIB}, \tag{10}$$

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 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 similar. The carbon intensity of bio-butanol 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, in order 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 [82]. It is assumed that all carbon consumed by the bacteria exits as CO_2 unless it exits in the products. 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 11 for a U.S. plant.

Table 11: Breakdown of greenhouse gas emissions data used in this study. All units are in gram CO_2 equivalent per GJ.

Description	**Value**	**Reference**
Feedstock Production and Harvesting	18,550	[83]
Land use changes, cultivation	-	[83]
Feedstock Transportation	2,000	[83]
Feedstock preprocessing	22,000	[83]
Well-to-gate greenhouse gas emissions for switchgrass	42,550	
Butanol dispensing	179	[84]
Butanol distribution and storage	1,458	[84]
Butanol combustion in a vehicle	63,430	Calculated with Aspen
Gate-to-wheel greenhouse gas emissions for bio-butanol	65,057	
Feedstock extraction	8,495	[84]
Feedstock Transportation	9,35	[84]
Land use changes, cultivation	2	[84]
Fuel production	12,968	[84]
Gas leaks and flares	2,643	[84]
Fuel dispensing	138	[84]
Fuel distribution and storage	575	[84]
Gasoline combustion in vehicle	67,870	[85]
Well-to-wheel greenhouse gas emissions for gasoline	93,626	
Well-to-gate greenhouse gas emissions for natural gas	8,400	[86]
Well-to-gate greenhouse gas emissions for electricity	21,260	[87]

Chapter 4: Results and discussion

Results will be presented in the following order: Section 4.1 will present the best separation train and corresponding economic and environmental analysis for the base case and each extractant. Following that, the extractants will be compared considering operating costs, capital costs, and the effect of wastewater treatment on the MBSP of each extractant. Finally, sensitivity analyses will be performed on key model and economic parameters.

4.1. Simulation and economic results for each extractant

4.1.1. Pure-distillation base-case results

The best separation train, with stream conditions, for the pure-distillation base-case can be viewed below in Figure 11. In this case, the optimizer removed water until heteroazeotropic conditions were achieved in the dehydration column. This was followed by recovery of acetone (99.9% recovery) at 0.5 bar. Next, ethanol was recovered (97% recovery) at 3 bar. Lastly, 99.8% of available butanol was recovered using the full azeotrope breaking method.

The total capital investment for this plant is \$332.5M. The largest contributor to capital investment in the base case is the wastewater treatment portion of the plant, which costs \$73M. Operating costs total \$185.6M/year. These operating costs are offset by \$51.5M/year in side-product revenue. Next to feedstock cost (\$58.87M/year), the largest contributions to operating cost were from the separation and pre-treatment, costing $27.1M/year and $26.7M/year respectively.

The MBSP for the pure-distillation base case is $2.15 per L or $2.47 per litre of gasoline equivalent (L_{ge}). The economic assessment for this case is summarized in Table 12. The corresponding CCA for this is 912.81/tonne CO_2e emissions avoided. The environmental assessment for this case is summarized in Table 13.

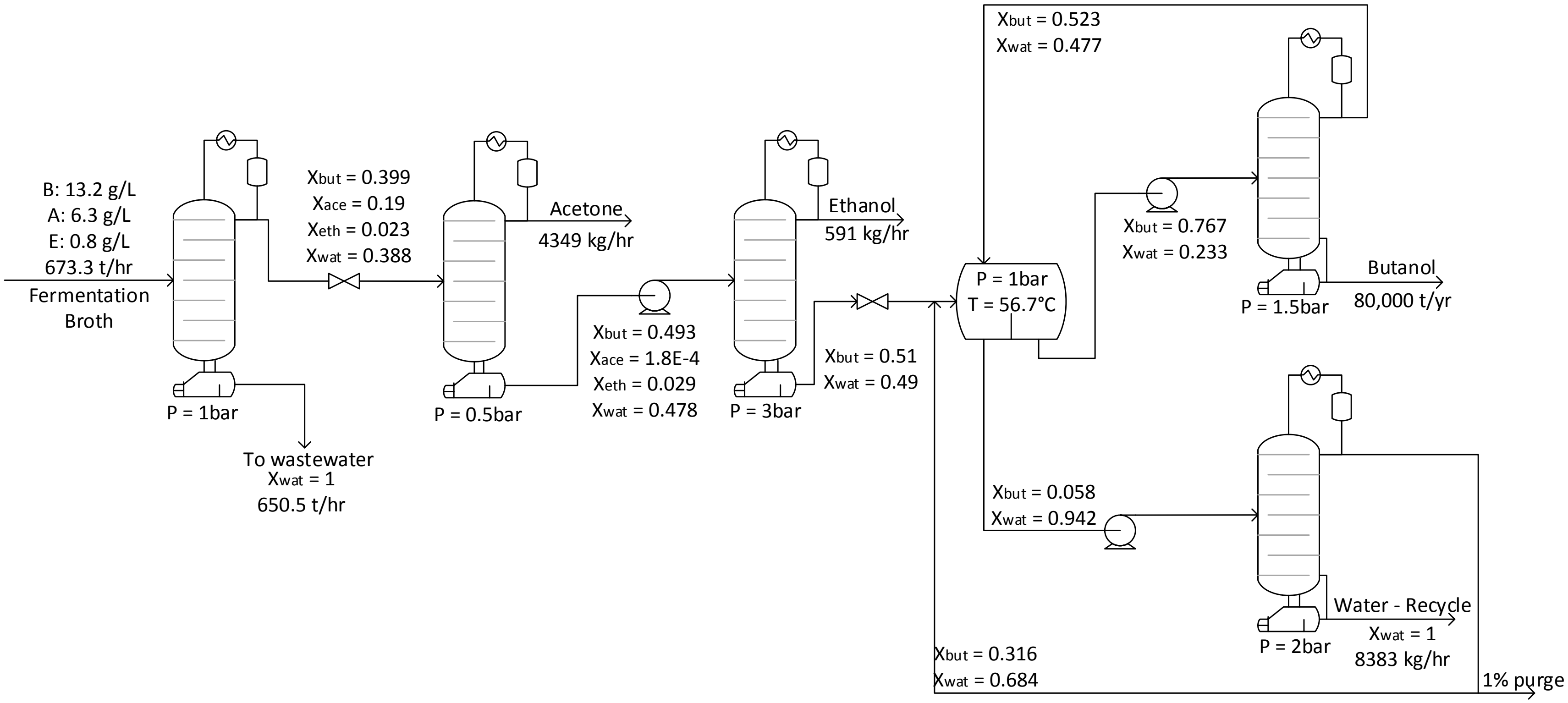

Figure 11: Best separation train configuration and corresponding process conditions for the pure-distillation base case. Products were recovered to their aforementioned purities.

4.1.2. Decane extraction-distillation results

The best separation train, with stream conditions, for the decane extraction-distillation separation method can be viewed in Figure 12. In this case, only three distillation columns were required to recover the products. Acetone was recovered first at 0.5 bar (99.9% recovery) followed by a column to separate butanol (99.6% recovery) and ethanol (93.8% recovery) at 1.5 bar. Ethanol was recovered slightly above fuel-grade purity to 92.5% by volume. This is because the selectivity of decane for butanol over water is very high, such that butanol and ethanol can be separated from each other at their required purities, thus needing no further processing.

Capital investment for this plant totalled \$369.4M with wastewater treatment (\$68.4M) and the fermentation section of the plant (\$46.8M) accounting for most of the cost. Annual operating cost for this case is \$212.7M with side product revenues totalling \$61.7M. Similar to the base case, the largest contributors to operating cost (alongside feedstock costs) are product recovery (\$52.2M/year) and pre-treatment (\$24.3M/year).

The MBSP for the decane extraction-distillation case is \$2.41/L or \$2.76/L_{ge}. The economic assessment for this case is summarized in Table 12. This case was worse than the base case because the butanol distribution coefficient for decane is so low that the mass flow rate of decane to the separation section is approximately 3.35 times the mass of the broth flow rate. This leads to exorbitantly high operating costs to recover the decane in the stripper. The corresponding CCA for this is \$1236.96/tonne CO_2e emissions avoided. Again, this is worse than the base case. This is partially due to the higher MBSP, but also due to increased emissions required to provide the necessary heating and cooling to the separation section of the plant. The environmental assessment for this case is summarized in Table 13.

