ECONOMIC RECOVERY OF BIOBUTANOL-A PLATFORM CHEMICAL FOR THE SUGARCANE BIOREFINERY

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DECLARATION

I, Frederick Kudzanai Chikava declare that:

The research reported in this dissertation/thesis, except where otherwise indicated, is my original work.

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ABSTRACT

In recent years, the South African sugar industry has faced challenges, such as drought, low prices and labour issues that have impacted negatively on the perceived sustainability. The adoption of the sugarcane biorefinery concept by the sugar industry is a possible solution to improving the sustainability of the industry amid these challenges. In this envisioned biorefinery, multiple products are created within an integrated system that maximises sustainability, as opposed to relying on producing one or very few products. In this study, the potential economic viability of the recovery of biobutanol was explored with the ultimate intention of using this biobutanol as a platform chemical for the production of higher value products to include in the biorefinery's product portfolio. Biobutanol is produced from biomass via the ABE (acetone, butanol, and ethanol) fermentation process.

Biobutanol production is characterised by very low butanol concentrations in the fermentation broth (around 2 wt. %) due to high inhibition, resulting in a very high cost of recovery (distillation) and the need for several downstream purification steps. Following a literature search on technologies that have been proposed and previously implemented for biobutanol production, processes integrating gas stripping and extraction were simulated on Aspen Plus® and techno economic analyses performed to determine the profitability based on cash flows over a 25 year period.

Gas stripping and liquid-liquid extraction experiments were first carried out in order to have a way of validating simulation results. Gas stripping experiments created scenario-based results of the expected butanol concentration in the gas phase once a steady state butanol concentration can be maintained in the fermenter. The extraction experiments were conducted to establish a quick way of evaluating the extractive properties of a solvent based on the distribution coefficients and selectivities with respect to butanol. Five solvents were evaluated including hexyl acetate and diethyl carbonate, which have not been reported on but have been previously applied in biomass processing. Distribution coefficients of 3.57 and 6.15 and selectivities of 367.09 and 396.00, with respect to butanol, were obtained for hexyl acetate and diethyl carbonate, respectively.

Four processes were then simulated on Aspen Plus® and they all assumed a fermentation process that make use of 281.67 t/h clear juice from a South African generic sugar mill

model. A study estimate type economic evaluation, accurate within $\pm 30\%$ error, was performed with profitability being assessed in terms of the Net Present Value (NPV) and the Internal Rate of Return (IRR) over the 25 year period. Process Scheme 1 was the benchmarking case and consists of the conventional series of five distillation columns. For this process a Total Capital Investment (TCI) of US$124.85 million was obtained and based on the sales and production costs a negative NPV of US$3.80 million was obtained. This indicates a non-viable process under the current economic conditions. Process Scheme 2 included *in situ* recovery by gas stripping and final purification using distillation. Five distillation columns were still required to purify the condensate from the stripper due to a large amount of water that is carried in. The increased productivity in the fermenter and the reduction the downstream column sizes in this process, compared to the benchmarking case, resulted in a reduced capital cost of US$67.43 million. This recovery process also yielded a potential to be profitable with a positive NPV of US$505.88 million and an IRR of 31%. This was attributed to the reduced TCI as well as the ability of the process to yield all the three ABE solvents to sellable purities.

Process Scheme 3 that included gas stripping and liquid-liquid extraction had almost the same TCI as Process Scheme 2 (US$68.94 million) but could only yield butanol to sellable quality due to the selective property of the solvent used (2-ethyl-hexanol). This reduction in sales led to an IRR of 6% which is below the discounted rate used (10%) although a positive NPV of US$82.38 million resulted. Process Scheme 4, making use of a two-stage gas stripping and distillation, was the most profitable process and it was concluded it would be the process to attach to the sugar mill model and also to be considered for the higher value chemical production. An NPV of US$524.09 and an IRR of 32% were realised for this process.

Sensitivity analyses on these four processes showed that the cost of the substrate (clear juice) and the butanol selling price have the major effects on the profitability. It was, therefore, recommended that other streams from the sugar mill be considered as substrates for higher value chemical products which can attract higher prices than butanol which is regulated by the petro based butanol. Finally, a structure of a functionalised ionic liquid was suggested based on group contribution methods to be a potential reactive extraction reactant for converting butanol to a higher value ester product.

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NOMENCLATURE

Symbols

Symbol	Description	Units
A	Bubble surface area	cm^2
C_s	Solute concentration in the aqueous phase	$g\ L^{-1}$
c_{10}	Bulk liquid concentration of butanol	$mol\ cm^{-3}$
F	Feed flow rate	$kg\ h^{-1}$
H	Heat of reaction	$kJ\ mol^{-1}$
K	Distribution coefficient	$g\ g^{-1}$
K_p	Overall gas side mass transfer coefficient	$mol\ cm^{-2}\ s^{-1}\ atm^{-1}$
K_sa	Stripping or removal rate constant	h^{-1}
N_1	Butanol flux	$mol\ cm^{-2}\ s^{-1}$
p_{10}	Butanol partial pressure in the bulk gas	atm
p_1^*	Hypothetical butanol partial pressure in equilibrium with bulk liquid concentration	atm
r	Bubble radius	cm
R	Molar gas constant	$cm^3\ atm\ mol^{-1}\ K^{-1}$
R_s	Stripping or removal rate	$g\ L^{-1}\ h^{-1}$
S	Solvent flow rate	$kg\ h^{-1}$
t	Time	s or h
T	Absolute temperature	K
V	Volume	cm^3
x_i	Molar fraction of component i	-

Greek letters

γ	Activity coefficient

Subscripts and Superscripts

0	Starting condition
θ	Standard conditions
aq	Aqueous phase
eq	Equilibrium
org	Organic phase
rxn	Reaction
∞	Infinite dilution

Abbreviations

ABE	Acetone-Butanol-Ethanol
BuOH	Butanol
DCF	Discounted Cash Flow
DDB	Dortmund Data Bank
FCI	Fixed Capital Investment
HOC	Hayden-O'Connell
IL	Ionic Liquid
IRR	Internal Rate of Return
LLE	Liquid-Liquid Equilibrium
NEV	Net Energy Value
NMR	Nuclear Magnetic Resonance

NRTL	Non-Random Two-Liquid
NPV	Net Present Value
ROI	Return on Investment
RV	Recoverable Value
SRK	Soave-Redlich-Kwong
TCI	Total Capital Investment
UNIFAC	UNIversal quasichemical Functional group Activity Coefficient
VLE	Vapour-Liquid Equilibrium
WC	Working Capital

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CHAPTER ONE

1. INTRODUCTION

1.1. Biobutanol

1.1.1. Butanol-An Introductory Overview

The rate at which fossil reserves are depleting coupled with the volatile crude oil price and environmental concerns like global warming and other geopolitical factors, has prompted the need to look into renewable resources for energy. Biofuels seem to be one of the potential alternative energy sources to substitute fossil-based liquid fuels, and a great deal of research has been conducted especially towards the design and optimisation of production processes. Butanol (butyl alcohol or n-butanol) produced from biomass (biobutanol), is one such potential biofuel to replace the conventional fossil-based fuels. As of the year 2012, the global market for butanol stood at 2.8 million tonnes (Mascal, 2012).

The use of butanol as an alternative fuel has shown so much potential as the butanol characteristics are similar to those of gasoline (Ranjan and Moholkar, 2012, Abdehagh et al., 2015). It is for this reason that butanol can be blended into gasoline in any proportion and used as fuel without the need to modify the existing car engines (Ranjan and Moholkar, 2012). Table 1-1 shows the characteristic properties of butanol when compared to the conventional fuel, gasoline, as well as to ethanol and methanol, which are common alcohol fuels. Additionally, compared to other biofuels, butanol is less volatile (low vapour pressure), less flammable and less corrosive making it safer to work with (Abdehagh et al., 2015). The low vapour pressure increases the ease of transportation through a pipeline (Ranjan and Moholkar, 2012, Ha et al., 2010, Harvey and Meylemans, 2011). Butanol also has a low solubility in water (7.7 g/100 mL at 20°C (Abdehagh et al., 2014, Visioli et al.,

2014)) which reduces the hazard of ground water contamination during pipeline transportation (Ranjan and Moholkar, 2012). It is described to be hygroscopic (Ha et al., 2010, Harvey and Meylemans, 2011).

Table 1-1: Comparison of butanol as a fuel

Parameter	Gasoline	Butanol	Ethanol	Methanol
Energy density (MJ/L)	32.5	29.2	19.6	15.6
Air-fuel ratio	14.6	11.2	9	6.5
Heat of vaporisation (MJ/kg)	0.23	0.43	0.92	1.2
Research octane number	91-99	96	129	136

More important than being a biofuel, butanol serves as a source of valuable materials which include:

- Solvent in chemical industry (Ishii et al., 1985, Ranjan and Moholkar, 2012) as well as for paints, dyes, coatings and varnishes (Wu et al., 2007, Faisal et al., 2014)
- Cosurfactant in micellar flooding (tertiary oil recovery) (Ishii et al., 1985)
- C_4 feedstock for chemical synthesis (esters, ethers, acetates etc.) (Zverlov et al., 2006, Ranjan and Moholkar, 2012). Butanol also makes a suitable platform chemical for further processing to advanced bio-fuels such as butyl levulinate (Kraemer et al., 2011)

1.1.2. Biobutanol Production History, Research and Developments

In the first part of the 20th century, acetone-butanol-ethanol (ABE) production from fermentation using solventogenic clostridia was ranked second only to ethanol (Ni and Sun, 2009, Kraemer et al., 2010). During this period, large commercial plants were in existence in the UK, Canada, France, the USA, Japan, India, China, Australia, South Africa (National Chemical Products in Germiston), Taiwan, Egypt, Brazil and Soviet Union (Zverlov et al., 2006, Qureshi and Ezeji, 2008). After World War 2, ABE fermentation could not compete with the petrochemically derived butanol as the industry was on the rise. Additionally, molasses became scarce particularly in USA where it was used in cattle feed (Jones and Woods, 1986). Between 1950 and 1960 ABE production completely ceased in Europe and North America (Ni and Sun, 2009). In South Africa, the fermentation was operational until 1982 due to the abundant supply of molasses, coal and the import restrictions. However,

the plant was forced to close due to shortages of molasses resulting from the severe drought in Southern Africa in early 1980 (Jones and Woods, 1986, Ranjan and Moholkar, 2012).

In recent years, focus has been rekindled towards the industrial production of biobutanol. In 2006, BP and DuPont announced a joined venture to develop and commercialise biobutanol. Plans were to produce 30 000 tons biobutanol per year in a modified ethanol plant of British Sugar in the UK (Ni and Sun, 2009). In China, an annual production of biobutanol amounting to 210 000 tons was reported in 2008 and this is expected to reach a million tons in the next few years (Ni and Sun, 2009). Brazil also has some plants that are currently operating.

The conventional biobutanol production suffers from the following challenges that have received a tremendous amount of research attention (Jones and Woods, 1986, Qureshi and Ezeji, 2008, Kraemer et al., 2011, Kumar and Gayen, 2011, Mariano and Maciel Filho, 2012):

i. Expensive feedstocks
ii. Low productivities (up to 0.6 g/L/h) and butanol yields (ABE yields of 0.3) of ABE fermentation
iii. High product inhibition especially by butanol (typically 20 g/L ABE with a mass ratio of 3:6:1)
iv. High cost of separation of ABE from dilute fermentation broth in the downstream processes

To address the challenge of cost associated with substrates, research attention has been directed towards making use of cheaper lignocellulosic feedstocks such as agricultural wastes and other energy crops such as switchgrass (a switch from the traditional molasses and corn). This is possible because the microorganisms for biobutanol production can catabolise a wide range of carbohydrates (Zverlov et al., 2006, Qureshi and Ezeji, 2008). The use of waste-type substrates is, however, associated with two challenges, i.e. they are usually not available in a concentrated form, and they may only be available seasonally (Lenz and Morelra, 1980).

Butanol productivity and yield from fermentation processes have been increased by employing continuous fermentation processes (as opposed to the conventional batch process). These continuous processes include the use of cell recycle membrane reactors and

immobilized cell reactors or packed bed reactors (Jones and Woods, 1986, Qureshi and Ezeji, 2008).

Microorganism growth inhibition by butanol in fermentation broth is the cause of the low product concentration which in turn requires a large amount of energy to separate and concentrate. Traditionally, distillation is used to recover and separate the products; however, the separation is not economically viable. The cost of separating butanol by a pure distillation downstream process requires more energy than the energy content of butanol (Kraemer et al., 2011). To reduce the product inhibition, hyper butanol-producing strains have been developed. For example, Qureshi and Blaschek (2001a) developed the strain *C. beijerinckii* BA101 which has been reported to produce up to 33 g/L ABE solvents and a total ABE concentration of 31.3 g/L (19.1 g/L butanol) was reported for *C. acetobutylicum* JB200 by Xue et al. (2012). However, economic analyses results have indicated that the use of improved fermentation strains alone is not sufficient to attain an economically viable process design, unless combined with cost effective separation processes (Van der Merwe et al., 2013).

In situ recovery of butanol from fermentation broth has received a great deal of research attention and the subject has been extensively investigated. The focus of the research has been towards the development of a suitable method that will both reduce the product inhibition as well as render the product concentration process economically viable. Techniques that have been investigated in detail include: liquid-liquid extraction, adsorption, gas stripping, pervaporation, perstraction (or membrane solvent extraction), reverse osmosis, as well as the use of hybrid processes.

Regardless of all the advances made in the ABE fermentation, product removal from fermentation broth still remains expensive and hinders the industrial production of biobutanol. The high energy cost associated with ABE recovery remains the bottleneck in the industrial production of biobutanol (Kraemer et al., 2010).

1.2. The Sugarcane Biorefinery Concept

The Sugar Milling Research Institute NPC (SMRI) aims to ensure sustainability of the sugarcane processing industry in Southern Africa in both the short and long term. It is involved in research work and offers technical services to the industry. In the SMRI annual

report for 2014-2015, it is stated that the South African sugar industry is showing signs of decline and there is need for change to ensure the industry still remains viable. One of the solutions to that effect is the adoption of the biorefinery approach, where *"multiple products are created within an integrated system that maximises profitability"*, as opposed to relying on producing one commodity (SMRI, 2015).

In its most general form, a biorefinery has been defined by the United States (U.S.) National Renewable Energy Laboratory[1] as *"a facility that integrates conversion processes and equipment to produce fuels, power and chemicals from biomass"*. Often, the biorefinery concept is compared to today's petroleum refineries where multiple products are produced from petroleum. At this present moment, sugar mills in South Africa can be considered as biorefineries for they use biomass (sugarcane) to produce sugar (sucrose) and molasses as products as well as bagasse which is used as fuel in the sugar mill (Rein, 2007). Some mills go on to use the molasses in the production of ethanol. The envisioned sugarcane biorefinery, however, may also produce a wide range of chemical intermediates (so-called platform chemicals) which represent the feedstocks for other products, in the same way as the production of bulk chemicals in an oil refinery.

The following are the advantages of a biorefinery (and hence, a sugarcane biorefinery) as compared to facilities that produce a single product (Lynd et al., 2005, Rein, 2007):

- It is possible to vary a mix of products to maximise revenue in the face of dynamic market conditions
- The selling price of the primary product can be significantly lowered by coproducing higher value, lower volume products
- There are integration benefits associated with coproduction e.g. making use of electricity and steam cogenerated from process residues
- Value generated from feedstock (biomass) is maximised in a biorefinery by making use of all the component fractions of biomass (cellulose, hemicellulose and lignin etc.)

[1] Homepage National Renewable Energy Laboratory, http:\www.nrel.gov/biomass/biorefinery.html, last accessed 28 June 2016

To increase the profitability and long term value of the (sugarcane) biorefinery, it is important to analyse a mix of high and low profit margin products and optimise the production capacities (Geraili et al., 2014).

1.3. Ionic Liquids and the Role of Green Chemistry in the Sugarcane Biorefinery

In order to turn the sugar industry in South Africa into a sustainable sugarcane biorefinery, it is important to ensure that the additional materials and chemicals that are being produced are based on green and sustainable supply chains. The application of green chemistry in the development of the sugarcane (or any other biomass) biorefinery offers an opportunity for the protection of the environment while meeting the needs of society.

By definition, green chemistry can be considered *"as a set of principles for the manufacture and application of products that aim to eliminate the use, or generation, of environmentally harmful and hazardous chemicals"* (H Clark et al., 2009). Therefore, in combining green chemistry with a biorefinery, the ultimate task is to produce genuinely green and sustainable chemical products (H Clark et al., 2009, Cherubini, 2010).

Ionic liquids (ILs) are organic salts that exist as liquids at low temperature (<100°C) and one of their most significant properties is their extremely low vapour pressure (Zhao et al., 2005, Ha et al., 2010). Although there is some level of debate, due to their negligible vapour pressure, ILs are generally regarded as 'green' solvents compared to the traditions volatile organic compounds (VOCs) (Earle and Seddon, 2000, Zhao et al., 2005). This combined with the fact that ILs can be designed and tuned to exhibit specific properties makes ILs an excellent resource in the sugarcane biorefinery as solvents, catalysts and in synthesis trails while producing materials and chemicals in a sustainable way.

1.4. Research Questions, Aims and Objectives

1.4.1. Project Aims and Objectives

The main objective of this study is to economically recover and concentrate butanol from the fermentation of sugars for the South African sugar industry. This is in line with supporting the South African sugar industry to adopt the sugarcane biorefinery concept. Butanol has the potential to become a platform intermediate for other chemicals. Options that could be considered include reacting butanol with an acid to produce high value ester

products, or reacting it with carbon dioxide, in the presence of a catalyst, to produce dibutyl carbonate.

To achieve the aim above, the following objectives have to be met:

1. Develop a scheme (process) that recovers and concentrates butanol from fermentation broth
2. Determine the profitability of the developed separation process based on the recoveries from the broth, capital and operating costs as well the energy performances
3. Determine the main factors that affect the profitability of the process and how that impacts on the decisions to be made in the context of the sugarcane biorefinery
4. Explore possible routes for the sustainable conversion of biobutanol into higher value products that can potentially be included in the mix of products in the sugarcane biorefinery

1.4.2. Thesis Layout

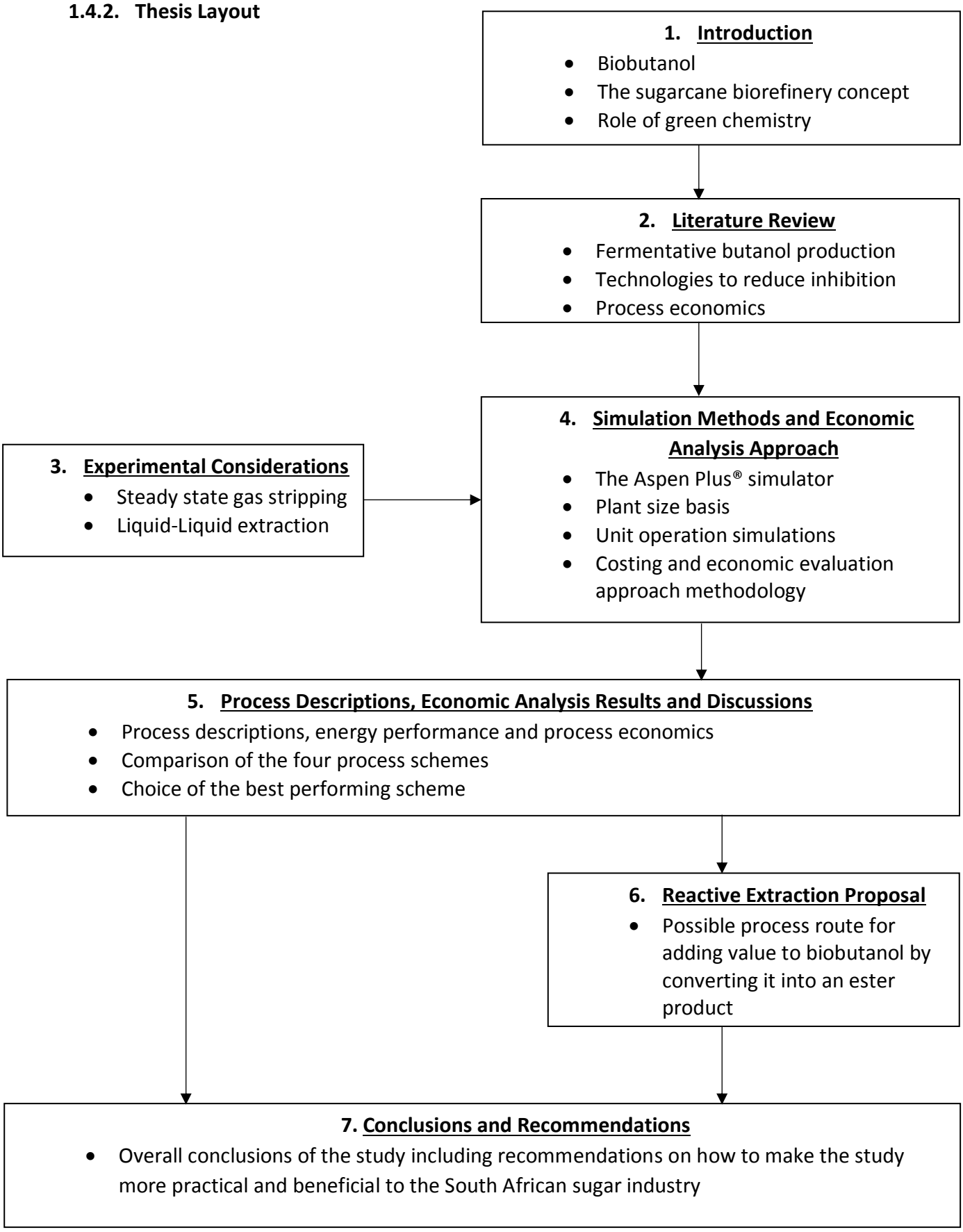

Figure 1-1: Thesis layout

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CHAPTER TWO

2. LITERATURE SURVEY

A number of reviews have been compiled describing butanol production by fermentation. These reviews cover areas like the production history, process conditions, the different substrates used, microorganisms, the process biochemistry, metabolism as well as the separation techniques that have been employed. Also covered are the improvements that have been achieved to make the conventional industrial process economically viable. Although a summary of all these aspects is also provided in this current review, emphasis has been placed on the product recovery and concentration techniques from a process engineering point of view. For additional information on the other aspects, the reader is referred to reviews by the following authors; Jones and Woods (1986), Qureshi and Ezeji (2008), Lee et al. (2008), Kumar and Gayen (2011) and Ranjan and Moholkar (2012).

