MULTI-OBJECTIVE OPTIMIZATION OF BUTANOL PRODUCTION DURING ABE FERMENTATION

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ABSTRACT

Liquid biofuels produced from biomass have the potential to partly replace gasoline. One of the most promising biofuels is butanol which is produced in acetone-butanol-ethanol (ABE) fermentation. The ABE fermentation is characterized by its low butanol concentration in the final fermentation broth. In this research, the simulation of three in situ recovery methods, namely, vacuum fermentation, gas stripping and pervaporation, were performed in order to increase the efficiency of the continuous ABE fermentation by decreasing the effect of butanol toxicity. The non-integrated and integrated butanol production systems were simulated and optimized based on a number of objectives such as maximizing the butanol productivity, butanol concentration, and butanol yield. In the optimization of complex industrial processes, where objectives are often conflicting, there exist numerous potentially-optimal solutions which are best obtained using multi-objective optimization (MOO). In this investigation, MOO was used to generate a set of alternative solutions, known as the Pareto domain. The Pareto domain allows to view very clearly the trade-offs existing between the various objective functions. In general, an increase in the butanol productivity resulted in a decrease of butanol yield and sugar conversion. To find the best solution within the Pareto domain, a ranking algorithm (Net Flow Method) was used to rank the solutions based on a set of relative weights and three preference thresholds. Comparing the best optimal solutions in each case study, it was clearly shown that integrating a recovery method with the ABE fermentation significantly increases the overall butanol concentration, butanol productivity, and sugar conversion, whereas butanol yield being microorganism-dependent, remains relatively constant.

RÉSUMÉ

Les biocarburants liquides ont le potentiel de remplacer en partie l'essence. Le biocarburant liquide qui démontre le plus grand potentiel est le butanol qui est produit lors de la fermentation ABE (acétone, butanol, éthanol). La fermentation pour produire simultanément l'acétone, le butanol et l'éthanol (ABE) est caractérisée par une faible concentration en butanol dans le bouillon de fermentation. Dans cette recherche, les simulations de trois méthodes de récupération in situ tels que la fermentation sous vide, l'absorption gazeuse et la pervaporation, ont été étudiées pour augmenter l'efficacité de la fermentation par une diminution de l'effet de la toxicité du butanol. Les systèmes de production de butanol non intégrés et intégrés ont été simulés et optimisés en fonction d'un certain nombre d'objectifs tels que la maximisation de la productivité du butanol, la concentration de butanol, et le rendement de butanol. Dans l'optimisation des procédés industriels complexes, il existe de nombreuses solutions potentiellement optimales qui sont obtenues plus efficacement en utilisant l'optimisation multi-objectif (OMO). Dans cette recherche, OMO a été utilisée pour générer un ensemble de solutions alternatives, connu sous le nom du domaine de Pareto. Le domaine de Pareto permet de visualiser les compromis entre les différentes fonctions objectives. Pour trouver la meilleure solution dans le domaine de Pareto, une méthode de classement (Net Flow Method) a été utilisée pour ordonner les solutions basées sur une série de poids relatifs et de trois seuils de préférence. Il a été clairement démontré que l'intégration d'une méthode de récupération à la fermentation ABE a considérablement augmenté la concentration de butanol, la productivité du butanol, et la conversion de sucre, tandis que le rendement de butanol, étant étroitement dépendant du type de microorganismes, est demeuré relativement constant.

ACKNOWLEDGEMENT

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Chapter 1.
INTRODUCTION

1.1. Biofuels

Energy is an indispensable element of our society. Our dependence on energy ranges from home appliances, communication, heating/cooling, and transportation to industrial purposes. About 80% of the energy consumption in the world is from fossil fuels such as petroleum, natural gas, and coal. The transportation sector contributes to 58% of fossil fuel consumption (Escobar et al., 2009). Figure 1.1 depicts the estimated world liquid fuel consumption over the next 25 years. The demand for liquid fuels in the transportation sector is predicted to increase more rapidly than any other end-use sectors according to the prediction of the U.S Energy Information Administration.

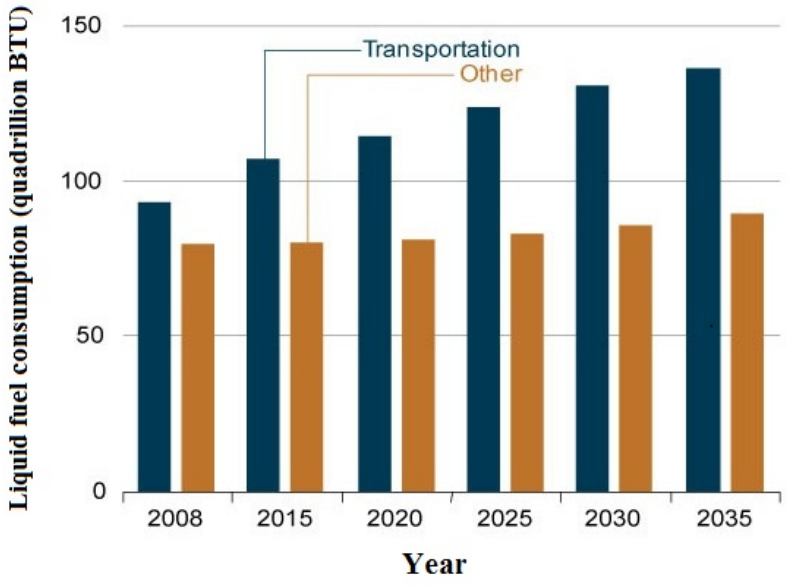

Figure 1.1: Estimated world liquid fuel consumption by end-use sector, 2008-2035 (US Energy Information Association, 2011)

Increasing oil prices, diminishing fossil fuel reserves, concerns over energy security, and elevated greenhouse gas (GHG) emissions (due to the fossil fuel combustion) have led to move toward a more sustainable, clean, and affordable energy resources. Renewable energies derived from wind, solar, geothermal, hydropower, and biomass have been extensively studied in order to develop their use. Energy from biomass resources is becoming increasingly important, since it can be used to partly displace conventional sources of energy that are used to produce electricity, heating, and transport fuels. Biomass is defined as any organic material that is derived on a renewable basis from living or recently living organisms.

Biofuels are produced from biomass and can be broadly classified as primary and secondary fuels. In a carbon fixation process, biomass recycles CO_2 (a contributor to climate change) by capturing it from the atmosphere in a process called photosynthesis whereby the solar energy is converted into biomass. Contrary to the primary biofuels such as wood which are used in an unprocessed form, secondary biofuels are produced from biomass by thermochemical means (e.g., biomass to liquid (BTL)) or by fermentation with microbes (Antoni and Zverlov, 2007). Figure 1.2 shows the secondary biofuel generation by a fermentation process.

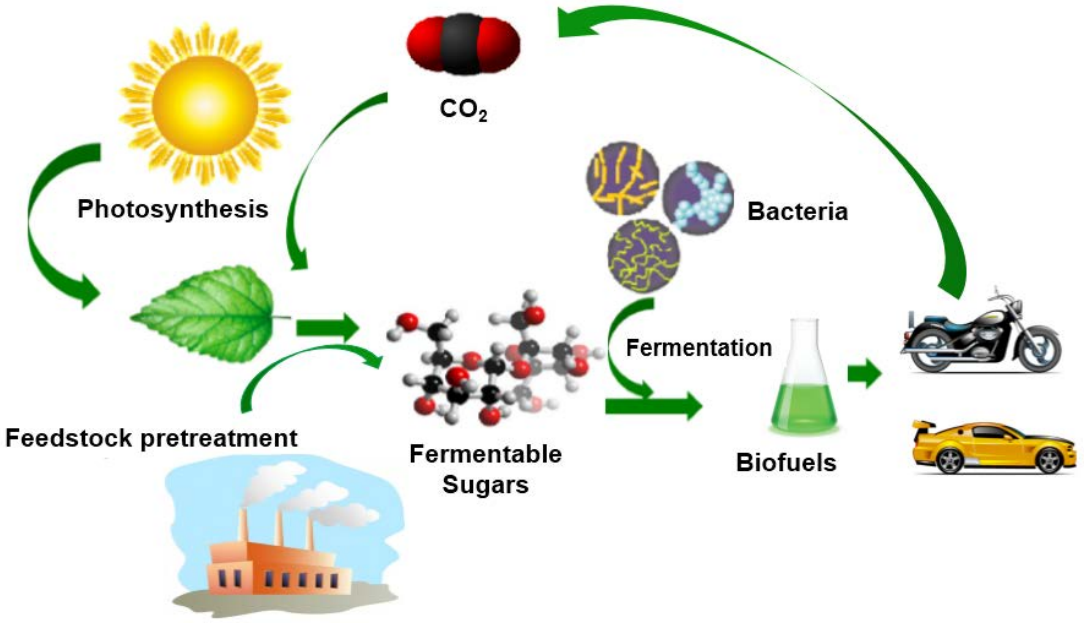

Figure 1.2: Conversion of solar energy into biofuels through fermentation.

Biofuels can be solid, such as charcoal, or liquid, such as ethanol and butanol, or gaseous, such as biogas. Liquid biofuels are being extensively studied mainly to replace conventional liquid fuels (petrol and diesel). Production of nearly carbon-neutral liquid fuels offers feasibility of more environmentally friendly transportation means without the necessity to shift to hydrogen-based or electrical vehicles. Due to their compatibility with existing vehicles and liquid fuel infrastructure, liquid biofuels are considered suitable alternative energy sources in the transportation sector. In order to meet the standards of engine applications, transportation safety, and energy density, liquid biofuels have to exhibit defined chemical and physical properties. Today, only diesel and ethanol are produced as a biofuel on an industrial scale.

1.1.1. Butanol vs. Ethanol

Ethanol production is by far the largest scale microbial process. Ethanol currently accounts for 94% of global biofuel production. Brazil and United States are world leaders of ethanol production, producing 70% of world bioethanol mainly from molasses and starch (Dufey, 2006). On the other hand, due to its superior properties over ethanol, butanol production by fermentation has attracted renewed attention and it has been extensively reviewed in the literature during the past few years (Antoni et al., 2007; Dürre, 2008). Performing a comparison of ethanol with butanol, one clearly sees the motivation toward the conversion of biomass to butanol instead of ethanol as a liquid biofuel for transportation applications.

Butanol as a biofuel has several advantages over ethanol including butanol's energy content which is 30% more than ethanol with a value that is closer to gasoline, resulting in a higher mileage (Table 1.1). Butanol has 116 000 kJ, whereas ethanol only has 88 000 kJ of energy per gallon (Chen and Blaschek, 1999). Due to butanol similar physical and chemical properties to gasoline, it can be used either pure or in any proportions with gasoline in unmodified car engines, while ethanol can only be mixed with gasoline up to 15 vol%, unless special engines are used. Butanol has a lower vapour pressure which makes it safer than ethanol to handle and store. Another important advantage is that butanol does not adsorb moisture from air because it is less hygroscopic than ethanol. Thus, the common problem of corrosion in ethanol transportation does not occur with butanol. This feature of butanol allows it to be used directly within the existing fuel infrastructure (i.e., tanks, pipelines, pumps, filling stations, etc.). Moreover, butanol is less hazardous and less flammable than ethanol (Dürre, 2007).

Table 1.1: Energy density and specific energy of butanol, ethanol and gasoline (data from Brown, 2003).

Fuel Type	Density (kg/m^3)	Specific energy (kJ/g)	Energy content (MJ/L)
n-butanol	810	36	29.2
Ethanol	794	26.5	23.5
Gasoline	740	44	32.6

1.2. Butanol

Butanol is a butyl alcohol produced from petroleum or via microbial fermentation. *n*-butanol is a four carbon, straight chained alcohol with a molecular formula of C_4H_9OH (MW 74.12 g/mol) and a boiling point of 118.8°C. It is a clear, flammable, and colorless liquid. Apart from being an attractive biofuel to replace gasoline, butanol is used as a chemical precursor for plastic solvents, detergents, polymers, paints, hydraulic fluids, and as an extractant in pharmaceutical processes.

1.2.1. Butanol Production History

The biological production of butanol dates back to 1862 when Louis Pasteur performed acetone-butanol-ethanol (ABE) fermentation to produce acetone (Pasteur, 1862). ABE fermentation made its way to industrial production which was counted as the second largest biotechnological process performed in the beginning of 20^{th} century. However, by 1950s, the ABE production by fermentation process declined due to low crude oil prices and increasing feedstock costs (molasses). Numerous ABE fermentation plants which used fermentation process to fulfill their industrial needs closed in USA, South Africa, China

and the former Soviet Union (Gabriel, 1928; Jones, 2001; Zverlov et al., 2006). Then until 2005, butanol was solely used as a chemical precursor for production of acrylate, methacrylate esters, glycol ethers, butyl acetate, etc. Later in 2007, BP and DuPont declared their collaboration for restarting the industrial ABE fermentation to produce butanol as a biofuel. In 2009, these two companies created a joint venture, called Butamax^{TM}, in Delware, USA (Butamax Advanced Biofuels LLC.). In addition, a few other companies such as Gevo and Green Biologics started biological butanol production which points to a bright future for ABE fermentation industrialization (Noorden, 2012).

1.2.2. ABE Fermentation Process

The ABE fermentation process uses a strain of *clostridia* to produce 6:3:1 mass ratio of butanol, acetone, and ethanol, respectively. Traditionally, butanol is produced in batch reactors typically having an initial concentration of 60 g/L glucose (usually molasses or cornstarch). First, the medium containing sugars and necessary nutrients is autoclaved at 121°C to sterilize the medium. After cooling, the medium is inoculated with the culture of solventogenic *clostridia* (e.g., *Clostridium acetobutylicum, Clostridium beijerinkii*) at which point the fermentation starts (Zheng et al., 2009).

During fermentation, ABE concentrations of up to 20-25 g/L are accumulated in 36-72 hours. Butanol is highly toxic to the microorganisms producing it. As a result, fermentation essentially ceases after butanol reaches concentrations as low as 5-10 g/L (Jones and Woods, 1986). The major end-products of ABE fermentation process are acetic acid, butyric acid, acetone, butanol, ethanol, carbon dioxide and hydrogen (Figure 1.3). Other end-products such as lactic acid, aceton and acetaldehyde can also be formed in minor

amounts. Low solvent concentration in batch fermentation results in low butanol yields (usually around 0.3 g/g) and low butanol productivities (around 0.5 g/L h) (Qureshi and Ezeji, 2008).

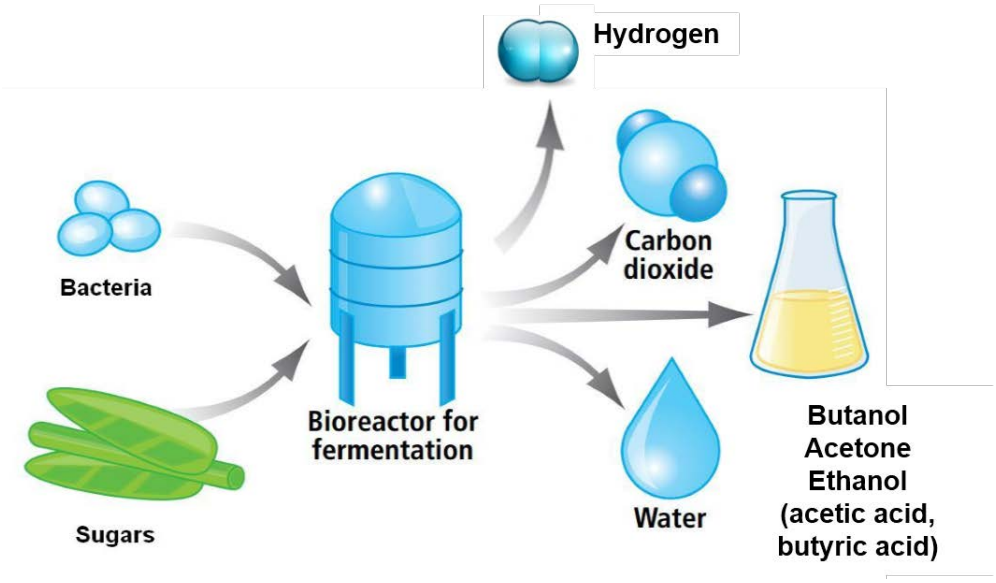

Figure 1.3: ABE fermentation process.

ABE fermentation consists of two stages of solventogenic and acidogenic pathways. The former occurs at the early stage of fermentation when microorganisms are growing exponentially. Products of this stage include butyric acid and acetic acid. After reaching certain amounts of acids in the fermentation broth, microorganisms enter the stationary growth phase and the second stage starts where the bacteria use the accumulated acids as an additional carbon source to produce the three main solvents: acetone, butanol and ethanol (Jones and Woods, 1986). The reason for this shift is the imminent threat of cell death by low pH. The conversion of butyric acid and acetic acid into solvents increases the pH again and keeps the cells metabolically active for a longer time (Gottwald and Gottschalk, 1985). Figure 1.4 shows the metabolic pathway of ABE fermentation carried out with

solventogenic bacteria. In spite of the fact that ABE fermentation has been studied for several decades, the mechanism of the metabolic shift from acidogenesis to solventogenesis is still unclear.

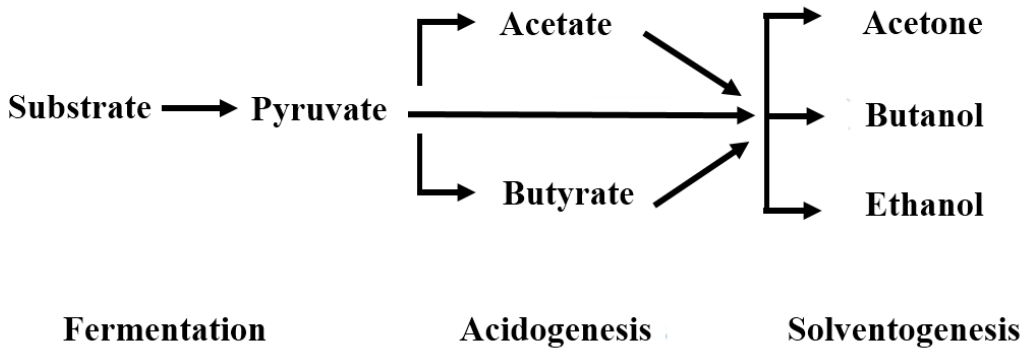

Figure 1.4: Phases of ABE fermentation process (Adapted from Qureshi and Ezeji, 2008).

1.2.3. Challenges in Biobutanol Production and Possible Solutions

ABE fermentation suffers from several disadvantages which makes the commercial scale fermentation of butanol currently unfavorable. High feedstock costs, low butanol concentrations ($g_{Butanol}/L$) in the final broth, low butanol yield ($g_{Butanol}/g_{Sugar\ consumed}$), low solvent productivity ($g_{Butanol}/L/h$), high costs of conventional separation methods including distillation, and high water usage during the fermentation process make the biological production of butanol very expensive (Ezeji et al., 2007; Kharkwal et al., 2009; Zheng et al., 2009).