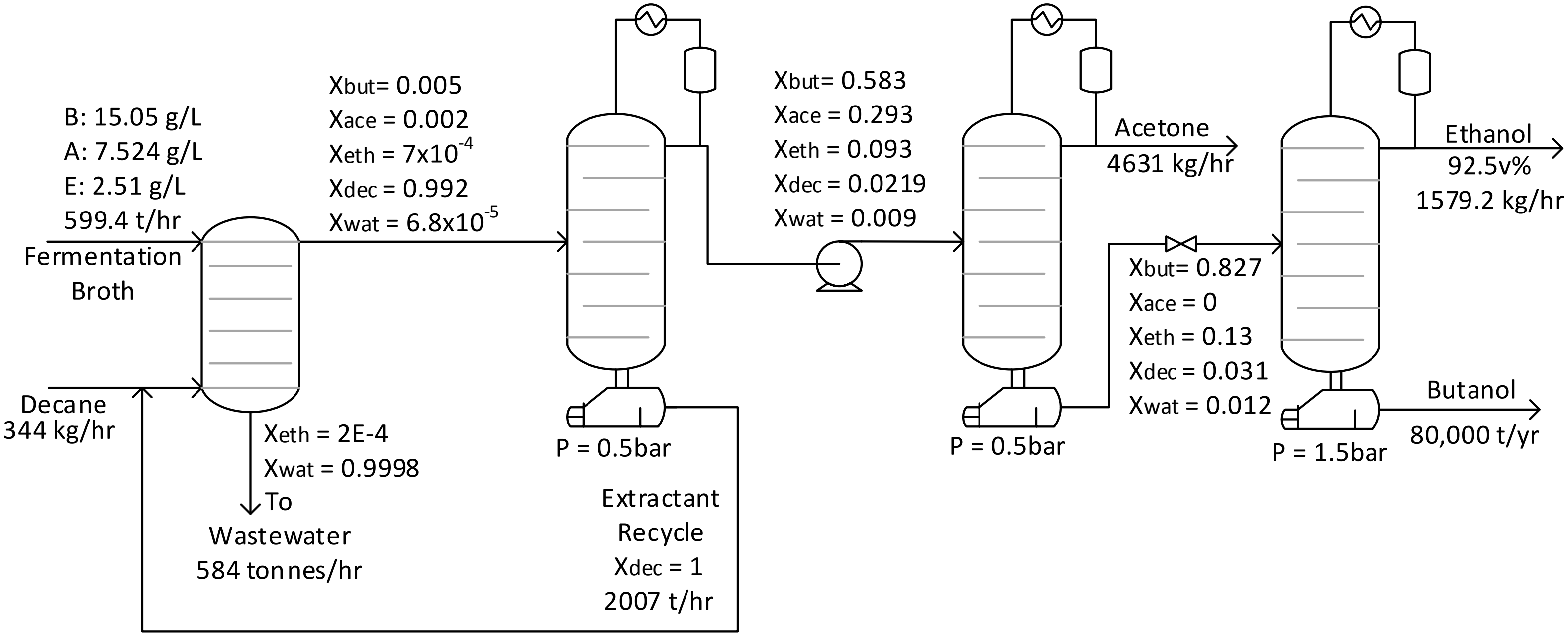

Figure 12: Best separation train configuration and corresponding process conditions for the decane extraction-distillation case. Products were recovered to their aforementioned purities unless otherwise noted.

4.1.3. Blend 1: decane/oleyl alcohol extraction-distillation results

The best separation train, with stream conditions, for the Blend 1 (decane/oleyl alcohol) extraction-distillation separation method can be viewed in Figure 13. This case required an additional distillation column compared to the pure decane case (due to the lower selectivity of the solvent blend), however it still avoided the heteroazeotrope. Butanol was removed first with a recovery of 99.7% followed by acetone (19.4% recovery) and lastly ethanol (15.6% recovery). Acetone and ethanol were recovered in small amounts as the distribution coefficient for butanol of this extractant, was much greater than those of acetone and ethanol. This results in all of the butanol being removed from the broth but relatively low acetone and ethanol removal.

Total capital investment for this case was \$332.2M with wastewater treatment accounting for \$56.2M of the total investment. Operating costs were \$161M/year despite with separation cost totalling \$11M/year. The MBSP for the decane extraction-distillation case is \$2.18/L or \$2.49/L_{ge}. The economic assessment for this case is summarized in Table 12. The flow rate of extractant in this case in considerably lower than the pure decane case (3.35 mass ratio for decane compared to 0.55 for the blend).

The corresponding CCA for this case is \$1006.00/tonne CO_2e emissions avoided. This is better than the base case CCA. The difference between the two cases lies in the fact that Blend 1 does not require natural gas imported to the plant as it produces enough biogas during wastewater treatment to meet its heating needs.

In addition, this configuration also produces less side products than the base-case meaning that butanol exits the plant with a larger portion of the total energy delivered from the plant as products. A summary table for the environmental assessment for this case can be viewed in Table 13.

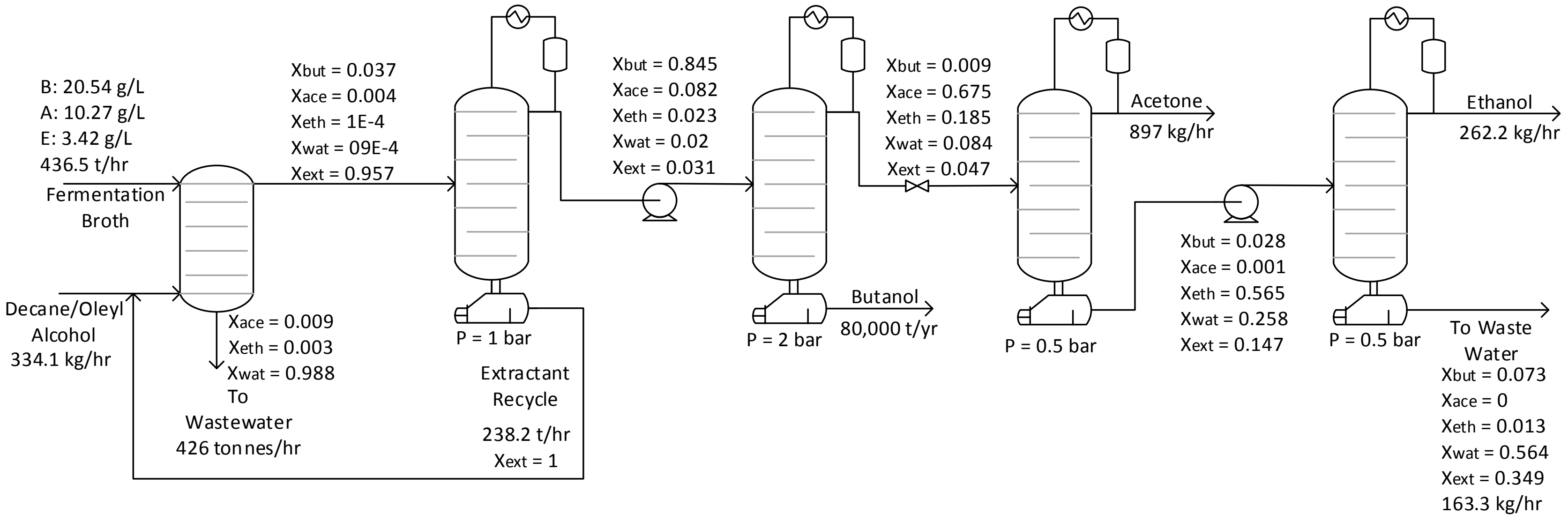

Figure 13: Best separation train configuration and corresponding process conditions for Blend 1 extraction-distillation case. Products were recovered to their aforementioned purities.

4.1.4. Decanol extraction-distillation results

The best separation train, with stream conditions, for the decanol extraction-distillation separation method can be viewed in Figure 14. In this case the heteroazeotrope was not avoided and it was found to be economically infeasible to recover ethanol. This is because the butanol distribution coefficient for decanol was much greater than that of ethanol, thus very little ethanol was removed from the fermentation broth. Though very little acetone was removed from the broth, it was still economic to recover it (7% recovery) at 0.5 bar. Following that, the full heteroazeotrope breaking method was used to recover butanol (99.9% recovery) and water for recycle.

Capital costs for this plant totalled \$342M, with wastewater treatment making up \$73.6M of the total cost. Operating costs for this plant totalled \$168M/year. The MBSP for the decane extraction-distillation case is \$2.36/L or \$2.70/L_{ge}. The economic assessment for this case is summarized in Table 12. The MBSP for this case was very high primarily because side product revenue was very low.

The corresponding CCA for this case is \$1246.65/tonne CO_2e emissions avoided. This is better than the base case CCA and quite similar to that of Blend 1. Decanol does also not require any natural gas input and the low percentage of products recovered means that butanol makes up a larger portion of the total recovered product energy. A summary table for the environmental assessment for this case can be viewed in Table 13.