2.1. Fermentative Butanol Production

The fermentation process to produce butanol is termed 'ABE fermentation' based on the major products which are acetone (A), butanol (B) and ethanol (E), with butanol being the major product of the three (Roffler et al., 1988). The ratio acetone:butanol:ethanol is typically 3:6:1, by weight (Abdehagh et al., 2013). ABE fermentation is sometimes also referred to as solvent fermentation (Qureshi et al., 2005). The term 'biobutanol' is often employed to specifically refer to butanol produced from biomass by fermentation-a biological process as opposed to 'petrobutanol' obtained from fossil resources via the oxo process (Lee et al., 2008, Ranjan and Moholkar, 2012, Van der Merwe et al., 2013).

The following are the major reactions involved in the glucose fermentation by *Clostridia* cultures (Wu et al., 2007, Liu et al., 2009):

$$C_6H_{12}O_6 + H_2O \rightarrow C_3H_6O_{(acetone)} + 3CO_2 + 4H_2 \quad [2\text{-}1]$$

$$C_6H_{12}O_6 \rightarrow C_4H_{10}O_{(butanol)} + 2CO_2 + H_2O \quad [2\text{-}2]$$

$$C_6H_{12}O_6 \rightarrow 2C_2H_6O_{(ethanol)} + 2CO_2 \quad [2\text{-}3]$$

$$C_6H_{12}O_6 \rightarrow C_4H_8O_{2\,(butyric\ acid)} + 2CO_2 + 2H_2 \quad [2\text{-}4]$$

$$C_6H_{12}O_6 \rightarrow 3C_2H_4O_{2\,(acetic\ acid)} \quad [2\text{-}5]$$

2.1.1. Microorganisms and Substrates for ABE Fermentation

The selection of the bacterial strains that are used in the production of biobutanol is dependent on the nature of the substrate, targeted productivity, the required relative concentration of the products, butanol tolerance as well as the need for additional nutrients (Jones and Woods, 1986, Kumar and Gayen, 2011). There are various microbial cultures that have been used to produce biobutanol but the most widely used are *Clostridium acetobutylicum* and *Clostridium beijerinckii* (Harvey and Meylemans, 2011), under anaerobic conditions. *Clostridium acetobutylicum* remains the best studied and most manipulated strain (Kumar and Gayen, 2011). These microorganisms have also been described as 'anaerobic solventogenic clostridia' (Kumar and Gayen, 2011, Abdehagh et al., 2013). The advantage of using these bacteria (or any other butanol-producing culture) is that they can utilise a wide variety of carbohydrates (e.g. cellbiose, sucrose, glucose, fructose, xylose etc.) (Zverlov et al., 2006, Qureshi and Ezeji, 2008) which is not possible for the traditional yeast that is used in ethanol production (Kraemer et al., 2011).

There are two phases that characterise the ABE fermentation by clostridial cultures, i.e. an acid production phase (acidogenesis) and a solvent production phase (solventogenesis)[2]. During the acidogenic phase, the pH of the fermentation broth drops from around 6.8-7 to between 4.5 and 5. During this phase, there is rapid cell growth and the secretion of the carboxylic acids, acetate, and butyrate (Kumar and Gayen, 2011, Ranjan and Moholkar, 2012, Mariano and Maciel Filho, 2012). At the final stage of the acidogenesis phase, acid production slows down due to effect of low pH. Organisms shift their metabolic activity to

[2] It should be noted that traditionally, ABE fermentation aimed at producing acetone, butanol and ethanol to be used as solvents, and hence this specific application lead to the usage of the somewhat ambiguous terms "solventogenesis" and "solvent fermentation".

the solventogenesis phase where the acetate and butyrate are consumed as substrates for the biosynthesis of acetone and butanol, while no growth is observed.

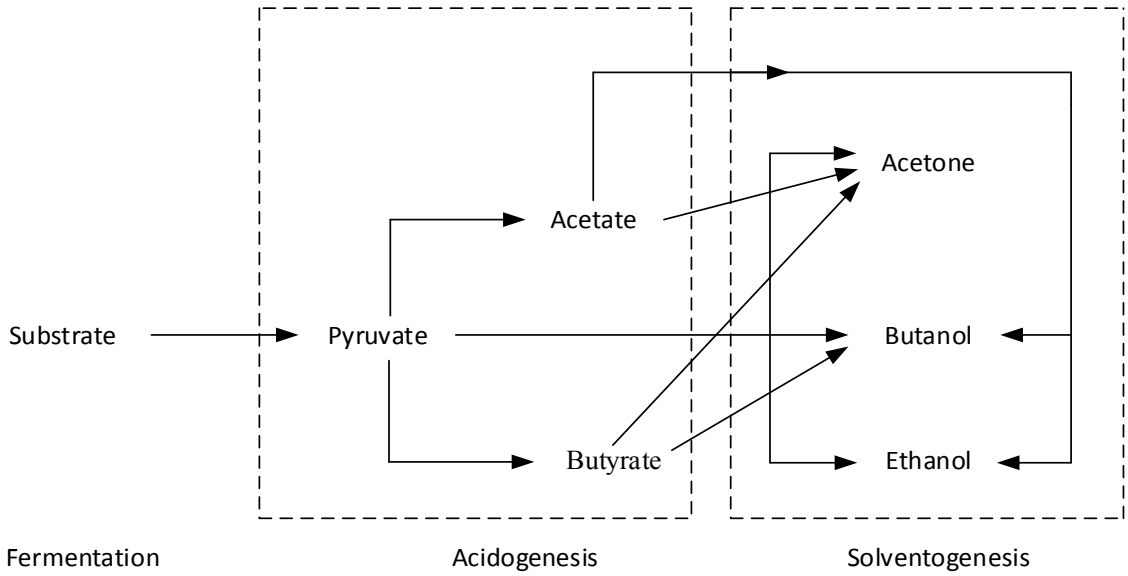


Figure 2-1: Phases of the ABE fermentation process (Qureshi and Ezeji, 2008)

Substrates that have been commonly considered for clostridia cultures include fibrous biomass containing hemicellulose and cellulose (e.g. wheat straw, rice straw); starchy biomass (such as ground corn and whey permeate); and fruits and vegetables containing fructose, glucose and xylose as basic components (Ranjan and Moholkar, 2012). However, the conventional substrates have been molasses, corn, wheat, millet and rye (Jones and Woods, 1986). In as much as Clostridia bacteria can ferment lignocellulosic material, acidic or enzymatic hydrolysis is essential to convert them into monosaccharides before using them as substrates in ABE fermentation (Kumar and Gayen, 2011). However, research is currently still in its infancy regarding the efficient hydrolysis of lignocellulose followed by fermentation.

Depending on the raw material (substrates) they are utilising, biorefineries can be classified into first generation and second generation biorefineries. In the first generation biorefineries, raw materials are sugar (sucrose) and cereal grains (starch) while for the second generation biorefineries, lignocellulosic materials (e.g. agriculture and forest wastes) are used as feedstocks. It is important to note that first generation feeds are food competitive while second generation feeds make use of non-edible biomass which are

cheaper and more readily available (Kumar and Gayen, 2011). In addition to the competition between food and fuel or chemical production, the production in first generation biorefineries may also lead to problems like deforestation by overuse of lands as well as the environmental risks associated with the use of fertilisers and pesticides (Geraili et al., 2014).

2.1.2. Conventional Industrial Process

Just like any other established fermentation process, the fermentative biobutanol production generally consists of the following six stages (Stanbury et al., 2013):

i. The formulation of the media to be used in culturing the process organism during the development of the inoculum and in the production fermenter.
ii. The sterilization of the medium, fermenters and ancillary equipment.
iii. The production of an active, pure culture in sufficient quantity to inoculate the production vessel.
iv. The growth of the organism in the production fermenter under optimum conditions for product formation.
v. The extraction of the product and its purification.
vi. The disposal of the effluents produced by the process.

Traditionally, the ABE fermentation was carried out in non-agitated batch fermenters with a capacity of 50 000 to 200 000 gallons (189 to 757 m^3). The product was recovered and concentrated by downstream distillation. The initial industrial process made use of maize mash (8 to 10%) which was first cooked for 60 to 90 min at 130 to 133°C. From the mid-30's going onwards molasses was used as the fermentation substrate. The molasses had to be cooked and sterilized at 107 to 120°C for 15 to 60 min and other sources of organic and inorganic nitrogen, phosphorus, and a buffering agent were added (Jones and Woods, 1986, Ranjan and Moholkar, 2012).

Typically, the batch fermentation system was initiated with a substrate concentration of around 60 g/L (glucose equivalent). The sterilized medium containing the substrate and nutrients is cooled under a blanket of oxygen-free nitrogen or carbon dioxide. Upon cooling, the fermenter reactor is inoculated with a Clostridium culture and fermentation started (Mariano and Maciel Filho, 2012, Roffler et al., 1987). Temperatures between 30 and 40 °C

have been reported to be optimum for the fermentation (Ranjan and Moholkar, 2012). Depending on the culture and substrate used, after a fermentation time of typically 36-72 hrs, ABE of up to 15-20 g/L (ratio usually 3:6:1) have accumulated.

In traditional butanol fermentation facilities, a series of five distillation columns was used to separate and purify the ABE solvents (Roffler et al., 1987, Mariano and Maciel Filho, 2012, Van der Merwe et al., 2013), with the last 2 columns solely designed to separate butanol from water (Figure 2-2).

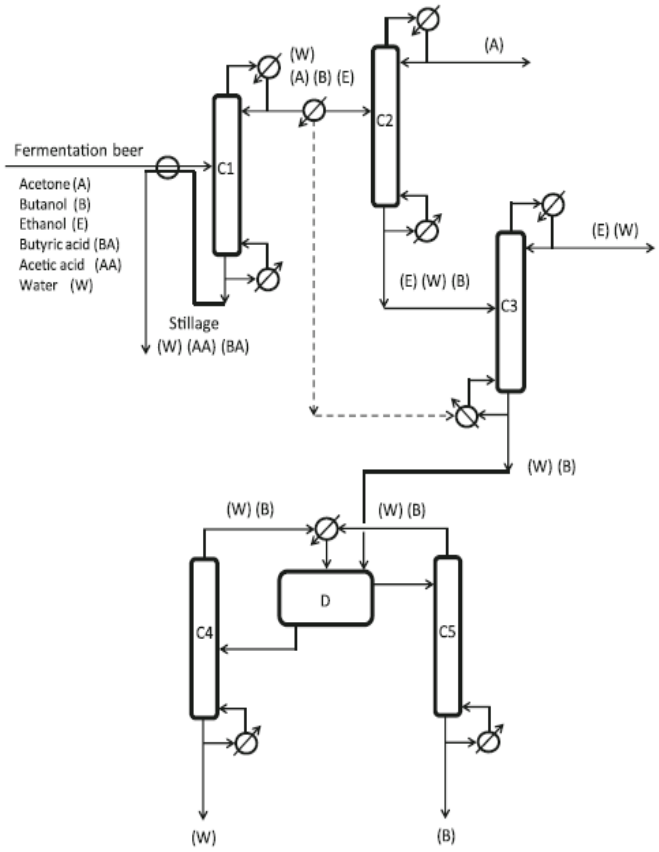


Figure 2-2: Conventional downstream distillation (Mariano and Maciel Filho, 2012)
C1 beer stripper, **C2** acetone column, **C3** ethanol column, **C4** water column, **C5** butanol column, **D** decanter

The separation of the butanol-water system is rendered complex by the existence of an azeotrope at a concentration 55.5 wt. % butanol at 101.3kPa. The azeotrope occurs above the solubility limit (7.7 wt% butanol) and thus, two liquid phases form, i.e. an upper phase containing 79.9 wt. % butanol and a lower phase containing 7.7 wt. % butanol are formed (Vane, 2008, Mariano and Maciel Filho, 2012, Visioli et al., 2014). The lower phase boils at lower temperatures (Visioli et al., 2014). This phase separation enables the heterogeneous

azeotrope to be separated by using a two distillation column system coupled with a decanter.

The top streams from the water and butanol columns are fed into a decanter. After butanol phase separation in the decanter, the water-rich phase is refluxed to the water column while the butanol-rich phase is refluxed to the butanol column. Typically, the bottom product (water) from the water column contains less than 0.1 wt% butanol while the bottom product (butanol) from the butanol column is approximately 99.9 wt% butanol (Mariano and Maciel Filho, 2012, Van der Merwe et al., 2013).

2.2. Developments and Improvements to the Conventional Process

2.2.1. Fed-batch Fermentation Process

In the fed-batch configuration, the process begins as a batch process with a relatively low substrate concentration and low volume. This mode is applied when a high substrate concentration is toxic to the microbial culture. As the substrate is being consumed, additional substrate is added at a slow rate being careful to keep the ABE concentration below the toxic level (Ezeji et al., 2004, Ranjan and Moholkar, 2012). Since butanol is also toxic to the culture, the fed-batch mode is to be coupled with a product-removal technique. Applying the fed-batch configuration together with a product-removal technique, therefore, solves two toxicity problems-substrate inhibition and butanol inhibition (Ezeji et al., 2004). The fed-batch fermentation configuration coupled with *in situ* gas stripping has been applied resulting in solvent productivities increases of up to 400% (Ezeji et al., 2004, Xue et al., 2012).

2.2.2. Continuous Fermentation Processes

Volumetric ABE productivity (g ABE/L fermentation broth/hr) is of major impact on the capital cost as it determines the size of the fermenters required. For instance, if productivity is doubled, capital expenditure can be reduced by approximately by 20%, coupled with some reductions in the operating costs (Green, 2011). Continuous fermentation processes are applied with the view to increase the reactor productivity which, however, is partly compensated by the relatively low butanol concentration when compared to the batch

process (Ranjan and Moholkar, 2012, Visioli et al., 2014). In China, there is a semi-continuous fermentation process which offers a 40% higher productivity than a conventional batch process (Ni and Sun, 2009). In continuous fermentations, concentrated sugar solutions can be used, product inhibition is reduced by integrated product removal and the cost of waste water treatment is reduced (Kraemer et al., 2011). There is also a reduction in the sterilization and inoculation time (Visioli et al., 2014).

The low productivity associated with the batch process (up to 0.6 g/L/h) is a consequence of various reasons which include the low cell concentration, down time and well as product inhibition. Cell concentrations in batch reactors are typically less than 4 g/L (Ezeji et al., 2007, Mariano and Maciel Filho, 2012). To increase the cell concentration, two techniques, namely 'immobilization' and 'cell recycle' have been reported.

2.2.2.1 Free Cell Continuous Fermentation

Free cell continuous fermentation is characterised by cells that are free to move within the fermentation broth due to agitation by a mechanically operated agitator or by air lifting (Kumar and Gayen, 2011). The microbial culture and nutrients are maintained in suspension and this aids in improving the mass transfer. The disadvantage of the continuous free cell fermentation is that high cell concentrations cannot be achieved and there is possible cell washout at high dilutions since there is no means to retain cells in the reactor (Qureshi and Ezeji, 2008).

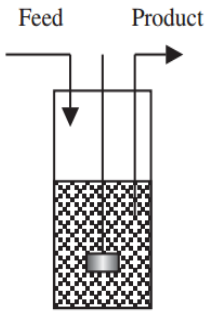


Figure 2-3:Free cell continuous reactor (Qureshi and Ezeji, 2008)

2.2.2.2 Immobilized and Cell Recycle Continuous Bioreactors

Immobilization serves to retain the microbial cells within the vessel. There is physical retention of the cells in the matrix which can be implemented in packed bed reactors as

shown in Figure 2-4 or fluidized type reactors. The lack of mechanical agitation in these reactors allows for long survival time of cells (Kumar and Gayen, 2011). Immobilization is, however, associated with mass transport limitations of substrate and products as well as activity loss due to immobilization. Additionally, there can be accumulation of fermentation gases within the matrix which reduce the productivity as the cells might not be in good contact with the substrate (Jones and Woods, 1986).

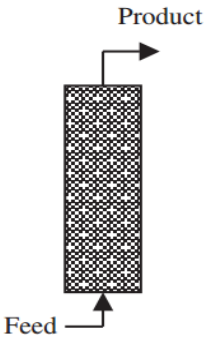


Figure 2-4: Immobilised cell packed bed reactor (Qureshi and Ezeji, 2008)

In as much as immobilized cell reactors increase the cell concentration inside the bioreactor, cell recycle membranes and filters also serve to increase cell concentration. As shown in Figure 2-5, a membrane or filter is used to prevent the cells from being removed from the broth with the out flow. Disadvantages of this scheme include: the possible fouling of the membrane with the fermentation broth as well as the high membrane cost (Qureshi and Ezeji, 2008).

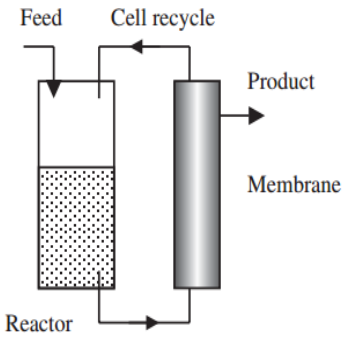


Figure 2-5: Membrane cell recycle reactor (Qureshi and Ezeji, 2008)

2.3. Biobutanol Inhibition and Recovery Techniques

Butanol, which is the major product of the ABE fermentation process, is toxic to microorganisms (Abdehagh et al., 2015) and inhibits the further ABE production at butanol concentrations above 10-15 g/L (Roffler et al., 1988, Ha et al., 2010, Abdehagh et al., 2015). As a result, the maximum attainable ABE concentration is about 20 g/L (Ishii et al., 1985) as the fermentation is brought to a halt. Roffler et al. (1988) summarises how butanol inhibition affects the economics of the ABE fermentation process as follows:

1. Fermenter productivity is lowered as butanol accumulates in the broth. This results in the need for larger fermenters.
2. The amount of substrates (sugars or saccharides) that can be consumed is reduced by the butanol inhibition. In traditional batch fermentation, sugar solutions of concentrations higher than 60 g/L cannot be used (Qureshi et al., 2005, Ranjan and Moholkar, 2012, Ishii et al., 1985, Ezeji et al., 2003). High sugar concentrations also come with feed inhibition effects.
3. It is expensive to recover the product by direct distillation due to the low final butanol concentration in the fermenter. There is need to remove large volumes of water during the recovery process because water has a lower boiling point than butanol (Qureshi and Blaschek, 2001b)-butanol boils at 117.7 °C.

To curb the inhibition effects of the butanol, there are two main solutions that have received research attention, i.e. to genetically modify the fermentation microorganisms such that they become more resistant to higher butanol concentrations and/or to design and develop efficient *in situ* (simultaneous and continuous) separation methods to remove butanol from the fermentation broth. Economic analyses of different biobutanol schemes with different strains have, however, indicated that the use of improved fermentation strains is not sufficient to attain an economically viable process design, unless combined with cost effective separation processes (Van der Merwe et al., 2013). This narrows the scope of the current study towards improving or optimising the recovery and concentration of biobutanol from fermentation using strains that are currently available on the market.

In situ recovery of butanol from fermentation broth, in integrated systems (fermentation and product recovery in the same vessel or coupled together), has received a great deal of

research attention. The focus of the research has been towards the development of a suitable separation method and Groot et al. (1990b) assert that such a separation method should not interfere with the microbial activity in the broth. Additionally, the selectivity of the separation should be high to reduce production costs, and capacity should be high to reduce investments costs. A number of methods have been investigated to recover butanol from model solutions as well fermentation broths and these include liquid-liquid extraction, adsorption, gas stripping, pervaporation, perstraction (or membrane solvent extraction) and reverse osmosis.

2.3.1. Adsorption

Seader and Henley (1998) define adsorption as a process *"….used to separate components in a gas or liquid mixture by adsorption on solids (adsorbents), followed by desorption to regenerate the adsorbents"*. In the recovery of butanol from model solutions and fermentation broths, much of the research has been directed towards finding the appropriate adsorbent. Adsorbents that have been studied include silicate, polymeric resins, zeolites, bone charcoal, activated charcoal, bonopore and polyvinylypyridine (Qureshi et al., 2005, Abdehagh et al., 2013). Hydrophobic adsorbents potentially show a higher selectivity for butanol over water (Visioli et al., 2014). Factors considered in adsorbent screening include: adsorption capacity, adsorption rate, selectivity for the butanol as well as the ease of desorption (Abdehagh et al., 2015).

Qureshi et al. (2005) reported the separation of butanol from model solutions and fermentation broth using silicate, bone charcoal/charcoal and polyvinylpyridine as adsorbents. Silicate was reported to be more attractive as it concentrated butanol from dilute solutions. The adsorbed solvent was completely desorbed with the regeneration of the silicate for reuse being conducted by heat treatment at 200°C. Butanol recovery by adsorption was proven as an energy efficient process with an energy requirement of 1 948kcal/kg (based on adsorption-desorption process) compared to 5 220 and 3 295kcal/kg for gas stripping and pervaporation, respectively (Qureshi et al., 2005).