Among the key factors determining the profitability of a butanol plant, feedstock cost has the largest impact on the overall cost. In a traditional fermentation plant which relies on conventional substrates, 79% of the total cost is accounted for feedstock while the operating cost of separation process is only 14% (Pfromm et al., 2010). Thus, the transition

to cheaper, non-edible feedstock is a necessity when penetrating into the commercial scale production of butanol. Another factor determining the butanol fermentation profitability is the oil price. Between the months of June to November 2008, the oil prices dropped and, as a result, butanol price decreased from $2400/t to $1000/t. It thus resulted in the closure of many butanol plants in China (Ni and Sun, 2009).

Solvent toxicity is one of the other critical problems in ABE fermentation. *Clostridial* cellular metabolism ceases in presence of 20 g/L or more solvents (Jones and Woods, 1986). Developing improved microbes with high solvent yields and concentrations, and applying cost-effective separation methods are two possible ways to address the problem with intrinsic low solvent concentrations. Solvent recovery by distillation is proven but is not economical due to the large amount of energy requirements. For example, for treating every one ton of solvent, about 12 ton of steam is required (Ni and Sun, 2005). Low butanol concentrations also produce large amounts of effluent and reduce sugar loadings (Green, 2011). Improvements in butanol separation can be made by applying non-conventional recovery methods such as vacuum fermentation, gas stripping, pervaporation, etc. (Jang et al., 2012).

1.2.4. Feedstock Type and Bacteria

Butanol is produced by *clostridia* fermentation. The solventogenic *clostridia* (e.g., *C. acetobutylicum*, *C. beijerinckii*, *C. pasteurianum*), a group of gram-positive and spore forming bacteria, are capable of using a wide range of sugars and carbohydrates including monosaccharides and polysaccharides. The solventogenic *clostridia* are able to secrete

various enzymes that facilitate the breakdown of polymeric carbohydrates (Ezeji et al., 2007).

ABE fermentation has traditionally used carbon substrates obtained from conventional crops such as sugar cane and sugar beets (sucrose), potato and corn (starch), etc. These feedstock sources are edible and are counted as the first-generation feedstock. First-generation feedstock are already available in large scales as they are produced for human and animal consumption. Since *Clostridium* has the essential enzymes to utilize starchy substrates, the substrate hydrolysis usually performed prior to the ABE fermentation is not needed (Qureshi and Blaschek, 2005; Jones and Woods, 1986). The cost of substrate has been always an important factor in determining the economics of ABE fermentation. Although the first-generation feedstock sources are significantly beneficial in achieving higher butanol concentrations due to their high sugar and starch contents, their consumption is considered unsustainable and hugely costly. Significant cost reduction can be achieved when lignocellulosic feedstock such as agricultural residues, corn cobs, sugar cane bagasse, wheat straw, and municipal solid waste (MSW) are used (Figure 1.5). These raw materials, known as second generation feedstock, are far more suitable for butanol generation since their utilization has no adverse effects on the food industry.

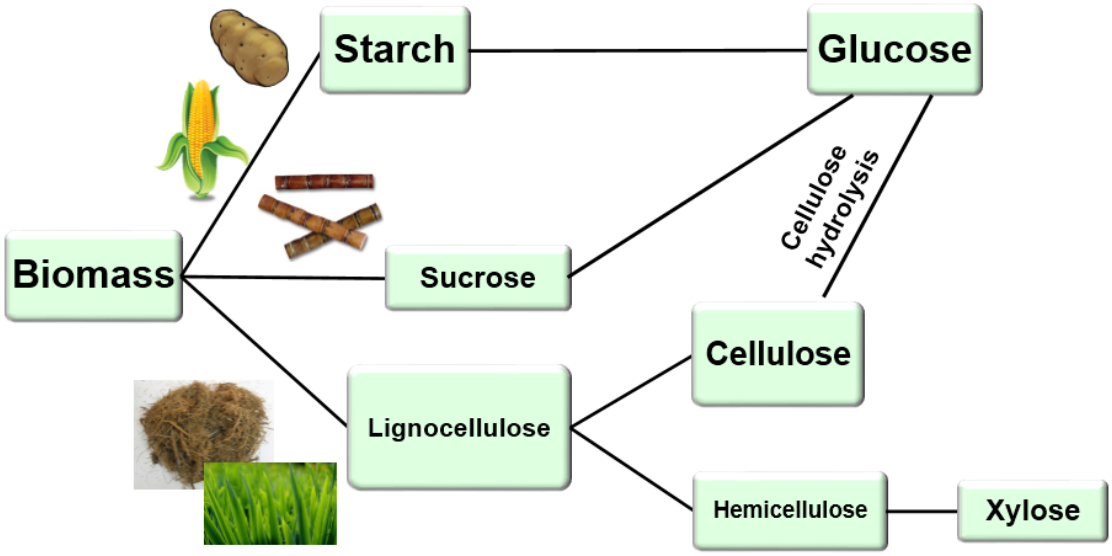

Figure 1.5: Various feedstock which may be used in ABE fermentation.

The major problems associated with ABE fermentation with solventogenic *clostridia* include solvent toxicity, strain degradation, undesirable spore formation, and formation of ethanol and acetone along with butanol. Although many researchers have worked on genetics of fermentation, solventogenic *clostridia* are still incapable of hydrolyzing fiber-rich agricultural residues. Hence, in order to obtain fermentable sugars from biomass, applying a pretreatment and hydrolysis step prior to the start of fermentation is imperative. However, organic acids and lignin produced during the hydrolysis process are toxic to the bacteria and their removal from the medium is a major challenge to be addressed. Moreover, most bacteria prefer glucose as the source of carbon and only when glucose finishes, the pentose sugars are utilized. It would be more economical when hexose and pentose sugars are utilized concurrently since the operation of fed-batch and continuous fermentation processes would be simplified (Ezeji et al., 2007). Thus, in order to improve the performance of solventogenic *clostridia*, new approaches to generate strains that can be

used in industrial biobutanol production are necessary. The butanol final concentration in the broth and the butanol yield are largely a function of the selection of the bacteria. Chemical mutagenesis and genetic manipulation offer better performances (Keis et al., 2001; Zverlov et al., 2006).

1.2.5. Fermentation Modes

ABE fermentation was largely operated in batch mode during the periods of its commercial production (Jones and Woods, 1986). Batch fermentation is easier to operate and has lesser chances of contamination. However, the conventional ABE fermentation in batch reactors results in productivities as low as 0.5 g/L/h due to the low cell concentration, downtime, and solvent toxicity. Solvent productivity (g solvent/L fermentation broth/h) significantly affects the process capital cost and is highly sensitive to the design of the fermenter. The most studied bioreactors are batch, fed-batch, and continuous. Continuous culture was shown to offer higher productivity compared to that of batch (Qureshi et al., 2004). In continuous fermentation, only one inoculum culture can carry the fermentation for a long time. Therefore, sterilization and inoculation time decreases which can lead to higher productivities. The most common strategies of the continuous fermentation include free cell, immobilized cell, and cell recycles that have been studied extensively in the literature (Nimcevic et al., 2002; Qureshi et al., 2004). Recycling and keeping cells within the fermenter have some advantages over simple continuous fermentation including longer continuous fermentation, more stable operations, and no cell washout. Contrary to free cell continuous reactors, immobilized cell and cell recycle continuous membranes offer higher solvent productivities because of the higher cell concentration that can be achieved. The

major limitation for achieving high cell densities and hence higher butanol productivities is the solvent toxicity in all fermentation modes. Advanced technologies for continuous product removal from fermentation broth prevent the inhibition by solvents. Thus, the cell life and butanol productivities improve.

1.2.6. Solvent Recovery Methods

Many attempts have been made to improve butanol production, but still the concentration of butanol in the final product is still too low to be economically viable. The major challenge to obtain high solvent productivities is due to the solvent toxicity. In order to overcome butanol toxicity and improve the productivity, various in-situ product recovery methods have been developed by selectively removing butanol. Some of these in-situ recovery methods include but not limited to vacuum fermentation, gas stripping, pervaporation, adsorption, reverse osmosis, and liquid-liquid extraction. Some of these methods, which were used in this research, are briefly explained in the following sections.

A. Gas Stripping

Gas stripping is a simple and cost effective in-situ separation technique to recover butanol during the fermentation process. ABE fermentation also produces H_2 and CO_2 gases. Bubbling these gases through the fermentation broth captures volatile solvents of ABE, and subsequently by passing the effluent gases through a condenser, volatile solvents are recovered. The gas exiting the cold trap is recycled back to the fermenter to capture more solvents. In some cases a separate gas stripper unit can be placed next to the fermenter to remove solvents, the effluent exiting the stripper is then recycled back to the fermenter (Ezeji et al., 2005).

B. Vacuum fermentation

Vacuum fermentation where volatile solvents can be removed during the fermentation process was first adopted in ethanol fermentation by Cysewski and Wilke (1977). In such a system, the fermenter remains at atmospheric pressure and the broth is circulated through a vacuum unit which is maintained under vacuum at the fermentation temperature. The fermentation broth is continuously boiled off and since butanol and other volatile solvents are more volatile than water, the butanol toxicity is thereby reduced. By separating the vacuum unit and the fermenter, carbon dioxide and hydrogen produced in the ABE fermentation are no longer needed to be compressed (Roffler et al., 1984).

C. Pervaporation

Pervaporation is the selective diffusion of solvents through a membrane resulting in the removal of volatile solvents from the fermentation broth. The liquid phase of fermentation broth is in contact with a hydrophobic membrane and the other side is a gaseous phase (vacuum or sweep gas). The permeate has to be volatile under the operating conditions of the membrane, regardless of vapor/liquid equilibrium. Based on the membrane physical characteristics, solvents in the fermentation broth have different selectivity values. The diffused solvent is in the form of vapour and is then recovered by condensation. In the selective removal process, the component of interest requires a heat of vaporization at the fermentation temperature. The efficiency of pervaporation is evaluated by selectivity (a measure of selective removal of volatile components) and flux (the rate of volatile stream passing through the membrane per membrane area). Pervaporation advantages over other recovery methods include low energy consumption and minimum risk of contamination. However, due to the swelling effect which makes membranes more permeable but less

selective, membranes must be changed at some point (Qureshi and Blaschek, 2005; Ezeji et al., 2006).

1.3. Process Simulation and Optimization

The economic feasibility of a fermentative process first requires a study of the process behavior. To reach this objective, mathematical modeling can be performed to investigate different operating conditions in order to predict large-scale bioreactor performance. Multi-objective optimization can be used to determine the optimal operating conditions of a continuous fermentation process coupled with an *in-situ* separation unit. To perform these tasks, finding a kinetic model for fermentation which adequately represents the ABE fermentation mechanism is crucial. After simulating the fermentation system coupled with various recovery units, the best operating conditions can be determined by the optimization of each setup.

1.3.1. Kinetic Model

The kinetic model of continuous fermentation used in this research is based on a model proposed by Mulchandani and Volesky (1986). They proposed a model to calculate the solvent production (acetone, butanol, and ethanol), the production of butyric acid and acetic acid, the formation of biomass, and the consumption of sugars in *Clostridium acetobutylicum* culture for a continuous production where the cells were retained inside the vessel. Their model was developed on the basis of the following assumptions: carbon substrate limitation and butanol and butyric acid inhibition. The kinetic equations proposed

by Mulchandani and Volesky (1986), which have been slightly corrected for minor typographical errors and missing terms, are presented in Chapter 2.

1.3.2. Pareto Domain

Optimization plays a major role in process modeling, design, and operation of chemical processes. To improve the performance, profitability, and safety; process operating conditions need to be optimized. Process optimization is often complex, nonlinear, and it is often required to optimize simultaneously several, often conflicting, process variables (or objectives). The mathematical relationship between the objectives to be optimized and decision variables determines the complexity of the optimization task. Until two decades ago, several objective functions were usually combined into a single objective criterion. However, this method suffers from several drawbacks as the various trade-offs between the objective functions are not visible and therefore not fully understood. In order to combine different objective functions into a single solution, each objective is assigned a weighting factor which carries the risk of losing optimal solutions, if not chosen properly (Chankong and Haimes, 1983).

To overcome single objective optimization shortcomings, multi-objective optimization can be used. In a typical multi-objective optimization problem, where optimal decisions are made in the presence of two or more conflicting objectives, there potentially exists more than one optimal solution. Multi-objective optimization (MOO) is an algorithm that has been developed to find the optimal solution(s) in the presence of tradeoffs among more than two conflicting objectives (Bhaskar et al., 2000; Rangaiah, 2008). In general, a MOO

problem has two or more objectives involving many decision variables. A MOO problem is defined as follows:

$$\text{Min/Max} \qquad F(x) = \left[f_1(x_1,\ldots, x_n), f_2(x_1,\ldots, x_n),\ldots, f_n(x_1,\ldots, x_n) \right] \tag{1.1}$$

where *F(x)* is the vector of individual objective functions to be optimized (minimize and or maximize) and *x* is the vector of decision variables or independent variables. The decision variables are usually selected within a realistic range between a lower and upper bound as defined by the decision maker.

$$x_{\text{i=1,...,n}}^{\text{lower bound}} \leq x_{\text{i=1,...,n}} \leq x_{\text{i=1,...,n}}^{\text{upper bound}} \tag{1.2}$$

In multi-objective optimization, instead of targeting a unique optimal solution, a number of optimal solutions are defined based on the concept of dominance. In this method, the trade-offs between individual objective functions mean that one objective improves while another objective is getting worse when moving from one optimal solution to another. The concept of dominance can be described by comparing two solutions. For a two-objective optimization, a solution A (x_A, $f_1(x_A)$, $f_2(x_A)$) is non-dominated by solution B (x_B, $f_1(x_B)$, $f_2(x_B)$) if at least one objective function of A is not worse than that of B. Moreover, if all the objective values of B are better than those of A, solution A is considered a dominated point.

The set of optimal solutions within a MOO problem is known as Pareto domain. Multi-objective optimization usually proceeds by circumscribing the Pareto domain comprised of a large number of non-dominated solutions. Several techniques to generate the Pareto domain have been proposed and applied for chemical engineering processes (Rangaiah, 2008). In this investigation, the Dual Population Evolutionary Algorithm (DPEA) was used

to obtain the Pareto domain for each fermenter configuration (Halsall-Whitney and Thibault, 2008). The procedure used can be summarized as follow:

1. A set of input values (decision variables) are randomly generated within their pre-determined ranges of variation to generate a specific population of solutions (M). Then, the objective functions are calculated for each set of input values of the population. In the Pareto domain, each point (solution) is defined based on its sets of decision variables and objective functions.
2. The objective functions are compared pairwise to calculate the number of times each solution is dominated. All non-dominated points, N_0, and a portion (survival fraction, FS) of dominated ones ($M - N_0$) are kept, resulting in N solutions retained for the next generation.

$$N = N_0 + INT[F_S(M - N_0)] \tag{1.3}$$

3. Then (M-N) points are generated to replace the discarded points in the population. To generate new points, two solutions from the N retained solutions are randomly chosen (one from dominated solutions and one from non-dominated solutions) and by a linear interpolation between their decision variables a new vector of decision variable is generated according to the following equation:

$$x_C = D_P x_A + (1 - D_P) x_B \tag{1.4}$$

In this equation D_P is randomly selected between 0 and 1. The objective values are calculated for the new set of decision variables.

4. These three steps are repeated until the desired number of non-dominated solutions is generated.

Figures 1.6 and 1.7 depict two-objective optimization plots for butanol production as an example. In Figure 1.6, the initial population (M) of 500 points or decision variables is presented. The two decision variables are the feed sugar concentration and the dilution rate. With each set of decision variables it is possible to calculate the corresponding two objective functions: butanol concentration and specific productivity (right plot of Figure 1.6). Each set of solutions implies a set of decision variables and corresponding objective functions. Both objective functions need to be maximized. Point x_A is in the decision variable space and the calculated objective functions $f(x_A)$ are depicted in Figure 1.6. Based on the concept of dominance, solution B (x_B, f (x_B)) clearly dominates solution A (x_A, f (x_A)), since both objective functions of point x_B are better than the values for the corresponding objective criteria for x_A. Thus, solution A will be discarded and all the other points which are non-dominated with respect to each other will be kept.

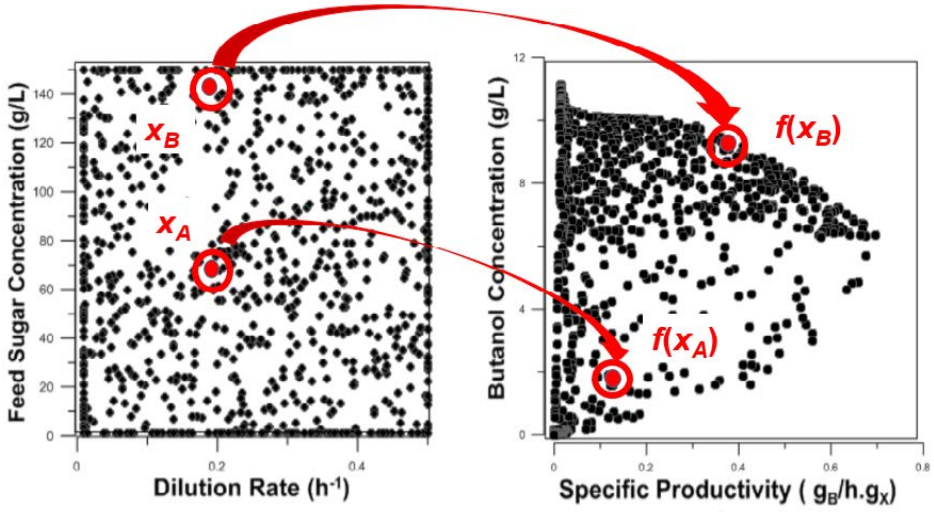

Figure 1.6: Plots of decision variables (left plot) and objective criteria (right plot) for the two-objective optimization of butanol production for the initial population.

Figure 1.7 shows 490 points of optimal non-dominated solutions (N_0) obtained for the butanol optimization problem after 6 generations with a population size of 500. It is clear that the two objectives are conflicting since specific productivity decreases with an increase in butanol concentration values. In this figure, every two optimal solutions are non-dominated with respect to each other. Any set of solutions that lie outside the zone shown on Figure 1.7 would lead to a dominated point and therefore would be worse than at least one solution that is within the Pareto domain.