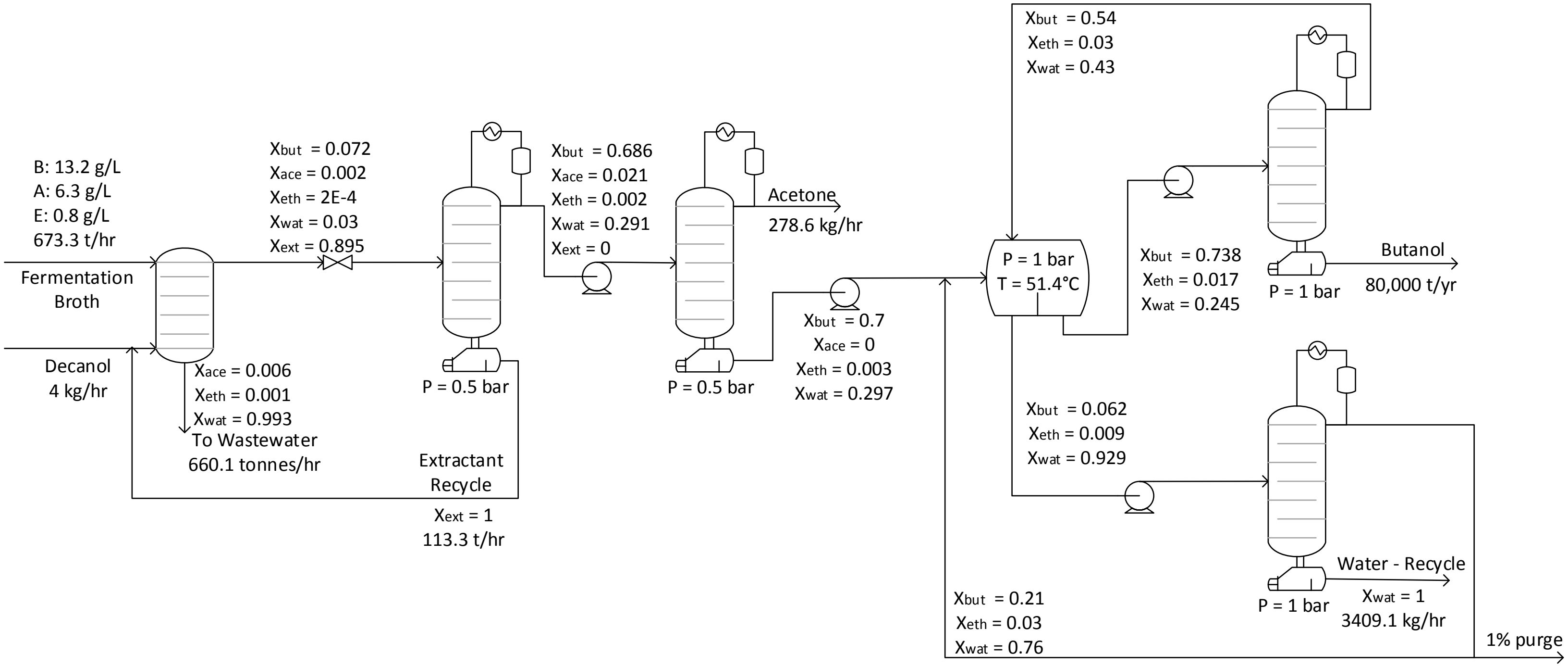

Figure 14: Best separation train configuration and corresponding process conditions for the decanol extraction-distillation case. Products were recovered to their aforementioned purities.

4.1.5. Blend 2: decanol/oleyl alcohol extraction-distillation results

The best separation train, with stream conditions, for the Blend 2 (decanol/oleyl alcohol) extraction-distillation separation method can be viewed below in Figure 15. This case was able to recover 99.5% of butanol using the half-azeotropic separation method. Immediately before the half-heteroazeotropic separation, ethanol is removed (8% recovery) at 2.3 bar. This is preceded by acetone removal (10% recovery) at 0.5 bar.

The MBSP for the Blend 2 extraction-distillation case is \$1.89/L or \$2.17/L_{ge}. Capital costs for this plant is \$275M with wastewater and pre-treatment contributing \$44M and \$43M respectively. Operating costs totalled \$142.5M/year with a low separation cost of \$5.13M and \$20.6M/year in side-product revenue. The economic assessment for this case is summarized in Table 12. Despite recovering low quantities of both acetone and ethanol, this case greatly benefits from increased fermentation yields. *In-situ* extraction increases fermentation yields to over double their batch values. This greatly increases product concentration in the broth entering the separation section both facilitating separation and lowers wastewater treatment costs.

The corresponding CCA for this case is \$853.84/tonne CO_2e emissions avoided. Similar to Blend 1, Blend 2 does not require natural gas imported to the plant. A summary table for the environmental assessment for this case can be viewed in Table 13.

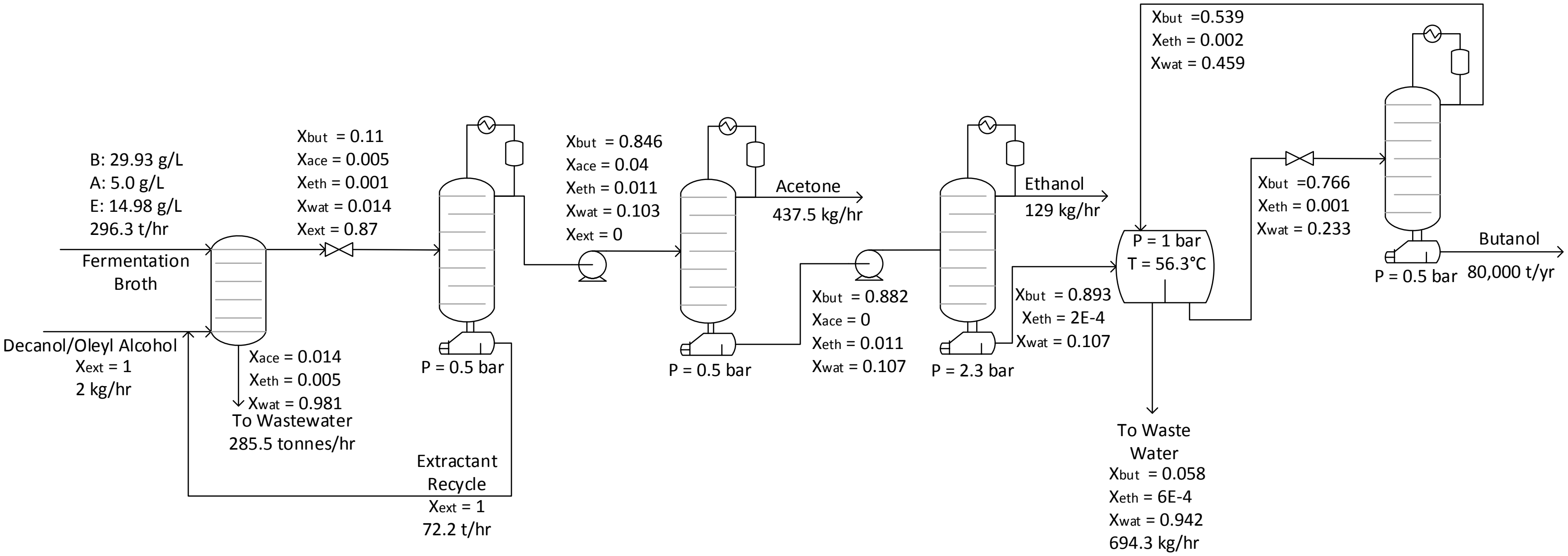

Figure 15: Best separation train configuration and corresponding process conditions for Blend 2 decanol/oleyl alcohol extraction-distillation case. Products were recovered to their aforementioned purities.

4.1.6. 2-Ethyl-1-Hexanol extraction-distillation results

The best separation train, with stream conditions, for the 2-Ethyl-Hexanol extraction-distillation separation method can be viewed below in Figure 16. This case recovered 92.4% of acetone at 0.5 bar, followed by 74% recovery of ethanol at 3 bar. Lastly butanol and water were separated using the full heteroazeotrope breaking method to recover 99.8% of the butanol present in the broth. This result is important, because the two other system-level studies that have considered 2-ethyl-hexanol failed to account for the heteroazeotrope possibly due to poor physical property models [60, 61].

Capital costs for this plant total \$248M with wastewater treatment making up \$39M of the total cost. Operating costs for this case are \$154M/year with separation accounting for \$23M. Side product revenue is \$56M/year. This results in an MBSP of \$1.58/L or \$1.81/L_{ge}. The economic assessment for this case is summarized in Table 12. This case performed quite well as it was able to recover fairly high amounts of both acetone and ethanol and the high concentration of products in the broth led to low wastewater treatment costs and increased side-product revenues.