Das et al. (1987) as quoted by Qureshi et al. (2005) studied the adsorption of butanol from model solutions into various charcoals. Bone charcoal was found to have a higher adsorption capacity than activated charcoal but with incomplete recovery on desorption.

There is still a need to address problems such as the interaction between adsorbents and nutrients, toxicity of adsorbents as well as the ease of desorption. Reaction intermediates can also be adsorbed onto some adsorbents.

Abdehagh et al. (2013) tested different types of zeolites and activated carbons in adsorbent screening experiments with the intention of investigating their performance as butanol adsorbents. Additionally, they investigated the effect of the presence of other fermentation broth components on the butanol production. Amongst the tested adsorbents, activated carbons F-400 and F-600 had the fastest kinetics for butanol adsorption. Equilibrium experimental results showed that F-400 had the highest adsorption capacity for butanol (300 mg/g) and selectivity results further showed that this adsorbent had the highest affinity for butanol with a low adsorption capacity for other broth components. Thus, F-400 was selected as the adsorbent of choice. The presence of sugars (glucose and xylose) showed no effect on butanol adsorption by F-400 while the presence of acetone caused a slight decrease in butanol adsorption capacity at low butanol concentrations. The presence of butyric acid had a significant and pronounced effect of the adsorbent capacity for butanol which led to the conclusion that acids compete with butanol for adsorption sites on the adsorbent. In a separate study, Abdehagh et al. (2015) carried out experiments to investigate the desorption of butanol from F-400 adsorbent using butanol-water and ABE model solutions. Based on the experimental results, the conclusion was that the adsorbed butanol and other compounds were quantitatively desorbed rendering activated carbon F-400 one of the most suitable adsorbents for butanol separation processes.

Overall, from the studies published in literature, it is not conclusive on what material constitutes the most promising or preferred adsorbent. A thorough performance comparison between the different adsorbents still needs to be conducted.

2.3.2. Gas Stripping

In gas stripping, a vapour (or gas) stream is used to remove one or more components from a liquid mixture. Gas stripping can be regarded as one-equilibrium-stage distillation (Seader and Henley, 1998). In biobutanol recovery by gas stripping, a gas (usually oxygen-free nitrogen or fermentation gas products (CO_2 and H_2)) is sparged through the fermentation broth taking with it volatiles from the broth which are condensed and recovered from a

condenser. The stripped gas is pumped and recycled back to the fermenter (Lee et al., 2008).

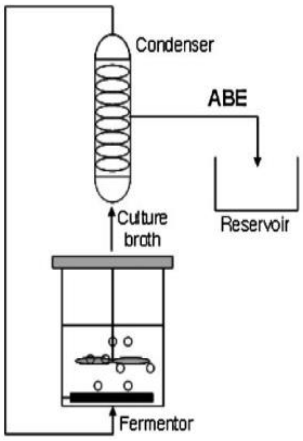


Figure 2-6: In situ recovery by gas stripping (Lee et al., 2008)

The volatility properties of the ABE permit easy product removal by gas stripping (Ezeji et al., 2003, Liu et al., 2004) since the process is governed by vapour-liquid equilibrium (Ranjan and Moholkar, 2012). The stripping of butanol from water has been found to be much faster than acetone and ethanol (Xue et al., 2012) and this property makes it possible for the concentration of butanol in the condensed stream. Gas stripping has the highest selectivity in separating butanol from water (compared to ethanol and acetone) even though butanol is higher boiling than acetone and ethanol (Xue et al., 2012). The selectivity of the stripping for butanol is defined as:

$$selectivity = \frac{y/(1-y)}{x/(1-x)} \qquad [2\text{-}6]$$

where x is the butanol concentration in the fermentation broth (in wt%) and y is the butanol concentration in the condensate.

Gas stripping has been applied in both batch and fed-batch fermentation processes resulting in solvent productivities increases of up to 400% (Ezeji et al., 2004). Qureshi and Blaschek (2001b) compiled a review on the butanol recovery by gas stripping and assert that sugar utilizations as high as 199 g/L have been realised compared to 30 g/L in non-integrated systems. Concentrated sugars solutions of up to 350 g/L have been used which has the

advantage of reducing the volume of waste water. ABE concentrations of between 9.1 and 120 g/L in the recovered stream have been achieved.

Of particular interest is the work reported by Xue et al. (2013). A two-stage gas stripping process was used to recover butanol from ABE fermentation by *Clostridium acetobutylicum* JB20. The process proved to be effective to produce high-titre butanol that can be purified with less energy. By making use of fermentation gases (H_2 and CO_2) Xue et al. (2013) obtained very high butanol and ABE concentrations of 429.3 g/L and 523.3 g/L, respectively, which were more than 20-fold higher than those obtained in conventional ABE fermentation. Although the energy requirement for the purification of this butanol product was not reported on, it was concluded that this two-stage gas stripping process can significantly reduce the energy requirement, thus providing an energy-efficient process for butanol production.

Factors that affect the recovery of butanol from fermentation broth include the concentration of butanol in broth, gas recycle rate and the bubble size of the stripping gas (Ezeji et al., 2003, Ezeji et al., 2004, Ezeji et al., 2005, Xue et al., 2012). When the bubble size is small, large amounts of antifoam is required and antifoam reduces the fermentation productivity (Ezeji et al., 2005). Xue et al. (2012) assert that gas stripping would be more effective when the butanol concentration in broth is higher than 8 g/L. This was demonstrated by intermittently applying gas stripping only when the butanol concentration was above 8 g/L, which resulted in a high concentration butanol condensate (above the solubility limit).

Advantages of using gas stripping are that it is a simple process and does not require expensive apparatus, it does not harm the culture and does not remove nutrients and reaction intermediates from the broth (Qureshi and Blaschek, 2001b, Ezeji et al., 2003, Kumar and Gayen, 2011, Xue et al., 2012). Gas stripping, however, has a low selectivity for butanol when compared to that of other separation techniques (Qureshi et al., 2005, Vane, 2008, Xue et al., 2012, Stoffers et al., 2013). This results in large amounts of water being carried to the condensed stream which requires a high energy input to separate.

2.3.3. Liquid-Liquid Extraction

In liquid-liquid extraction (or solvent extraction or liquid extraction), a liquid feed of two or more components is separated by contact with a second liquid phase, the solvent (extractant), which partially dissolves certain components of the liquid feed (Seader and Henley, 1998). Separation is driven by the differences in the distribution coefficients of chemicals (Lee et al., 2008). If butanol is more soluble in the extractant (organic phase) than in the fermentation broth (aqueous phase) it becomes concentrated in the extractant. Extractive fermentation is used to describe fermentation that incorporates the use of a solvent to recover butanol from the fermentation broth (Roffler et al., 1988). The selection of the appropriate solvent for the extractive fermentation has received a great deal of research attention. Solvents that have been investigated range from organic solvents (Roffler et al., 1988) to ionic liquids (Ha et al., 2010, Fadeev and Meagher, 2001) as well as mixtures of solvents (Roffler et al., 1988). The advantage of liquid-liquid extraction is the high capacity of the solvent and the high selectivity of the butanol/water separation (Groot et al., 1990b, Ha et al., 2010). Additionally, it is possible to conduct the extraction concurrently-inside the fermenter (Ha et al., 2010), provided the solvent is not harmful to the microorganisms.

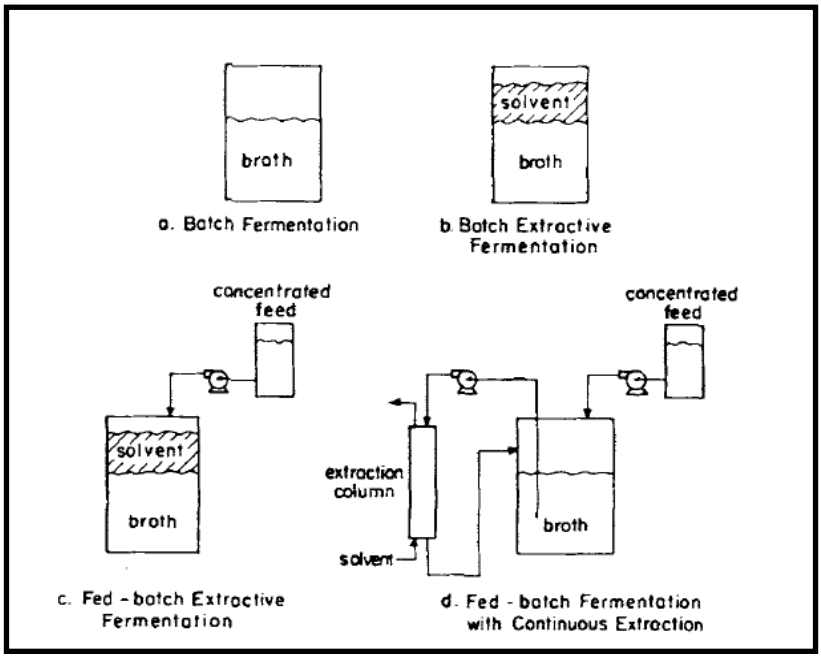


Figure 2-7: Extractive fermentation process configurations (Roffler et al., 1988)

Figure 2-7 shows the three extractive fermentation process configurations compared to the conventional batch. In the batch extractive configuration, the immiscible solvent is directly added to the batch culture of microorganisms. Butanol dissolves into the solvent as the fermentation proceeds which reduces the inhibition effects. However, the solvent eventually becomes saturated. There still remains a problem of large amounts of waste water produced although the fermenter productivity is increased (Roffler et al., 1988). In the fed-batch configuration, substrate is added into the broth at a slow rate to keep the butanol concentration below the toxic level (Ranjan and Moholkar, 2012). The butanol concentration, however, eventually exceeds the toxic concentration as the solvent becomes saturated with product (Roffler et al., 1988). Thus, the batch-fed fermentation has to be coupled to a suitable ABE recovery technique to prevent product inhibition of the microorganisms. Additionally, it has been reported that there is formation of emulsions from the high shear rate generated by the impeller (Ranjan and Moholkar, 2012, Roffler et al., 1988).

This necessitates the implementation of the continuous extraction unit in which butanol from the broth is continuously extracted from the broth in a separate unit into which fresh or regenerated solvent is continuously introduced. Continuous processes have high capital costs, however, they tend to be more economical over batch and fed-batch processes (Kumar and Gayen, 2011). Roffler et al. (1988) used oleyl alcohol as the extraction solvent in all of the four configurations illustrated above. Table 2-1 shows a summary of the results obtained.

Table 2-1: Comparison of batch culture and extractive fermentation using oleyl alcohol (Roffler et al., 1988)

Fermentation	**Overall butanol productivity (g/L h)**	**Concentration of glucose fermented (g/L)**	**Total glucose fermented (g/L)**
Batch	0.58	81	81
Batch extractive	0.72	98	98
Fed-batch extractive	1.5	333	207
Fed-batch with continuous extraction	1.0	300	241

The results show that there was a 70% increase in volumetric productivity when continuous extraction was used compared to the conventional batch. The Karr reciprocating plate extraction column was used and the process can easily be integrated into a large scale extractive fermentation system.

Oleyl alcohol (*cis*-9-octadecen-1-ol) was also selected as a suitable solvent for butanol extraction together with C-20 guerbet alcohol (branched-chain alcohol of carbon number 20) (Ishii et al., 1985). This choice was based on the non-toxicity to the microorganisms, partition coefficients etc. from a group of 29 solvents which included aliphatic alcohols, higher fatty acids and fluorinated alcohols. Partition coefficients of between 3.5 and 4.3 were realised for the two solvents which are quite high compared to those for ethanol and acetone which were between 0.17 and 0.52. In the same study, castor oil was relegated as a solvent due to its toxicity to microorganisms, high specific gravity which makes it difficult to separate as well as the low partition coefficient for butanol.

The use of ionic liquids (ILs) has also received some level of research attention in the production and recovery of alcohols. Room temperature ionic liquids (IL) are salts that have melting points below 100°C and are entirely composed if ions (Ha et al., 2010). They principally consist of large organic cations and inorganic or organic anions (Stark, 2011). They have been described as *'designer solvents'* (Ha et al., 2010) as their distinct physico-chemical properties (melting point, polarity, viscosity, solvation properties, phase behaviour, chemical and thermal stability) depend on the choice of the anions and cations in each IL (Stark, 2011). ILs have extremely low vapour pressure, low flammability and can possess low solubility in water. The fact that they can be designed to possess low toxicities makes them interesting and feasible solvents for butanol extraction. The selectivity of alcohol extraction is affected by the water solubility in IL and IL solubility in water (Fadeev and Meagher, 2001).

Ha et al. (2010) investigated the extraction behaviour of butanol from aqueous media by liquid-liquid extraction using a variety of imidazolium based ILs with alkyl chains of varying length in combination with anions such as tetrafluoroborate ($[BF_4]^-$), trifluoromethanesulfonate ($[TfO]^-$), hexafluorophosphate ($[PF_6]^-$) and

bis(trifluoromethylsulfonyl)imide ($[Tf_2N]^-$ or BTI). Extraction efficiencies and selectivity were found to be directly proportional to the IL polarity as determined by the dielectric constant. Results showed that BTI-based ILs have the potential to work as a solvent in recovering butanol from aqueous media. $[C_8mim][BTI]$ was able to extract more than 74% of the initial butanol with a selectivity of 132 in one cycle of extraction. However, these ILs were not applied to actual fermentation broths and thus, their toxicity against microorganisms cannot be ascertained.

Disadvantages that arise from the use of liquid-liquid extraction include the complications that arise from the introduction of a new liquid phase into the fermentation broth and the fouling of the solvents (Groot et al., 1990b).

2.3.4. Perstraction (Membrane Solvent Extraction)

Perstraction is a liquid-liquid extraction process coupled with membrane extraction. The idea is to mitigate the shortcomings of liquid-liquid extraction, namely solvent toxicity and the formation of emulsions as reported in batch-fed fermentations. In this set-up, the solvent is separated from the broth by a membrane offering a dispersion free extraction environment (Groot et al., 1990b). The technique also offers an advantage of independent control over the flow rate of the broth and the extractant (Ranjan and Moholkar, 2012). Mass transfer in the membrane becomes an important parameter (Groot et al., 1990b, Ranjan and Moholkar, 2012). The overall mass transfer is a function of the individual mass transfer coefficient on aqueous (fermentation broth) and, the extractant side, as well as the mass transfer through the membrane (Ranjan and Moholkar, 2012).

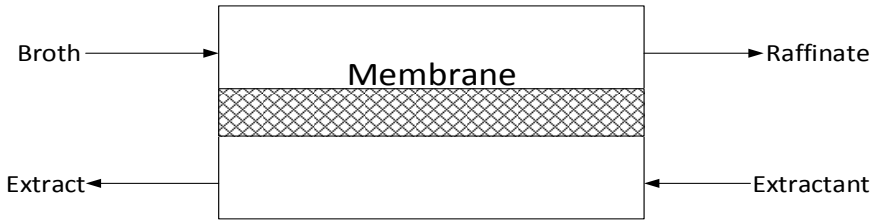


Figure 2-8: Concept of membrane solvent extraction (Groot et al., 1990b)

Silicone rubber membranes were used in a study by Groot et al. (1990b) and these offer preferential permeation of butanol over water. Disadvantages of membrane extraction

include the need to install a membrane area and membrane fouling, hence adding onto costs (Groot et al., 1990b).

2.3.5. Pervaporation

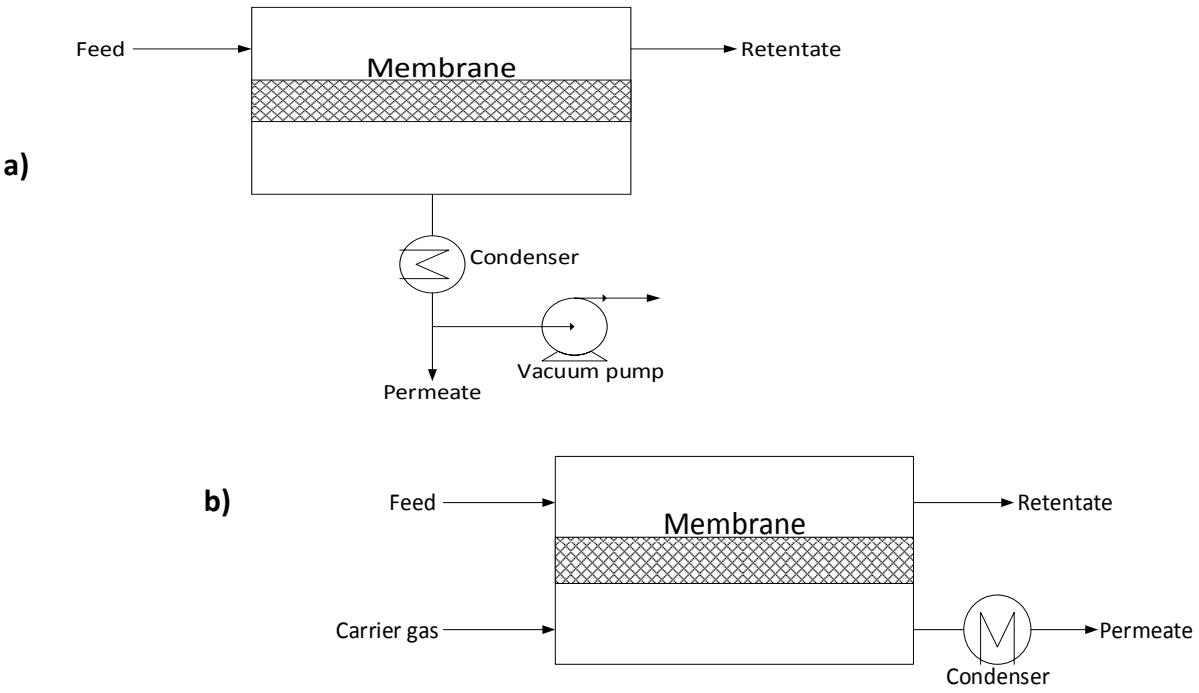


Figure 2-9: Alternative operation of pervaporation a) Vacuum operation b) Carrier gas pervaporation (Feng and Huang, 1997)

Pervaporation is a process in which the component of interest is separated from a liquid mixture (feed) through a membrane by application of a differential pressure between the walls sufficient to bring the component into a gaseous state and get removed on the other side of the membrane (Jaimes et al., 2014). Thus, a stream with high concentration of the desired component (permeate) is obtained in a gas state and another stream with low concentration of the desired component (retentate). A condenser is incorporated to condense and recover the permeate gas. The differential pressure is usually established by using a vacuum pump or through the use of a carrier (sweep) gas (Seader and Henley, 1998).

Pervaporation has been reported as one of the promising methods of recovering butanol (Heitmann et al, 2013). Pervaporation can be used to separate butanol from water as the permeation of butanol through the membrane is faster than the permeation of water (Groot et al., 1990b). It has also been investigated as a recovery process for ethanol from wine (Jaimes et al., 2014). When pervaporation is applied to the recovery of butanol from

fermentation broth, the membrane is placed in contact with the fermentation broth and the volatile butanol diffuses through the membrane as vapour which is recovered by condensation. The butanol (or ABE solvents) first get solubilised into the membrane and then they diffuse through the membrane and evaporate on the permeate side at low pressure (Ranjan and Moholkar, 2012). This transfer mechanism if often referred to as solution-diffusion mechanism (Ranjan and Moholkar, 2012).

The selection of materials and design of pervaporation membranes has received a great deal of research attention as researchers try to find membranes showing better mass transfer properties and selectivities. Both, liquid and solid membranes have been used in pervaporation (Jin et al., 2011). The two parameters that determine the efficacy of a membrane are the selectivity and the flux through the membrane (rate of passage of volatile components per unit time per unit area) (Ranjan and Moholkar, 2012). Membrane stability is also a factor to consider as the membrane is continuously used.

Qureshi et al. (2001) used a silicate-silicone composite membrane to recover butanol from fed-batch reactor operating with *Clostridium acetobutylicum.* An ultrafiltration membrane was incorporated in front of the pervaporation membrane, and as a result, the membrane was not fouled. A total of 154.97 g/L solvents was obtained with a yield between 0.31 and 0.35 compared to a yield between 0.29 and 0.30 obtained in the batch reactor. Heitmann et al. (2013) investigated the separation behaviour of polydimethylsiloxane (PDMS) membrane and membranes based on a poly(ether block amide) and created a database for these two polymers that have been applied to recover organics.

It is also worth noting that the membrane permeate contains acetone, butanol and ethanol and distillation is still required for further purification (Jin et al., 2011). Pervaporation has the advantage of its operational simplicity but the separation must be carried out outside the fermenter (Ha et al., 2010).

2.3.6. Summary of Biobutanol Recovery Techniques

Table 2-2 gives an overview of the butanol recovery methods to which a review has been given. The challenge is to compare experimental results from various researchers as the

conditions and scale of the experiment are so different. It is even more difficult to compare results for different techniques for example, comparing results from liquid-liquid extraction and pervaporation, as there are no defined comparison criteria available. However, it is apparent that adsorption, liquid-liquid extraction and pervaporation have been investigated in more detail and show advantage and potential over the other methods. These technologies have also been previously identified as the having the highest potential by Groot et al. (1990a) and Stoffers et al. (2013).

It was, therefore, initially, decided to include these three technologies in full techno-economic analyses (together with distillation). The use of each technique at a certain stage, however, depends on a number of factors including the size and composition of streams. Section 2.4 below is a review of how these technologies have been previously integrated in full scale processes which gave motivation towards the configurations that were included in the current analysis.