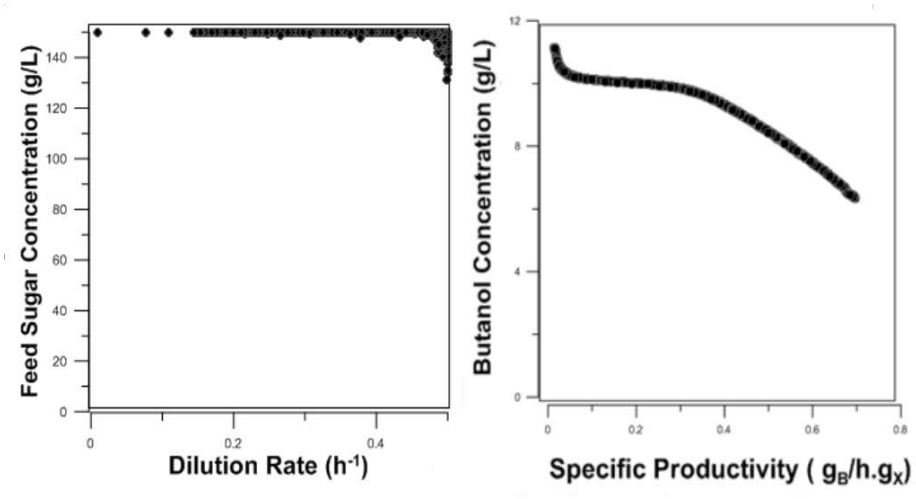

Figure 1.7: Plots of decision variables (left) and objective criteria (right) for the two-objective optimization of butanol production after converging to the Pareto domain.

1.3.3. Net Flow Method

For many simple problems, the decision maker can choose the optimal solution strictly based on the Pareto domain. However, for more complex problems, a ranking algorithm can be used to determine the optimal region of operation. In this study, the Net Flow Method (NFM) was used for ranking all solutions of the Pareto domain. NFM uses

knowledge from an expert or decision maker to perform the ranking based on a set of weights and thresholds. The detailed description of NFM is presented in Chapter 2.

Figure 1.8 shows the ranked optimal solutions for the two-objective optimization of butanol production. The red point is the best ranked solution. And, the black, dark grey, and light grey regions represent the best 5%, next 45%, and the last 50% ranked regions, respectively.

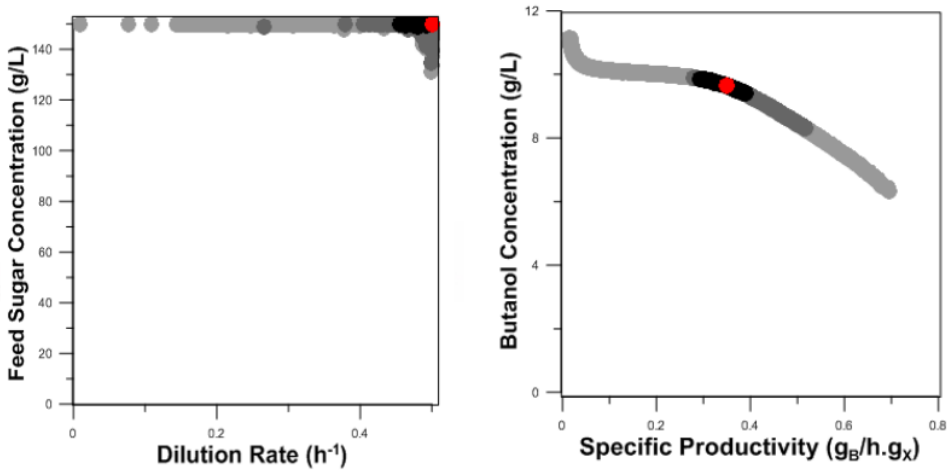

Figure 1.8: Ranked Pareto domain for the two-objective optimization of butanol production.

1.4. Thesis Objectives

The aim of this research is to model and optimize the ABE fermentation processes integrated with various continuous solvent removal units. Three recovery methods of vacuum fermentation, gas stripping and pervaporation, are considered for evaluation during the fermentative process. The fermentation processes coupled with solvent recovery units are to be simulated and optimized for different sets of objectives. Multi-objective optimization method is used to generate a Pareto domain in which a set of non-dominated,

optimal solutions are circumscribed. The decision variables that are used to obtain the Pareto domain include: inlet sugar concentration, dilution rate, biomass retention factor, evaporation rate factor (vacuum fermentation), CO_2 flow rate (gas stripping), cold trap temperature (gas stripping), membrane area (pervaporation). Multiple objective functions are desired to be maximized or minimized in the fermentation process, namely, butanol productivity, butanol concentration, butanol yield, sugar conversion, membrane area (pervaporation), and cold trap temperature (gas stripping). The operating conditions of the best solution in each case will be determined and discussed.

1.5. Thesis Outline

The thesis is divided into four chapters. The second chapter focuses on the design and optimization of a continuous butanol fermentation system coupled with a vacuum unit. In this chapter, the MOO results are depicted for standard fermentation and vacuum fermentation and the best ranked points are compared. This chapter is prepared in a journal manuscript format and will be submitted to the Biotechnology and Bioprocess Engineering Journal.

Chapter three focuses on optimizing the butanol fermentation production coupled with three different recovery units of: vacuum fermentation, gas stripping, and pervaporation. The Pareto-optimal points are shown for each case and the best solutions are compared with respect to each other in order to select the best recovery system among the three methods. This chapter is prepared in a journal manuscript format and will be submitted to the Applied Biochemistry and Biotechnology Journal.

Chapter four presents the overall conclusions of this research and recommendations for future investigation.

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Chapter 2.
MULTI-OBJECTIVE OPTIMIZATION OF BIOBUTANOL PRODUCTION: CONTINUOUS FERMENTATION COUPLED WITH A VACUUM SEPARATION UNIT

***Abstract*—** To produce butanol more economically from acetone-butanol-ethanol (ABE) fermentation, it is required to operate the process under optimal conditions. In this work, multi-objective optimization was used to determine Pareto-optimal solutions for this process. Based on an available kinetic model and a set of related mass balances for ABE fermentation, a continuous fermentation system coupled with a vacuum separation unit was simulated and a large number of Pareto-optimal solutions were obtained based on four decision variables and three objective functions. The optimal solutions were then ranked using the Net Flow Method (NFM) and were compared to the continuous fermentation without the vacuum separation unit. It was found that for the best solution, the selective removal of solvents via the vacuum separation unit enhanced butanol specific productivity ($g_{Butanol}/L/h/g_{Biomass}$), and its average concentration ($g_{Butanol}/L$). In addition, an optimal substrate conversion of 96% was obtained in the vacuum fermentation, compared with 83% in the non-integrated process. Adding a vacuum unit to the fermentation process allowed the inlet feed sugar concentration to increase from 55 g/L in the non-integrated fermentation to 150 g/L in the vacuum fermentation. Two additional multi-objective optimization cases were investigated in order to find the best set of objective functions for vacuum fermentation. Comparing the results of each case has shown that replacing the butanol specific productivity ($g_{Butanol}/L/h/g_{Biomass}$) by productivity ($g_{Butanol}/L/h$) as an

objective resulted in an increase in microorganism concentrations. Higher amounts of microorganisms in the fermenter led to an improvement in the butanol yield ($g_{Butanol}/ g_{Sugar\ consumed}$), butanol concentration ($g_{Butanol}/L$), and butanol productivity ($g_{Butanol}/L/h$) values.

2.1 Introduction

In recent years, biofuels have gained significant attention driven by factors such as limited supply of fossil fuels, the increasing and fluctuating prices of oil, and concerns over greenhouse gas emissions from fossil fuels leading to global warming. Amongst liquid biofuels, butanol produced from biomass has attracted special attention with its potential to be an alternative environmentally-sustainable fuel for petroleum gasoline due to its highly similar physical properties as well as its energy content.

The process for the production of butanol from biomass is commonly known as acetone-butanol-ethanol (ABE) fermentation. The economics of ABE production is directly influenced by the type of fermenter used (batch, continuous, fed-batch, etc.), the solvent recovery technique, the extent of sugar conversion, solvent yield, solvent concentration, and productivity. In the ABE fermentation process, butanol toxicity to the fermenting microorganisms results in product inhibition and limits butanol concentration in the broth. This in turn results in the cost of butanol recovery to be high, and more energy than the energy content of butanol may be required for its recovery. Therefore, by increasing butanol concentration in the final broth, significant energy saving can be attained.

To partly alleviate product inhibition, the concentration of solvent products in the broth should be maintained below the inhibition level by removing a portion of these products (Groot et al., 1991). To achieve this objective, several methods have been investigated in

literature: pervaporation (Groot and Kossen, 1984), liquid-liquid extraction (Evans and Wang, 1988; Roffler et al., 1987), gas stripping (Bailey and Ollis, 1986; Ezeji et al., 2003; Groot et al., 1989), reverse osmosis (Qureshi and Blaschek, 2001), and adsorption (Abdehagh et al., 2013; Garcia et al., 1986). Another technique to remove the volatile solvents in the fermentation broth is vacuum fermentation during which the fermenter or a separate unit connected to the fermenter is kept under vacuum conditions via a vacuum pump. This technique was first used by Cysewski and Wilke (1977) in ethanol fermentation in order to reduce ethanol inhibition of the yeast. They have demonstrated that by performing the process under vacuum, rapid and complete fermentation of concentrated sugar solutions was achieved. The higher boiling point of butanol (118°C) over that of water (100°C) could lead to believe that vacuum fermentation cannot be used in ABE fermentation. However, using computational simulation, Mariano et al. (2010) have shown the technical feasibility of vacuum fermentation integrated with butanol fermentation. Water and butanol form an azeotropic mixture: from which butanol can be boiled off at temperatures lower than the individual boiling point of butanol and water. Therefore, at butanol concentrations of interest in the fermentation broth, butanol is significantly more volatile than water and, as a result, butanol concentration in the vapour phase would be much higher than the one in liquid fermentation broth.

To assess the economic feasibility of a fermentative process, a study on the process behavior is first required. In this sense, mathematical modeling is performed to investigate different operating conditions in order to predict large-scale bioreactor performance. In this paper, multi-objective optimization was used to determine the optimal operating conditions of a continuous fermentation process coupled with a vacuum separation unit. To compare the advantage of using such a system, a comparison with the same process but without the

vacuum fermentation unit was also performed. The impact of the selected set of objective functions was investigated by considering two additional optimization scenarios for the vacuum fermentation.

2.2. Process Description

The ABE fermentation is usually carried out using bacteria such as *Clostridium acetobutylicum* or *Clostridium biejerinkii*. For most strains, the inhibition concentration of acetone, butanol, and ethanol solvents is approximately 20 g/L, with a butanol concentration of 13 g/L or less (Jones and Woods, 1986). This inhibition means that the fermentation process essentially ceases after the solvent concentration reaches this limit, resulting in a low butanol yield (Mariano et al., 2012). It has been demonstrated that continuous fermentation mode provides some advantages over batch mode where higher productivities can be achieved by maintaining a higher biomass concentration in the fermenter (Jones and Woods, 1986; Qureshi et al., 2000). Moreover, with relatively high dilution rates, a cell retention system can be used to prevent the washout phenomenon (the condition where culture is not able to sustain itself through the fermenter due to high dilution rates) (Groot et al., 1989). In continuous fermentation, it is desired to achieve steady-state operation rapidly. The fermentation is performed at atmospheric pressure and 37^{o}C. The fermentation process is usually initiated in batch mode and, then at a suitable time, it is switched to continuous mode of operation where eventually steady-state operation is achieved. In continuous fermentation, a feed stream containing fermentable sugar and nutrients enters the fermenter where sugar is converted into desired products by

the microorganisms. To maintain steady-state operation, an equivalent stream of the fermentation broth must exit the fermenter.

The fermentation process evaluated in this work is schematically represented in Figure 2.1. This system is used for both the standard continuous fermentation and the fermentation coupled with a vacuum separation unit. In the latter case, a stream (Stream 2), which is withdrawn from the fermentation broth, passes through a heat exchanger to add the necessary latent heat of vaporization to sustain the desired rate of evaporation prior to entering the vacuum flash unit where a fraction of the inlet stream is vaporized. The flash unit operates at 37^0C with a pressure in the vicinity of 7 kPa which corresponds to the boiling point of the fermentation broth at 37^0C. Because ABE solvents are more volatile than the water in the fermentation broth, the vaporized stream (Stream 8) is more concentrated with these solvents. It is therefore possible to partly remove butanol and therefore reducing its inhibition. In order to create vacuum, a condenser is used to condense and separate the solvents in Stream 8 in addition to a vacuum pump. It is assumed that all the volatile solvents that were evaporated are recovered in the condenser (Stream 3) and the vapour stream leaving the condenser (Stream 9) carries negligible amounts of solvents. The liquid stream leaving the vacuum unit (Stream 4) is pumped and sent to a cell retention unit where part of the liquid permeates through a membrane (Stream 7). The retentate stream is then split into two streams: a purge stream (Stream 5) to maintain the biomass concentration constant and a recycle stream (Stream 6) to the fermenter. Under steady-state, the feed stream flow rate must equal that of the three streams exiting the fermentation system (i.e., $F_1 = F_3 + F_5 + F_7 + F_9$). In the case of a standard continuous fermentation, the

vacuum separation unit and the heat exchanger are simply bypassed. The performance of both configurations were optimized and compared in this paper.

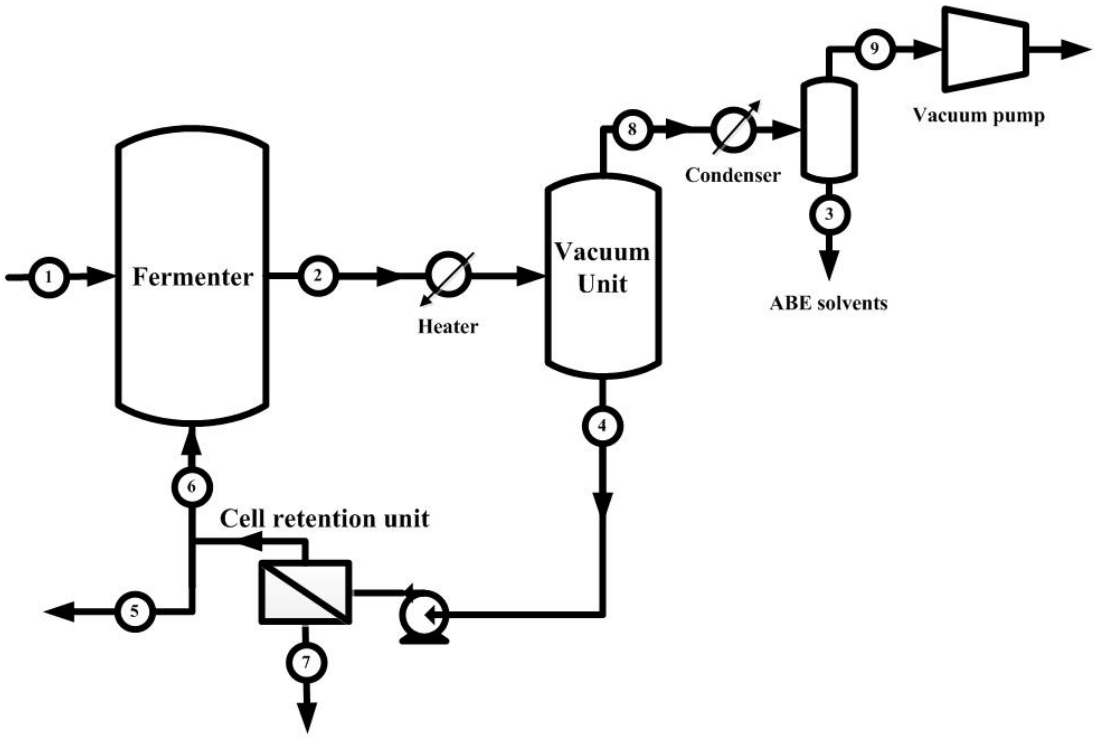

Figure 2.1: Schematic of a continuous fermenter equipped with a cell retention and a vacuum unit. 1 (Feed stream); 2 (Stream to the vacuum unit); 3 (Solvent condensate); 4 (Broth stream out of the vacuum unit); 5 (Bleed stream); 6 (Recycle stream back to the fermenter); 7 (Permeate stream from cell retention unit); 8 (Vacuum unit vapour stream); 9 (Vapour stream out of condenser/separator).

2.2.1. ABE Fermentation Kinetic Model

The kinetic model used in this research to simulate the continuous fermentation is based on a model proposed by Mulchandani and Volesky (1986). They proposed a model to calculate the solvent production (acetone, butanol, ethanol), the production of butyric acid and acetic acid, the formation of biomass, and the consumption of sugars in *Clostridium acetobutylicum* culture for a continuous production where the cells were retained inside the

vessel. Their model was developed on the basis of the following assumptions: carbon substrate limitation only and product inhibition. The kinetic model proposed by Mulchandani and Volesky (1986), which has been slightly modified for minor typographical errors and missing terms, is presented in the following equations. The model contains a product inhibition factor, *F(I)*:

$$\begin{aligned} F(I) &= \exp(-\,0.01BBA) && BBA \le 8 \text{ g/L} \\ F(I) &= -\,0.153BBA + 2.16 && 8 \le BBA \le 13.9 \text{ g/L} \end{aligned} \tag{2.1}$$

The term BBA corresponds to the total concentration of butanol and butyric acid. The cell growth rate (r_x) is based on the Monod equation (Monod, 1949):

$$r_x = \mu_m \frac{C_S}{C_S + K_S} F(I) X \tag{2.2}$$

The substrate consumption rate (r_s) is expressed as:

$$-r_S = k_3 \mu X F(I) + k_4 X F(I) + k_1 \frac{C_S}{C_S + K_S} \frac{BA}{BA + K_{BA}} X + k_2 \frac{C_S}{C_S + K_S} \frac{AA}{AA + K_{AA}} X \tag{2.3}$$

The following equations represent the rate of acid production, including acetic acid and butyric acid, which are considered as intermediate metabolites and are eventually reduced to acetone and butanol, respectively:

$$r_{AA} = k_8[k_3\mu_m \frac{C_S}{C_S + K_S} F(I)X + k_4 F(I)X] - k_9 \frac{C_{AA}}{C_{AA} + K_{AA}} \frac{C_S}{C_S + K_S} X \quad (2.4)$$

$$r_{BA} = k_5[k_3\mu_m \frac{C_S}{C_S + K_S} F(I)X + k_4 F(I)X] - k_6 \frac{C_{BA}}{C_{BA} + K_{BA}} \frac{C_S}{C_S + K_S} X \quad (2.5)$$

$$r_A = k_{10}[k_3\mu_m \frac{C_S}{C_S + K_S} F(I)X + k_4 F(I)X] + k_{15} \frac{C_{AA}}{C_{AA} + K_{AA}} \frac{C_S}{C_S + K_S} X \quad (2.6)$$

$$r_B = k_7[k_3\mu_m \frac{C_S}{C_S + K_S} F(I)X + k_4 F(I)X] + k_{14} \frac{C_{BA}}{C_{BA} + K_{BA}} \frac{C_S}{C_S + K_S} X \quad (2.7)$$

Ethanol production (r_E) is solely based on substrate consumption:

$$r_E = k_{11}[k_3\mu_m \frac{C_S}{C_S + K_S} F(I)X + k_4 F(I)X] \quad (2.8)$$

The change in concentration of all species in the fermenter is obtained by an overall mass balance around the fermenter with constant volume (Figure 2.1) as shown in Equation (2.9).

$$\frac{dC_i}{dt} = \frac{1}{V}\left[F_1 C_{i,1} + F_6 C_{i,6} - F_2 C_{i,2} + r_i V\right] \quad (2.9)$$

where C_i stands for the product concentration for each species: butanol, ethanol, acetone, butyric acid, acetic acid, and sugar. A similar mass balance can be written for biomass as follows:

$$\frac{dX}{dt} = \frac{1}{V}\left[F_6 X_6 - F_2 X_2 + r_X V\right] \quad (2.10)$$

where

$$F_1 = F_3 + F_5 + F_7 + F_9 = D\,V \tag{2.11}$$

$$F_2 = 20F_1 \tag{2.12}$$

$$F_6 = F_4 - F_5 - F_7 \tag{2.13}$$

It is assumed that the feed stream contains no biomass. All the kinetic constants in the aforementioned equations can be found in Mulchandani and Volesky (1986). For completeness, the table of constants in the kinetic model are given in Appendix I. The set of differential equations were solved by finite differences and the mass balances were solved at each integration time step. Visual Basic for Applications (VBA) program was used as the simulation platform and the required thermodynamic information was obtained by calling Honeywell UniSim® software from VBA.