The corresponding CCA for this case is \$471.57/tonne CO_2e emissions avoided. This case requires an external source of natural gas, however the low marginal biofuel cost leads to a comparatively low CCA. A summary of the CCA calculation can be viewed in Table 13.

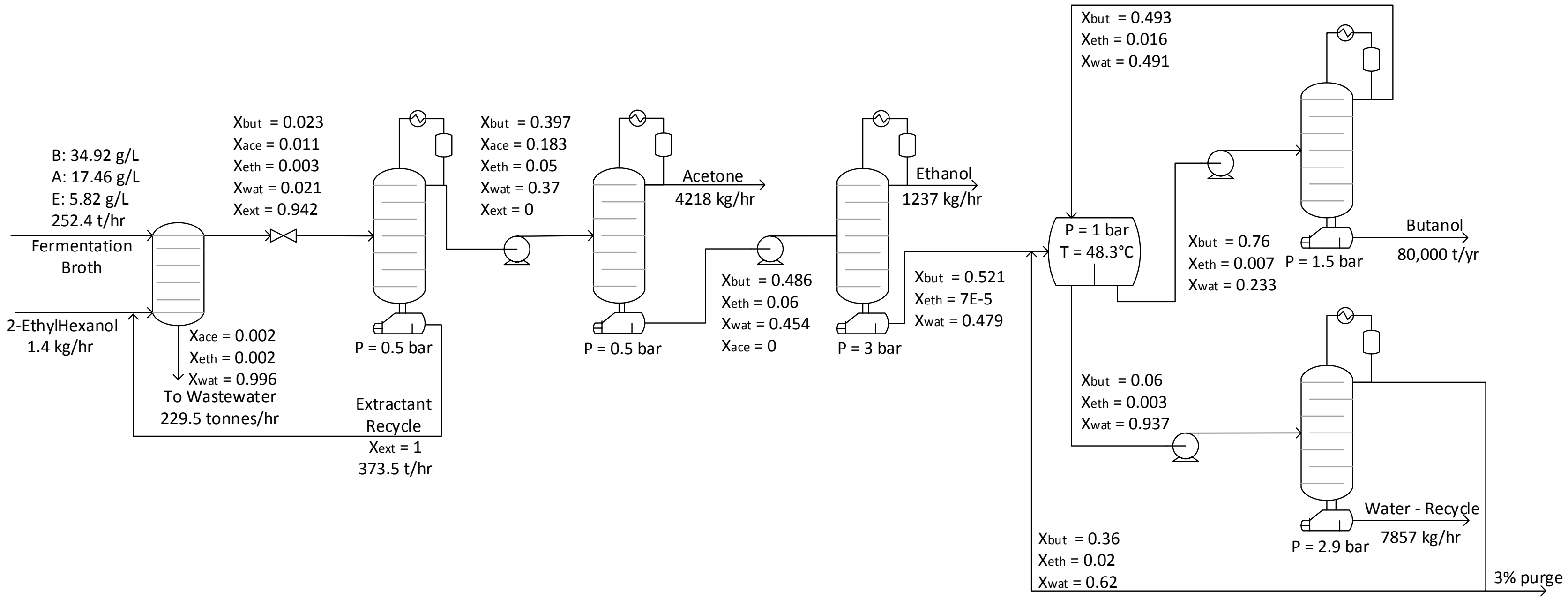

Figure 16: Best separation train configuration and corresponding process conditions for the 2-ethyl-1-hexanol case. Products were recovered to their aforementioned purities.

4.1.7. Hexanol extraction-distillation results

The optimal separation train for the hexanol extraction-distillation separation method (including stream conditions) can be seen below in Figure 17. The butanol distribution coefficient of hexanol is so high relative to that of ethanol that it was found to be uneconomic to recover ethanol. The acetone distribution coefficient is also relatively low, however it was found to be economical to recover acetone at 0.5 bar (4% recovery). Following the removal of acetone, the butanol-water heteroazeotrope (99.7% butanol recovery) was broken using the full heteroazeotropic separation method.

The MBSP for the hexanol extraction-distillation case is \$2.41/L or \$2.76/L_{ge}. Capital costs totalled \$356M with wastewater treatment costing \$73M. Operating costs for this case are \$170M with a mere \$15M in side produce revenue. The economic assessment for this case is summarized in Table 12. This extractant performed quite poorly as very little side product revenue was generated.

The corresponding CCA for this case is \$1314.35/tonne CO_2e emissions avoided. Similar to other cases with low product recovery, no additional natural gas was needed to provide heating to the plant. A summary table of the CCA calculation can be viewed in Table 13.

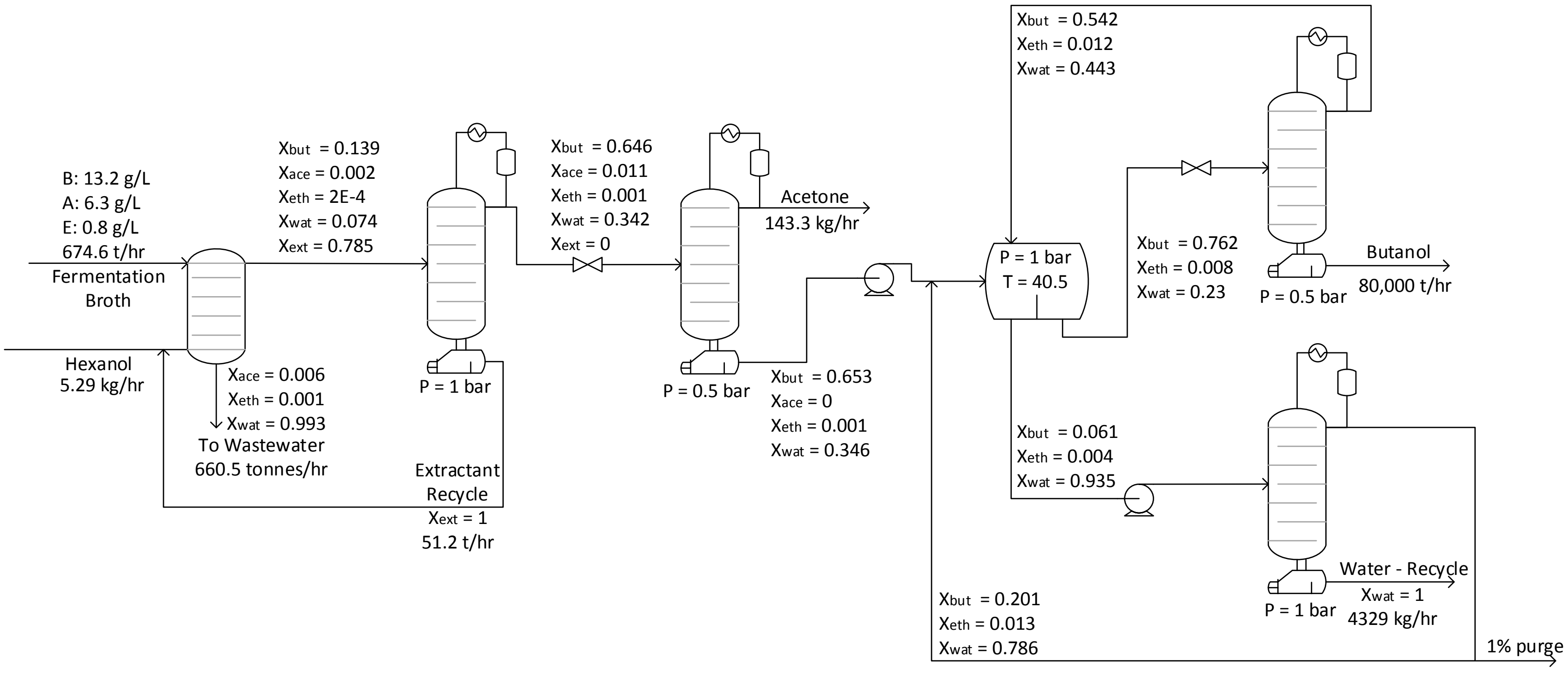

Figure 17*:* Best separation train configuration and corresponding process conditions for the hexanol case. Products were recovered to their aforementioned ASTM purities.

4.1.8. Mesitylene extraction-distillation results

The best separation train, with stream conditions, for the mesitylene extraction-distillation case can be viewed below in Figure 18. This method avoids the butanol-water heteroazeotrope so a modification of the reverse-direct sequence was found to be the best separation order. Butanol was removed first at 2.7 bar (99% recovery) followed by acetone removal at 0.5 bar (94.6% recovery) and lastly ethanol recovery at 2.8 bar (10% recovery).