Table 2-2: Summary of biobutanol recovery techniques

Recovery method	Advantages	Disadvantages
Adsorption	• Simple and economical • Does not affect culture	• Competition for adsorption sides as adsorbent is added to the broth
Gas stripping	• Simple and economical • Does not affect culture, concentration of nutrients and reaction intermediates • Free of emulsion formation	• Low condensate concentration • Low selectivity • Foam formation
Liquid-liquid extraction	• Can be carried out within the fermenter • High capacity and selectivity solvents can be found • Extensive work has been done	• Complications due to introduction of another liquid phase • Solvent toxicity to the cells • Emulsion formation • Loss and fouling of extraction solvent
Pervaporation	• Operational simplicity • Does not harm the microorganisms • Independent control of the broth and extractant flows	• Must be carried out outside the fermenter • Possible membrane fouling • Rate of removal of solvents limited by mass transfer resistances
Perstraction (Membrane solvent extraction)	• Toxicity of solvent for the cells does not occur • Offers a dispersion free environment	• Need for a membrane increases cost • Possible membrane fouling

2.4. Biobutanol Recovery Economics

What is clear from all the studies that are reported in literature is that it is not possible to use a single unit operation, based on the above techniques, for the recovery of butanol from fermentation broth. Neither a single distillation column nor an extraction or pervaporation step alone can produce biobutanol with high purity (Stoffers et al., 2013, Xue et al., 2014). The integration of two or more unit operations in order to achieve economic configurations has been explored in a number of studies. The general idea is to be able harness the advantages of different technologies and reap from them in a single process scheme or flowsheet that delivers butanol at a high purity. Processes that combine two or more different unit operations or technologies to improve efficiency are often referred to as hybrid processes (Seader and Henley, 1998).

There is generally limited real plant data available in literature concerning processes for biobutanol production. This limits the number of techno-economic studies that can be undertaken with high degrees of accuracy as many assumptions have to be made to scale laboratory data to industrial scale. Despite this drawback, literature contains a number of studies that have included the economic analysis of the biobutanol production process and these studies have been mainly conducted to determine the profitability of different process routes based on different fermentation strains, feedstocks or purification technologies. The main indicators widely used in engineering economics to assess different process alternatives include the payback period, net present value (NPV), internal rate of return (IRR) and the cost of production (Bonomi et al., 2015). A cash flow analysis of each process is prepared and this requires information about the investment, all expenses and revenues for the expected lifetime for the project (Bonomi et al., 2015).

Lenz and Morelra (1980) evaluated the economic benefit of using liquid whey matter as a substrate over molasses in a batch fermentation system. Molasses costs accounted for 62% of the overall production cost resulting in a production cost slightly higher than the total annual income. The economics of the process were turned from a loss making process using molasses to an economically viable process by using whey matter as a substrate. A 19% increase in revenues was realised and a discounted cash flow rate of return of 28% was determined for a 10-20 year plant life.

Stoffers et al. (2013) reported on both an integrated extraction-distillation process that utilises an ionic liquid as a solvent for extraction, and an integrated pervaporation-distillation process. In both instances, the stages before the distillation, i.e. extraction and pervaporation, are designed to remove as much water as possible such that in the downstream only a stream with an azeotropic butanol-water composition is available, which can be purified with less columns than in the conventional case. The input into these processes consisted of a simplified butanol-water feed which resulted in generally low total capital investments due to less downstream distillation columns being required, e.g. the distillation case required a total capital investment of €2.2 million. More distillation columns would be required if the other fermentation products, i.e. acetone and ethanol, were also included. The models were, however, sufficient to show than the process that included extraction could reduce the purification costs from €0.289/kg butanol, in the benchmarking case, to €0.230/kg butanol. An increase in purification costs (to €0.296/kg butanol) was reported for the case that included pervaporation (Stoffers et al., 2013).

A study by Roffler et al. (1987) examined the economics of producing biobutanol by extractive fermentation compared to the conventional batch fermentation followed by a trail of the five distillation columns. The use of an extractive solvent increased the fermenter productivity to 1.5 g/L h, from 0.58 g/L h in the conventional case, and this led to a 20% decrease in the equipment cost. The higher productivity results in fewer fermenters, which are a major contributor towards the total capital investment. The use of extraction was also reported to reduce the energy requirements of the whole process.

A study widely quoted in the current study is one by Van der Merwe et al. (2013) who developed process models to compare three different possible process designs for biobutanol production from sugarcane molasses. Since the study was peromed in South Africa, it brings familier context and assumptions. The first route consisted of batch fermentation and stream stripping while in the second route some of the distillation columns were replaced by a liquid-liquid extraction column. The third route incorporated fed-batch fermentation and gas stripping with CO_2. Process modelling in ASPEN PLUS® and economic analyses in ASPEN Icarus® showed that the third process route was the only one of the three that would potentially be profitable in the current economic conditions in South

Africa. The incoporation of the gas stripping stage was shown to be effective in improving the economics of biobutanol production.

A more recent report by Naleli (2016) examines the economics of biobutanol production from lignocellulosic biomass which would be of interest to the sugar industry as bagasse could be used in hydrolysis. The study examined the effects of having different fermentation methods, fermentation technology improvements as well as the purifcation. It was concluded that the simultaneous sacharrification and fermentation (SSF) integrated with gas stripping and distillation as well SSF integrated with gas stripping and extraction were the most economic process configurations. This analysis was based on obtained NPVs and IRR. The overall conclusion was also that the molasses based biobutanol process of Van der Merwe et al. (2013) had better economics (for the same butanol capaicity) than the lignocellusic biomass based biobutanol.

2.5. Development of Research Questions, Aims and Objectives

From the literatire review that was conducted, it can be concluded that there has not been any butanol recovery technologies, or a combination thereof, that can be conclusively regarded as economically viable. Additionally, economic evaluations of the biobutanol production process are reported for processes producing fuel grade butanol that is meant to compete with the petro-based butanol. The production of higher value chemical products from biobutanol has not been reported on in detail.

Gas stripping, extraction and adsorption techniques seem to be promising steps that can be combined with distillation to design economically viable recovery processes. The research questions that therefore arose were as follows:

1. Can biobutanol production from streams in the current South African sugar mill be made economically viable by integrating the fermentation process with gas stripping, extraction, adsorption and distillation?
2. What are the major factors that affect the profitability of such integrated processes in the current South African economic conditions?
3. What opportunities would such processes present for the conversion of the biobutanol to higher value, fully bio-based chemical products?

In an attempt to answer these questions, different flowsheets are generated on Aspen Plus® and techno economic analysis conducted to determine the profitability of the considered processes. An experimental section is included to validate some of the simulation results where possibe.

This current study is a pioneering work carried out in the SMRI Sugarcane Biorefinery Research Group in the conversion of the current sugar industry in South Africa into a fully fledged 'sugarcane biorefinery' producing a wide variety of chemical products and energy. The concept is to use the different streams in the sugar mill to generate higher value (and maybe smaller volume) products and establishing different biorefinery models that give different economic scenarios. This will present the industry with valuable alternatives from which to pick a scenario that best suits their requirement. The inclusion of the experimental part in this study also sets a precedence in terms of verifying simulation results as opposed to depending on literature values that are not always verifiable.

3

CHAPTER THREE

3. EXPERIMENTAL CONSIDERATIONS

The experimental part of this study was included in order to have experimental values to use as inputs into Aspen Plus® as well as to validate the results obtained from the simulator. The gas stripping and liquid-liquid extraction experiments are reported on in this section of the dissertation.

3.1. Gas Stripping

3.1.1. Introduction

The use of gas stripping as a method for reducing the inhibition effects of butanol in ABE fermentation has been extensively investigated using model broth solutions as well as in laboratory scale fermenters (Ezeji et al., 2004, Lu et al., 2012, Xue et al., 2012). The main aims have been to investigate how much of the products can be recovered from both batch and continuous fermenters by the gas stream and how well the process can be optimised to increase the concentration of organics recovered. Factors that have been found to affect the efficiency and effectiveness of the process include the nature of the stripping gas, temperature, butanol concentration in the broth, the gas recycle rate, bubble size and the presence of co-solvents (i.e. acetone and ethanol). These factors have been sufficiently investigated and optimised process conditions applied in some recovery processes (Ezeji et al., 2005, Xue et al., 2014, Liao et al., 2014).

Before butanol recovery by gas stripping can be incorporated in a commercial process or pilot plant stage, its performance and benefits should first be ascertained and verified. This can be done using simulators, like Aspen Plus®, to simulate conceptual process designs which can be analysed for economic performance. The ultimate aim of the current gas

stripping experimental work was, therefore, neither to investigate the factors affecting the gas stripping process nor to determine what product concentrations can be obtained from a certain fermenter setup, but to use Aspen Plus® as a simulator to determine the economic performance of gas stripping incorporated in different process schemes. This was to be done by developing a predictive Aspen Plus® flowsheet that is verified by experimental results.

Gas stripping has previously been incorporated in a full Aspen Plus® process for both ethanol (Ponce et al., 2014) and butanol (Van der Merwe et al., 2013) fermentation processes. Van der Merwe et al. (2013) used concentration profiles reported by Ezeji et al. (2004) from a fed-batch reactor coupled with gas stripping for the reduction of product inhibition. Since Aspen Plus® requires a steady-state concentration as input, Van der Merwe et al. (2013) used a concentration of 5 g/L total ABE as an input to the gas stripper. This was from the recognition that from the concentration profiles, the total ABE concentration in the fermenter was always greater than this value but not necessarily the average concentration during the whole fermentation time. Designing for this concentration would, hence, represent the worst case scenario in terms of energy requirements in the downstream purification. This approach is sufficient for simulating results from one fermenter, however, challenges are encountered when attempting to extend the same approach to a different bioreactor that uses a different strain and substrate. Gas stripping experiments were, therefore, taken up in order to create a scenario based approach to the steady state concentration in the fermenter.

There is no published work that has reported on such experiments before. Ideally, before measuring a new set of measurements, a well-known test system is first measured in order to validate the equipment as well as the method. There is a great deal of fermentation equipment reported in literature and these are so specific to a certain scenario and depend on the available resources. It was, therefore, not possible to have a certain fermenter set-up reconstructed and replicated in order to have test system to validate the method. The validation of the results and method was performed by comparing the concentrations of the organics in the condensed gas stream with results reported in literature. If the method is applicable, the modelled fermenter system would have to produce results that are in the same range with those reported for various fermentation systems that make use of

different strains, substrates and gas stripping equipment. This comparison was performed in Section 4.5.1.1 after the gas stripping experiment results had been simulated on Aspen Plus®.

The designed experimental approach was to create steady state (realistically, pseudo-steady state) concentration levels in the fermenter while stripping and measuring the concentration of the organics in the gas leaving the fermenter/stripper unit. If a fermenter operating in a fed-batch mode and coupled with gas stripping is able to maintain a certain steady state concentration (i.e. when the stripping rate equals the production rate), then the output ABE concentration can always be read out from the results of the experiments. Simulating these results using Aspen Plus® then makes this approach suitable for incorporation into a full conceptual process design for economic analysis or production of other valuable products in the downstream processes.

3.1.2. Theory of Gas Stripping

The stripping of organic chemicals dissolved in water follows a first order process expressed as (Truong and Blackburn, 1984):

$$R_s = -\frac{\mathrm{d}C_s}{\mathrm{d}t} = K_s a C_s \qquad [3\text{-}1]$$

where $\frac{\mathrm{d}C_s}{\mathrm{d}t}$ is the instantaneous rate of change of concentration of an organic component in the aqueous phase. The stripping rate is directly proportional to the component stripping rate constant ($K_s a$) and the component concentration in the aqueous phase (C_s). This dependence of the stripping rate on the solute concentration in the aqueous phase has been investigated and verified for butanol stripping from model solutions as well as fermentation broth in number of studies (Ezeji et al., 2005, de Vrije et al., 2013, Liao et al., 2014).

For a fermentation process coupled with gas stripping, steady state concentrations of organics in the broth can be approached when the stripping rate equals the rate at which the microorganisms are producing the organics.

The gas-liquid contact in the stripper should be such that the gas becomes saturated with the organic solute. A mass transfer analysis in the stripper can be performed in the same

approach conducted by Ezeji et al. (2005). As the carbon dioxide gas bubbles rise from the distributor through the solution in the stripping cell, butanol (and acetone and ethanol) is transferred from the bulk solution to the gas bubble. Assuming that the butanol concentration in the bulk liquid does not significantly change as one bubble passes through the stripping cell (< 1s) and that the radius of the bubble does not change, the following equations apply (Ezeji et al., 2005):

The overall mass balance can be expressed as (where, N_1 is the butanol flux);

$$\frac{V}{RT}\frac{\mathrm{d}p_{10}}{\mathrm{d}t} = N_1 A \qquad [3\text{-}2]$$

where $V = \frac{4}{3}\pi r^3$ and $A = 4\pi r^2$ (volume and area of a sphere, respectively).

The equation proposed by Cussler (2009) is also valid for the calculation of the butanol flux:

$$N_1 = (p_1^* - p_{10})K_p \qquad [3\text{-}3]$$

Combining equations 2-2 and 2-3 yields equation 2-4:

$$\frac{\mathrm{d}p_{10}}{(p_1^* - p_{10})} = \frac{3RTK_p}{r}\mathrm{d}t \qquad [3\text{-}4]$$

The value of K_p is calculated using equations given by Cussler (2009).

Integrating equation 3-4 with the following boundary conditions yields the relationship depicted in Figure 3-1, i.e. $r = 1.287t$ (where t is in s):

$p_{10} = 0$ at $t = 0$ and $p_{10} = 0.99p_1^*$ at t = t

Figure 3-1 shows the contact time required for bubbles of up to 6mm radius to reach 99% saturation with butanol in the stripping cell.

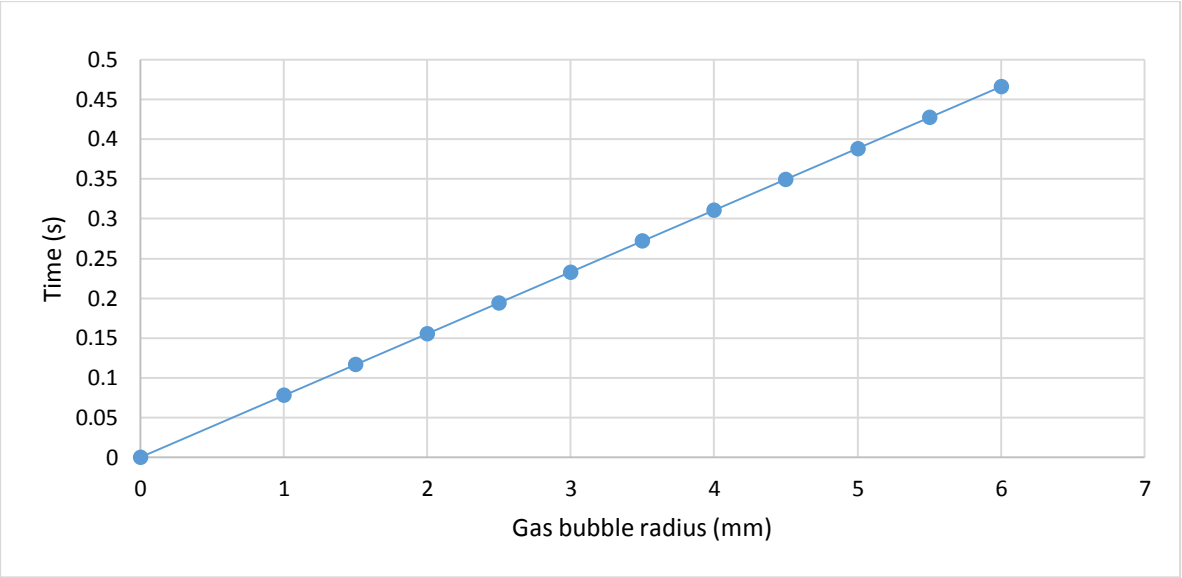


Figure 3-1: Time taken for gas bubbles to reach 99% saturation with butanol, independence of bubble size

3.1.3. Materials and Methods

3.1.3.1. Experimental Set-up and Procedure

The experimentation procedure started with the stabilisation of the gas chromatograph (GC) as well as the water bath temperature being allowed to reach and stabilise at the reaction (typical fermentation) temperature (35-36°C). The stabilisation of the GC required roughly an hour. The stripping cell was made up of a 250 cm^3 reagent bottle (solvent volume was approximately 220 cm^3). Carbon dioxide gas was introduced into the stripping cell via an aquarium gas distributor (Figure 3-2) which worked as a gas sparger. Due to the amount of carbon dioxide produced relative to the hydrogen, it was assumed that the hydrogen has a negligible effect on the on both the stripping and the condensation.

Figure 3-2: Aquarium gas distributor (gas sparger)

A rotameter was used to measure the gas flow rate into the stripping cell. The gas was introduced through a 1/8 inch pipe coil immersed in the water bath which ensured that the gas had reached the experimentation temperature before stripping. As the gas bubbles rose through the cell, the ABE solvents in solution were continuously stripped from the liquid phase into the gas phase. A sampling (6-port) valve was used to direct the gas from the stripping cell either to the GC for analysis ("inject position") or towards the fume hood ('fill position"). Gas lines to the sampling valve and to the GC were heated by means of nichrome wire and maintained at 190°C to avoid any of the gas constituents condensing before getting to the GC.

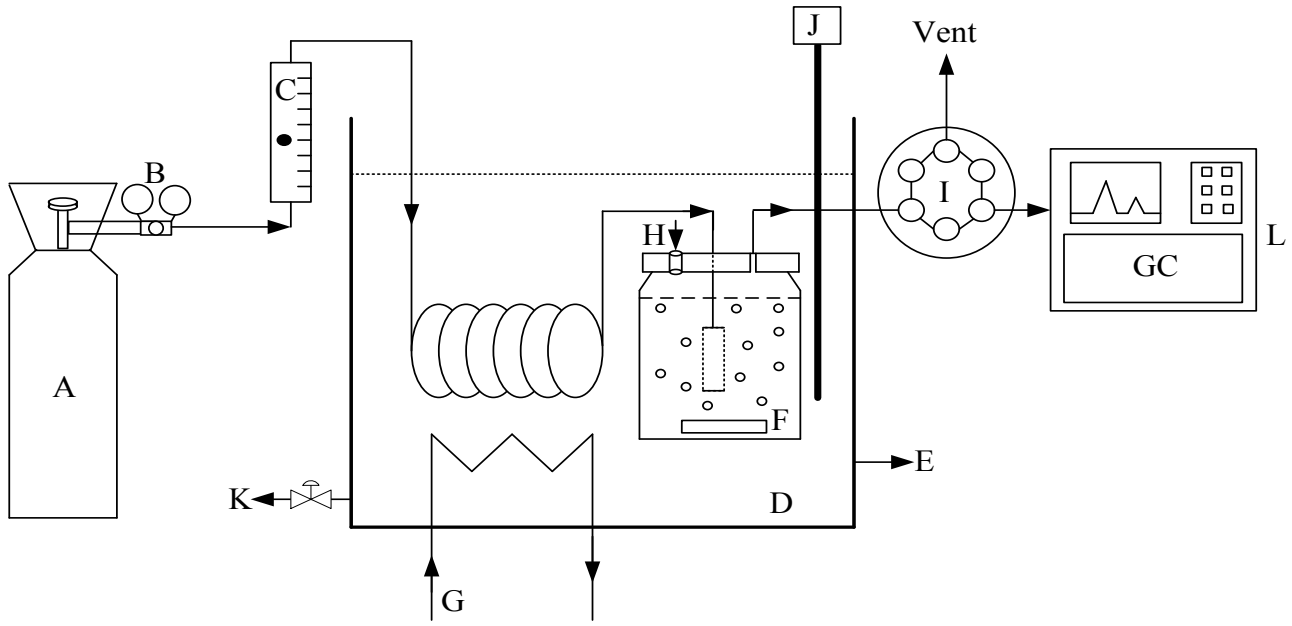


Figure 3-3: Gas stripping experimental set up

A-Carbon dioxide tank, **B**-Pressure regulator, **C**-Rotameter, **E**-Water tank, **F**-Stirring bar, **G**-Water cooler/heater, **H**-Septum, **I**-Sampling valve, **J**-Temperature sensor, **L**-GC

The changes in concentration in the liquid phase (the cell) were monitored by withdrawing samples through a septum on top of the cell using a GC syringe and manually injecting into the GC. The liquid was sampled every hour. The same septum was also used to introduce butanol into the stripping cell during the steady state modelling. The initial experiments were conducted with model broth solutions containing ABE in water and the stripping of these organics was monitored in the unsteady state mode for 9 hours. For simplicity, steady

state (SS) experiments were then conducted using a simplified broth solution consisting of water and butanol only.

To model the steady state operation, the unsteady state butanol composition profile in the liquid phase was first obtained. The stripping was then repeated with the same initial butanol concentration but with intermittent loading of the cell with butanol through the septum. The loading rate was determined by the stripping rate obtained from the unsteady state experiment run. The gas and liquid phases were sampled such that the sampling does not coincide with the cell loading. There were 15 minutes between each loading and the next sampling time.

Three steady state concentration levels were investigated. These represent the low (3.1g L^{-1}), medium (8.67 g L^{-1}) and high (21.62 g L^{-1}) level butanol concentrations in the broth, considering that butanol inhibition brings the fermentation process to a complete halt at around 12 g/L (Jones and Woods, 1986).