2.2.2. Multi-objective Optimization

Multi-objective optimization (MOO) has been applied in many complex chemical engineering processes where the simultaneous optimization of more than one objective function is required. When a precise kinetic model of the process is available, multi-objective optimization enables examining the different decision variables without performing costly and time consuming experiments in order to evaluate the desired objective criteria. It is therefore possible to determine from the model the optimal process design.

The aim of the present paper was to model, simulate and optimize a continuous ABE fermentation process integrated with a vacuum separation unit to selectively remove a portion of the solvents and reduce product inhibition. In such a case, changing the operating

conditions such as vacuum pressure in the separation unit, dilution rate, initial sugar concentration, and evaporation rate has a direct impact on the objectives of interest such as butanol specific productivity, butanol productivity, butanol yield, butanol average concentration in the outlet streams, and sugar conversion. Two scenarios were defined and evaluated: the first scenario compared the standard fermentation with the vacuum fermentation configuration, and in the second scenario, the choice of the set of objective functions in the multi-objective optimization were evaluated for the vacuum fermentation configuration.

2.2.3. Pareto Domain

Optimization plays a major role in process modeling, design, and operation of chemical processes. To improve the process performance, profitability, and safety, it is required to operate the process under optimal conditions. Process optimization is often complex and nonlinear, and usually requires optimizing simultaneously several, often conflicting, process variables (or objectives). The mathematical relationship between the objectives to be optimized and the decision variables determines the complexity of the optimization task. Until two decades ago, the numerous objective functions were usually combined into a single objective criterion. However, this method suffers from several drawbacks as the various trade-offs between objective functions are not visible and therefore not fully understood. In order to combine different objective functions into a single solution, each objective is assigned a weighting factor which carries the risk of not achieving the most desired optimal solution, if not chosen properly (Chankong and Haimes, 1983).

To overcome single objective optimization shortcomings, multi-objective optimization can be used (Doumpos and Zopounidis, 2002). In a typical multi-objective optimization problem, where optimal decisions are made in the presence of two or more conflicting objectives, there is more than one optimal solution. Multi-objective optimization usually proceeds by circumscribing the Pareto domain with a large number of non-dominated solutions. The concept of dominance can be described by comparing two solutions: a solution A is non-dominated by solution B if at least one of the objective functions of A is not worse than that of B and it is better with respect to at least one objective. Moreover, if all the objective function values of A are better than those of B, then solution B is considered a dominated solution. Several techniques to generate the Pareto domain have been proposed and applied for chemical engineering processes (Rangaiah, 2008). In this investigation, the Dual Population Evolutionary Algorithm (DPEA) was used to obtain the Pareto domain for each fermenter configuration (Halsall-Whitney and Thibault, 2008). The procedure used is as follows:

1. A set of input values (decision variables) are randomly generated within their pre-determined range of variation to create an initial population of solutions (M). Then, the objective functions are calculated for each set of input values of the population. In the Pareto domain, each point (solution) is defined based on its sets of decision variables and associated objective functions.
2. The objective functions are compared pairwise to calculate the number of times each solution is dominated. All non-dominated solutions, N_0, and a portion (survival

fraction, F_S) of the dominated solutions ($M - N_0$) are kept, resulting in N solutions retained for the next generation.

$$N = N_0 + INT\ [F_S(M - N_0)] \tag{2.14}$$

3. Then (M-N) new solutions are generated to replace the discarded points in the population. To generate new points, two solutions from the N retained solutions are randomly chosen (one from the dominated solutions and one from the non-dominated solutions) and by a linear random interpolation between their decision variables a new vector of decision variables is generated. The objective functions are calculated for the new set of decision variables.
4. These three steps are repeated until the desired number of non-dominated solutions is generated.

2.2.4. Net Flow Method

For many simple problems having only few objectives, the decision maker can choose the optimal solution strictly based on the Pareto domain. However, for more complex problems, a ranking algorithm can be used to determine the optimal region of operation. In this study, the Net Flow Method (NFM) was used for ranking all solutions of the Pareto domain. NFM uses knowledge from an expert or decision maker to perform this ranking based on the following four sets of ranking parameters:

1. The relative importance of each objective function is expressed by a set of normalized relative weights:

$$\sum_{K=1}^{n} W_K = 1 \tag{2.15}$$

2. The range of variation of each criterion for which the decision maker is not able to prefer one objective function of a given solution over the same objective function of another solution is called the indifference threshold (Q_K). Every two objective functions placed in this range are considered to be indiscernible with respect to each other.
3. The minimum difference between two values for a given criterion that the decision maker starts to prefer between two values is called the preference threshold (P_K). Above this threshold, priority is given to the larger value if a criterion is to be maximized and to a smaller value for a minimization problem.
4. The difference between two values of a criterion which is considered too high to be tolerated refers to the veto threshold (V_K). A solution is banned relative to another if the veto threshold is violated for at least one objective function in a solution.

For each objective function the following relationship exists between the three thresholds:

$$0 \le Q_K \le P_K \le V_K$$

These NFM parameters give the importance that each criterion has to the eyes of the decision maker. Based on the relative weights and the three thresholds, each solution is given a score. The whole Pareto domain is then ranked based on these scores. The NFM algorithm to perform the ranking executes as follow:

1. First for each two solutions of *i* and *j* in the Pareto domain, the difference between the values of F_k of each objective function (K) is calculated by the following equation, the difference is calculated for all the solutions (M) in Pareto domain pairwise:

$$\Delta_K[i,j] = F_K(i) - F_K(j) \begin{cases} i \in [1,M] \\ j \in [1,M] \\ k \in [i,n] \end{cases} \tag{2.16}$$

2. The concordance index C_K [i, j] is then calculated for each objective function for every pair of solutions in the Pareto domain using equation (2.17).

$$C_K[i,j] = \begin{cases} 1 & \text{if } \Delta_K[i,j] \le Q_K \\ \dfrac{P_K - \Delta_K[i,j]}{P_K - Q_K} & \text{if } Q_K < \Delta_K[i,j] \le P_K \\ 0 & \text{if } \Delta_K[i,j] > P_K \end{cases} \tag{2.17}$$

Based on the indifference and preference thresholds for a given objective function (K), the concordance index measures the strength of the argument when the value of a criterion for solution i ($F_K(i)$) is at least as good as the same value ($F_K(j)$) in solution j. For differences below the indifference threshold, the concordance index equals unity while for differences over the preference threshold it equals zero. For a difference value between Q_K and P_K, the concordance index varies linearly between 0 and 1.

3. To determine the global concordance index, the weighted sum of individual concordance indices is calculated for each two solutions.

$$C[i,j] = \sum_{K=1}^{n} W_K C_K[i,j] \quad \begin{cases} i \in [1,M] \\ j \in [1,M] \end{cases} \tag{2.18}$$

4. Then the discordance index (D_K) is calculated based on the preference and veto thresholds of each criterion for a pair of solutions.

$$D_K[i,j]=\begin{cases} 0 & \text{if } \Delta_K[i,j]\le P_K \\ \dfrac{\Delta_K[i,j]-P_K}{V_K-P_K} & \text{if } P_K<\Delta_K[i,j]\le V_K \\ 1 & \text{if } \Delta_K[i,j]>V_K \end{cases} \quad (2.19)$$

The discordance index measures the strength of the argument for the solutions when the value of a criterion for solution *i* ($F_K(i)$) is significantly worse than the same value ($F_K(j)$) in solution *j*. For differences below the preference threshold, the discordance index equals zero while for differences over veto threshold it equals unity. For the difference values varying between Q_K and V_K, it varies linearly between 0 and 1.

5. The global concordance and discordance values are used to show the performance of each pair of solutions in the Pareto domain. Considering all objective functions, the quality of solution i relative to solution j is calculated by the following equation:

$$\sigma[i,j]=C[i,j]\left(\prod_{K=1}^{n}[1-(D_K[i,j])^3]\right) \quad \begin{cases} i\in[1,M] \\ j\in[1,M] \end{cases} \quad (2.20)$$

When σ[*i*, *j*] is close to zero, it indicates that solution *j* outranks solution *i*. If the value is close to 1 then solution *i* either outranks solution *j* or both solutions are in each other's vicinity.

At the end, the final ranking is done by summing up all the individual outranking elements for each solution in the Pareto domain.

$$\sigma_i=\sum_{j=1}^{M}\sigma\,[i,j]-\sum_{j=1}^{M}\sigma\,[j,i] \quad (2.21)$$

The first term compares the performance of solution *i* relative to other solutions while the second term compares the performance of other solutions relative to solution *i*. After scoring each solution as it was indicated above then solutions are sorted from highest to lowest. The solution with the highest ranking value is the solution that suits the decision-maker problem best. A more detailed description of Net Flow Method can be found in the literature (Thibault, 2008; Thibault et al., 2012).

2.2.5. Definitions of Objective Functions and Decision Variables

A. Standard versus Vacuum Fermentation

To evaluate the benefits of incorporating a vacuum separation unit in the fermentation process, the standard continuous ABE fermentation process (Case 1) was optimized and compared with the continuous fermentation coupled with a vacuum solvent removal unit (Case 2) also under optimal conditions. Both cases consist of three objective functions, with three and four decision variables, respectively. All three objective functions need to be maximized:

Case 1:	Case 2:
$f_1(\phi_1,\phi_2,\phi_3) = SP_B$	$f_1(\phi_1,\phi_2,\phi_3,\phi_4) = SP_B$
$f_2(\phi_1,\phi_2,\phi_3) = C_B$	$f_2(\phi_1,\phi_2,\phi_3,\phi_4) = C_{B(avg)}$
$f_3(\phi_1,\phi_2,\phi_3) = Con_S$	$f_3(\phi_1,\phi_2,\phi_3,\phi_4) = Con_S$

Table 2.1 presents the definition of all objective functions and decision variables used in this study. In both Cases 1 and 2, the three objective functions are the maximization of butanol specific productivity, average butanol concentration, and sugar conversion. The butanol specific productivity is the butanol productivity divided by the cell concentration which serves at the same time to prevent the biomass from reaching very high values. On

the other hand, the one added to the cell concentration in the denominator is a soft constraint to prevent the biomass reaching very small values in order to create a very high butanol specific productivity. The decision variables used were the dilution rate (ϕ_1), sugar concentration in the feed (ϕ_2), biomass retention factor (ϕ_3), and evaporation rate factor (ϕ_4). The biomass retention factor is obtained by adjusting the bleed stream flow ratio (F_5/ ($F_{5+}F_7$)). To satisfy the steady-state mass balance, the evaporation rate factor for Case 2 was expressed as a fraction of stream F_2 and was manipulated by changing the vapour fraction of the vacuum unit. Since vacuum unit did not exist in standard fermentation, ϕ_4 was not used as a decision variable in Case 1. The Pareto-optimal solutions for both cases were ranked by the Net Flow Method to find the best point. The NFM relative weights and thresholds used for each case are presented in Table 2.2.

Table 2.1: Definition of objective functions and decision variables with their lower and upper bounds.

	Parameters	Definitions	
Objectives Functions	Butanol specific productivity, SP_B (g_B/L.h.g_x)	$\frac{1}{V}\frac{[C_{B,3}MW_BF_3 + C_{B,4}MW_B(F_7+F_5)]}{X+1}$	
	Average butanol concentration, C_B (g/L)	$\frac{C_{B,3}MW_BF_3 + C_{B,4}MW_B(F_7+F_5)}{F_1}$	
	Sugar conversion, Con_S (fraction)	$1-\frac{C_{S,7}(F_7+F_5)}{C_{S,1}F_1}$	
	Butanol yield, Y_B (g/g)	$\frac{C_{B,3}MW_BF_3 + C_{B,4}MW_B(F_7+F_5)}{C_{S,1}F_1MW_S - C_{S,7}(F_7+F_5)MW_S}$	
	Butanol productivity, P_B (g/L.h)	$\frac{1}{V}[C_{B,3}MW_BF_3 + C_{B,4}MW_B(F_7+F_5)]$	
Decision Variables	Dilution rate, ϕ_1 (h^{-1})	$\frac{F_1}{V}$	$0.01 \le \phi_1 \le 0.8$
	Inlet feed sugar concentration, ϕ_2 (g/L)	$C_{S,1}MW_S$	$5 \le \phi_2 \le 150$
	Biomass retention factor, ϕ_3 (m^3.h/m^3.h)	$\frac{F_5}{F_7+F_5}$	$0.05 \le \phi_3 \le 1$
	Evaporation rate factor, ϕ_4 (m^3.h/m^3.h)	$\frac{F_8}{F_2}$	$0 \le \phi_4 \le 0.04$

B. Two Additional Vacuum Fermentation Cases

It will be shown in the results that vacuum fermentation (Case 2) leads to higher values of all three objective functions when compared to the standard fermentation (Case 1). It will also be shown that the decision variables for the best Pareto-optimal solutions for Case 2 were mostly concentrated around the maximum sugar concentrations set at 150 g/L. Since the sugar feedstock and pre-treatment methods are generally fixed in industrial ABE fermentation plants, sugar concentrations in feed streams are almost invariant, it was decided for the remaining case studies to keep the sugar concentration in the inlet feed

stream at 150 g/L. As a result, the inlet sugar feed concentration is excluded from the decision variable set. Two additional case studies were conducted for the continuous vacuum fermentation configuration to examine the choice of the objective functions on the performance of the fermentation unit. Cases 3 and 4 are defined as follow:

Case 3:
$f_1(\phi_1, \phi_3, \phi_4) = SP_B$
$f_2(\phi_1, \phi_3, \phi_4) = Y_B$
$f_3(\phi_1, \phi_3, \phi_4) = Con_S$

Case 4:
$f_1(\phi_1, \phi_3, \phi_4) = P_B$
$f_2(\phi_1, \phi_3, \phi_4) = Y_B$
$f_3(\phi_1, \phi_3, \phi_4) = Con_S$

Table 2.2: Net Flow Method parameters used to rank the Pareto-optimal solutions for Cases 1-4.

Mode	Criteria	Relative Weights	Thresholds		
			Indifference	Preference	Veto
Case 1	SP_B	0.4	0.05	0.1	0.2
	C_B	0.2	1	2	6
	Con_S	0.4	0.05	0.1	0.3
Case 2	SP_B	0.4	0.05	0.1	0.2
	C_B	0.2	2	5	12
	Con_S	0.4	0.05	0.1	0.3
Case 3	SP_B	0.4	0.05	0.1	0.2
	Y_B	0.2	0.005	0.01	0.03
	Con_S	0.4	0.05	0.1	0.3
Case 4	P_B	0.4	2	3	7
	Y_B	0.2	0.005	0.01	0.03
	Con_S	0.4	0.05	0.1	0.3

2.3. Results and Discussion

The Pareto domain for each case study was obtained by determining 1000 Pareto-optimal solutions using the DPEA genetic algorithm. These 1000 solutions were then ranked using the Net Flow Method based on the relative weights and threshold values presented in Table 2.2. The plots of the three objective functions for the ranked Pareto domains for Cases 1 and 2 are presented in Figures 2.2 and 2.3. In these plots, the red dot represents the best Pareto-optimal solution. The black, medium grey and light grey regions represent the best 5%, the next 45% and the last 50% ranked solutions, respectively. Figures 2.2 and 2.3, for Cases 1 and 2, clearly show the trade-offs that exist between the three objective functions. An increase in the butanol concentration was accompanied by a decrease in its specific productivity. For Case 1, the trade-off is even more striking between the butanol specific productivity and sugar conversion where an increase in specific productivity is accompanied by a drastic reduction in sugar conversion. A possible explanation is that at low dilution rates, a greater amount of sugar is consumed within the fermenter and, as a result, more butanol is produced. However, low dilution rates result in lower specific productivity.

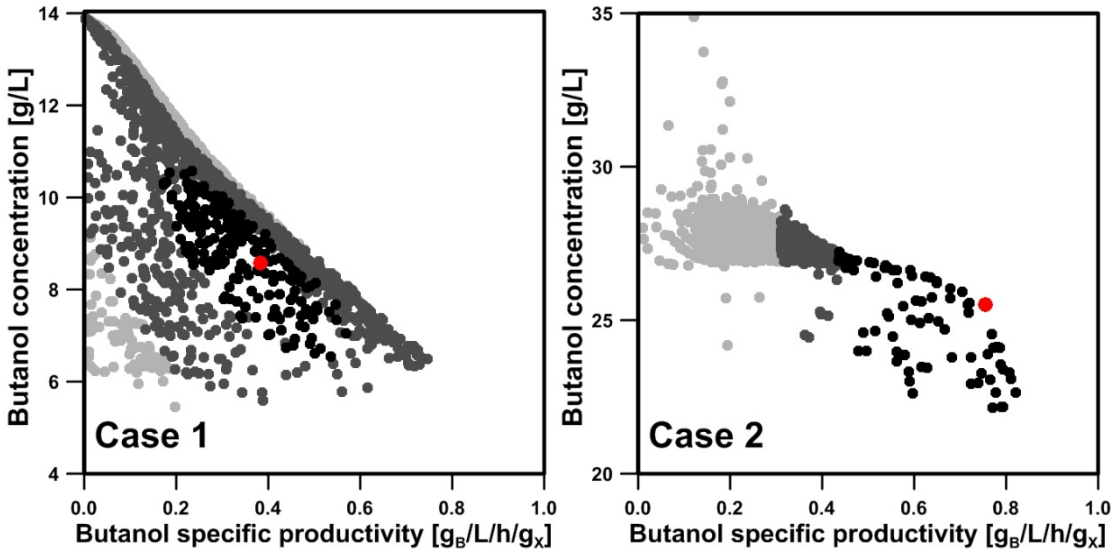

Figure 2.2: Plot of butanol average concentration versus butanol specific productivity for Cases 1 and 2.