The capital investment for wastewater treatment in this case was \$73M, the largest contribution to a total capital investment of \$341M. Operating costs are \$176M with separation accounting for \$16M annually. Side product revenue for this case was \$47M/year. This resulted in an MBSP of \$2.13/L or \$2.44/L_{ge}. Operating cost of separation for mesitylene is quite low, however this is offset by the recovery of less side products than other cases. A summary of the economic results for mesitylene can be viewed below in Table 12.

The corresponding CCA for this case is \$842.99/tonne CO_2e emissions avoided. Natural gas import was required to the plant and the high energy cost but the smaller marginal biofuel cost decreased the CCA as compared to the base case. A summary table of the CCA calculation can be viewed in Table 13.

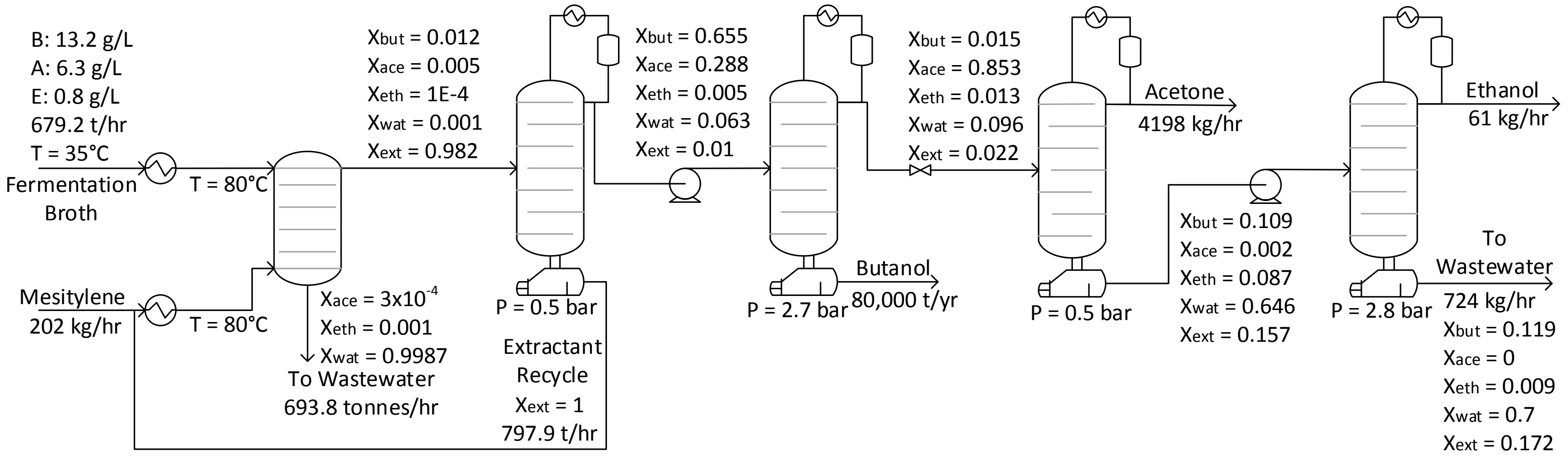

Figure 18: Best separation train configuration for the mesitylene extraction-distillation case. Products were recovered to their aforementioned ASTM purities.

4.1.9. Oleyl alcohol extraction-distillation results

The optimal separation train for Oleyl-alcohol can be viewed below in Figure 19. In this sequence, 16.2% of acetone in the broth was removed first, followed by 13% of the ethanol. Lastly, 99.1% of the butanol was recovered using the half-azeotrope recovery method.

Total capital investment for this plant is $284M. The wastewater treatment plant in this case cost only $46M. Total operating costs were $151M per year with $24M in side product revenue generated annually. This resulted in an MBSP of $1.97/L ($2.25/L_{ge}) for the oleyl alcohol extractive-distillation case. In this case, low side-product recoveries were offset by high broth concentrations, leading to a smaller required wastewater treatment section. A summary table of the economic results for this case can be viewed in Table 12.

The corresponding CCA for this case is $878.99/tonne CO_2e emissions avoided. No natural gas import to the plant was required in this case. A summary table of the CCA calculation can be viewed in Table 13.

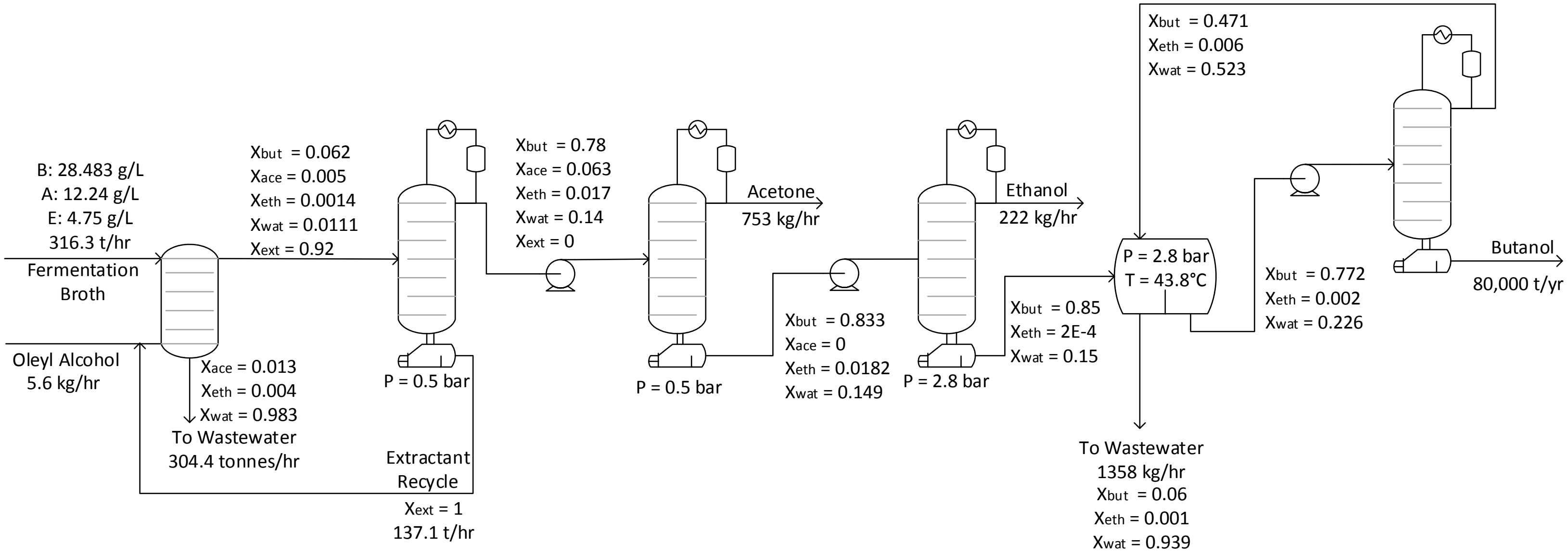

Figure 19: Best separation train configuration for the oleyl alcohol extractive-distillation case. Products were recovered to their aforementioned ASTM purities.

Table 12: Summary of economic results for each of the extractants

	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

Table 13: Summary of CO_2e emissions avoided for each of the extractants

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)	-1687.0	-1687.0	-1687.0	-1687.0	-1687.0	-1687.0	-1687.0	-1687.0	-1687.0
Wall-to-gate GHG emissions for switchgrass import	728.5	728.5	728.5	728.5	728.5	728.5	728.5	728.5	728.5
Biomass to bio-butanol plant emissions (from Aspen Plus)	816.0	813.7	883.95	902.7	898.3	795.7	906.9	823.3	890.9
Well-to-gate GHG emissions for natural gas use	27.5	56.3	0	0	0	14.18	0	11.0	0
Well-to-gate emissions for electricity import	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	-141.8	-45.0	-117.3	-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	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)	912.81	1236.96	1006.00	1246.65	853.84	471.57	1314.35	842.99	878.99

4.2. Comparison of extractants

To facilitate comparison between the extractants, a summary table outlining key economic and simulation metrics can be viewed in Table 14. The order of separation methods from lowest to highest MBSP is as follows: 2-ethyl-hexanol ($1.58/L); Blend 2: decanol/oleyl alcohol ($1.89/L); oleyl alcohol ($1.97/L); mesitylene ($2.13/L); pure distillation ($2.15L); Blend 1: decane/oleyl alcohol ($2.18/L); decanol ($2.36/L); and finally decane and hexanol, each at $2.41/L.

The three non-toxic extractants that performed better than the base case greatly benefitted from higher broth concentrations. The pre-treatment section for the base-case contributed 21.2% ($26.7M/year) of operating costs while for 2-ethyl-hexanol, Blend 2 and oleyl alcohol it only contributed around 15% (≈ $15M/year). This difference in operating costs is due to the fact that there is a higher solids fraction in the slurry entering the pre-treatment section (due to the higher allowable sugar concentration in the fermenters) which reduces the cost of acid to the pre-treatment reactor and ammonia to the conditioning reactor as they are added in amounts per unit quantity of liquid hydrolysate.