Table 3-1: Steady state gas stripping experiment conditions

Experiment	**1**	**2**	**3**
SS butanol concentration (g L^{-1})	3.10	8.67	21.62
Butanol loading rate (cm^3 h^{-1})	0.10	0.25	0.44
Carbon dioxide flow (L min^{-1})	0.25	0.25	0.25

3.1.3.2. Analytical Procedure

Analysis of the ABE solvents was performed using a GC-2010 (Shimadzu, Japan) equipped with a thermal conductivity detector (TCD). Separation was effected in a 30 m RESTEK capillary column of internal diameter (ID) 0.25 mm coated with polyethylene glycol (film thickness 0.25 µm). Helium was used as a carrier gas at a flow rate of 2 mL/min and pressure of 150 kPa. The injector was maintained a temperature of 220°C and the TCD was kept at 250°C. The oven temperature program was maintained at 55°C at all times.

The calibration of the detector was conducted by preparing standard, known broth (ABE) solutions in distilled water and calculating the actual mass of ABE and water injected into

the GC. Lower level concentrations were obtained by diluting the standard solutions using acetonitrile. In each chromatogram obtained, the peak areas were used to calculate the mass of each component available and converting these to mass fractions and ultimately to concentrations using the density. Carbon dioxide was not quantified in the gas phase and all concentration values were reported on a carbon dioxide free basis. Good recovery and linearity was obtained for all the components. Calibration curves are shown in the Appendix A1.

3.1.3.3. Bubble Size Analysis

Bubble size analysis was carried out using Image Pro +6, which is an image processor. Pictures of the bubbles were taken as they rise through the ABE solution at the operating gas flow rate and these were analysed for size by making use of a calibration rod inserted in the stripping cell at the time of taking the picture. A sample of 30 bubbles was used in each analysis. Figure 3-4 shows one such picture of the bubbles as they leave the sparger as well as the calibration rod which is a 1/8 inch diameter gas pipe.

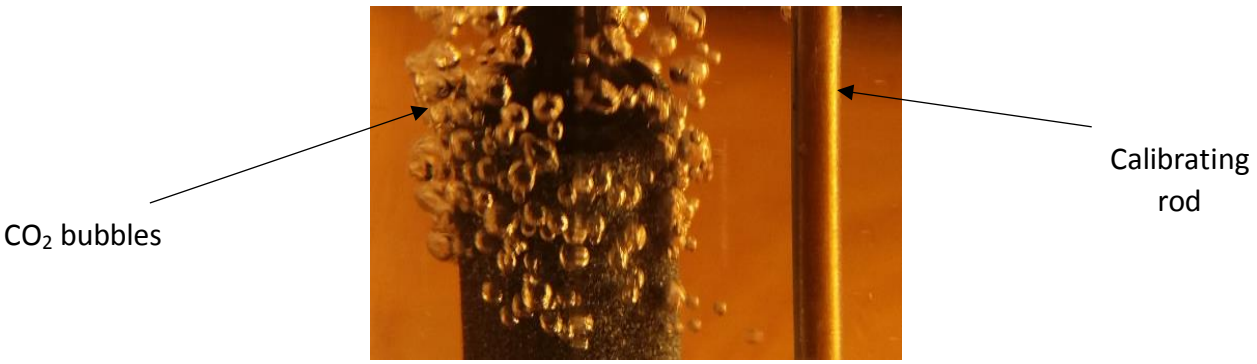


Figure 3-4: Carbon dioxide gas bubbles as they leave the sparger

3.1.4. Results and Discussions

3.1.4.1. Bubble Size Analysis

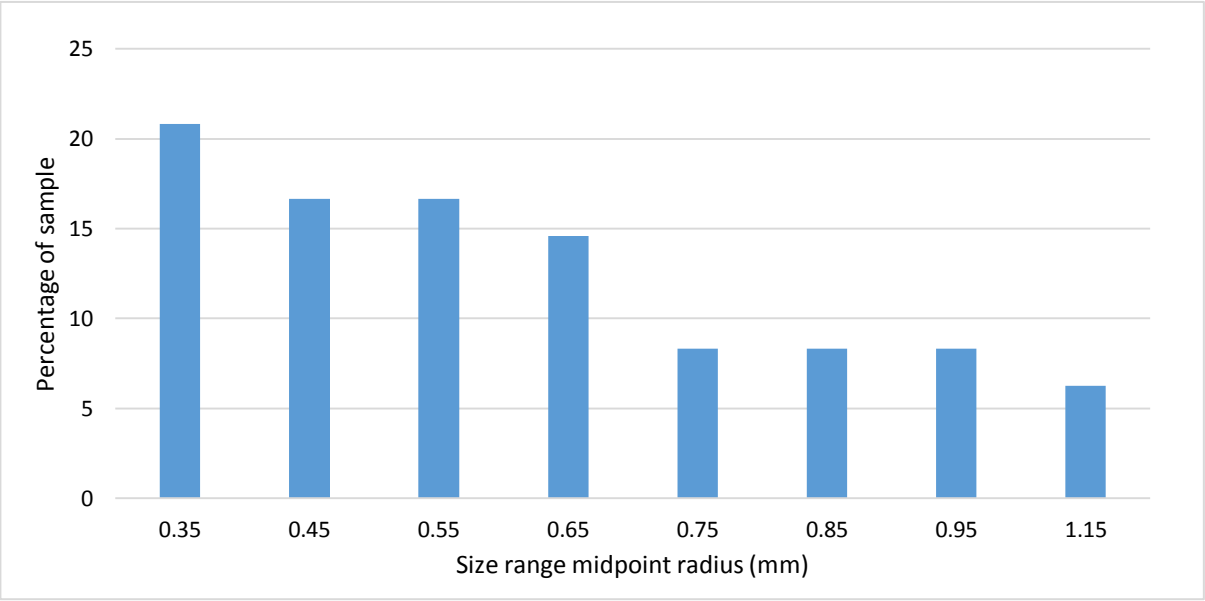


Figure 3-5: Bubble size analysis of the bubbles in the stripping cell

Bubble analysis showed that the sparger does not produce uniformly sized bubbles. Figure 3-5 shows the bubble size distribution obtained and bubbles with radii between 0.3 mm to 1.25 mm were produced. Around 90% for the bubbles have an overall radius of less than 1 mm. The difference in bubble sizes does not pose any mass transfer problem as long as the produced bubbles are small enough for quick butanol saturation during their contact time with the liquid phase (Ezeji et al., 2005). Comparing the size range above to the saturation time to bubble radius depicted on Figure 3-1, it can be seen that all the bubbles produced by the sparger would reach saturation by the time they reach the liquid surface in the 250 mL stripper cell. Acquainted with the bubble size analysis results and having established that all the gas bubbles were being saturated with the organics, experimentation was then proceeded to.

3.1.4.2. Unsteady State Gas Stripping

An initial model broth solution containing ABE in the ratio of 3:6:1 yielded the results shown in Figure 3-6.

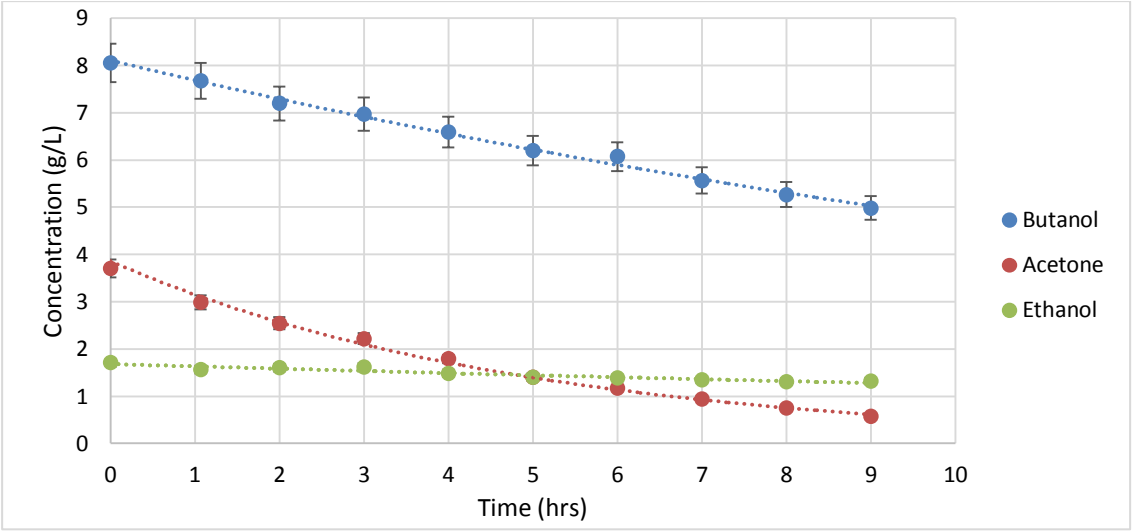


Figure 3-6: Unsteady state stripping of ABE solution with carbon dioxide at 0.25 L/min and T = 36 °C

The concentrations of the three solvents decrease smoothly and uniformly with time as carbon dioxide is sparged through the stripping cell. The ethanol concentration in the solution is low which results in a very low stripping rate; however, it was also observed that acetone is stripped much more easily out of the solution. The effects of the higher vapour pressure associated with acetone relative to ethanol (46kPa for acetone compared to 15.6 kPa for ethanol at 37°C) can be the reason for the trend observed. Generally, the trend obtained is synonymous to the relationships obtained for the stripping of organics from dilute solvents using gases carbon dioxide, nitrogen, oxygen or air (Xue et al., 2012, Xue et al., 2013).

The three components in the broth strip at different rates and to accurately load the cell for steady state concentrations of all three would require more robust equipment than available. In a real fermenter, it would not be any easier as microorganisms have a complicated production cycle which is affected by a number of variables which may not be in sequence with the required control system. A fed batch approach, integrated with gas stripping, can approach steady state much better but for a single product. Lu et al. (2012) approached fairly close to steady state concentrations for all the product concentrations in fed batch fermenter only after 72 hours of the process.

Figure 3-6 plots were, therefore, produced for simplified butanol-water solutions at each of the three concentration levels investigated. In the steady state modelling, the stripping

rates obtained from these plots were used to determine the cell loading rate required in each case.

3.1.4.3. Steady State Gas Stripping

Figure 3-7 shows the experimental steady state results using a simplified model broth of only butanol and water.

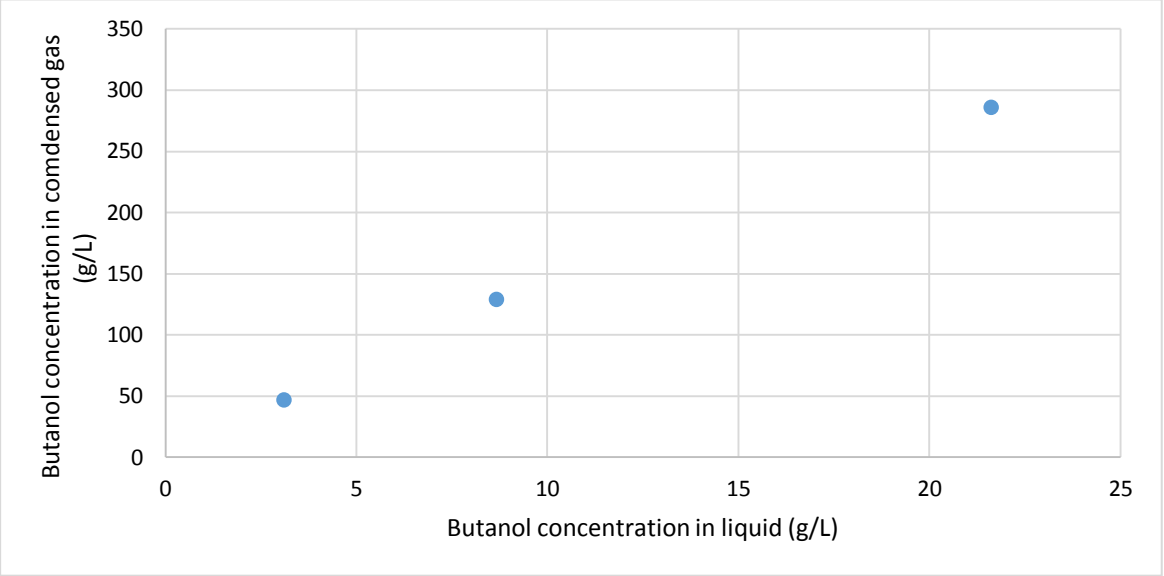


Figure 3-7: Experimental steady state stripping results, CO_2 at 0.25 L/min and T = 36 °C

The ordinate shows the concentration of the gas stream leaving the stripper cell (fermenter), evaluated on a carbon dioxide free basis. Ideally, this gas stream would be sent to a condenser to condense all the organics, followed by an analysis of the liquid condensate. This would have required a larger stripping cell in order to obtain a reasonable amount of solvent that would also be a good representation. The condensation of this gas stream was evaluated by means of an Aspen Plus® simulation as described in Section 4.5.1.1.

From Figure 3-7 one can get an indication of the expected output concentration from the stripper once a certain steady state butanol concentration is maintained in the fermenter. The establishment of such steady state concentration is not a trivial issue. It can be established by having a fed-batch control system that is able to operate in sync and in quick response to the microorganisms' activity on the fermenter.

3.1.5. Conclusions

The experimental results from this section of the gas stripping created a scenario based approach to steady state butanol concentrations in the fermenter, although it might not be practically feasible to obtain such controlled steady state concentration as used in the current experiments, if an average value of concentration can be approached, the results of Figure 3-7 can be used to estimate the expected gas phase compositions.

The next task was then to include this gas stripping stage in full scale process simulation for economic performance analysis. How this gas stripping stage was simulated on Aspen Plus® and how the results obtained from the simulation flowsheet compare with the experimental results is explained in Section 4.5.1.1 after giving the details on how the simulator works and its shortcoming and limitations.

3.2. Liquid-Liquid Extraction

3.2.1. Introduction

As previously mentioned, the use of liquid-liquid extraction in the recovery of biobutanol has shown great potential in improving the economics of the process. When used directly in the fermenter, liquid-liquid extraction increases the productivity of the fermenter system which reduces the fermenter sizes (major reduction in capital costs). When used downstream to fermentation, extraction reduces the amount of water that is sent to the downstream distillation columns. This reduces the utilities required in the reboilers as well as the size of the downstream distillation columns (both a reduction in capital and operating costs).

Liquid-liquid extraction, as a separation technology, is developed and has been applied at industrial level. For the case of biobutanol, industry level production that involves extraction has not been reported on. However, laboratory investigations have shown that equipment such as the Karr reciprocating-plate extraction column can be successfully used and applied in the extraction of biobutanol (Roffler et al., 1987, Roffler et al., 1988) and the fabrication and scale-up of such equipment has been reported to be relatively straight forward (Karr, 1959). Considering these advantages of liquid-liquid extraction and the level and state of

research, extraction experiments were carried out to choose a solvent to use in the extraction column design included in one of the processes for techno economic analysis.

Broadly speaking, the aim of the experiments was to have a quick way of evaluating a potential solvent for biobutanol extraction. The results were also important in improving the simulation results of an extraction column which in previous studies have been performed by using separation factors on Aspen Plus® (van der Merwe, 2010). The solvents' extractive properties evaluation was done using the partition coefficient and the selectivity.

The partition (or distribution) coefficient and selectivity of a solvent can be used to determine its extractive performance. A high value of the distribution coefficient is an indication of the high affinity for butanol and, therefore, leading to a low solvent/feed ratio. The distribution coefficients are evaluated from the equilibrium weight fractions in the aqueous phase (*aq*), the raffinate, and the extract or organic phase (*org*). Equations 3-5 and 3-6 give the calculation of the distribution coefficients of butanol and water after equilibrium has been established.

$$K_{BuOH} = \frac{[BuOH]_{org}}{[BuOH]_{aq}} \quad [3\text{-}5]$$

$$K_{H_2O} = \frac{[H_2O]_{org}}{[H_2O]_{aq}} \quad [3\text{-}6]$$

The selectivity is given by the ratio of the distribution coefficients. It is a measure of the preference of the solvent for butanol over water. The selectivity of a solvent for butanol shows how much of water (undesirable) is also extracted into the solvent phase together with the butanol (desirable). The higher the selectivity, the better the extractive properties of the solvent.

$$S_{BuOH} = \frac{K_{BuOH}}{K_{H_2O}} \quad [3\text{-}7]$$

The experimental values of K_{BuOH} and S_{BuOH} (Equations 3-5 and 3-7) can be directly used in Aspen Plus® for an extraction column design as demonstrated by Garcia-Chavez et al. (2012) by making use of the K_{LL} correlation subroutine. The experimental results obtained in this section were applied as such as described in Section 4.5.2.

3.2.2. Solvent Selection

Several solvent selection criteria and procedures have been reported and applied in literature to obtain the ideal solvent for butanol extraction from fermentation broth. Broadly speaking, the selection of an ideal solvent for extraction of fermentation products from broth considers the following factors (Vogel and Todaro, 1996):

- Capacity and selectivity
- Availability
- Immiscibility with the feed
- Density differential
- Reasonable physical properties, e.g. high viscosity impedes mass transfer and capacity
- Toxicity
- Corrosiveness
- Ease of recovery
- Price

For the particular case of biobutanol, solvents for butanol extraction have be selected mainly based on their capacity and selectivity for butanol as well as the toxicity to the microorganism, i.e. if contacted *in situ* (in the fermenter). For extraction that occurs downstream to the fermenter, solvent solubility in water and toxicity will not offer any hazard to the microorganism in the fermenter although an extra recovery step might be necessary.

A number of solvents selection methods for biobutanol recovery have also been employed. Some of these solvent screening methods include estimating capacities by using UNIFAC coefficients (Kollerup and Daugulis, 1985, Gmehling and Schedemann, 2014) and the use of computer-aided molecular design.

Table 3-2 gives the properties of butanol and the five solvents for which the distribution coefficients and selectivities were successfully measured. It has been shown in literature that alcohols exhibit higher values of distribution coefficients, with oleyl alcohol being the most reported solvent of choice. This is because oleyl alcohol is one of the few alcohols that are non-toxic to clostridia (Stoffers et al., 2013). Alkanes are also a group of compounds that

are relatively non-toxic, however, they exhibit low distribution coefficients (Kim et al., 1999, Stoffers et al., 2013).

Table 3-2: Extraction solvents and properties, as compared to butanol

Solvent	Melting point (°C)	Boiling point (°C)	Density (g/ml)	Solubility in water	Purity or Assay
Butanol	-89	117.7	0.810	73g/L	≥99.95%
Oleyl alcohol	15	330	0.845	Immiscible	85%
2-ethyl-1-hexanol	-76	183	0.833	0.7g/L	≥99%
1-octanol	-16	195	0.824	0.46 g/L	≥99.95%
Diethyl carbonate	-43	127	0.975	Insoluble	≥99%
Hexyl acetate	-80	155	0.8673	0.4 g/L	≥98%

It was also of interest in this study to include solvents that have already found applications in the biorefinery arena, even if they may not possess ideal properties (such as too high a density in the case of diethyl carbonate) for the extraction from aqueous solution. The reason for this approach is that once the basic properties are understood, molecular design principles could be used in the future to devise an optimised solvent featuring the required functionality. The use of such biorefinery-based solvents enables the production of chemicals that meet a strict processing route, e.g. in the case where a 100% “green” or sustainable product is required and specified. Additionally, if this solvent can be produced from other feedstock in the biorefinery, it means it comes at a cost of production rather than the market price.

Diethyl carbonate has been used for extraction in the production of xylan from biomass (Kavakka and Gramstrom, 2016). It has also been used in the recovery of biopolymers (polyhydroxyalkanoate) produced from biomass (Noda and Schechtman, 1999). Diethyl carbonate (as well as dimethyl carbonate) has also been regarded as a ‘green’ solvent (Fischmeister and Doucet, 2011).

Hexyl acetate is a sweet smelling ester and by its composition could be produced in a biorefinery. Although a number of esters have been considered and investigated for butanol extraction, hexyl acetate is not reported anywhere and just by looking at its properties, it was considered a feasible solvent for extraction.

Other solvents which were initially considered include diethyl succinate, ethyl levulinate, isoamyl alcohol, methyl-isobutyl ketone and valerolactone. These solvents belong either to a class of solvents that have already found application in biorefineries or could be possibly made from biomass. However, they were discarded as solvents for butanol extraction based on density and solubility in water or by having too close boiling points to butanol which would make the downstream solvent recovery impossible or too expensive.

3.2.3. Experimental Procedure

A procedure similar to that used by Gonzalez-Penas et al. (2014) for solvent screening for *in situ* ABE extractive fermentation was employed for all solvents reported in Table 3-3. Equal masses of the organic and aqueous phases were added into graduated cylinders (tubes) with tightening caps such that the total volume was between 4.5 and 5 mL, in each. The starting aqueous phase was a standard solution of 1.2 wt. % butanol in water, which represents the final tolerable butanol concentration in typical fermenters (Jones and Woods, 1986).

The tubes were vigorously shaken in a horizontal position for 4 hours to enable the formation of emulsion of both phases. The tubes were then allowed to settle in a vertical position for 24 hours in a temperature controlled water bath at 30$\pm$1°C. Before the organic and the aqueous phases were removed for analysis, the final volumes of the aqueous and organic phases were read off the graduated cylinder.

3.2.4. Analysis and Analytical Procedure

The following mass balance can be formulated:

$$[BuOH]_0.V_0 = [BuOH]_{aq}.V_{aq} + [BuOH]_{org}.V_{org} \quad [3\text{-}8]$$

V_0 represents the initial volume of the contacted aqueous phase and its respective butanol concentration, $[BuOH]_0$, while V_{aq} and V_{org} are the final volumes of the final aqueous (raffinate) and the organic phases, respectively.