The comparison of Cases 1 and 2 in Figure 2.3 indicates that the sugar conversion remains fairly high over a wider range of specific productivity for fermentation coupled with a vacuum separation unit. The values of all objective functions and the decision variables as well as few important selected variables for the best ranked Pareto-optimal solutions for both cases are reported in Table 2.3. Values associated with the highest-ranked Pareto-optimal solution in Table 2.3 indicate that most of the key factors determining the profitablity of an ABE fermentation plant are superior when a vacuum separation unit is used. In Case 2, the average concentration of butanol by combining the three output streams (F_3, F_5, F_7) is 25.9 g/L which represents a three-fold increase compared to that of Case 1. High butanol concentration in the final fermentation broth is greatly advantageous since it results in lower separation costs for butanol recovery from the dilute broth. It was demonstrated by Philips and Humphrey (1983) that as butanol concentration increases from 10 g/L to 40 g/L, the ratio of energy input over recovered butanol decreases from 1.5 to 0.25. Moreover, due to the

higher average butanol concentration and higher dilution rate, the butanol specific productivity was increased by 75% for Case 2, when compared to Case 1.

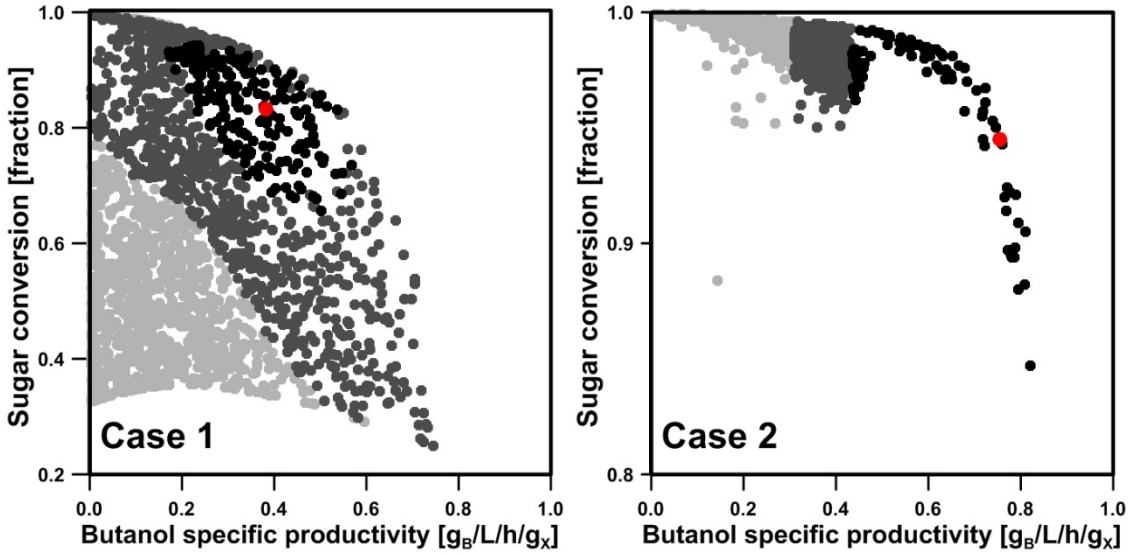

Figure 2.3: Plot of sugar conversion versus butanol specific productivity for Cases 1 and 2.

Higher biomass leads to higher conversion of sugars to butanol and because of the selective removal of solvents from the fermenter, inhibition was partly mitigated and thus the butanol production could progress further. The inhibition factor of "1" in equation (2.1) represents no inhibition in fermentation and as the factor decreases, butanol and butyric acid toxicity increases which eventually leads to biomass growth cessation when the factor reaches "0". In Case 2, due to the reduced solvent inhibition compared to that of Case 1, biomass concentration is higher which means higher butanol concentration is attainable. With respect to decision variables, Figure 2.4 shows the plots of the inlet feed sugar concentration as a function of dilution rate for Cases 1 and 2. The highest ranked solution for the standard fermentation has a feed sugar concentration of 55 g/L and a diluton rate of 0.71 h^{-1} whereas for Case 2 they are 150 g/L and 0.8 h^{-1}, respectively.

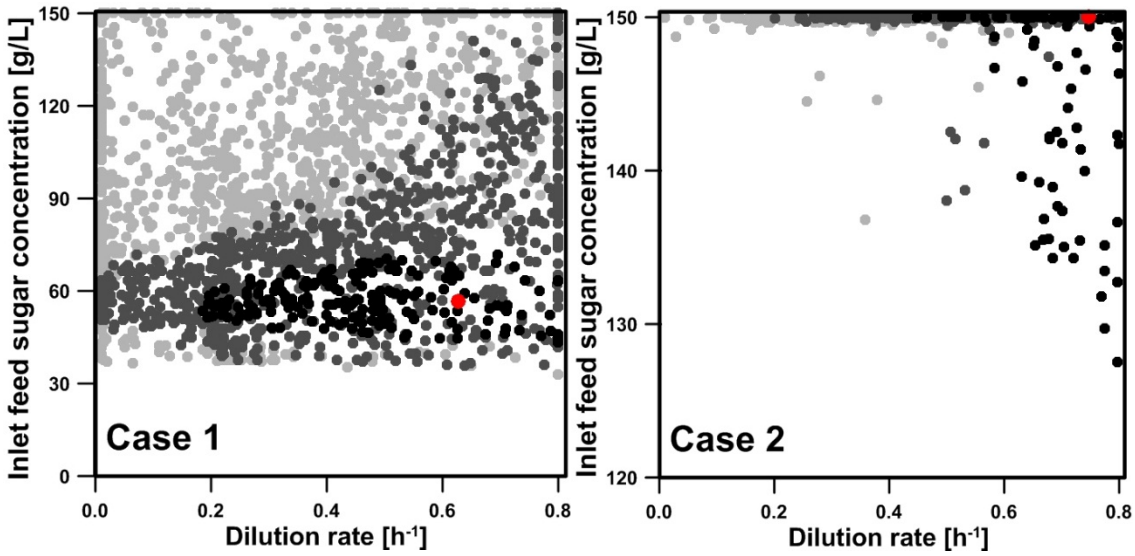

Figure 2.4: Plot of inlet feed sugar concentration versus dilution rate for Cases 1 and 2.

The significant difference in the inlet feed sugar concentration between the standard and the vacuum fermentation is due to the lowered butanol toxicity in the fermenter because of the partial extraction of solvents from the fermentation broth in the latter case. When butanol concentration is maintained at a concentration lower than its inhibiting level in Case 2, the inlet sugar concentration is 2.7 times greater than the one in Case 1. The results are consistent with previous experimental results presented by Mariano et al. (2011).

Although the inlet sugar concentration is less in Case 1, the sugar conversion is higher in Case 2 due to the higher sugar consumption rates associated with lower butanol concentration in the fermenter. Since the butanol specific productivity is directly proportional to the dilution rate, the best 5% ranked Pareto-optimal solutions for Case 2 have higher dilution rates. In Cases 1 and 2, however, the butanol yield is relatively low at 0.18 g/g. Therefore, in Case 3 the average butanol concentration was replaced by the butanol yield as one of the three objective functions whereas the other two objective

functions (butanol specific productivity and sugar conversion) remained unchanged. Also, based on the optimal decision variables in Case 2, the inlet feed sugar concentration was set at 150 g/L for Case 3. Figure 2.5 shows the plots of the three objective functions for Case 3. In general, the butanol specific productivity decreased with increasing butanol specific productivity, and the best 5% ranked solutions (black region) was divided into two parts: a part with high butanol yield and low specific productivity, and the other with low butanol yield and high specific productivity. The best optimal solution for Case 3 is located at specific productivity of 0.75 $g_B/L/h/g_X$, butanol yield of 0.18 g/g, and sugar conversion of 95%. As it is depicted in Figure 2.5, except for the butanol yield value, the other two objective function, namely the specific productivity and sugar conversion, have approximately reached their maximum values. A possible reason for low butanol yield of the best ranked solution is the low relative weight of butanol yield (only 20%) in the ranking algorithm when compared to other two objective functions (the relative weights are 40% for butanol specific productivity, and 40% for sugar conversion) in NFM (Table 2.2). Thus for economic reasons, a decision maker might change the relative weights to obtain higher butanol yield at the expense of lower productivity.

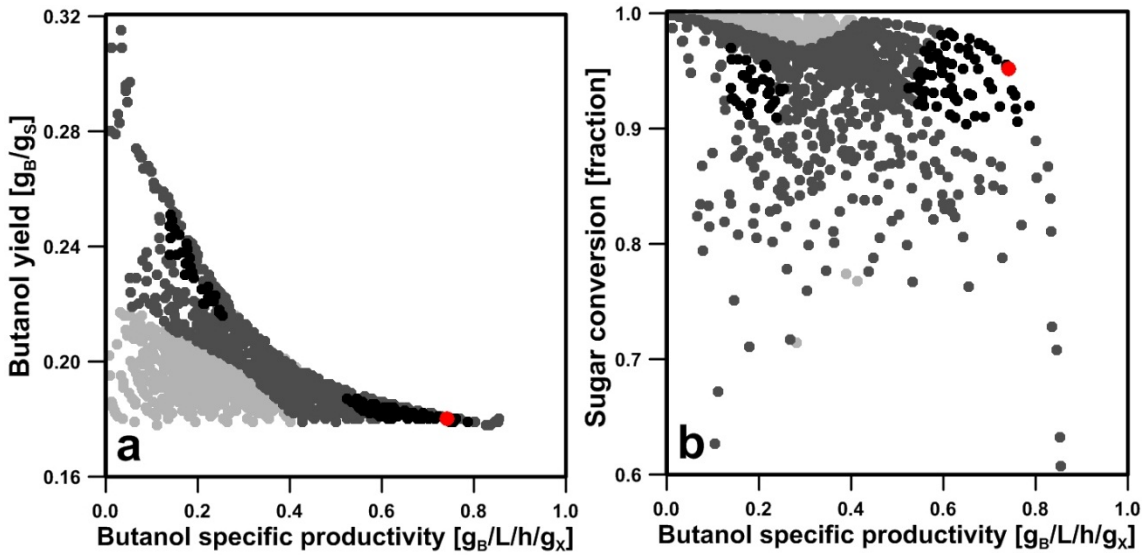

Figure 2.5: Plots of objective functions for Case 3. (a) Butanol yield versus butanol specific productivity; and (b) Sugar conversion versus butanol specific productivity.

The summary of results in Table 2.3 shows that the change of butanol average concentration to butanol yield as an objective function in Case 3 did not influence the yield value for the best solution in Case 3. Other calculated parameters in Case 3 are also very close to those in Case 2. Hence, changing one of the objective functions in Case 3 did not significantly affect the final results.

In the first three cases, the specific productivity was used as one of the objective functions. The specific productivity is defined as the mass of butanol produced per unit volume and unit time divided by the biomass concentration. The motivation to divide the productivity (g/L/h) by the biomass concentration is to indirectly place a constraint on the biomass concentration. Thus, in Case 4, the specific productivity was replaced by the productivity as one of the three objectives whereas the other two objectives were the butanol yield and sugar conversion. The plots of the objective functions for Case 4 are presented in Figure 2.6. For this case study, the best Pareto-optimal solution was obtained at the highest

productivity and yield while sugar conversion remained close to that in the previous vacuum fermentation cases.

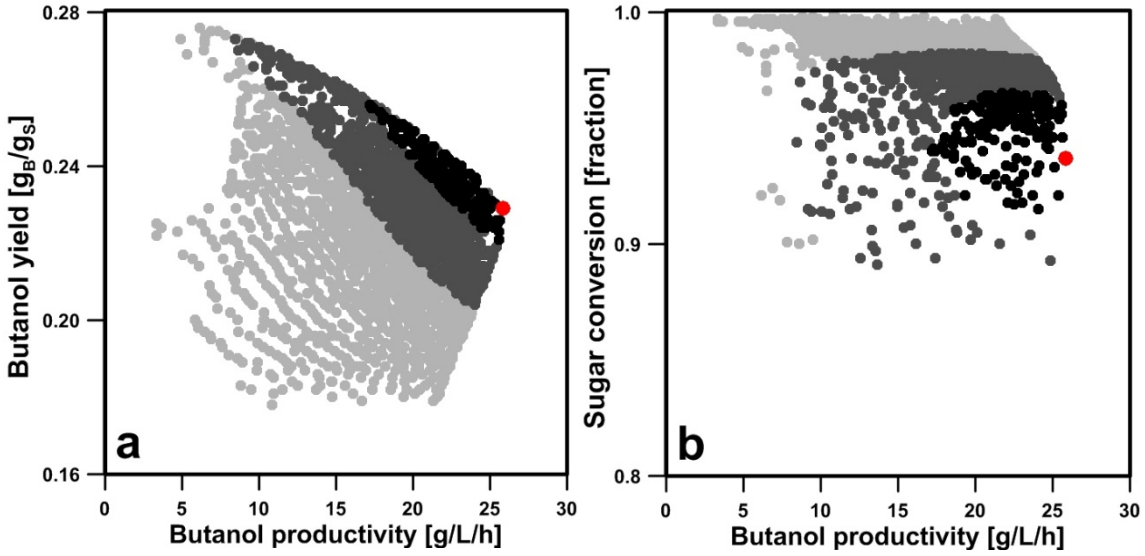

Figure 2.6: Plots of objective functions for Case 4. (a): Butanol yield versus butanol productivity; and (b): Sugar conversion versus butanol productivity.

In Case 4, the butanol productivity reached 26.4 g/L/h while the specific productivity decreased to 0.19 $g_B/L/h/g_X$. Using the butanol specific productivity as an objective function attempts to have the highest possible butanol productivity while placing a constraint on the biomass concentration in the fermenter. Since the butanol productivity is not divided by the biomass concentration, the biomass concentration in fermenter can reach much higher values. Results of Figure 2.6 show that the butanol yield for the best solution in Case 4 is 0.23 g/g which represents an increase of 28% compared to those in Cases 2 and 3. In Case 4, the sugar conversion remained approximately the same as in Cases 2 and 3. In Case 4, butanol concentration for the optimal solution was 32.3 g/L which implies an improvement of 25% when compared to those in Cases 2 and 3. The average ABE concentration also increased from 41.1 g/L in Cases 2 and 3 to 56 g/L in Case 4. This is due

to the fact that the concentrations of the fermentation intermediates (acetic acid and butyric acid) decreased in the fermenter in Case 4 (Table 2.3). Lower acid concentration in the fermenter is beneficial since decreased acid concentrations means more intermediates were converted into the solvents of interest. Moreover, the presence of acids in the fermentation broth contributes to higher inhibition levels. Biomass concentration in Case 4 is 139 g/L which is more than 5 times higher than that in other vacuum fermentation cases. This significant increase in biomass concentration in Case 4 resulted in higher butanol concentration and productivity. Nevertheless, in order to maintain high biomass concentrations within the fermenter, more substrate is needed.

Table 2.3: Summary of decision variables and objective functions associated with the best Pareto-optimal solutions for Cases 1-4.

Parameters	Case 1	Case 2	Case 3	Case 4
Butanol specific productivity ($g_B/L.h.g_X$)	0.42[a]	0.75[a]	0.741[a]	0.19
Butanol productivity (g/L.h)	5.8	20.6	20.6	26.4[a]
Butanol yield (g/g)	0.18	0.18	0.18[a]	0.23[a]
Butanol concentration (avg) (g/L)	8.18[a]	25.9[a]	25.71	32.3
ABE concentration (avg) (g/L)	13.27	41.21	41.01	56
Acetic acid concentration in the fermenter (g/L)	2.24	6.3	6.3	2.06
Butyric acid concentration in the fermenter (g/L)	2.03	5.8	5.8	2.7
Butanol concentration in the condensate (g/L)	-	36.83	36.83	166
Butanol concentration in the fermenter (g/L)	8.18	2.67	2.67	10.4
Inhibition factor	0.6	0.866	0.866	0.153
Sugar conversion (%)	83[a]	96[a]	95[a]	95[a]
Inlet feed sugar concentration (g/L)	55[b]	150[b]	150	150
Residual Sugar (g/L)	9.4	17.8	19.52	12.09
Cell retention ratio ($m^3.h/m^3.h$)	0.2[b]	0.98[b]	0.93[b]	0.05[b]
Biomass concentration (g/L)	12.9	27.4	26.9	139
Dilution rate (h^{-1})	0.71[b]	0.8[b]	0.8[b]	0.8[b]
Stream F_3 flow rate (m^3/h)	-	220.4	214.3	50.8
Stream F_5 flow rate (m^3/h)	56.8	96.5	97.9	13.46
Stream F_7 flow rate (m^3/h)	227.2	2.3	7.8	256.1

[a] Objective functions
[b] Decision variables

It is important to note that the reason for choosing the specific productivity as an objective function in Cases 1-3 was to increase the fermentation efficiency by maintaining low amount of microorganism in the fermenter. However, there is a trade-off between high butanol concentration and low biomass concentration. In Cases 2 and 3, the biomass retention factor is close to 1 (F_7 is very low compared to F_5) which implies that it would be possible to eliminate the cell retention unit. Removing the cell retention unit would lead to

a cost reduction in the fermentation process. In this case, the biomass concentration would simply be controlled by the bleed flow rate F_5. The evaporation rate in Case 4 (50.8 m^3/h) decreased and the butanol concentration in the condensate increased from 36.83 g/L (in Cases 2 and 3) to 166 g/L (in Case 4). Thus, the energy consumption for solvent condensation in Case 4 can be reduced while the average butanol concentration was improved. High dilution rates resulted in higher productivities and higher evaporation rates. Consequently, for all three cases for vacuum fermentation (Cases 2-4), the dilution rate for the best Pareto-optimal solution is at the highest value of 0.8 h^{-1}.

2.4. Conclusions

The aim of this work was to optimize the production of butanol in a continuous fermentation process coupled with a vacuum separation unit with three different scenarios, and to compare the optimization results with the standard continuous fermentation. After performing process simulation, obtaining the Pareto domain for both configurations, and ranking the Pareto-optimal solutions with the Net Flow Method, the optimal operating region was identified. Higher butanol productivities and average butanol concentrations were observed in the vacuum fermentation compared to the standard continuous fermentation. However, butanol yield values were found to be fairly low in standard and vacuum fermentation cases. It was also shown that the biomass concentration in the fermenter determines the butanol yield values. Moreover, higher sugar consumption in the vacuum fermentation was observed which is an important factor highly affecting the butanol production economics. Investigating three vacuum fermentation cases with distinct set of objective functions in each case, the optimal solution was determined.