All extractants that performed better than the base case (including mesitylene) had considerably lower separation costs than the base-case. Because it was found to be the most cost-effective extractant, Table 15 below breaks down the operating costs for 2-ethyl-hexanol and compares them to the base-case.

Table 14: Summary of key parameters and breakdown of capital costs, operating costs and revenues for each of the extractants

	Base case	Decane (Non-toxic)	Blend 1 (Non-toxic)	Decanol (Toxic)	Blend 2 (Non-toxic)	Ethyl-Hexanol (Non-toxic)	Hexanol (Toxic)	Mesitylene (Toxic)	Oleyl alcohol (Non-toxic)
Butanol recovery	99.8%	99.6%	99.7%	99.9%	99.5%	99.8%	99.7%	99.0%	99.1%
Acetone recovery	99.9%	99.9%	19.4%	7%	10%	92.4%	4%	94.6%	16.2%
Ethanol recovery	97%	93.8%	15.6%	-	8%	74%	-	10%	13%
Butanol Broth Concentration (g/L)	13.2	15.05	20.54	13.2	29.93	34.92	13.2	13.2	28.483
Heteroazeotrope Avoided	No	Yes	Yes	No	No	No	No	Yes	No
MBSP ($/L)	2.15	2.41	2.18	2.36	1.89	1.58	2.41	2.13	1.97
CCA ($/tonne CO$_2$ avoided)	912.81	1236.96	1006.00	1246.65	853.84	471.57	1314.35	842.99	878.99
Total installed equipment cost	175,668	193.049	174,517	183,899	144,925	129,639	188,430	180,338	149,517
Solids Processing	1.9	1.7	1.9	1.8	2.3	2.5	1.7	1.8	2.2
Pre-treatment %	26.7	24.0	25.6	25.1	29.8	32.8	24.9	26.1	29.1
Fermentation %	12.9	24.2	17.9	12.3	13.0	12.2	12.1	12.6	13.6
Separation %	7.2	5.6	6.9	6.0	5.3	7.9	8.1	8.0	6.1
Wastewater %	41.6	35.4	32.2	40.0	30.4	30	38.9	41.0	30.6
Utility Gen. %	9.8	9	15.5	14.4	19.3	14.4	14.2	10.4	18.4
Total variable OC ($M/yr)	125,616	148,045	101,567	106,172	89,679	104,147	106,610	115,476	96,732
Solids Processing %	3.7	3.2	4.6	4.4	5.2	1.5	4.4	4.1	4.9
Pre-treatment %	21.2	16.4	18.7	25.1	16.2	12.6	25.1	23.3	15.7
Fermentation %	1.2	0.9	1.0	1.4	7.3	0.5	1.4	1.3	0.7
Biomass %	46.9	39.8	58.0	55.4	65.8	56.5	55.3	51.4	61.3
Separation %	21.5	35.2	11.7	7.2	5.7	21.6	7.4	13.9	11.5
Wastewater %	5.4	4.5	6	6.4	6.3	5.2	6.4	6.0	5.9
Total side product Revenue ($M/yr)	51,509	61,731	25,077	16,733	20,640	56,302	15,775	46,914	23,753
Acetone %	78	69.3	33.1	15.4	19.6	69.2	8.4	82.1	29.3
Ethanol %	8.7	19.3	7.9	-	4.7	16.7	-	1	7.1
Utility Gen %	13.3	11.3	58.9	84.6	75.6	14.2	91.6	16.9	63.6

Table 15: Breakdown of operating costs for 2-Ethyl-Hexanol and the base case

Operating Cost	**2-Ethyl-Hexanol**			**Pure-distillation Base-Case**	
	Unit	Annual Amount	Annual Cost ($M)	Annual Amount	Annual Cost ($M)
Switchgrass	tonnes	869,907	58.869	869,906	58.869
Sulfuric Acid	tonnes	138,480	2.512	310,067	5.623
Net Water	tonnes	70,891	4.750	73,643	4.934
Enzymes	tonnes	1,121	4.749	1,121	4.749
Ammonia	tonnes	9,752	3.970	27,118	11.025
CSL	tonnes	9,956	0.552	27,682	1.535
Total Heating	GJ	2,682,457	22.533	3,625,572	30.455
Total Cooling	GJ	1,886,640	0.668	3,971,300	1.406
Total Electricity	kWh	76,998,611	4.657	80,012,222	4.840
Wastewater	N/A	N/A	5.4	N/A	7.158

The increase in broth concentration also has a large impact on the cost of wastewater treatment. For the base-case, wastewater treatment accounts for 41.6% of the total installed equipment cost, while for the three non-toxic extractants that performed better than the base case, wastewater treatment only made up about 30% of total installed equipment cost. Wastewater treatment also contributed approximately 5% of total variable operating costs for each case. This large contribution of wastewater treatment to capital, and to a lesser degree operating cost, indicates that it is an important consideration when calculating the economics of ABE fermentation, which is often neglected in other studies and can result in overly optimistic predictions of MBSP and performance. To further illustrate this point, Table 16 shows the MBSP for the five best separation options if wastewater treatment is omitted.

Table 16: Comparison of MBSP when considering and neglecting wastewater

	Base-case	**Mesitylene**	**2-Ethyl-Hexanol**	**Blend 2**	**Oleyl alcohol**
MBSP with wastewater ($/L)	2.15	2.13	1.58	1.89	1.97
MBSP neglecting wastewater ($/L)	1.62	1.59	1.28	1.56	1.62

4.3. Sensitivity analyses

Figure 20 shows a sensitivity of 2-ethyl-hexanol to changes in fermentation broth concentration. The sensitivity results show that even with a 33% reduction in broth concentration, 2-ethyl-hexanol still greatly outperforms the base-case.

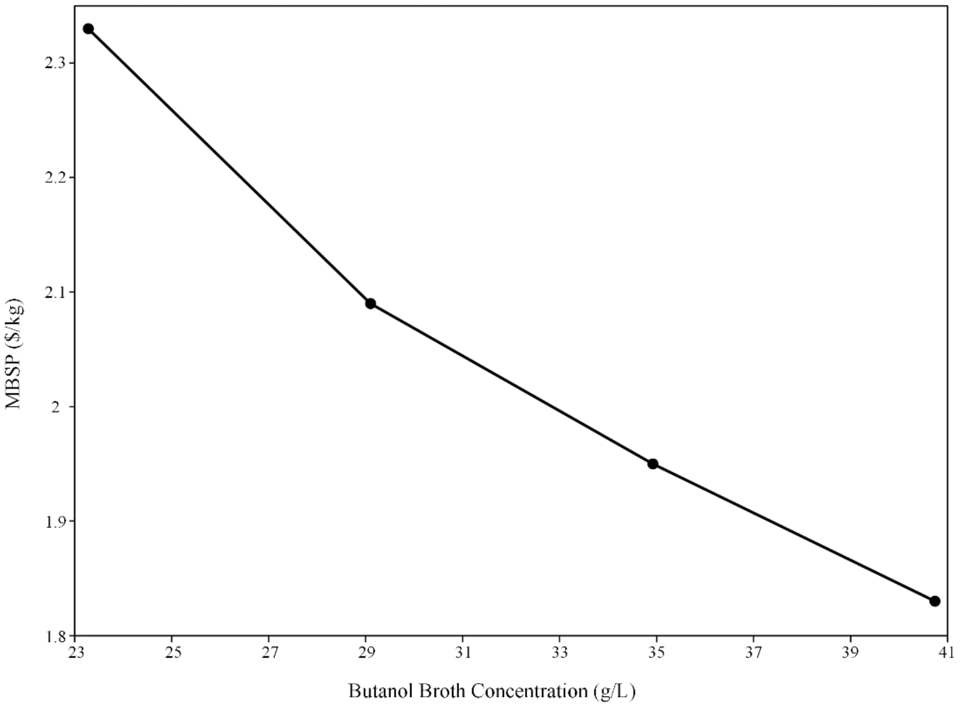

Figure 20: Sensitivity analysis on 2-Ethyl-Hexanol broth yield

Next to broth concentration, it was found that the production rate (and thus separation) of side-products had very significant impacts on plant economics. For example, mesitylene was the only toxic extractant to perform better than the base-case because it was able to recover a large percentage of acetone in the broth for side revenue, which the other toxic extractants could not do without very high extractant flow rates, significantly increasing operating costs. A similar trend is noticed in the non-toxic extractants that performed better than the base-case. 2-ethyl-hexanol performed better than Blend 2 and oleyl alcohol as it was able to recover 92.4% of the acetone in the broth, compared to 10% and 16.2% for Blend 2 and oleyl alcohol respectively.