At equilibrium, Equation 2-8 reduces to:

$$\frac{[BuOH]_0}{[BuOH]_{aq}}.V_0 = V_{aq} + K_{BuOH}.V_{org} \quad [3\text{-}9]$$

Gas Chromatography (GC) was used to determine the final butanol concentration in the raffinate. As was the case for gas stripping experiments, a GC-2010 (Shimadzu, Japan) equipped with a thermal conductivity detector (TCD) was used. Separation was effected in a 30 m RESTEK capillary column of internal diameter (ID) 0.25 mm coated with polyethylene glycol (film thickness 0.25 µm). Helium was used as a carrier gas at a flow rate of 2 mL/min and pressure of 150 kPa. The injector was maintained a temperature of 220°C and the TCD was kept at 250°C. The oven temperature program was maintained at 55°C at all times.

Initial tests were performed to determine if any solvent would be detectable in the raffinate phase at the end of the settling period. For the solvents shown on Table 3-2, they were not detectable and this was also confirmed by NMR analysis (the limit of detection of 1H NMR spectroscopy is estimated to be < 1 mol. %). The raffinate phase, therefore, consisted of only water and butanol. Figure 3-8 shows the TCD detection of the raffinate butanol-water compositions. The calibration follows the area ratio method suggested by Raal and Mühlbauer (1998). The full details are given in Appendix A2. A recovery of 105% was obtained. Each phase was injected 3 times.

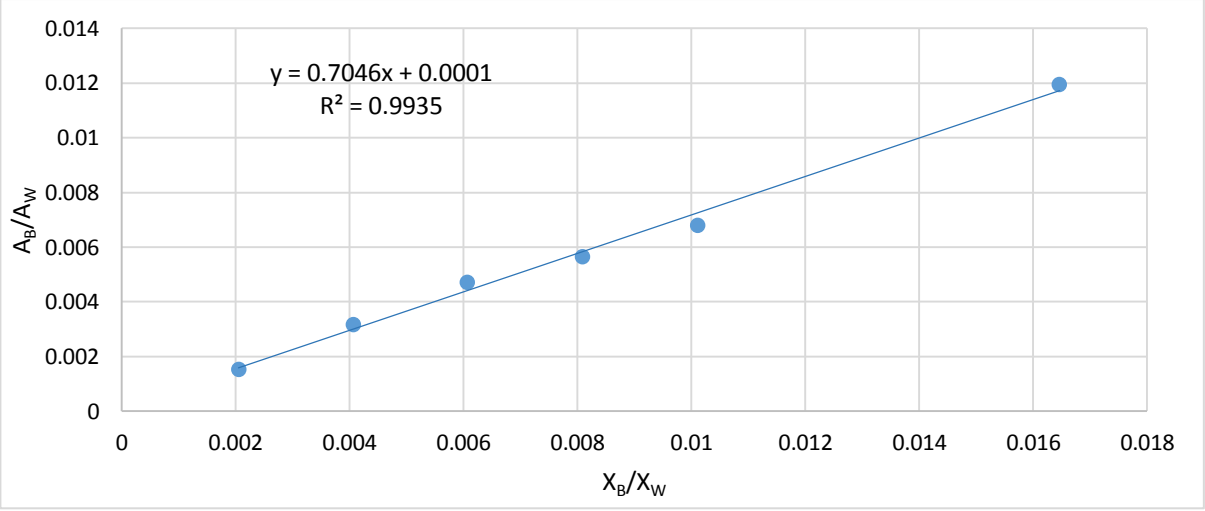


Figure 3-8: Extraction experiments butanol-water calibration

In order to calculate the water distribution coefficient, a Karl Fisher Moisture Titrator (MKS-500) was used to determine the water composition in the final organic phase.

3.2.5. Results, Discussions and Conclusions

Table 3-3 gives the results of the extraction experiments that were successfully carried out with the five solvents. For the repeat analyses on all the samples, the relative standard deviations, given by Equation 2-10, were all below 10% indicating a good reproducibility. The raw data is reported in Table A1 (Appendix A).

$$\frac{Standard\ Deviation}{Average} \times 100\% \qquad [3\text{-}10]$$

The validation of the extraction experimental method and analysis was performed by comparing the distribution coefficients reported in literature for oleyl alcohol and those obtained from the current study. This is because oleyl alcohol remains the most reported on and benchmarking solvent for butanol extraction. Furthermore, in the case of 2-ethyl-hexanol, experimental results reported by Ghanadzadeh and Ghanadzadeh (2004) were plotted together with the results from the current study to see how close these values lie on the binodal curve.

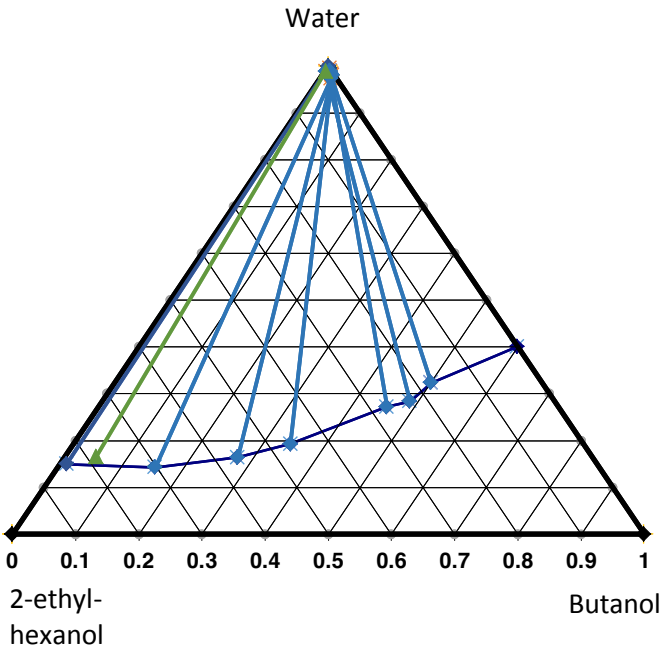


Figure 3-9: Literature (Ghanadzadeh and Ghanadzadeh, 2004) (◆) and current study (▲) water-butanol-2-ethyl-hexanol LLE data at 30°C

Figure 3-9 shows how the experimental results reported by Ghanadzadeh and Ghanadzadeh (2004) (in mole fractions) compare to the results obtained using the method used in the current study. Only experimental results data points are shown as these were also successfully correlated and modelled using the UNIQUAC property method. Figure 3-9 shows that the measured data point lies very close to the binodal curve and that the

direction and gradient of the tie line is also in the same order. From Figure 3-9 as well as the distribution coefficient values reported in Table 3-3 it can be concluded that the experimental method was sufficient to provide for a quick way of selecting potential solvents for butanol extraction. The obtained slight differences can be attributed to a number of factors including the differences in temperatures at which equilibrium is established. The extractive properties of a solvent vary with temperature as other properties like viscosity and density vary as well. The other source of the differences could be the purity of the chemicals that were used which is not always reported in publications.

The two new solvents that were investigated for the distribution coefficients show potential to compete with the conventional alcohols. As mentioned, higher alcohols as a class of compounds have been found to be good extractants for butanol. The obtained distribution coefficient of hexyl acetate (3.57) is almost equal to that reported for butyl acetate, i.e. 3.58 (Kim et al., 1999). The two compounds are similar ester compounds, which explain their similar extractive properties. It is always worth noting that the extractive properties of the 2 new solvents are almost the same to much better than oleyl alcohol, as the case for diethyl carbonate.

Table 3-3: Liquid-liquid extraction experimental results

Solvent	Current Work (30°C)		Literature			
	K_{BuOH}	S_{BuOH}	K_{BuOH}	S_{BuOH}	T(°C)/BuOH conc.	Reference
Oleyl alcohol	3.90	237	3.97	-	25°C /1.5wt%	Malinowski and Daugulis (1994)
			4.57	294.7	24°C /1.5wt%	Gonzalez-Penas et al. (2014)
			4.30	-	37°C/1.3wt%	Ishii et al. (1985)
			3.42	194	25°C/1wt%	Garcia-Chavez et al. (2012)
2-ethyl-1-hexanol	8.50	215.38	7.95	311.1	24°C /1.5wt%	Gonzalez-Penas et al. (2014)
			6.10	276	28°C/2 % vol	Kim et al. (1999)
1-octanol	6.12	95.97	5.6-7.33	-	-	Kim et al. (1999)
			10	130	37°C/2wt%	Groot et al. (1990a)
Hexyl acetate	3.57	367.09	-	-	-	-
Diethyl carbonate	6.15	396.00	-	-	-	-

Although the 24hr settling time was sufficient for complete phase separation in all cases, hexyl acetate and diethyl carbonate required more time than the alcohols. This can be attributed to their densities (Table 3-2) that are almost equal to water, which makes phase splitting not as spontaneous as when a much lower density extractant is used. Duration of phase splitting is of paramount importance when a multistage extraction should be applied (Stoffers et al., 2013) and realistically, multistage extraction equipment would need to be applied in the current case. The use of these two solvents would only make sense, therefore, if they are readily available in the biorefinery as by-products of other processing

steps or as products available at nearly no cost. This would be an economic motivation that offsets their undesirable density properties. Alternatively, these solvents can be designed e.g., dibutyl carbonate can be made from biorefinery-based products.

Although oleyl alcohol has historically been reported as a benchmarking solvent for butanol extraction, the current measurements confirmed that 2-ethyl-hexanol has superior extractive properties to oleyl alcohol. The toxicity of this solvent was not an issue of concern in this current study as the extraction would not be performed directly in the fermenter. 2-Ethyl-hexanol was, therefore, used as solvent for extraction in this current study. Another motivation towards the use of this solvent was the fact that it has been previously used in the extraction of biobutanol from molasses and included in a full techno economic analysis (Van der Merwe et al., 2013). The process that includes this extraction column was found to be the most economically viable process. It was, however, reported that the simulation of the extraction column was not performed with accuracy due to the lack of distribution coefficient data (van der Merwe, 2010). Using the same solvent in this current study improves the simulation as well as contextualises this process to investigate if the same profitability reported can be obtained even when a different substrate is used, e.g. clear juice as used in this current study.

The use of 2-ethyl-hexanol in this current study in the extraction column design is explained in Section 4.5.2. It is important to note that this is just an example of how such a solvent can be used in the simulation when the distribution coefficients are known. By looking at a number of solvents that have been investigated for the recovery of fermentation products from broths (Kim et al., 1999), it is clear that one solvent cannot have the same extractive properties towards the different valuable broth components. For example, 2-ethyl-hexanol has very low capacity for acetone and ethanol (Kim et al., 1999). When all the broth components are of value and need to be recovered by extraction, one would have to think towards using a mixture of solvents or more effectively, the use of ionic liquids that can be tailor made to suit the specific application. The work presented in Chapter 6 will be extended to work towards such a designed solvent for the separation of ABE fermentation products.

4

CHAPTER FOUR

4. SIMULATION METHODS AND ECONOMIC ANALYSIS APPROACH

This chapter begins with an outlook on the overall strategy that was employed to meet the study objectives. This is followed by a brief outlook of the advantages and limitations of the tool that was used to simulate the processes i.e. the Aspen Plus® software. It then goes on to describe and explain the methodology that was applied first for the simulation of the individual unit operations within the considered processes on Aspen Plus® and then the overall approach to the economic assessment. Also included is the equipment sizing and cost estimation.

4.1. Overall Strategy to Study

To meet the objectives of the study, and based on the studies reported in literature, four process schemes were considered. These processes were simulated and techno economic analyses performed in order to determine their potential profitability. Results from the experimental work reported in Chapter 3 were used as inputs and validation of the simulation results obtained. The four processes were designed to produce fuel grade biobutanol (at least 99.5 wt % butanol) and the other two co-products (acetone and ethanol) to the highest purity which could possibly be attained in each case. The techno-economics of investing and operating the four processes were assessed to decide on the process alternative to include into the sugarcane biorefinery.

Process Scheme 1 represents the conventional five column distillation trail for biobutanol recovery and this was used as the benchmarking case. This process is suitable for benchmarking as it is the most reported process in literature and number of economic evaluations has been reported on (Lenz and Morelra, 1980, Roffler et al., 1987, van der

Merwe, 2010, Naleli, 2016). Process Scheme 2 consists of recovery by single stage gas stripping followed by distillation. This was meant to ascertain the actual gain that gas stripping affords to the process. In Process Scheme 3, gas stripping was followed by liquid-liquid extraction (and subsequently, distillation). This is a process scheme that was found to be profitable by Van der Merwe et al. (2013) using molasses as a carbon source. It was, therefore, included in this study to ascertain if it holds using a different carbon source in the mill as well as standardising the process to the same assumptions and methods. Generally, it is difficult having to compare different processes simulated by different research groups as the underlying assumptions, design approach and methodology as well as the availability of the data are usually different in each case. The strength of this current study is that it includes an experimental part of the extraction experiments, which were not successful in the study by van der Merwe (2010), as well as an the experimentally validated gas stripping model.

The incorporation of a two-stage gas stripping as suggested by Xue et al. (2013) was investigated in Process Schemes 4. The two-stage gas stripping has not been included in any full-plant techno economic analysis to date.

4.2. Simulation on Aspen Plus®

Aspen Plus® (Version 8.6) software, was used as the simulation tool in this study in order to predict the performance of the biobutanol recovery schemes. This, ultimately, allowed for the identification of the best economically viable scheme for higher value chemical production that can be appended to an existing sugar mill. Aspen Plus® is currently the industry market-leading process simulation environment (Bonomi et al., 2015). It can solve a large number of equation sets that are encountered in process development in, typically, a very short space of time. It has a refined user interface and online component databases which makes it a better tool than programming languages like MATLAB® and C++. These mathematically based programming languages (e.g. MATLAB®) also have limitations in the number of the main equipment items they can model (Gorgens et al., 2015). Aspen Plus® allows for a rigorous process definition, equipment and utility requirements and the outputs from the models are inputs to the economic analyses for a preferred process scheme.

In the Aspen Plus® simulator, modelling tools are used to perform rigorous material and energy balances and other underlying physical relationships (e.g. thermodynamic equilibrium, rate equations) are also applied in the prediction of process performance (e.g. operating conditions and equipment sizes). It is, however, critical to understand the fundamental models, methods and data sets that the simulator is using as this determines how much the results can be trusted and relied on. The right choice of the physical property method is important, which is a collection of all equations used to estimate the properties. Contained in each method are equations to calculate properties like enthalpy, density etc. Phase equilibrium calculation methods are also contained in the chosen property method. Property methods range from equation of state models to activity coefficient models and special methods that have been designed for specific applications (e.g. API Sour-Water Method).

The system under consideration in this study is highly complex, consisting of possibly carboxylic acids (by products: butyric and acetic acids), polar alcohols (ethanol and butanol), water and gases above their critical temperature (CO_2 and H_2). This makes it impossible for one property method to correctly represent the biobutanol recovery and purification process at all its stages. However, the non-random two-liquid activity coefficient model using the Hayden-O'Connell model for the vapour phase (NRTL-HOC) was deemed sufficient for the current application (except for gas stripping as explained in Section 4.5.1). By means of regression of experimental data, especially as measured by Stockhardt and Hull (1931), literature has validated the appropriateness of this physical property method (van der Merwe, 2010, Mariano et al., 2011). The NRTL is used to predict highly non-ideal liquid mixtures and the HOC equation predicts solvation of polar compounds and dimerization in the vapour phase which occurs with carboxylic acids (acetic and butyric acid). It has also been shown that the NRTL model is able to describe the vapour-liquid equilibria and especially the miscibility gap in systems containing water, alcohol and ionic liquid (Stoffers et al., 2013). This will be important as this study continues according to the proposal in Chapter 6.

The analysis on Aspen Plus® is steady state based and this allows for the assessment of energy efficiencies for different operating points. There is, however, no guarantee that the economic optimum that results from this assessment is indeed the global optimum. For

example, in the case of distillation columns, the attainment of steady state conditions is determined by the effectiveness of the control system. It might, however, happen that the determined steady state economic optimum is not necessarily attainable due to controllability issues (Nelson, 2012) and hence, the controllability of steady state design must be evaluated via dynamic simulation (Seader et al., 2004). This was not included in the scope of the current study but is necessary for the final design that is put forward for implementation.

Another shortcoming of the simulator is the reduced interaction with the problem and this can possibly lead to the user missing some crucial concepts of the problem (Gorgens et al., 2015). This calls for a critical understanding of the problem statement before approaching the simulation environment for all the different processes and unit operations. Additionally, for other unit operations, no reliable property databanks are currently available. As an example, membrane operations (pervaporation) could not be included in the current processes as there are no reliable parameters for the membrane describing concentration, temperature and permeate pressure tendencies (Stoffers et al., 2013). Experiments would have to be conducted in order to obtain these.

Despite the noted shortcomings of the software, Aspen Plus® remains an invaluable tool for process development in research and development and was used extensively in this study as it provides a risk-free analysis of what-if scenarios (Gorgens et al., 2015). Aspen Plus® flowsheets were created and the results enabled for a quantitative comparison of the considered four process configurations. Although some laboratory experiments were included in the study, the use of the software cut down on the possible number of experiments that could have been considered. For example, it was not necessary to measure the VLE data of all the component systems as necessary for distillation column designs as such data is already contained in Aspen Plus® databases. The optimised process schemes on Aspen Plus® were used for energy and economic performance comparison. Another advantage of using Aspen Plus® in this study arises from the fact that there is a South African generic sugar mill that is being modelled on Aspen Plus® (Guest, 2017) and combining results from this current study to that sugar mill model will allow for the analysis of the economics of the overall sugarcane biorefinery with great ease and flexibility.

4.3. Determination of the Plant Capacity

One of the unique and fundamental works being carried out by the SMRI Sugarcane Biorefinery Research Team is the development of an Aspen Plus® based South African generic raw sugar mill. Previously, a MATLAB® based model was developed by the SMRI as part of the Bio-refinery Techno Economic Modelling (BTTEM) project which was a part of the Sugar Technology Enabling Programme for Bio-Energy (STEP-Bio)[3] (Starzak and Davis, 2016). The conversion into an Aspen Plus® will provide a model to which a number of future biorefinery downstream models can be appended to assess how the overall economics of the sugar mill will be impacted.

Preliminary results from the Aspen Plus® based generic sugar mill model were used to determine the plant capacity in this study. A brief description of the sugar production process is given for context before going into the results from the model that was used.

4.3.1. Raw Sugar Production Process

A typical sugar production process in South Africa consists of five stages, which are: juice extraction, clarification, evaporation, crystallization and sugar drying. As shown in Figure 4-1, before sucrose (sugar) is extracted from the cane, cane is prepared for extraction by means of cane knives and/or shredders, to make the sucrose accessible. The bulk of sugar mills in South Africa make use of chain diffusers for the extraction process. Sucrose is leached from the sugarcane by spraying hot water onto a moving bed in a counter current flow pattern. Typically, a diffuser consists of 10 to 18 stages (Rein, 1995). The extracted sucrose leaves the diffuser as draft juice while the fibre of the cane, bagasse, is dried and typically taken to boilers for steam production.

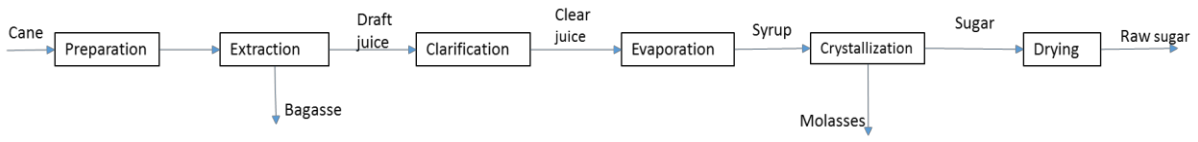


Figure 4-1: Flow diagram of a typical raw sugar mill

[3] A private-public partnership co-funded by the Department of Science and Technology (DST) and the South African Sugar industry under the DST's Sector Innovation Fund.

The clarification stage aims to remove the impurities in the draft juice. The clarification process is enhanced by the addition of chemicals like lime to remove suspended solid particles which settle as mud and are filtered. The resulting clear juice is then sent to the evaporators where the sucrose is concentrated. The concentration process takes place in multiple effect evaporators and the resulting concentrated stream (now called syrup) is sent for crystallisation.

The crystallization process (consisting of a series of crystallisation pans, centrifugals and re-melters) is usually carried out in three stages and aims to crystallise the maximum amount of sugar possible from the syrup. The process is improved by the addition of seed grains or semi-crystallised slurry. The final residue of the process is referred to as molasses. In the final drying stage, the surface moisture content of the sugar crystals is reduced by means of evaporation. The final raw sugar is a final product that can be sold but it can also be further refined to make white sugar.

4.3.2. Plant Size Design Basis

To determine the plant size for the downstream biobutanol production, streams in the sugar mill model were analysed for compositions. Table 4-1 gives the preliminary results from the Aspen Plus® generic sugar mill model (Guest, 2017). Stream flows and compositions are given in relation to the sugar production process described in Section 4.3.1 above. To find the basis for the designs in the current study, streams from Table 4-1 were analysed for composition and compared to what fermentation requires. As previously mentioned, traditional butanol fermenters use up to a maximum of 60 g/L (~ 6 wt %) sugar solutions (Jones and Woods, 1986) while in fermenters that incorporate continuous gas stripping, concentrations of up to 600 g/L (approximately 50 wt. % sugar) have been used (Xue et al., 2012). That means from the draft juice stream, all streams will need to be diluted if they are to be directed towards batch fermentation, but there is no need for dilution in the case of gas stripping coupled fermentation. The clear juice[4] stream was, hence, chosen to be the carbon source in the current study. This was based on the mentioned sugar concentration and also on the fact that suspended solids and other impurities would have been removed as these might interfere with the fermentation microorganisms.