Nomenclature

ϕ_1 - Dilution rate [h^{-1}]
ϕ_2 - Inlet feed sugar concentration [g/L]
ϕ_3 - Biomass retention factor [m^3.h/m^3.h]
ϕ_4 - Evaporation rate factor [m^3.h/m^3.h]
A - Acetone
AA - Acetic acid
B - Butanol
BA - Butyric acid
BBA - Combined Butanol and butyric acid
Con_S - Sugar conversion [mmol/mmol]
C_i - Concentration of species i [mmol/L]
$C_{B(avg)}$ - Butanol average concentration [g/L]
E - Ethanol
F_n - Stream volumetric flowrate [m^3/h]
i - Denotes species: A, AA, B, BA, BBA, E, S
MW_i - Molecular weight of species i [g/mmol]
n - Stream number
r_i - Production rate of species i [mmol/L/h]
r_X - Biomass growth rate [g/L.h]
P_B - Butanol productivity [g_B/L.h]
SP_B - Butanol specific productivity [g_B/L.h. g_X]
S - Sugar
V - Fermenter volume [m^3]
X - Biomass concentration [g/L]
Y_B - Butanol yield [g/g]

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SIMULTECH 2012: 2nd International Conference on Simulation and Modeling Methodologies, Technologies and Applications, Rome, Italy, 79-86.

APPENDIX 2.I: List of model constants (Mulchandani and Voleskey, 1986)

Constants	Values
μ_m	0.35 [h^{-1}]
K_1	0.35 [mmol/g/h]
K_2	0.59 [mmol/g.h]
K_3	89.0 [mmol/g]
K_4	0.45 [mmol/g/h]
K_5	0.11
K_6	0.5 [mmol/g/h]
K_7	0.39
K_8	0.19
K_9	0.9 [mmol/g.h]
K_{10}	0.22
K_{11}	0.059
K_{14}	2.0 [mmol/g/h]
K_{15}	2.2 [mmol/g/h]
K_s	21.14 [mmol/L]
K_{AA}	10.10 [mmol/L]
K_{BA}	15.9 [mmol/L]

Chapter 3.

MULTI-OBJECTIVE OPTIMIZATION OF BIOBUTANOL PRODUCTION BY CONTINUOUS FERMENTATION WITH IN-SITU RECOVERY BY GAS STRIPPING, PERVAPORATION, OR VACUUM SEPARATION

Abstract— Acetone, butanol, and ethanol (ABE) continuous fermentation was simulated and optimized for three case studies where the ABE fermentation process was integrated in turn with gas stripping, pervaporation, and vacuum separation methods in an attempt to partly mitigate the product inhibition effect. Following the multi-objective optimization of the three integrated processes, the Pareto-optimal solutions were ranked using the Net Flow Method. Results were compared to the standard continuous fermentation process without an integrated recovery method. The integrated butanol recovery methods has significantly improved butanol productivity, butanol concentration, and sugar conversion whereas butanol yield remained unchanged.

3.1. Introduction

Production of biofuels (e.g. ethanol and butanol) has attracted renewed global attention due to the diminishing fossil fuel resources and increased concerns over climate change. Ethanol production has dominated the biofuel industry in the past decade. However, butanol offers a number of superior properties over ethanol as a renewable transportation liquid and has been the subject of significant research interest. Butanol is a four-carbon alcohol with a molecular formula of C_4H_9OH and a boiling point of 118^0C. Compared to ethanol, butanol has a higher energy density per liter of fuel, is less miscible with water, has lower freezing point, and can be blended with gasoline in all proportions. Butanol can be produced synthetically from petroleum or biologically by the fermentation of carbohydrates. The latter happens in a process frequently referred to as the acetone-butanol-ethanol (ABE) fermentation. Commercial scale ABE fermentation was first performed in the UK in 1912 and it was developed rapidly during the first and second world wars. In 1950s, due to the high price of fermentation substrates and costly separation methods, the biological production of butanol was unable to compete with its synthetic equivalent (Qureshi and Ezeji, 2008). During the past few years, researchers have been making progress in promoting butanol as a new renewable energy source.

Butanol production by means of ABE fermentation suffers from a number of limitations including low butanol concentrations, yield, and productivity. Using a strain of bacteria such as *Clostridium acetobutylicum* or *Clostridium beijerinckii*, the total solvent (ABE) concentration in the final fermentation broth is approximately 20 g/L of which butanol is only 13 g/L (Qureshi and Blaschek, 2001a). The low solvent concentration is caused by the end-product inhibition and leads to costly butanol recovery. In general switching to cheaper

feedstock (e.g. agricultural residues), altering the butanol producing bacteria strains to produce and tolerate higher concentrations of butanol, and using energy-efficient separation techniques to replace the energy intensive methods, e.g. conventional distillation, are some of the possible approaches to address the challenges with ABE fermentation commercialization (Chen and Blaschek, 1999; Parekh et al., 1998). Evaluating the economics of distillation, it was shown that a tremendous amount of energy can be saved when the concentration of butanol increases from 10 to 40 g/L in the final fermentation broth (Philips and Humphrey, 1984). Extractive fermentation is considered to be an efficient approach to reduce the cost of butanol production since the recovery and removal of inhibitory components directly from the fermenter is possible. In extractive fermentation, where fermentation and solvent recovery are combined, inhibition is partly alleviated which results in higher sugar consumption and higher butanol average concentration. Other energy efficient recovery methods include pervaporation (Bengtson et al., 1991; Friedl et al., 1991; Groot and Luyben 1987), vacuum (or flash) fermentation (Mariano et al., 2012), gas stripping (Ennis et al., 1986, Groot et al. 1989), liquid-liquid extraction (Eckert and Schugerl, 1987; Maddox et al., 1992), and adsorption (Groot and Luyben, 1986; Neilson et al., 1988). The goal of this study is to simulate and optimize a continuous ABE fermentation process coupled with a separation unit. Three recovery methods, namely gas stripping, pervaporation, and vacuum fermentation, are used in this investigation as the separation unit in the integrated fermentation process. The kinetic model to simulate ABE fermentation is the one proposed by Mulchandani and Volesky (1986). The integrated fermentation process, with glucose as feedstock, was optimized for butanol productivity, butanol concentration, and sugar conversion simultaneously.

3.2. Fermentation System

The fermentation process was performed under steady state conditions using continuous culture operation. The schematic diagram of the ABE fermentation process for vacuum fermentation was previously presented in Chapter 2 (Figure 2.1). In this system, the feed continuously enters the fermenter at a constant sugar concentration and the product streams leave the fermenter at the same flow rate. Thus, the working volume of fermenter always remains constant and in this study it was set at 400 m^3. A cell retention unit (i.e. microfiltration membrane) coupled with a bleed stream is used to control the biomass concentration in the fermenter. Such a system is advantageous for two reasons; first, the cell retention unit keeps sufficient amounts of cells in the fermenter to prevent the washout phenomenon, and second, it removes enough cells to maintain the steady state within the fermenter. In addition to controlling the biomass concentration within the fermenter, the bleed stream is also necessary to maintain metabolites, not removed through the product recovery system, at a level below an inhibitory level (Ezeji and Qureshi, 2013). A stream of the fermentation broth is circulated through the cell retention unit where a fraction of the aqueous broth solution permeates through the membrane while cells remain in the retentate stream. Altering the ratio of the retentate to permeate stream along with the bleed stream, one can manipulate the biomass concentration in the fermenter. In the integrated ABE fermentation method, where the butanol production and solvent recovery are performed simultaneously, a vapor stream rich in volatile solvents leaves the fermenter (or the recovery unit) followed by condensation in the cold trap to capture the solvent products. Subsequently, the product stream exiting the recovery unit, the permeate stream of the cell

retention unit and the bleed stream are sent to the distillation unit for further butanol purification.

3.2.1. Fermentation with gas stripping

Gas stripping is a simple technique which can be integrated with the ABE fermentation process to relieve the product inhibition in the fermentation broth. The integration of gas stripping into the ABE fermentation was demonstrated by Ennis et al. (1986). Using nitrogen as the stripping gas in batch fermentation, Ennis et al. demonstrated that sugar utilization increased significantly. CO_2 and H_2 formed during the ABE fermentation are not sufficient to adequately decrease the inhibition in the fermentation broth; therefore, an additional stripping gas stream is circulated through the fermenter to strip out some of the volatile solvents.

Figure 3.1 shows the schematic diagram of a continuous solvent removal integrated process using gas stripping where fermentation gases, mainly CO_2, is used as the stripping gas. Stripped solvents are cooled and the desired products are captured in the condenser (Stream 3). Since the gas stream exiting the condenser, assumed to be saturated at the condenser temperature, still contains some of uncondensed volatiles (mostly acetone), it is recycled back to the fermenter for another solvent absorption cycle. The gas stream exiting the condenser needs to be brought back to the fermentation temperature of 37°C before entering the fermenter. The energy to increase the temperature of the gas stripping stream is provided by a heat exchanger that exchanges heat with the gas stream leaving the fermenter and an additional heat exchanger to reach the required temperature. A make-up or bleed gas stream (Stream 9) is used to maintain the stripping gas flow rate constant. The biomass

concentration in the fermenter is maintained constant via a cell retention unit. The two exit Streams of 5 and 7 are used to control the outlet flow rates to maintain steady state operation.

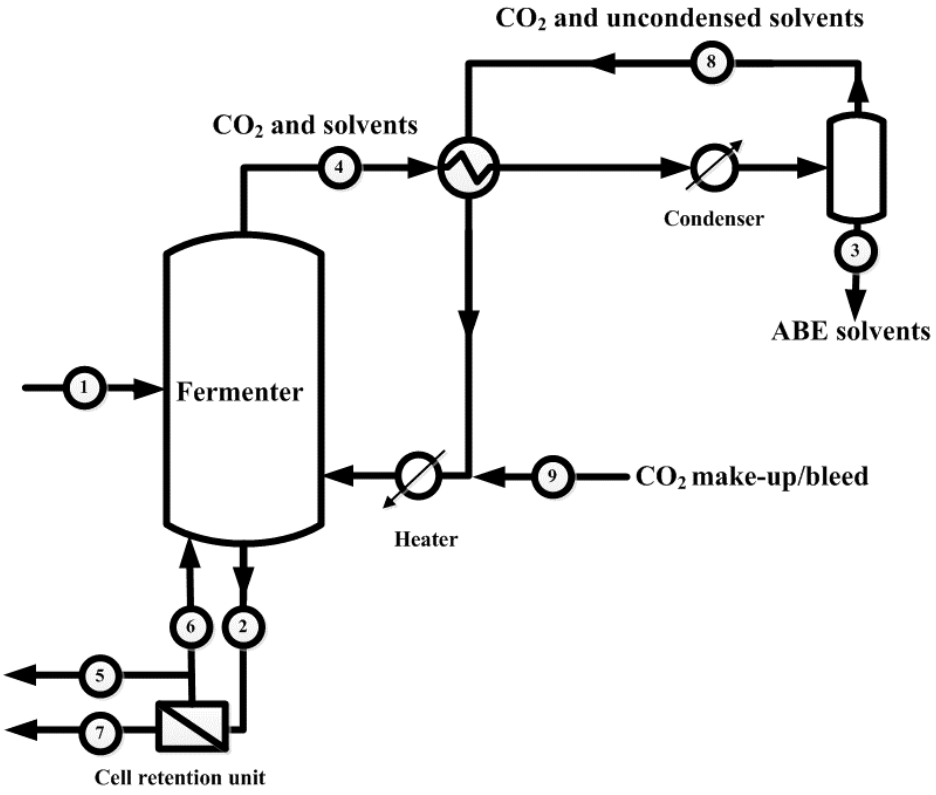

Figure 3.1: Schematic diagram of a fermentation system integrated with gas stripping.

3.2.2. Fermentation with Pervaporation

Pervaporation is considered to be a promising separation method for butanol removal due to its low energy requirement and the fact that it has no adverse effects on the microorganisms in the fermenter. Pervaporation is a membrane-based technology that mitigates solvent inhibition by the selective removal of volatile components from fermentation broth. Some membranes which have been investigated for butanol removal in ABE fermentation include polydimethylsiloxane (PDMS), polypropylene, silicone, and

immobilized liquid membranes (Huang and Meagher, 2001). The desired characteristics for choosing an appropriate membrane for removing butanol are membrane stability, high butanol selectivity (a measure of the efficiency of removal of solvents from water which is defined as [y/(1-y)]/[x/(1-x)], where x and y are the weight fractions of components in the permeate and feed), and high permeation flux (which is defined as W/A/t, where W is the weight of collected permeate (g), A is the effective area of the membrane (m^2), and t is the collection time (s)). Application of pervaporation in ABE fermentation systems has been extensively studied by other researchers (Qureshi and Ezeji, 2008).

Figure 3.2 shows the schematic diagram of a continuous ABE fermentation system coupled with a PDMS/ceramic composite membrane as suggested by Wu et al. (2012). On the upstream side (Stream 2) where the fermentation broth comes in contact with a polymeric membrane, solvents diffuse selectively through the membrane. To induce the solvent diffusion through the membrane, vacuum is created on the downstream side by a vacuum pump. As a result, volatiles exit the membrane as a vapor (Stream 8) and pass through a condenser where they will be captured. The retentate stream of the pervaporation unit (Stream 4) is pumped and sent to a cell retention unit where part of the liquid permeates through the membrane (Stream 7). The retentate stream is then split into two streams: a bleed stream (Stream 5) to maintain the biomass concentration constant in the fermenter and a recycle stream (Stream 6) back to the fermenter. Stream 9, which contains non-condensable gases, exits the system after leaving the condenser. Under steady state, the feed stream (Stream 1) must equal the three streams exiting the fermentation system (i.e., $F_3 + F_5 + F_7 + F_9$).

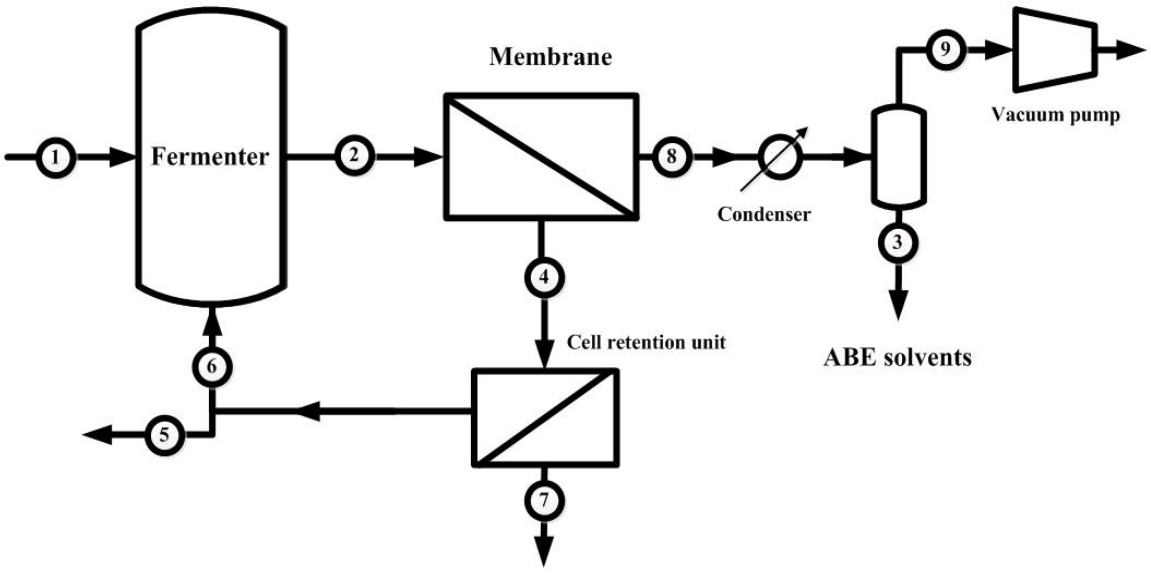

Figure 3.2: Schematic of a continuous fermenter coupled with a pervaporation module using a PDMS membrane.

The values of the experimental selectivity for acetone, butanol, ethanol, and water as well as the average permeation flux were taken from Wu et al. (2012) and are presented in Table 3.1. In the absence of specific information and due to the similar molecular shape and size of butyric acid to butanol and acetic acid to acetone, their selectivity values are assumed to be identical. Moreover, the biomass selectivity is assumed to be zero and the fouling effects are not considered. The experiments of Wu et al. (2012) were performed in a batch ABE fermentation system coupled with a PDMS/composite membrane. In this work, the separation factors listed in Table 3.1 were assumed to be constant along the membrane for the continuous ABE fermentation coupled with pervaporation and only the permeation flux for each component, which is a function of the solvent concentration in the broth, was calculated using the data in Table 3.1.

Table 3.1: Average flux and separation factors for ABE and water in the PDMS/ceramic composite membrane (Wu et al., 2012).

Average Flux ($kg/m^2/h$)	Separation factor (α)			
	Ethanol	**Acetone**	**Butanol**	**Water**
0.993	7.15	27.78	16.56	0.044

3.2.3. Vacuum Fermentation

Another technique to remove the volatile solvents from the fermentation broth is vacuum fermentation during which the fermenter or a separate unit connected to the fermenter is kept under vacuum conditions. This technique was first used by Cysewski and Wilke (1977) in ethanol fermentation in order to reduce ethanol inhibition. They demonstrated that by performing the process under vacuum, rapid and complete fermentation of concentrated sugar solutions was achieved. Due to the higher boiling point of butanol (118°C) over that of water (100°C), engineering heuristics suggest that water would be more volatile and, as a result, vacuum has not been used widely in ABE fermentation. However, vapour-liquid diagrams are confirmed by computational simulation and the technical feasibility of vacuum fermentation for butanol fermentation is proved (Mariano et al., 2008). Indeed, water and butanol form an azeotropic mixture and in the range of butanol concentration encountered in the fermentation broth, butanol is significantly more volatile than water. The presence of other solvents such as acetone and ethanol does not change significantly the thermodynamic behavior of butanol relative to water.

Figure 3.3 shows the schematic diagram of the ABE fermentation process coupled with a vacuum unit. In this system, stream F_2 is withdrawn from the fermentation broth and passes through a heat exchanger to add the necessary latent heat of vaporization to sustain the

desired rate of evaporation prior to entering the vacuum flash unit where a fraction of the inlet stream is vaporized. The flash unit operates at 37°C with a pressure in the vicinity of 7 kPa which corresponds approximately to the boiling point of the fermentation broth at 37°C. Because ABE solvents are more volatile than the water in the fermentation broth, the vapor stream (Steam 8) is more concentrated with these solvents. It is therefore possible to partly remove butanol and therefore reducing its inhibition.