These observations strongly indicate that the acetone and ethanol selling prices and distribution coefficients for a given extractant are important for the plant's economic performance. If side-products are not recovered, they are digested in wastewater treatment, converted to methane and CO_2 and combusted. However, cases with less side-product recovery require little-to-no natural gas to be imported to the plant (although they still require electricity input), which *decreases* operating costs. Thus, each extractant will respond differently to a change to the price of natural gas or the attainable prices of each of the side products. Sensitivity analyses on the prices of acetone, ethanol, and natural gas can be seen below in Figure 21 Figure 22, and Figure 23. Note that the natural gas price is also assumed to affect electricity price, but by one third of the relative deviation in natural gas price, as previously noted in literature [88].

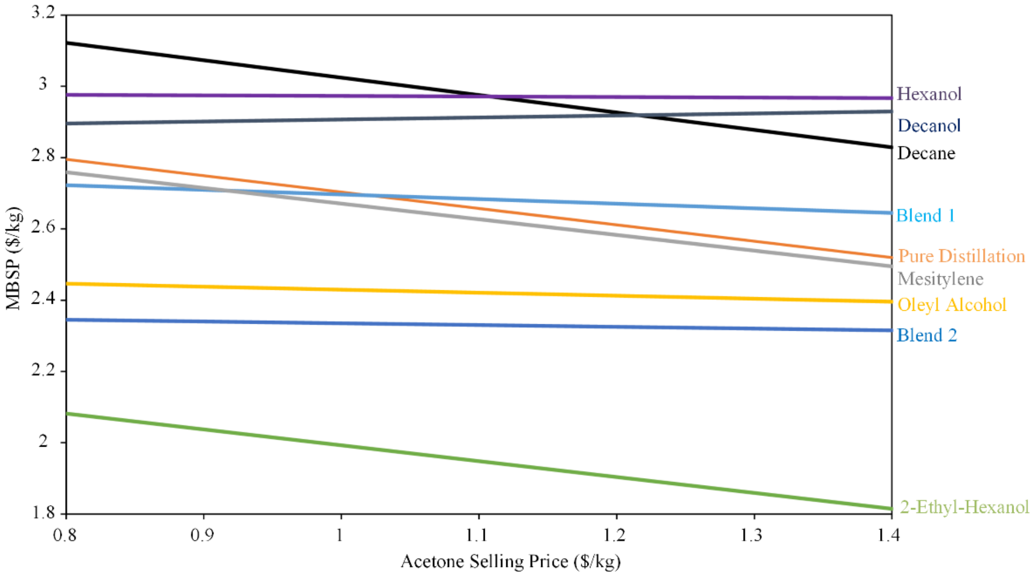

Figure 21: Sensitivity of acetone selling price

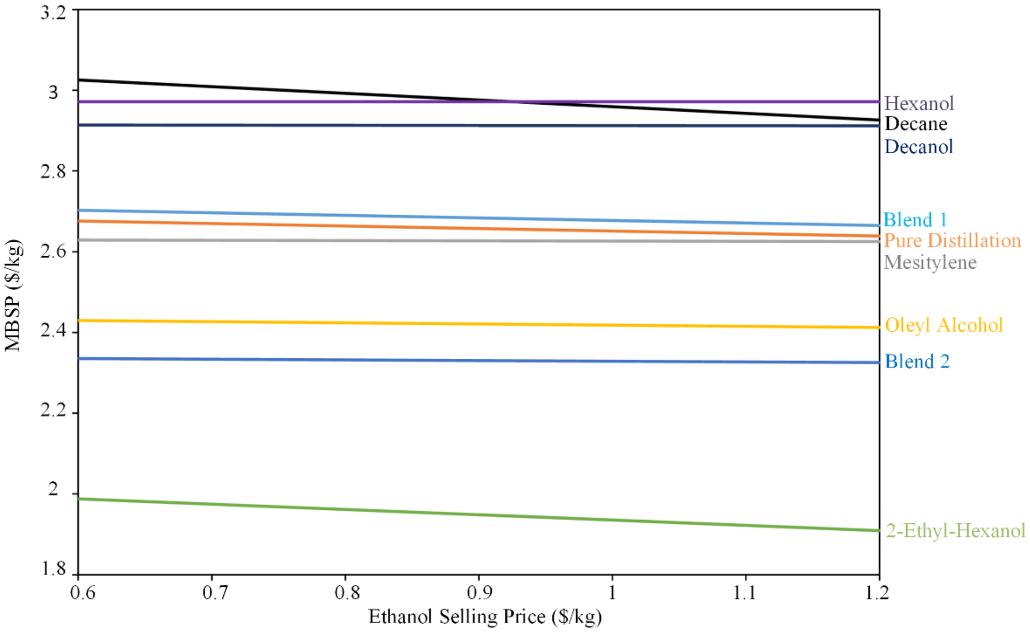

Figure 22: Sensitivity analysis of ethanol selling price

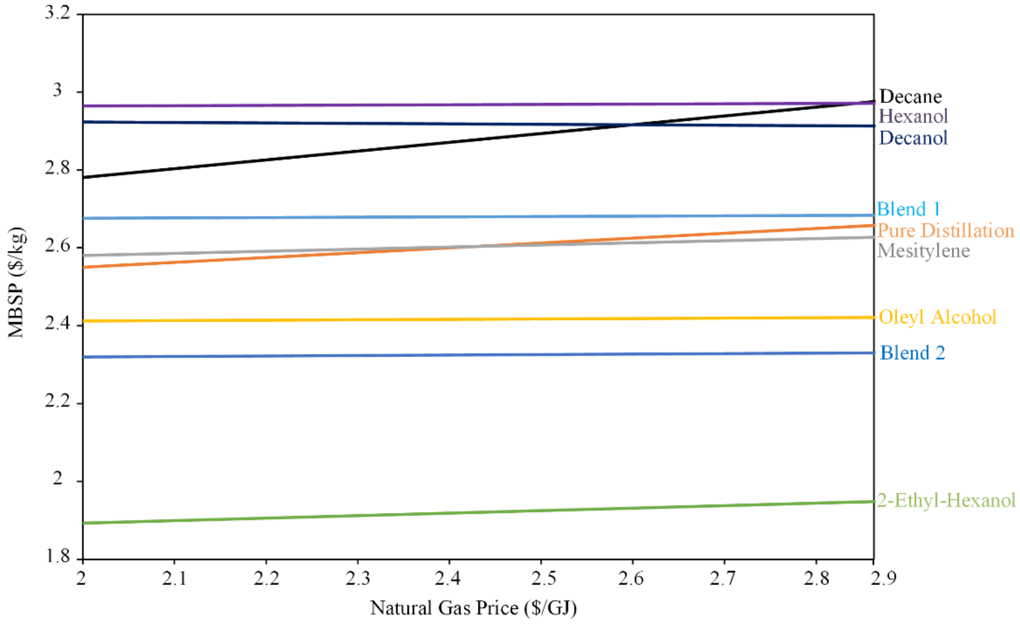

Figure 23: Sensitivity analysis on natural gas price

The cases that recover high amounts of acetone (decane, base-case, mesitylene and ethyl-hexanol) are logically much more sensitive to acetone and natural gas prices than their counterparts, which recover less acetone. Selling price of ethanol has very little effect on MBSP as it is recovered in such small quantities.

As previously mentioned, the acetone and ethanol distribution coefficients of some of the extractants were not yet reported in literature and thus values were assumed sensitivity analyses on these parameters can be seen in Figure 24 and Figure 25. Note that these sensitivities were performed assuming that the best identified separation train did not change.