[4] Draft juice is transferred to a mixed juice tank along with filtrate juice (recycled from vacuum filters) and sludge (recycled from syrup filter). Together, these leave the mixed juice tank and are called mixed juice.

Table 4-1: Preliminary flow results from the sugar mill model

Item	Overall throughput ($t\ h^{-1}$)	Composition (wt %)				
		Water	Sugar (Sucrose)	Non-sugar (Glucose and Fructose)	Fibre	Lime
Cane	244.18	68.53	14.17	2.24	15.06	-
Mixed (draft) juice	313.46	85.61	12.02	1.97	0.35	0.05
Clear juice	281.67	86.32	11.83	1.85	-	-
Syrup	58.20	35.20	55.90	8.90	-	-
Raw sugar	28.86	0.08	99.17	0.48	-	-
Molasses	10.89	20.19	32.45	46.63	-	-

How much biobutanol (and subsequently, the higher value ester product that can be produced from it) is produced is dependent on the demand and commodity prices of the ester product, raw sugar and any other co-product coming from the biorefinery at that point. Therefore, in this economic analysis, an arbitrary basis was chosen in which all of the clear juice stream is taken to biobutanol production-the largest possible scale (at mill level) and hence a scenario benefiting from economies of scale. The inclusion of the biobutanol into the raw sugar mill model, at a later stage, will enable the determination of the economic impact of this particular scenario.

This, however, still leaves the option to select a different stream at a later stage if a lower volume, higher value product has come into focus. This will be done as more information is gathered following the proposal outlined in Chapter 7 and the finalisation of the Aspen Plus® sugar mill model. Additionally, since clear juice is specified as the carbon source, the current analysis is based on the normal length of milling season of 36 weeks. Historically, the milling season in South Africa ranges between 34 and 38 weeks (Moor and Wynne, 2001). In the off-seasons, a different raw material can be considered but this comes with different productivities (from another strain) and assumptions which cannot be simultaneously included in this current study.

4.4. The Fermentation Process

To begin with, fermentation as a process or unit operation was not simulated on Aspen Plus® but was included using a theoretical calculation to account mainly for the cost of fermenters and the output flows. Same values of fermenter cost cannot be used for all the scenarios as technologies like gas stripping have been shown to reduce fermenter sizes compared to the conventional batch case (10-fold higher sucrose concentration). Previously, studies have been carried out where the fermentation process was simulated by making use of the simplified stoichiometric equations of Section 2.1 and assigning fractional conversions to match results from a certain fermenter (van der Merwe, 2010). As argued in the case of gas stripping, this limits the applicability of such a model in the case where a different carbon source has to be used to the one reported for that fermenter. Also, the model does not have predictive abilities when conditions are slightly changed. For the fermenter model to be predictive on Aspen Plus® there is the need for well-known kinetics that are studied and obtained from experiments and cover a wide range of scenarios.

Additionally, in these previous simulations, the fermenter is modelled as one big reactor with the required outputs (van der Merwe, 2010). Databases were then consulted and offshore calculations were then performed to determine the number of fermenters required to meet the reactor designed based on realistic fermenter sizes. This also means that the costing of these fermenters is done external to the simulator, and that the simulator only produces a broth stream that meets some literature specifications. For the current study, several publications were consulted and average values of the sugar utilization, butanol yield and the reactor productivity were used to determine the fermenter sizes for a given process scheme. Since it was the amount of the carbon source (clear juice) that was constant in all the process schemes analysed, fermenter sizes are the same for all the processes involving gas stripping and only different in the base case conventional (batch) fermentation process.

The fermenter parameters, which determine the broth compositions, for the conventional base case were determined by using productivities as well as product yields. This was the simplest case because batch fermentation is allowed to reach completion (once the inhibition is strong enough to kill the clostridia) before purification is employed. In the case

of processes involving gas stripping, productivities that are reported are based on the condensed stream that is obtained. These productivities neither indicate the productivity in the isolated fermenters nor do they report the effectiveness of the gas stripping process in recovering the produced organics. For this reason, in the case of gas stripping, sugar utilization and yields were used to both determine fermenter outputs and sizes.

Also important to note is that under the STEP-Bio programme, the University of Cape Town (UCT) is undertaking work on improving the biobutanol fermentation efficiency and to develop kinetics that can be used in the simulator. This work is ongoing and collaboration plans are in place to take the developed kinetics and include them in the simulation. This will be important especially for the reactive extraction work that is proposed in Chapter 7 of this dissertation.

4.5. Processes Simulations

The process simulations relate to how the individual blocks and unit operations in the four process schemes that were considered were actually sized and simulated on Aspen Plus®. Equally important is the costing of these blocks and their contribution towards the purchased equipment costs.

4.5.1. Gas Stripping

The simulation of the gas stripping and its inclusion into the processes for economic analysis followed the experiments conducted and reported in Section 3.1. The term “first gas stripping stage” refers to gas stripping that is integrated and conducted in the fermenters as the ABE organics are produced making use of the fermentation gases. This improves the fermenter productivities as the inhibition effects of butanol are reduced. Where applicable, the second gas stripping stage refers to gas stripping conducted outside the fermenter, i.e. on the condensate from the first stage gas stripping. This is meant to reduce the amount of water sent to the downstream purification steps.

4.5.1.1. First Gas Stripping Stage

Following the steady state experimental modelling of the gas stripping integrated fermentation, the task was to develop an Aspen Plus® model simulation (flowsheet) that would sufficiently predict the results for the whole range covered by the three

concentration levels considered. Since gas stripping has been described as a one-equilibrium-stage distillation (Seader and Henley, 1998), initially, a single flash drum on Aspen Plus® was considered using the NRTL-HOC method. Table 4-2 shows the results obtained from a simulation that assumes a steady state ABE concentration of 5 g/L. The condensate from the flash was compared to the results reported by Ezeji et al. (2004) as a starting point, as this was the same model used and reported by van der Merwe (2010). As it can be seen in Table 4-2, the single flash drum was not sufficient to predict the gas stripping. The same insufficiency was reported by van der Merwe (2010) who, however, obtained a better prediction by changing the property method to Soave-Redlich-Kwong (SRK) equation-of-state. An attempt to use of the SRK equation of state together with a single flash drum gave even lower concentrations than those reported in Table 4-2.

Table 4-2: Gas stripping results using flash drum and NRTL-HOC (ABE concentration: 5 g/L)

Component	**Mass fractions in condensate**	
	Ezeji et al. (2004)	**This Work: NRTL-HOC**
Acetone	0.078	3.873×10^{-3}
Butanol	0.152	0.012
Ethanol	0.003	8.407×10^{-4}

This led to the conclusion that a single equilibrium stage cannot represent the process sufficiently. A feasible explanation to this hypothesis is that of back-condensation. As the gas moves in the liquid and from the top of the liquid in the stripper cell (and in practical fermenters), it is possible that some of the gas condenses back into the liquid. Condensation of parts of the gas results in more than one equilibrium stage in the stripper being established with the actual number of established stages being difficult, or impossible to determine practically.

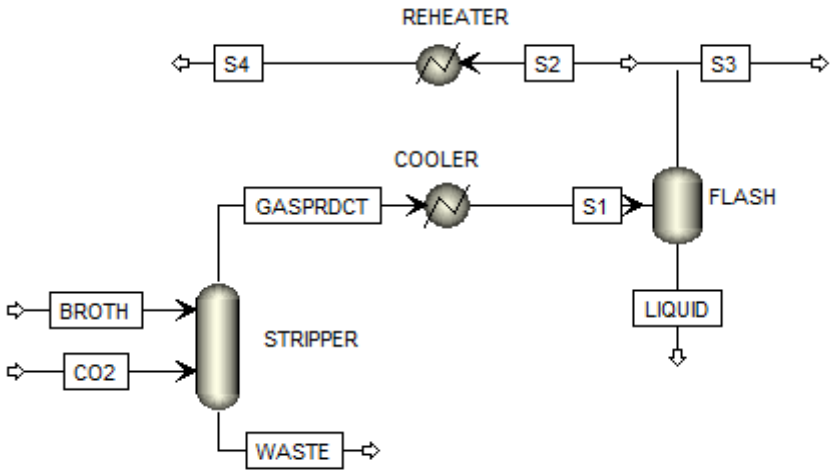


Figure 4-2: Screen shot of the first stage gas stripping model on Aspen Plus®

Ultimately, the first stage was successfully simulated and modelled as a RadFrac stripper column using the SRK equation of state. Figure 4-2 shows the screenshot of the Aspen Plus® flowsheet of the first stage gas stripping. The stripper column consists of 4 equilibrium stages, without a condenser and reboiler. The fermentation broth is fed into the top of the column (on stage 1) while the carbon dioxide is added from the bottom of the column (on stage 4). The stripping unit is only a tool to make a prediction on the composition of the resulting gas from the fermenter but it does not add to the cost of the process as it is not physically available.

The process begins with a fermentation broth containing the ABE (or initially just butanol) solvents in water as well as a stream of carbon dioxide being contacted in the stripper. The gas stream from the top of the column (GASPRDCT) containing mainly carbon dioxide as well as the stripped organics and water is sent to a cooler operating at -10°C and 10 bar for possible complete condensation of water and the ABE. The cost of electricity use in gas compression was taken into account in the economic analysis. The flash drum after the cooler facilitates the gas liquid separation and it operates at the same conditions as the cooler. Some of the uncondensed gas stream is purged (S3) while the rest is sent to a heat exchanger where it is reheated and adjusted to the fermenter conditions in order for it to be recycled for stripping (S4). The condensate is the product stream for further downstream purification.

The simulation started with a simplified broth of butanol and water feed as per steady state experiments in Section 3-1. The simulations were then repeated with the other products of the fermentation added, i.e. the co-solvents acetone and ethanol, to see the effect they would have on the recovered gas stream. For this purpose, an ABE ratio of 3:6:1 by weight was used as it is the typical concentration ratio in traditional batch fermenters (Jones and Woods, 1986, Qureshi and Ezeji, 2008, Mariano and Maciel Filho, 2012).

The calculation of the overall stream flow rate used for the Aspen Plus® model was based on the butanol loading rate during the experiments in each run. The butanol loading rate represents a flow rate of the pure butanol which is also maintained at a certain constant composition in solution. The water flow was then normalised using its composition in solution relative to the butanol in solution.

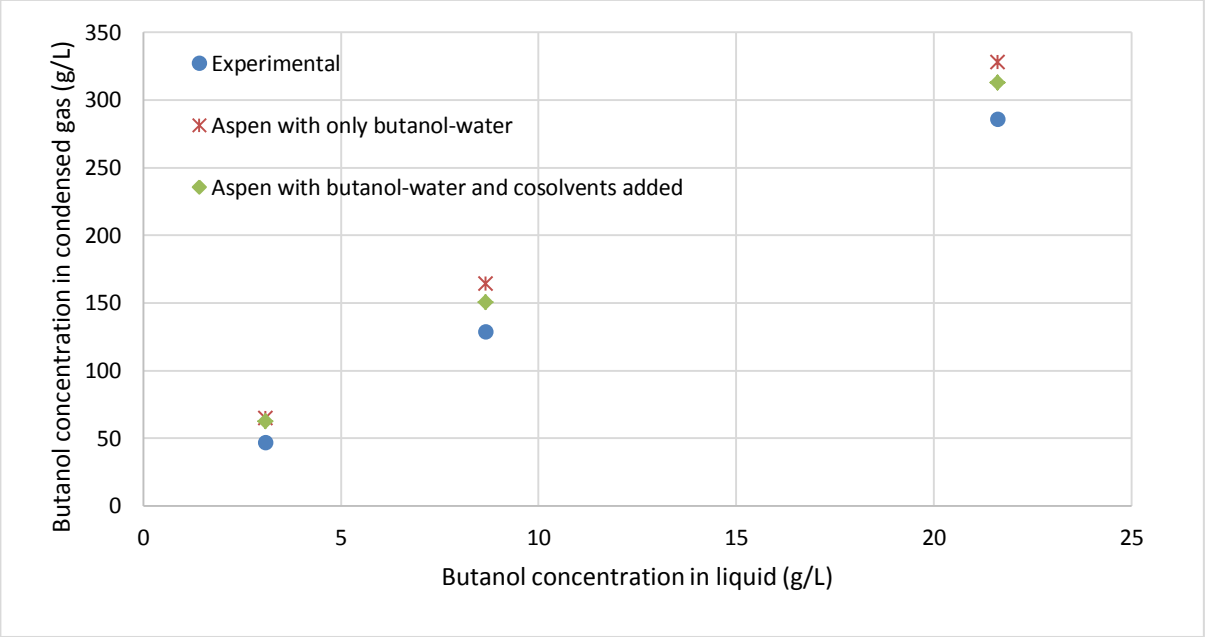


Figure 4-3: Comparison between experimental and simulated results

In Figure 4-3 the comparison between the experimental steady state results and the results obtained from the Aspen simulation are shown. The ordinate shows the concentration of the gas stream leaving the stripping unit (fermenter), on a carbon dioxide free basis. There is a close agreement between the simulated and the experimental results with the simulations predicting a higher concentration in the gas phase than obtained. The relative error between the experimental and simulated values decreases from the low to the high concentration levels. Table 4-3 gives the composition of the condensed stream as predicted

by Aspen Plus® for the three concentration levels in the case where the co-solvents were added.

Table 4-3: Predicted composition of the condensate with co-solvents added

Steady state butanol concentration (g L^{-1})	**Concentration in the condensate stream (g/L)**		
	Acetone (A)	**Butanol (B)**	**Ethanol (E)**
3.10	3.67	47.48	2.10
8.67	20.20	151.41	8.41
21.62	54.81	312.66	18.56

The final stage in this section was to choose the inlet butanol concentration and determine how the composition of the condensate stream at this concentration compares to the fermenters coupled with gas stripping that are reported in literature. A concentration of 8 g L^{-1} butanol was used as a feed into the gas stripping model. This concentration represents a good compromise between stripping rate and product inhibition. Furthermore, characterisation studies in gas stripping have shown that for gas stripping to be effective in recovering butanol, the concentration of butanol in solution should be at least 5 g L^{-1}. The lower the concentration in the broth, the less product can be recovered and stripping rates are also low (Xue et al., 2013, Xue et al., 2012). Gas stripping has, in laboratory experiments, been initiated when the butanol concentration in the fermenter is between 5 and 10 g L^{-1} (Ezeji et al., 2004, Liu et al., 2009, Xue et al., 2012). The condensate stream from the first stage gas stripper has a butanol concentration of 146.8 g L^{-1} and this is compared to values reported in literature in Table 4-4.

Table 4-4: Fed-batch fermenters with gas stripping reported in literature

Reference	Experimentation time (hours)	Microorganism	Substrate	Butanol in condensed stream (g L^{-1})
Ezeji et al. (2004)	201	*Clostridium beijerinckii* BA101	Glucose	151.7
Lu et al. (2012)	168 & 264	*Clostridium acetobutylicum*	Cassava bagasse hydrolysate	100-150
Xue et al. (2012)	330	*Clostridium acetobutylicum* JB200	Glucose	150.5
Xue et al. (2014)	200	*Clostridium acetobutylicum* JB200	Glucose	147.2

4.5.1.2. Second Gas Stripping Stage

As previously mentioned, Xue et al. (2013) reported on a two-stage gas stripping unit which can improve the energy required for downstream biobutanol purification and Xue et al. (2014) reported on the characterisation of the second-stage gas stripping unit. In all studies reported in literature, this second-stage gas stripping has not been simulated and included in an economic analysis of any full-scale process.

The butanol solubility in water at 20°C is 7.7 wt. % (Xue et al., 2014) which enables the condensate from the first gas striping stage to separate into two phases. The organic phase is transferred to the downstream purification steps while the aqueous phase is stripped again in a second stage gas stripper. The condensate from this second stage gas stripping is then mixed with the organic phase from the first-stage stripper and sent for further purification.

The second stage gas stripping was simulated using the same model developed for the first stage gas stripping using experimental results. Since the gas stripping takes place away from the fermenter, temperature can be regulated to give the best of stripping rates and concentrations in the condensate. In the characterisation, Xue et al. (2014) report a temperature of 55°C being the most ideal for this operation. A sensitivity analysis on Aspen Plus® confirmed that the ideal temperature is in that range. Sensitivity analyses were also performed to determine the right carbon dioxide flow rate and the cooling temperature of the stripped gas stream. Cooling is performed in a condenser operating at 10°C and 1 bar which is a higher temperature than in the first gas stripping stage. However, the gas recycle has to be heated back to 55°C as opposed to the fermentation temperature in the first stage (37°C). Table 4-5 shows the flow results from the second-stage stripping and how these compare with results reported by Xue et al. (2013).

Table 4-5: Second gas stripping stage flow results

Component	First-stage gas stripping				Condensate from second-stage gas stripping	
	Xue et al. (2013)		Current study		Xue et al. (2013)	Current study
	Organic phase	Aqueous phase	Organic phase	Aqueous phase		
Acetone (g/L)	39.3	43.4	84.3	51.7	118.7	227.0
Butanol (g/L)	612.3	101.3	146.8	104.5	336.6	467.0
Ethanol (g/L)	9.1	8.5	22.2	20.7	22.1	88.5

Although the values are in the same range, the difference emanates from the difference in the composition of the broth right from the fermenter. These bring differences in the compositions of the aqueous and condensate phases after separation. The presence of acetone and ethanol increases the solubility of butanol in water (Xue et al., 2013, Xue et al., 2014).

The current analysis assumes that the amount of carbon dioxide that the fermentation stage produces is sufficient to cater for the needs of both gas stripping stages. The analysis from the fermentation of molasses to butanol showed that the fermentation produces carbon dioxide that exceeds the carbon dioxide requirement of the first gas stripping stage and

thus, some of it is purged from the system (van der Merwe, 2010). Liu et al. (2009) also reports the same about corn fermentation. Assuming that the same is valid for clear juice fermentation, the extra carbon dioxide can be harnessed and be used in the second stage. Otherwise, alternative gases like air and nitrogen can be considered. The use of these other gases will, however, come with extra cost implications as they would need to be purchased. If carbon dioxide would be recycled (and some purged out of the system to avoid the build-up of toxins), the rate of carbon dioxide production must be such that it matches the stripping requirements.

Finally, the costing of both the first and second stage gas stripping was not based on the Aspen Plus® model of the stripper but on the sizes of the fermenters and tanks that would be required at a practical level. The costing excludes other pieces of equipment that are necessary, e.g. gas spargers. Spargers would have to be custom made for particular fermenter and tank sizes and their prices are not readily accessible and available. Prices of auxiliary equipment are much smaller compared to the fermenters themselves, and should hence be negligible.

4.5.2. Liquid-Liquid Extraction Column

The design and simulation of the extraction column on Aspen Plus® was performed using the distribution coefficients and selectivities measured in Chapter 3 supplemented with literature values. The "K_{LL} correlation" is a subroutine in Aspen Plus® which enables for the inclusion of distribution coefficients and selectivities directly into the simulation for liquid-liquid equilibrium prediction. The correlation gives the temperature dependency of the K values for different solvents as given below:

$$lnK_{LL} = a + \frac{b}{T} + clnT + dT \qquad [4\text{-}1]$$

K_{LL} is the liquid-liquid distribution coefficient value and *a*, *b*, *c* and *d* are regression coefficients and *T* is the temperature. In this study, the temperature dependency was not established and therefore, the values of constants *b* to *d* were set to zero. The extraction column was designed to operate at 30°C which is the temperature at which the measurements were taken. To validate the correlation prediction at a different temperature, a decanter can be set up on Aspen Plus® at that specific temperature and the

output compared to a known point in literature (Shah et al., 2016). Table 4-6 gives the values that were used in Process Scheme 3. The distribution coefficients of the other co-products were obtained from literature that had the K values for butanol agreeing with current experiments conducted.

Table 4-6: Extraction parameters used in the K_{LL} correlation

Solvent/Chemical	$\boldsymbol{lnK}$	**Source**
Acetone	0.22	Ghanadzadeh et al. (2004)
Butanol	2.14	Current study
Ethanol	-0.245	Solimo (1990)
Water	-3.57	Current study
2-Ethyl-1-hexanol	6.56	Solimo (1990)

Optimisation of the column was performed by the use the extraction factor, E. Generally, extraction columns are designed with extraction factors between 1.5 and 2 (Perry and Green, 1999).

$$E = K\frac{S}{F} \qquad [4\text{-}2]$$

S and F are the solvent and feed flowrates, respectively and K is the distribution coefficient in terms of mass fractions. Figure 4-5 shows the design and optimisation of an extraction column in Process Scheme 3 that uses 2-ethyl-hexanol as the extraction solvent. In this case, the column has 6 theoretical stages and a solvent flow of 14 000 kg/h. As opposed to vapour-liquid systems (as in distillation, for example), liquid-liquid systems have very low tray efficiencies which range from 5 to 30% (Vogel and Todaro, 1996). Using an efficiency of 20% translates to 30 real stages which is a realistic column size. The diameter of the column was calculated and its cost determined from the reported Karr extraction columns which have been used in the recovery of butanol (Roffler et al., 1987, Roffler et al., 1988). The procedure for costing of equipment based on a cost of a similar equipment of a different size is outlined further below (Section 4.7).