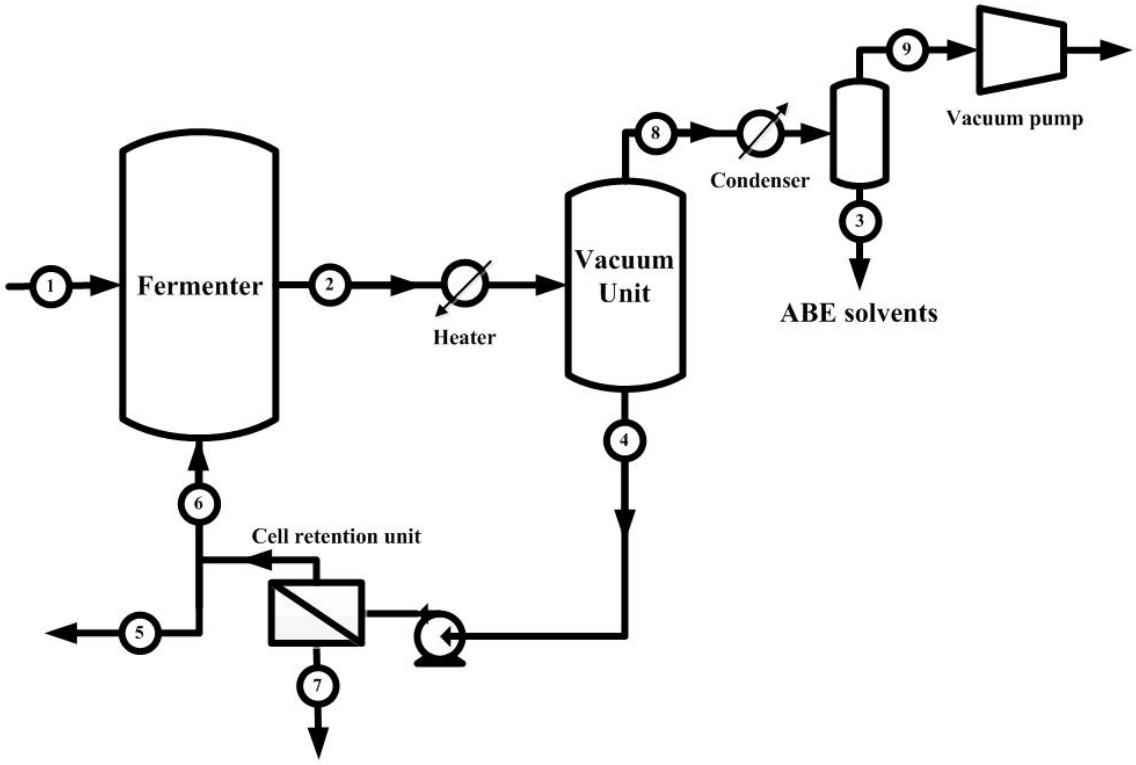

Figure 3.3: Schematic diagram of a continuous fermentation coupled with a vacuum unit.

3.3. Multi-objective Optimization

This study considers the optimization of a continuous fermentation process coupled with three butanol recovery methods: gas stripping, pervaporation, and vacuum fermentation. For these three cases, fermenter dimensions, fermentation temperature, and inlet feed sugar concentration were kept constant. Based on our previous optimization results for vacuum

fermentation, feed inlet sugar concentration was fixed at 150 g/L. The working volume of the fermenter was 400 m^3, and the fermentation was conducted at 37°C and 1 atm. Possible objectives for optimizing a continuous ABE fermentation are the butanol productivity, butanol yield, and sugar conversion where all three objective functions need to be maximized. An additional objective that could be used in gas stripping and pervaporation cases is to maximize the cold trap temperature and minimize the membrane area, respectively.

The definition of all objective functions and decision variables are presented in Table 3.2. In gas stripping, a higher cold trap temperature results in lower ABE condensed solvent flow rate (F_3) exiting the cold trap (Figure 3.1). However, since the solvents in the vapor phase (CO_2 stream and the uncondensed solvents out of the cold trap) are recycled back to the fermenter, using higher cold trap temperatures could lead to energy savings without the loss of ABE solvents. The cold trap temperature in the vacuum fermentation and pervaporation methods was set constant at a value low enough such that the majority of the ABE solvents are captured and only traces of ABE remains present in the vapor phase leaving the condenser.

In the pervaporation process, the membrane cost is the major factor in the economic viability of ABE fermentation; thus, minimizing the membrane area as an objective leads to lower capital and operating costs. The decision variables used in the different case studies are the dilution rate, the biomass retention factor, the cold trap temperature (gas stripping), the carbon dioxide flow rate (gas stripping), the membrane area (pervaporation), and the evaporation rate (vacuum fermentation). The Pareto-optimal solutions for both cases were ranked by the Net Flow Method (NFM) to find the best point of operation. The NFM

relative weights and thresholds used for each case are represented in Table 3.3. A detailed description of multi-objective optimization, NFM method, and the kinetic model of ABE fermentation with their related equations were presented in Chapter 2.

Table 3.2: Definition of objective functions and decision variables with their lower and upper bounds.

	Parameters	Definitions	
Objectives Functions	Butanol productivity, P_B [a,b,c] (g/L.h)	$\frac{1}{V}[C_{B,3}MW_B F_3 + C_{B,4}MW_B(F_7+F_5)]$	
	Butanol yield, Y_B [a,b,c] (g/g)	$\frac{C_{B,3}MW_B F_3 + C_{B,4}MW_B(F_7+F_5)}{C_{S,1}F_1MW_S - C_{S,7}(F_7+F_5)MW_S}$	
	Sugar conversion, Con_S [a,b,c] (fraction)	$1-\frac{C_{S,7}(F_7+F_5)}{C_{S,1}F_1}$	
	Cold trap temperature, T[a] (°C)		
	Membrane area[b] , A_M (m^2)		
Decision Variables	Dilution rate, D [a,b,c] (h^{-1})	$\frac{F_1}{V}$	$0 \le D \le 0.8$
	Biomass retention factor ,α [a,b,c](m^3.h/m^3.h)	$\frac{F_5}{F_7+F_5}$	$0.1 \le \alpha \le 1$
	Evaporation rate factor, X_4[c] (m^3.h/m^3.h)	$\frac{F_3}{F_2}$	$0 \le X_4 \le 0.04$
	Cold trap temperature, T[a] (°C)	T	$-40 \le T \le 5$
	CO_2 flow rate, F_{CO2}[a] (m^3/s)	F_{CO2}	$1.6 \le F_{CO2} \le 650$
	Membrane area, A_M[b] (m^2)	A_M	$0.05 \le A_M \le 200$

[a] Gas stripping
[b] Pervaporation
[c] Vacuum fermentation

Table 3.3: Net Flow Method parameters used to rank Pareto-optimal solutions.

Mode	Criteria	Relative Weights	Thresholds		
			Indifference	Preference	Veto
Gas Stripping	P_B	0.3	2	3	7
	Y_B	0.2	0.005	0.01	0.03
	Con_S	0.3	0.05	0.1	0.3
	T	0.2	3	5	10
Pervaporation	P_B	0.3	2	3	7
	Y_B	0.2	0.005	0.01	0.03
	Con_S	0.3	0.05	0.1	0.3
	A_M	0.2	3	10	40
Vacuum	P_B	0.4	2	3	7
	Y_B	0.2	0.005	0.01	0.03
	Con_S	0.4	0.05	0.1	0.3

3.4. Results and Discussion

The Pareto domain for the continuous fermentation integrated with each of the three separation methods was obtained by determining 1000 Pareto-optimal solutions using the Dual Population Evolutionary Algorithm (DPEA) (Halsall-Whitney and Thibault, 2008). These 1000 solutions were then ranked using the Net Flow Method based on the relative weights and threshold values presented in Table 3.3. The plots of the three objective functions for the ranked Pareto domains for gas stripping, pervaporation, and vacuum fermentation are presented in Figures 3.4-3.6. In these plots, the red dot represents the best ranked Pareto-optimal solution. The black, medium grey and light grey regions represent the best 5%, the next 45% and the last 50% ranked solutions, respectively.

The ranked Pareto-optimal results obtained for the gas stripping recovery method are presented in Figure 3.4. Figures 3.4a and 3.4b present the four objective functions plotted as two two-dimensional projections. Figure 3.4a presents the plot of the butanol yield as a function of butanol productivity. The best ranked solution is located at the maximum butanol productivity of 23 g/L/h and a butanol yield in the vicinity of 0.21 g/g. The trade-

off between butanol productivity and butanol yield is clearly shown. In the upper region of the Pareto domain, an increase in butanol productivity leads to a decrease in butanol yield. This trade-off is due to the fact that high butanol productivity is linked to high dilution rates and a higher dilution rate leads to a lower butanol yield. The best ranked solution is obtained at the maximum value of butanol productivity which is obtained by compromising on butanol yield. Figure 3.4b presents the plot of the Pareto domain for the other two objective functions that is the sugar conversion versus the cold trap temperature. The best ranked solution indicates that the optimal trade-off is obtained when the cold trap temperature is at its maximum value whereas a light trade-off for the sugar conversion is observed. In summary for gas stripping, the best ranked solution is obtained at maximum butanol productivity and cold trap temperature and to achieve these maxima it is necessary to accept slightly lower butanol yield and sugar conversion. Figure 3.4c shows the plot of two decision variables associated to the Pareto domain: CO_2 flow rate versus dilution rate for gas stripping. An increase in the gas flow rate leads to an increase in the dilution rate because a larger fraction of the broth is removed, including more butanol which has a consequence to reduce product inhibition. Associating the results of Figures 3.4a and 3.4c, it can be concluded that an increase in the gas flow rate leads to an increase in butanol productivity. It is important to note, however, that increasing the gas flow rate also leads to an increase in the operating costs. Figure 3.4d presents the plot of butanol productivity versus the cold trap temperature where it can be observed that the majority of the best 50% of the ranked solutions are concentrated around a cold trap temperature of 5°C. Since in gas stripping, the cold trap temperature is an objective function to be maximized, the majority of optimal solutions are kept close to high cold trap temperatures. Cold trap temperatures of less than 5°C might be expected to result in higher butanol productivities. However, as it

was shown in Figure 3.1, recycling the gas stream F_8, which carries the uncondensed solvents, increases the concentration of solvents in the fermenter. As a result, no solvent is lost and under steady state the saturated gas stream leaving the fermenter will contain a higher proportion of the more volatile solvent.

Figure 3.5 shows the concentration of the solvents in the fermenter as a function of time for the best ranked solution at 5°C and compared with another solution with the same operating conditions but a different cold trap temperature of -10°C. It is shown in Figure 3.5 that at a cold trap temperature of -10°C, the acetone and butanol concentrations are 5 and 6.5 g/L whereas, they are respectively 13.85 g/L and 11 g/L at 5°C. Since acetone is the more volatile solvent, using a higher cold trap temperature results in a higher fraction of acetone being recycled to the fermenter. Eventually, a steady state concentration level for each solvent is obtained. Recycling the uncondensed solvents therefore resulted in elevated solvent concentrations in the fermenter and high butanol productivities. However, high butanol concentrations make the fermentation broth more toxic to the microorganisms and limit the solvent production.

In the kinetic model of Mulchandani and Voleskey (1986), which was used in this study, the acetone is not considered to be toxic to the microorganisms, but it would be necessary to conduct fermentation experiments to investigate at which concentration acetone becomes toxic. On the other hand, changing the cold trap temperature from 5 to -10°C slightly decreased ethanol concentration in the fermenter.

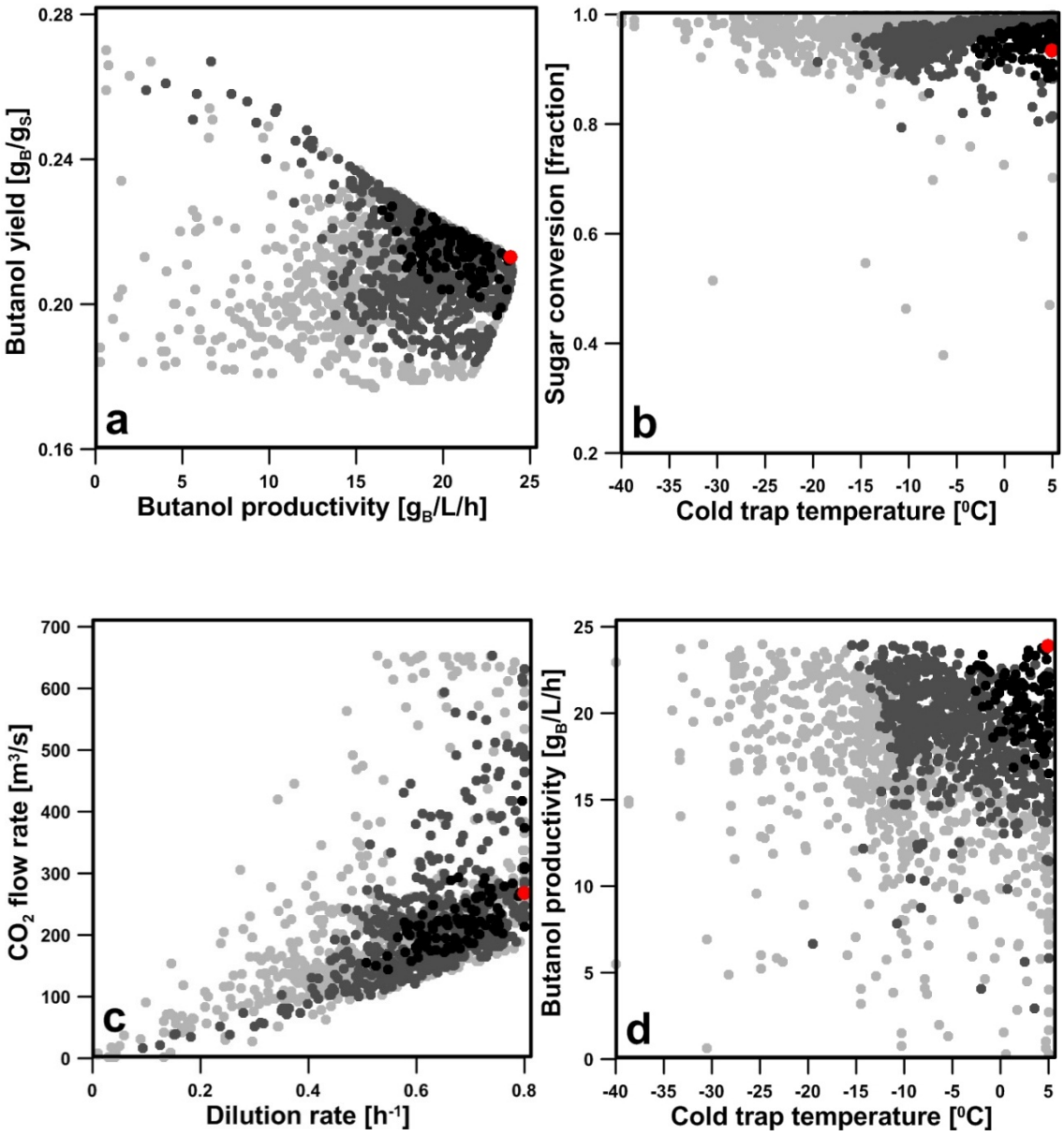

Figure 3.4: Plots of objective and decision variables for gas stripping method. (a) Butanol yield versus butanol productivity, (b) Sugar conversion versus cold trap temperature, (c) CO_2 flow rate versus dilution rate, and (d) Butanol productivity versus cold trap temperature.

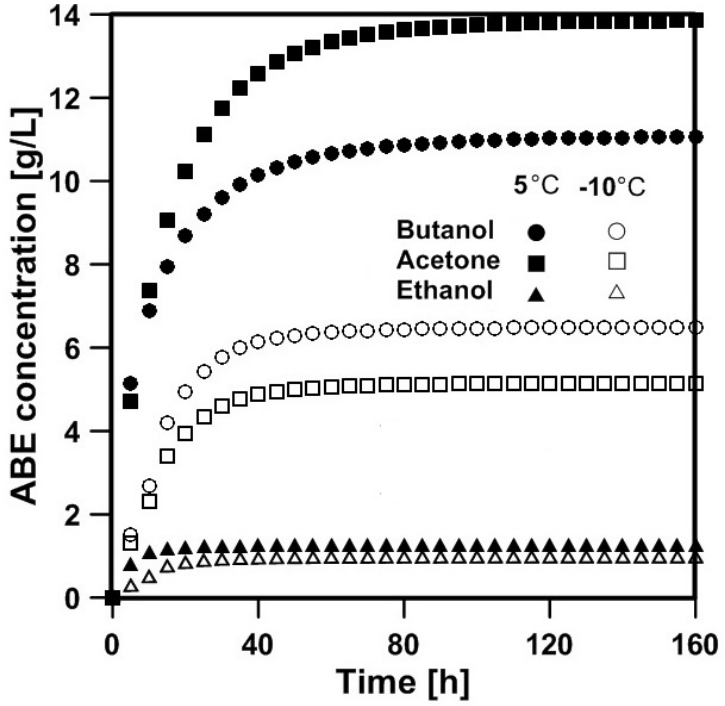

Figure 3.5: ABE solvent concentration in the fermenter for cold trap temperatures of -10°C and 5°C for the fermentation system integrated with gas stripping.

Figure 3.6 shows the plots of the Pareto-optimal solutions for the continuous fermenter coupled with the pervaporation recovery system. Figure 3.6a presents the plot of butanol yield as a function of butanol productivity whereas Figure 3.6b presents the plot of sugar conversion versus membrane area. These two plots clearly show the trade-off for all four criteria that was struck to achieve the best ranked solutions of the Pareto domain. The best ranked solution for the integrated pervaporation module lies at a butanol productivity of 13.17 g/L/h, a butanol yield of 0.22 g/g, a substrate conversion of 93% and a membrane area of 23.46 m^2.

Figure 3.6b shows clearly the impact of the membrane area on sugar conversion. Under the operating conditions leading the Pareto domain, a conversion of less than 35% is obtained when the membrane module is inoperative, i.e. standard continuous fermentation, and then

increases steadily as the membrane area increases. A sugar conversion of 100% is obtained for membrane areas larger than 45 m^2. A higher membrane area results in higher solvent removal which mitigates product inhibition and in higher sugar conversion. As a consequence, as clearly indicated in Figure 3.6c, when the membrane area is large enough to sufficiently remove the inhibition, higher feed flow rates (or dilution rate) can be processed through the fermenter.