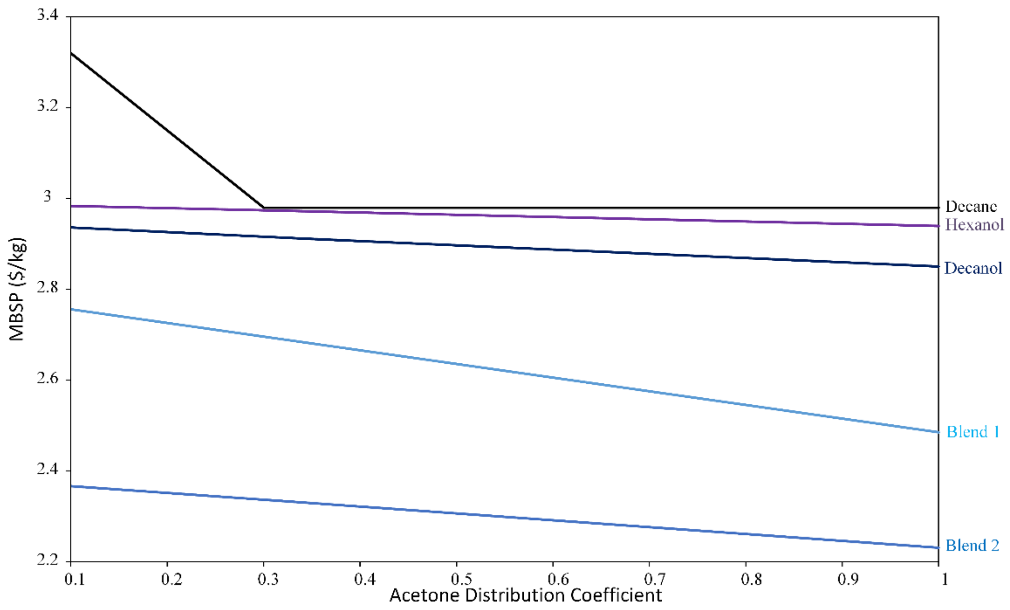

Figure 24: Sensitivity analysis on acetone distribution coefficient for extractants with unreported coefficient values

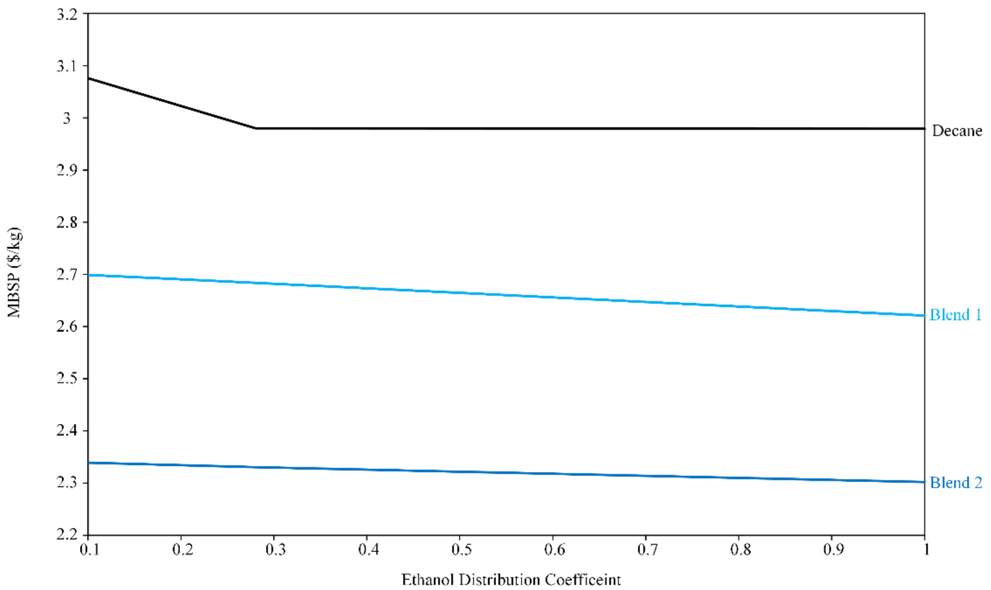

Figure 25: Sensitivity analysis on ethanol distribution coefficient for extractants with unreported coefficient values

Similar to price, the MBSP is quite sensitive to the distribution coefficient for acetone but less for that of ethanol. In the case of Blend 1, the MBSP changed by nearly $0.2/L over the range of distribution coefficients tested. It is the author's opinion that candidate butanol extractants also should be tested for their acetone distribution coefficients in lab-scale studies.

The CCA for biochemical bio-butanol ranged from 471.57 to 1314.35 dollars per tonne CO_2e emissions avoided. The economic best extractant, 2-ethyl-hexanol, also reported the lower CCA. Intuitively, cases which recovered more side products generally had lower CCA values. This is because more of the carbon entering the plant, ended up in the products, instead of being emitted.

The target mark for CCA generally discussed by policy makers is $50/tonne CO_2e emissions avoided [89]. Though all of the biochemical bio-butanol production routes studied are higher than this value, it is certainly plausible that this target can be achieved if improvements are made to the biomass supply chain. Plant emissions and biomass growth emissions were similar for all cases. 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. In addition all the cases were associated with positive net lifecycle emissions, this calls into question the common misconception that biofuels are carbon neutral.

The final MBSP for extractants in this study were relatively high compared to other values in literature ($1.06/L [58], $0.48/L [17]), however this is the first study to take the significant on-site wastewater treatment costs (both capital and operating) into account. Moreover, unlike the others, this study performed rigorous modelling of the separation section, as opposed to heuristic-based estimates providing a more detailed cost analysis than previous studies. Sensitivity analyses were also performed showing that acetone price, and extractant distribution coefficient were quite impactful to MBSP. In general, the sections with the highest capital costs are wastewater treatment and pre-treatment/saccharification. As other studies have noted, the most expensive operating costs for any plant are biomass, pre-treatment and separation costs. Further reducing these costs could make bio-butanol competitive with petrochemical butanol.

Chapter 5: Conclusions and future work

There were three main objectives of this work: (1) to test the efficacy of various commonly studied butanol extraction chemicals by detailed modelling of their separation properties; (2) to integrate these models into both up and down-stream units, including wastewater treatment, to determine an accurate MBSP for each of the studied extractants; (3) to compare each of the extractants on an environmental basis by calculating their respective costs per tonne CO_2e emissions avoided.

Chapter 3 described the general design of the proposed bio-butanol plant and its associated unit operation models as well as the parameters for the economic and environmental analyses. Fermentation models were utilized to predict the increase in fermentation productivity as a result of *in-situ* fermentation. These fermentation yields were integrated with rigorous models of the separation sequence for each extractant. The separation sections were designed to produce 80,000 tonnes/year of butanol and the rest of the plant, including up-stream solids processing, pre-treatment/saccharification, fermentation, downstream utility generation, and wastewater treatment were sized accordingly to determine the MBSP for each extractant. Using these results, it was then possible to determine the CCA for each extractant.

Chapter 4 presented the economic best separation configurations and associated MBSP and CCA for each extractant. A summary table of the MBSP and the CCA for each extractant can be viewed in Table 17.

Table 17: MBSP and CCA Summary Table

Separation Case	MBSP ($/L)	CCA ($/tonne CO_2 avoided)
Pure-Distillation Base-Case	2.15	912.81
Decane	2.41	1236.96
Blend 1	2.18	1006.00
Decanol	2.36	1246.65
Blend 2	1.89	853.84
2-Ethyl-Hexanol	1.58	471.57
Hexanol	2.41	1314.35
Mesitylene	2.13	842.99
Oleyl Alcohol	1.97	878.99

This work determined 2-ethyl-hexanol to be the best overall extractant both economically and environmentally. All MBSPs reported in this work are higher than other reported values in literature. This is partly due to the addition of wastewater treatment, which accounts for at least 30% of total installed capital for all cases. It is also partly due to more realistic sugar losses throughout pre-treatment and fermentation than considered in other studies. The cost of bio-butanol could be greatly improved through less expensive wastewater treatment (perhaps through a more highly concentrated fermentation broth) and more efficient pre-treatment and saccharification methods.

CCA for all cases were also higher than the target of \$50/tonne CO_2 equivalent emissions avoided. It is the author's opinion that with emission reductions in the biomass supply chain this target can be achieved.

5.1. Future work

There is a significant amount of work still required to once again industrialize ABE fermentation. Three main areas of study are identified:

5.1.1 Lab scale studies

Lab scale studies could still be useful in many ways to the ABE fermentation area. As previously noted, potential butanol extraction chemicals should be investigated to determine their acetone distribution coefficients as side-product revenue has been shown to have a large effect on MBSP. In addition, fermentation studies could also be conducted to better quantify the effects of *in-situ* extraction on ABE fermentation yield. This could be done with batch, fed-batch and continuous reactor configurations.

5.1.2. Process intensification

To further decrease the cost of separation, process intensification techniques such divided-wall columns or semi-continuous distillation could be utilized. Both of these techniques condense a three-component separation, normally requiring two distillation columns in series, into a single column. These techniques have been shown to lower total annualized cost of separation in certain production ranges [90, 91].

5.1.3. Wastewater treatment

Wastewater treatment has been identified as a large cost in the production of both bio-butanol and bioethanol [62]. Wastewater treatment of bio-butanol has not been studied in great detail to determine how it is different than wastewater treatment for bioethanol production. This would allow a more accurate estimation of ABE wastewater treatment costs. Furthermore, if the cost of wastewater treatment were reduced it could have a moderate impact on the MBSP for any given extractant. In addition, the carbon emissions associated with wastewater treatment should be better investigated to see how the impact of residual sugars, affects wastewater carbon emissions.

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