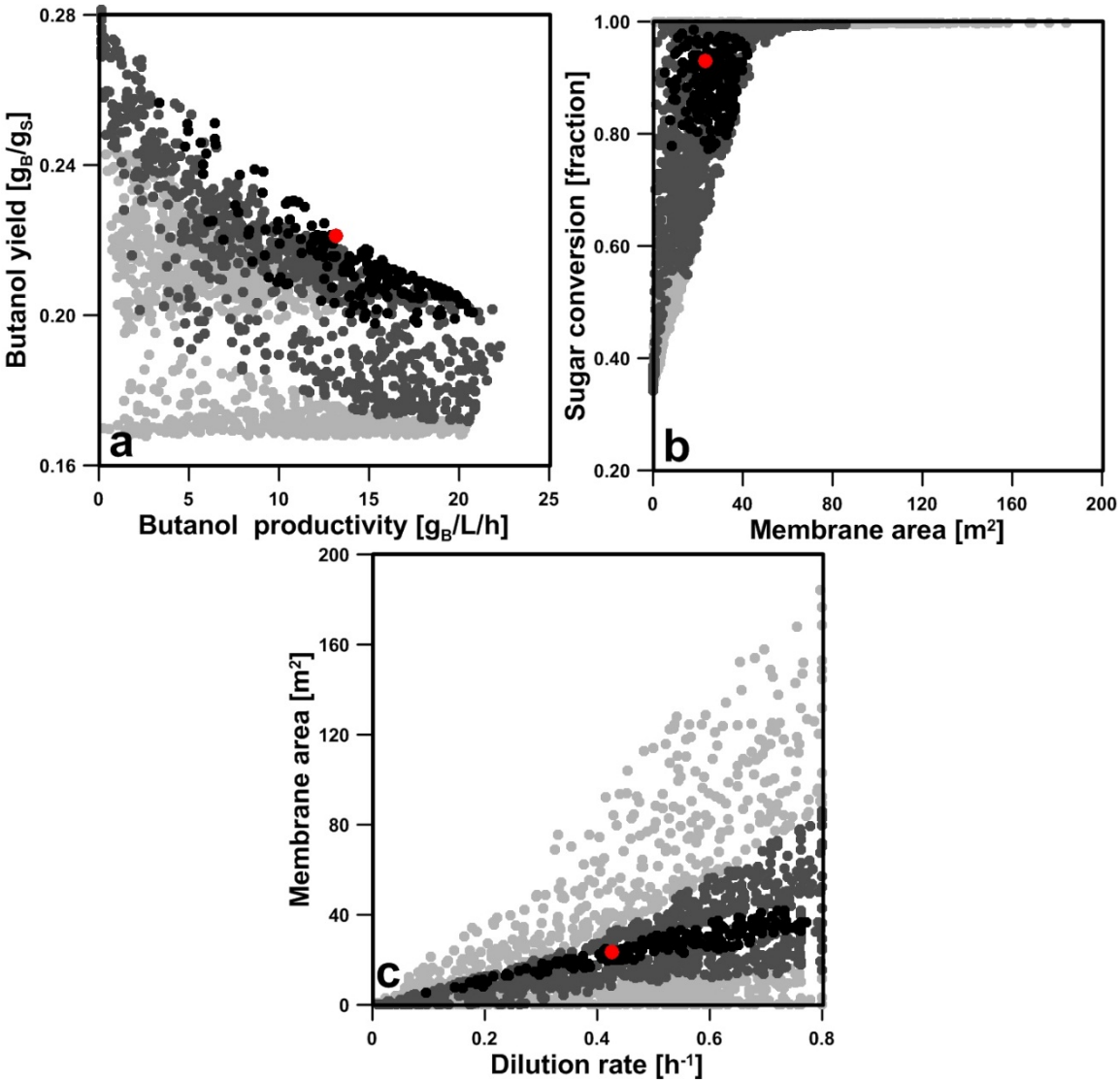

Figure 3.6: Plots of objective functions and few decision variables for the fermentation process along with pervaporation method. (a) Butanol yield versus butanol productivity, (b) Sugar conversion versus membrane area, and (c) membrane area versus dilution rate.

Figure 3.7 shows the plots of the three objective functions and two decision variables for the continuous fermentation coupled with a vacuum evaporation unit. As can be seen in Figure 3.7a for the upper region of the Pareto domain, an increase in butanol productivity results in a decrease in butanol yield. From Figure 3.7b it is evident that sugar conversion remains relatively high over the whole range of butanol productivity. Figures 3.7a and 3.7b clearly show that, for the best ranked Pareto-optimal solution, the maximum butanol

productivity is achieved with a trade-off between the butanol yield and sugar conversion. The best ranked solution was obtained for a butanol productivity of 23.35 g/L/h, a butanol yield of 0.21 g/g, and a sugar conversion of 95%. Figure 3.7c shows the plot of the dilution rate as a function of the evaporation rate factor. The best zone of operation corresponds to a high dilution rate and a low evaporation rate. Low evaporation rates result in higher solvent saturated vapor stream leaving the vacuum separation unit. The product stream F_3 leaving the condenser in combination with bleed streams of F_5 and F_7 result in the average butanol productivity and concentration which was shown to be higher at lower evaporation rates (Figure 3.3).

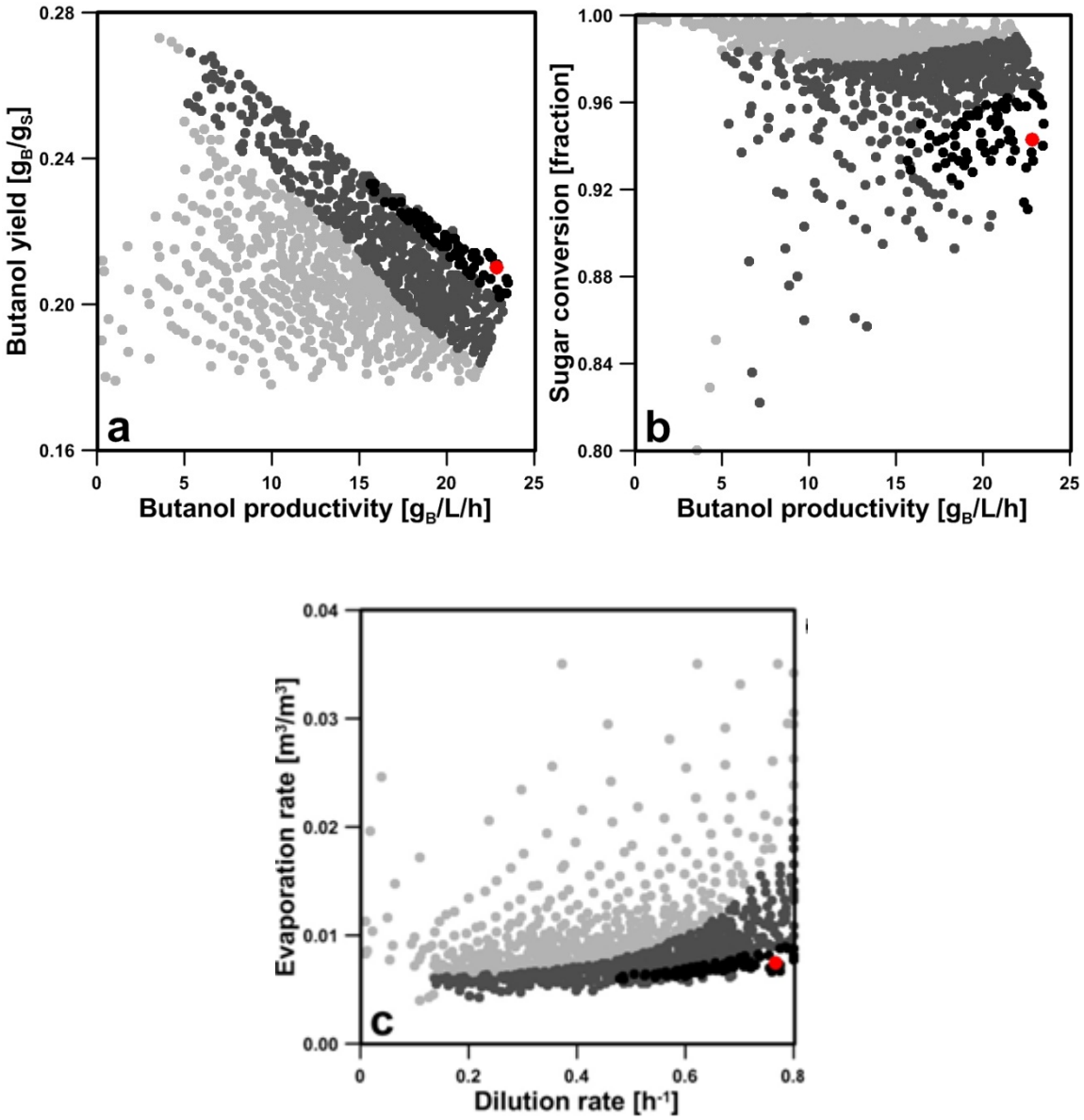

Figure 3.7: Plots of the objective functions and few decision variables for the continuous fermentation coupled with a vacuum separation unit. (a) Butanol yield versus butanol productivity, (b) Sugar conversion versus Butanol productivity, and (c) Evaporation rate factor versus butanol productivity.

Table 3.4 presents the values for the best solution for each optimization case study. In order to clearly highlight the advantages of adding each separation method to the continuous fermentation, the results of the non-integrated continuous ABE fermentation is also presented in this table. The operating conditions for the non-integrated fermentation were

selected to be similar to those obtained for the best ranked Pareto-optimal solutions of the three case studies. Among the three integrated fermentation methods, gas stripping and vacuum fermentation have similar butanol productivity, butanol yield, and sugar conversion. This is due to the fact that, for these two methods, butanol concentration in the condensate (Stream 3) is higher than the butanol concentration obtained with pervaporation method. Moreover, the condensate flow rate for gas stripping is higher than that of pervaporation and is nearly similar to that of vacuum fermentation.

The butanol productivity of the best solution for all three integrated methods has improved between six to ten times of the one in the non-integrated fermentation. However, the yield values did not change significantly in the integrated methods when compared to non-integrated fermentation. The reason is that yield value is highly dependent on the strain of microorganisms producing butanol and since the strain is the same in all cases, applying a separation method has little effect on butanol yield values.

Results of Table 3.4 indicate that the butanol average concentration for the process with integrated separation based on all exit streams is approximately three times higher when compared to the non-integrated fermentation, with values of 29.98 g/L, 30.88 g/L, and 29.2 g/L for gas stripping, pervaporation, and vacuum fermentation, respectively. The higher concentration of butanol in integrated fermentation is due to the lower inhibition factor in the fermenter. As it is presented in Table 3.4, the inhibition factor in the non-integrated method is very close to “0” (inhibition factor of “0” corresponds to the full inhibition), whereas the inhibition factor is 0.27 for gas stripping and vacuum and 0.14 for pervaporation.

Moreover, the most important advantage of using integrated fermentation methods is the high sugar conversions, resulting in low residual sugar concentrations. Sugar conversion has increased by 180% when compared to the non-integrated fermentation system. Since in the non-integrated method, inhibition mitigation by selective solvent recovery does not occur, the solvent toxicity limits the biomass growth and butanol production. Thus, the biomass concentration in the non-integrated method is only around 25.9 g/L, while in the integrated separation methods this number reaches as high as 93.7 g/L in the vacuum fermentation method.

The fermenters coupled with a separation unit also have higher dilution rates. This essentialy means that in the integrated separation methods the butanol production rate is very high compared to the non-integrated fermentation and increasing the dilution rate does not have adverese effects on sugar conversion or average sugar concentration. The lower dilution rate of 0.43 h^{-1} in pervaporation, which is 50% less than that of gas stripping and vacuum fermentation, is due to the limited solvent recovery in this method. This is due to the fact that in the pervaporation method, the condensate flow rate is relatively low when compared to gas stripping and vacuum fermentation. This is because low permeation flux of the membrane and a higher membrane area would be required to increase the total permeate flow rate.

Table 3.4 shows that acetone concentration in the fermenter with gas stripping method is 10.6 g/L which is close to that of non-integrated method but much higher than that of other separation methods. This shows that at cold trap temperature of 5°C only a small fraction of acetone is recovered in the condenser. In pervaporation and vacuum fermentation methods,

it was assumed that all solvents in the vapor stream out of the whole process are recovered and there was no need to recycle the gas stream. Acetic acid and butyric acid concentrations in the gas stripping and vacuum fermentation are much higher than the pervaporation and the non-integrated method.

The accumulation of acids in the fermenter is not favorable since it shows that acids are not efficiently converted to the product solvents. Moreover, butyric acid is more toxic than acetic acid to the culture and its removal is essential to decrease the inhibition level (Ezeji et al. 2004). The low concentration of butyric acid and acetic acid in the non-integrated fermentation is due to the low biomass concentration, where the low amount of biomass is not able to convert high amounts of sugar to intermediate acids and solvents. Since the selectivity of butanol and acetone are assumed to be equal to butyric acid and acetic acid, respectively, the acids concentration in the condensate are higher with pervaporation method than that of the other separation methods. As a result, another reason for the lower butanol productivity and butanol concentration of the pervaporation method could be the high rate of intermediates removal as in the solventogenesis phase of fermentation. As a result, there are less intermediate products to be converted to the desired solvents. Loss of fermentation intermediates by diffusion through the membrane as well as membrane fouling are reported to be the main drawbacks of applying pervaporation technique for product recovery in ABE fermentation (Ezeji et al., 2010). The acids loss problem in pervaporation could be solved by finding a membrane with a higher selectivity to butanol than other acids and solvents.

Table 3.4: Summary of decision variables and objective functions associated with the best Pareto-optimal solutions for integrated and non-integrated fermentation systems.

Parameters	Gas stripping	Pervaporation	Vacuum fermentation	Non-integrated fermentation
Butanol productivity (g/L. h)	23.98	13.17	23.35	2.27
Butanol yield (g/g)	0.21	0.22	0.21	0.25
Butanol concentration (avg) (g/L)	29.98	30.88	29.2	13.21
Butanol concentration in the condensate (g/L)	149.97	152	137.3	-
Butanol concentration in the fermenter (g/L)	8.14	11.9	7.93	13.21
Acetone concentration in the fermenter (g/L)	10.60	5.14	2.80	9.07
Ethanol concentration in the fermenter (g/L)	1.22	1.09	0.86	0.67
Butyric acid concentration in the fermenter (g/L)	4.18	1.25	4.38	0.56
Acetic acid concentration in the fermenter (g/L)	4.25	0.76	4.40	0.28
Sugar conversion (%)	94	93	95	34
Residual Sugar (g/L)	10.60	12.2	8.12	98.31
Cell retention ratio ($m^3.h/m^3.h$)	0.1	0.1	0.1	0.1
Biomass concentration (g/L)	90	85	93.7	25.9
Dilution rate (h^{-1})	0.8	0.43	0.8	0.17
Stream F_3 flow rate (m^3 /h)	49.26	24	55.67	-
Inhibition factor	0.27	0.14	0.27	0.05
Cold trap temperature (°C)	5.00	-	-	-
Gas flow rate (m^3/s)	268	-	-	-
Membrane area (m^2)	-	23.46	-	-

3.5. Conclusions

The ABE continuous fermentation system integrated with one in situ recovery method was simulated and optimized. Three separation methods were individually integrated to the ABE fermentation: gas stripping, pervaporation and vacuum fermentation. The operating conditions of the fermenter including the inlet feed sugar concentration, temperature and pressure were kept constant for all methods. Applying an integrated separation method improved sugar conversion drastically. The average butanol concentration and butanol productivity values were increased significantly in gas stripping, pervaporation, and vacuum fermentation when compared to the non-integrated fermentation. Butanol yield was not affected by performing fermentation integrated with a separation method as it remained nearly the same as in the non-integrated fermentation. The integration of a solvent removal method decreased solvent inhibition and resulted in higher biomass concentrations in the fermenter. Results of gas stripping and vacuum methods were very similar and superior to pervaporation in the terms of butanol productivity and average concentration. Future studies should be directed to performing an economic analysis of each method in order to determine the most viable technique.

Nomenclature

A_M - Membrane area (m^2)

B - Butanol

Con_S - Sugar conversion [mmol/mmol]

C_i - Concentration of species i [mmol/L]

$C_{B(avg)}$ - Butanol average concentration [g/L]

CO_2 - Carbon dioxide

D - Dilution rate [h^{-1}]

F_n - Stream volumetric flowrate [m^3/h]

i - Denotes species: B, S, CO_2

MW_i - Molecular weight of species i [g/mmol]

n - Stream number

P_B - Butanol productivity [g_B/L.h]

S - Sugar

T - Cold trap temperature (°C)

V - Fermenter volume [m^3]

X - Biomass concentration [g/L]

Y_B - Butanol yield [g/g]

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Chapter 4.
CONCLUSIONS AND RECOMMENDATIONS

Butanol toxicity to microorganisms which leads to low butanol concentration in the final fermentation broth of ABE fermentation is one of the major challenges with the commercialization of biobutanol fermentation process. To address this problem, in this research three case studies, where a separation technique (vacuum fermentation, gas stripping or pervaporation) integrated with a continuous ABE fermentation, were evaluated for their potential to partly alleviate the butanol toxicity. The goal of this thesis was to simulate and optimize a continuous fermentation system coupled with a separation unit and to compare the optimized solutions to the non-integrated fermentation process. In order to assess the performance of the ABE fermentation process, multi-objective optimization technique was used to generate a Pareto domain region where more than 500 non-dominated solutions were circumscribed based on a set of decision variables. The graphs of the Pareto domain clearly showed the trade-offs which existed between objective functions.

In Chapter 2 vacuum fermentation system was optimized based on three objective functions (i.e. butanol specific productivity, butanol concentration, and sugar conversion) and three decision variables (i.e. dilution rate, inlet feed sugar concentration, and evaporation rate factor). 500 Pareto-optimal solutions were generated and the solutions were ranked by the Net Flow Method to obtain the best ranked solution. The optimization results for vacuum fermentation case studies were compared with the best ranked solution of the non-

integrated fermentation. It was shown that integrating a vacuum separation unit within the fermentation process improved butanol specific productivity, overall butanol concentration and sugar conversion. However, butanol yield remained constant at 0.18 g/g in both cases. Therefore, two additional vacuum fermentation cases with a modified set of objectives were optimized. It was demonstrated that in the second vacuum fermentation case replacing butanol concentration by butanol yield did not increase the butanol yield of the best ranked solution. In the third vacuum fermentation case, however, replacing butanol specific productivity by butanol productivity increased the butanol yield for the best ranked point. It was shown that higher biomass concentrations obtained with the cell retention unit leads to higher sugar conversion, butanol concentration and butanol yield.

In Chapter 3, three separation methods, namely, gas stripping, vacuum fermentation and pervaporation, were integrated with the continuous ABE fermentation and optimized. Results for the best optimal solutions showed that gas stripping and vacuum fermentation methods had nearly the same objective values. In gas stripping method, the cold trap temperature, which was used both as a decision variable and objective function, was in the vicinity of the maximum cold trap temperature for a large number of Pareto-optimal solutions. For the continuous ABE fermentation integrated with pervaporation, optimization results indicated that butanol productivity and sugar conversion were lower when compared to the ABE fermentation coupled with vacuum fermentation and gas stripping methods. Increasing butanol productivity in pervaporation requires higher membrane area which in turn increases the overall process costs.

Future works should be directed towards performing the economic analysis on the best ranked solutions in each fermentation method in order to assess the viability of biobutanol commercialization via these techniques. Moreover, since the optimization process was performed in VBA and thermodynamic data was provided by calling UniSim HYSYS within VBA, the processing times were very long. Therefore, finding a method to decrease the optimization times should also be the scope of future works.

The kinetic model which was adapted from Mulchandani and Volesky (1986) did not include potential sugar, acetone, ethanol, and acetic acid inhibition terms within the set of equations. Finding a more comprehensive kinetic method to describe the ABE fermentation metabolic pathways is desired. With respect to the fermentation microorganisms, using different strains of *Clostridia* could be examined in order to increase the butanol yield. Moreover, with respect to the fermentation set-up, a process could be examined and optimized where a second fermenter would be added in series to the first fermenter in order to consume the residual sugar exiting the first fermenter.