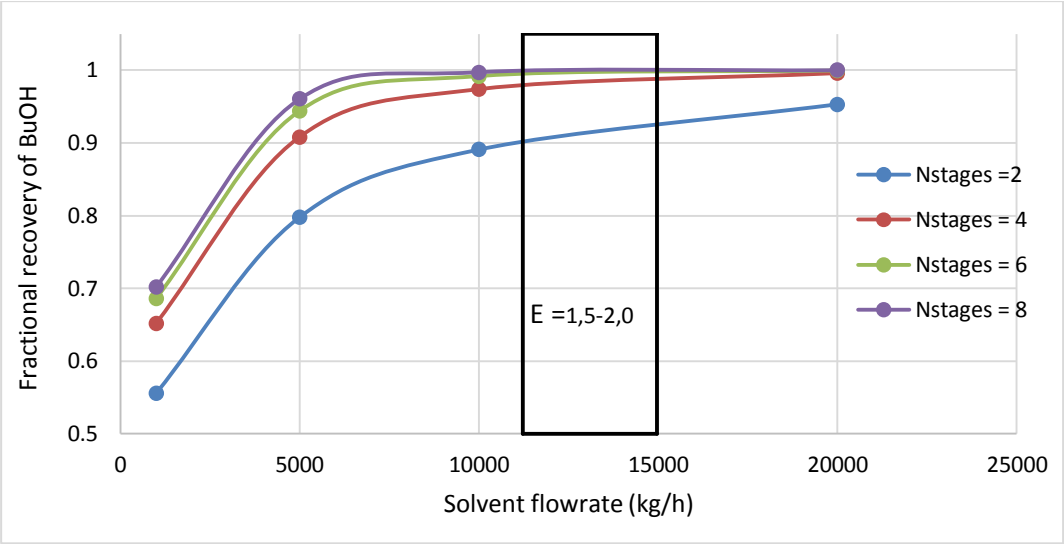


Figure 4-4: Process Scheme 3-Extraction column optimisation

4.5.3. Distillation Columns

The desired outcome of the distillation column design was design columns that result in the separation of the available components from the broth to the required purities while representing the best compromise between capital and operating costs. The components and the composition of the streams to these distillation columns were variable in each of the four process schemes considered. The determination of the optimal column sequencing in the processes investigated was not particularly complex and in all cases heuristics discussed by Seider et al. (2009) were conformed to (Appendix B).

Table 4-7: Boiling point properties of the broth components (Perry and Green, 1999)

Component of broth	Normal boiling point (°C)
Acetone	56.14
Ethanol	78.31
Water	100.00
Butanol	117.75

Also shown in Appendix B are the residue curve maps demonstrating the different distillation boundaries encountered in the broth components. Table 4-7 shows the boiling points of the broth components (in order of increasing boiling point). Where applicable, broth components were removed and recovered in that order.

The RadFrac model on Aspen Plus® was used to design all distillation columns. RadFrac is the Aspen Plus®'s rigorous distillation model and is capable of performing simulation, sizing and rating of tray and packed columns. Before simulating the columns using RadFrac, shortcut methods that make use of the Winn-Underwood-Gilliland design equations were first used to obtain the initial guesses of the column specifications.

All the distillation columns are tray columns and sizing was performed with Aspen Plus® using the tray sizing tool which estimates the diameter of each column. The choice of the tray columns over packed columns is based on the realisation that the broth could realistically contain compounds that can foul the column internals. Tray columns are less susceptible to fouling than packed columns (Seider et al., 2009). The costing of these columns also included the condensers, reflux drums, reflux pumps and the reboilers. A full column costing was therefore possible.

The conventional process has the last two columns meant to separate the butanol-water azeotrope by making use of a decanter. The top products from the two columns are recycled back to the decanter leading to a stream recycle problem which results in convergence issues on Aspen Plus® if a recycle block is to be used. Due to these inherent convergence problems this work did not include the recycle blocks at this preliminary design stage. An iterative procedure was used where the recycle streams were spilt and the tops output from the two columns being continuously fed into the streams into the decanter till they matched, within a reasonable tolerance. This is the same procedure applied by Shah et al. (2016) to obtain the recycle stream in an extractive distillation process and is a generally acceptable method. Another method would be to use calculator blocks on Aspen Plus®.

4.5.4. Other Equipment

Other pieces of equipment including pumps, storage, and surge tanks were also included. Storage tanks were designed and costed to have a one week capacity based on the flow rates and vendor quotes. Storage tanks were included for clear juice as well as the final organic products from the distillation columns. Surge tanks were included inside the processes in order to provide a constant feed to distillation and extraction columns.

All pumps were designed as centrifugal pumps and their electricity consumption determined depending on where they are applied.

4.6. Energy Performance

The bulk of the studies that have been conducted so far aims at producing the fuel grade biobutanol (purity of nearly 100 wt. %) and hence energy performance assessments results have been part of such reports. The results are usually used to compare biobutanol to other biofuels like ethanol. Literature particularly contains a great deal of research into the energy performance of fuel ethanol produced from various carbon sources including molasses and cassava (Nguyen et al., 2008, Nguyen et al., 2007). Although the focus of the current study is to produce butanol for higher value product production, the energy performance of each process alternative was evaluated for comparison purposes to literature as a way of validating the design and analysis approach. Two quantities were calculated, i.e. the Net Energy Value and the Process Energy Demand.

The Net Energy Value (NEV) weighs energy output against energy input and it is a conventional key indicator in identifying whether the production and use of a fuel results in an overall gain or loss of energy (Nguyen et al., 2008). The energy content of a fuel is weighed against the energy inputs in the fuel production cycle. In this current study, only the main product butanol was considered as a fuel. It is, however, recognised that the inclusion of the other 2 products will change the determined NEV as the choice of on the process schemes are narrowed down. Also left for further analysis in the final choice of designs is low grade or waste energy that could be used in the ABE recovery process as well as field and transport energy.

$$NEV = Energy\ content\ of\ biofuel\ (butanol) - Net\ energy\ inputs \qquad [4\text{-}3]$$

The energy input is the total of all fossil and non-fossil energy inputs, excluding energy recovered from system co-products, e.g. acetone.

The Process Energy Demand is calculated from the total energy required for processes (from steam, Q_{steam}, and from any other power source, Q_{power}) and the total amount of butanol produced M_{BuOH}.

$$Q_{ED} = \frac{Q_{steam} + Q_{power}}{M_{BuOH}} \qquad [4\text{-}4]$$

The values of the energy demand for different process routes and alternatives for biobutanol production are well documented in literature (Roffler et al., 1987, Van der Merwe et al., 2013, Naleli, 2016). In this study, this was determined for the four process schemes evaluated to add to the criteria for assessing the best performing process. The energy input into the fermentation was excluded in this evaluation since only the purification stages were designed in detail.

4.7. Process Economics Analysis Approach

A study estimate (factored estimate) type economic evaluation was carried out to determine the profitability of the biobutanol recovery schemes. Such an analysis is based on the knowledge of major items of equipment and is accurate within ±30% error (Peters et al., 1968, Lenz and Morelra, 1980). In analysing costs in industrial processes, capital investments costs, manufacturing costs, and general expenses including income taxes must be taken into considerations.

4.7.1. Total Production Costs

The production cost estimation entails costs associated with operating the plant and selling of products. As opposed to capital expenditures which are incurred once during the life of a project, production costs are recurring expenses and therefore, affect the cash flow and the profitability of the project (Kolmetz and Sari, 2014). Production costs are generally divided into manufacturing (or operating) costs and general expenses.

4.7.1.1. Manufacturing Costs

Manufacturing costs are divided into three categories, i.e. direct production costs, fixed charges and plant overhead costs (Peters et al., 1968). These are expenses that incur to make the product as well as to make it ready for shipment (Kolmetz and Sari, 2014). Table 4-8 gives the basis on which all the components of the manufacturing costs were calculated for all the process schemes considered in this study. The percentages fall into the ranges recommended in literature based on historical data from chemical processing plants (Kolmetz and Sari, 2014).

The term "Raw materials" in this study mainly refers to the clear juice which is the carbon source in the fermentation process. The cost of clear juice was estimated using the

Recoverable Value (RV) system that is used for cane payment in South Africa. The reasoning behind this was to be able to determine the opportunity cost associated with using the clear juice for fermentation as opposed to producing raw sugar. The RV rate available currently is only for cane and thus, this value was used to estimate the rate for clear juice that indicates the value addition that happens to the cane as it is converted to clear juice. A rate of R 4 529.92/t RV was used as a cost of clear juice and Appendix B (Section B2) gives the detail of the calculation based on the 2015/2016 milling season.

Table 4-8: Components of the manufacturing costs (Max et al., 1991)

Component	Basis	Percentage
	Direct cost	
Raw material	Material balance (clear juice cost)	-
Operating labour	Itemised according manpower requirements	-
Direct supervisory and clerical labour	Operating labour	15
Utilities	Process' water, steam and electricity requirements	-
Maintenance and repairs	Fixed capital investment	6
Operating supplies	Maintenance and repairs	15
Laboratory charges	Operating labour	10
Patent and royalties	Sales	1
	Fixed charges	
Insurance	Fixed capital investment	1
Local taxes	Fixed capital expenditure	1
Plant overhead costs	Operating labour + supervision + maintenance	55

The products acetone, butanol and ethanol were the only considered sellable products. The potential sale of fermentation gases (CO_2 and H_2) for by-product credit was not included in the analysis. The selling prices of commodities are often found in trade journals, e.g. The Chemical Marketing Reporter and The European Chemical News. The values obtained from these sources are, however, subject to short-term fluctuations and hence, long term

forecasting can be necessary for investment analysis (Smith, 2005). Table 4-9 shows the commodity prices used in the economic analysis to determine the potential cash flows from each Process Schemes. These prices are calculated averages from various sources and suppliers for the year 2016.

Table 4-9: Commodity selling prices

Product	Selling price (US$/kg)
Acetone	1.14
Butanol	1.89
Ethanol	0.51

Since the biobutanol production process (or ultimately, the higher value product process) will be, ideally, next to a sugar mill, it is expected that utilities are already established and would come from the sugar mill. Three utility types were considered, i.e. steam, water and electricity to provide for the energy needs of the process. The cost of high pressure steam (HPS) was determined by calculating the amount of fuel that is required to produce the HPS, including any loses (Smith, 2005). This is a hypothetical worst case scenario basis where coal is used after bagasse has been, possibly, used for higher value product production. The details of the calculation are shown in Appendix B3 using coal as the fuel from which the steam is produced. The cost of electricity was considered at the standard electricity price although most sugar mills are electricity self-sufficient and only buy electricity during the off-crop season. Table 4-10 gives the costs of the standard utilities.

Table 4-10: Utilities costs

Utility	Condition	Cost
Steam	HPS (at 31 bar and 390°C)	US$ 6.07/t
Portable water	At 23.5°C	US$ 0.07/t
Electricity	220/230 V AC	US$ 0.08/kWh

The solvent used for extraction and the refrigerant for cooling the gas from the gas stripping can also be defined utilities as there is need to constantly top up due to losses during recycle. Values of US$ 0.250/ t for the Freon 12 refrigerant and US$ 1.81/kg for the solvent 2-ethyl-1-hexanol were used.

To improve the energy efficiency of the process, heat integration is often performed using pinch analysis technology. Pinch analysis principally minimises the dependency of the process on externally supplied utilities. Cold and hot streams in the process are matched in a heat exchanger network. Pinch analysis was not included at this preliminary stage of the study and will only be included in the overall process that includes the mill as the whole biorefinery is analysed holistically. A few streams were, however, matched for energy transfer based on the traditional biobutanol processing route, e.g. the stillage stream from the beer stripper supplies the necessary energy to preheat the broth before the first distillation column.

Finally, operating labour refers to the manpower responsible for running the equipment. Each major piece of equipment that is shown on the flowsheet requires a certain number of operators. In recent years, equipment has become highly instrumented and as such the operating labour is independent of the size of the equipment or vessel but is proportional to the number of the available units (Ulrich, 1984). In this study, the number of operators required was estimated from the operator requirements for various types of process equipment given by Ulrich (1984) as shown on Table 4-11. These values are based on continuous operation. Each operator works an 8 hour shift with 3 shifts in a day. On average, an equipment operator is paid R116 029 per year in South Africa[5].

Table 4-11: Operator requirement for various process equipment (Ulrich, 1984)

Generic Equipment Type	Operators per Unit per Shift
Wastewater treatment plants	2
Blowers and compressors	0.2
Heat exchangers	0.1
Mixers	0.3
Towers (incl. auxiliary pumps and exchangers)	0.5

4.7.1.2. General Expenses

These are other expenses that are involved in the operations of a company. They can be classified as administrative expenses, distribution and marketing expenses, research and

[5] http://www.payscale.com/research/ZA/Job=Equipment_Operator/Salary

development expenses, and financing expenses. They often incur remote from the plant, e.g. in a central corporate headquarters (Ulrich, 1984).

In the same way as in the case of manufacturing costs, Table 4-12 gives the basis on which the general expenses were calculated for all the process schemes considered in this study. The percentages fall into the ranges recommended in literature based on historical data from chemical processing plants (Kolmetz and Sari, 2014).

Table 4-12: General expenses parameters (Max et al., 1991)

Component	Basis	Percentage
Administration costs	Operating labour	20
Distribution and selling costs	Sales	4
Research and development	Sales	3
Financing	Total capital investment	5

4.7.2. Capital Investments

This is a large amount of money that must be supplied to purchase and install all the necessary machinery and equipment. This money is required before an industrial plant can be put into operation and also includes capital required for the plant operation. The Total Capital Investment (TCI) is made up of the Fixed Capital investment (FCI) and the Working Capital (WC).

$$\textit{Total Capital investment} = \textit{Fixed Capital Investment} + \textit{Working Capital} \quad [4\text{-}5]$$

4.7.2.1. Fixed Capital Investment (FCI)

FCI can be defined as the total cost of processing installations, buildings, auxiliary services and all the engineering involved in the creation of a new plant. FCI usually makes up 85 to 90% of the TCI (Kolmetz and Sari, 2014). A number of methods for calculating FCI have been proposed. In this study, however, only one method was used throughout for all the process schemes. Firstly, the total cost of purchased process equipment was determined mainly from Aspen and then all the other components of the direct cost were estimated individually as equivalent to percentages of the equipment cost. Table 4-13 gives typical

variations in component costs as percentages of the FCI for multipurpose grass-roots plants or large battery limits additions (Max et al., 1991, Peters et al., 1968, Kolmetz and Sari, 2014). A grass-roots plant is a complete plant that is erected on a new site while the term 'battery limit' relates to the geographical boundary defining the coverage of a specific limit (Peters et al., 1968, Kolmetz and Sari, 2014). The process schemes in this current study are battery-limited additions as they are, eventually, going to be extensions to existing sugar mills.

Contingency is added to the fixed capital investment to compensate for unpredictable expense, minor process changes, price changes as well as estimation errors. A 10% contingency (Kolmetz and Sari, 2014) was added to all the process schemes considered in this study.

Table 4-13: Components of the fixed capital investment

Component	**Range, % of FCI**
Direct costs	
Purchased equipment	15-40
Purchased equipment installation	6-14
Instrumentation and controls (installed)	2-8
Piping (installed)	3-20
Electrical (installed)	2-10
Buildings (including services)	3-18
Yard improvements	2-5
Service facilities (installed)	8-20
Land	1-2
Indirect costs	
Engineering and supervision	4-21
Construction expense	4-14
Contractor's fee	2-6
Contingency	5-15

The cost of major equipment (which includes columns and heat exchangers) was obtained from the Aspen Plus® Economic Evaluator Package. It is also possible to obtain prices of

equipment from real quotes through published literature and reports. The cost estimation of specialised equipment (e.g. reactors, generators, boilers) is generally regarded as unreliable (Humbird et al., 2011). The prices obtained from Aspen Plus® version 8.6 are quoted at 2013 and cost indexes were used to update these prices to 2016.

Cost indexes are used to update cost data applicable at a past date to costs that represent conditions at a later date (Kolmetz and Sari, 2014). They numerically reflect the historical change in engineering costs. It is only a general estimate as there is no index that can factor in all variables, e.g. special technological advancements or local conditions (Peters et al., 1968). Equation 4-6 is a basic ratio relationship that can be used to update historical costs.

$$M_2 = M_1 \left(\frac{I_2}{I_1}\right) \quad [4\text{-}6]$$

Where,

M_1= original money/cost

M_2 = cost at expected/present time

I_2 = Index value at expected/present time

I_1 = Index value at time original cost was obtained

Many types of cost indexes are published regularly and some of these apply to specific items, e.g. equipment costs, others apply to labour or other specified fields. The most common indexes include the Marshal and Swift (M&S) Equipment Cost Indexes, Chemical Engineering Plant Cost Indexes (CEPCI) and the Nelson Refinery Construction Index (Peters et al., 1968, Kolmetz and Sari, 2014). The CEPCI[6] were used in this study as either the CEPCI or the M&S are generally adequate for chemical process industries (Kolmetz and Sari, 2014). The M&S indexes are not available for periods beyond 2012.

Finally, in the case of sizing storage tanks, no cost data was available for the capacities required. Therefore, the *six-tenths factor rule* was applied. According to the rule, if a new piece of equipment is similar to one of another capacity for which cost data are available,

[6] http://www.chemengonline.com/economic-indicators-3/?printmode=1

Equation 4-7 below can be used to estimate the unknown cost (Peters et al., 1968, Kolmetz and Sari, 2014):

$$E_b = E_a \left(\frac{C_b}{C_a}\right)^{0.6} \quad [4\text{-}7]$$

Where,

C_a = capacity of equipment *a*

C_b = capacity of equipment *b*

E_a = cost of equipment *a*

E_b = cost of equipment *b*

Equations 4-6 and 4-7 were applied to estimate the costs of the fermenters and tanks using data from vendors as reported by Roffler et al. (1987) and then normalised to 2016 values.

4.7.2.2. Working Capital

The Working Capital (WC) represents the money that is required to keep the business afloat and running before there is any cash flow in terms of revenues. The WC, therefore, consists of the total amount of money invested in raw materials, finished products in stock, cash kept to pay salaries and wages and any accounts and taxes payable (Peters et al., 1968, Douglas, 1988). In this study, the WC was kept at 15% of the FCI (Peters et al., 1968, Douglas, 1988, Kolmetz and Sari, 2014).

4.7.3. Profitability Indicators and Assessment

This stage represents the final and ultimate analysis methodology of the process schemes that were designed. A profitability assessment is necessary to evaluate how much profit can be obtained from investing capital in a certain process compared to other alternatives. The most commonly used methods for evaluating profitability are: Rate of Return On Investment (ROI), Discounted Cash Flow (DCF) based on full-life performance, Net Present Value (NPV), capitalised costs and the payout period (Peters et al., 1968, Anderson and Fennell, 2013). The DCF analysis method was used to evaluate the economic viability of the four process

schemes. The explanations, definitions, and advantages and disadvantages of the other methods are well recorded in literature (Peters et al., 1968, Ulrich, 1984, Douglas, 1988).

The DCF analysis is based on the projections of the cash flow during the life span of the project (Smith, 2005). From the predicted cumulative cash flow curve, an evaluation of the payback period and the NPV can be deduced. Net cash flow is the remaining money after all the expenses have been paid and cash flows that are predicted to happen in future are discounted to reflect their reduced value in the present time (Anderson and Fennell, 2013). It is important to note that the discounting rate reflects the opportunity cost of the funds to the investor and is a reflection of how much one can get from investing with established banks. The NPV sums up all the discounted cash flows generated in the span of the project. It is an indication of the total cash flow that would be generated by a project if all revenues and expenses incurred in the running of the project were reduced to the present time (Anderson and Fennell, 2013).

Table 4-14: Discounted cash flow analysis parameters

Parameter	**Value**
Year of project inception	2016
Economic Project Life	25 years
Depreciation (straight line)	25 years
Tax Rate	28 %/year
Discount Rate	10 %
Currency cross rate	1 US$ = R 13.15
Operating hours per year	6 048 h
Escalation parameters: Total production costs	9 %/year
Sales	9.5 %/year

The greater the positive NPV of a project, the more profitable and economically attractive it is. A negative NPV indicates a non-profitable investment that will not return the opportunity cost of the project. The NPV is zero when the product breaks even, i.e. the discounted investments are equal to the discounted returns, for a given discount rate. The discount rate at this point is called the Internal Rate of Return (IRR). In Table 4-14 the parameters used for the DCF analysis are shown.

The economic performance of each scheme was, therefore, determined by looking at the NPV after 25 years as well as the IRR. The IRR has to be greater than the discount rate for it to make sense to invest in the process.

4.7.4. Sensitivity Analysis

The determination of NPVs depends on assumptions that may not hold and hence performing a sensitivity analysis enables one to determine how variances in the inputs to the analysis affect the output. The sensitivity analysis was performed on the following factors and their effect on the NPV and the IRR evaluated:

a) Feedstock (clear juice) cost.
b) Utility costs (water, steam and electricity).
c) Capital expenditure.
d) Butanol selling price.
e) The Rand to US Dollar cross rate.

The sensitivity analysis of the above factors was performed on all the four process schemes, whether profitable or not, in order to see what factors need to be improved in order to move towards complete viability. A ±15% variance in all the above factors was evaluated.

5

CHAPTER FIVE

5. PROCESS DESCRIPTIONS, ECONOMIC ANALYSIS RESULTS AND DISCUSSIONS

5.1. Process Scheme 1: Conventional Distillation

5.1.1. Process Description

The conventional distillation process for biobutanol recovery and concentration from fermentation was used as a base case for the comparison with the other proposed processes. This benchmarking case was designed as described in literature (Roffler et al., 1987, Mariano et al., 2011, Mariano and Maciel Filho, 2012). The design of the process assumes a batch fermentation process as in the conventional case and thus, a continuous downstream process is attainable by operating various batch fermenters on a staggered schedule (Roffler et al., 1987, van der Merwe, 2010). Table 5-1 gives the fermentation parameters that were used.

Table 5-1: Process Scheme 1-Fermentation parameters

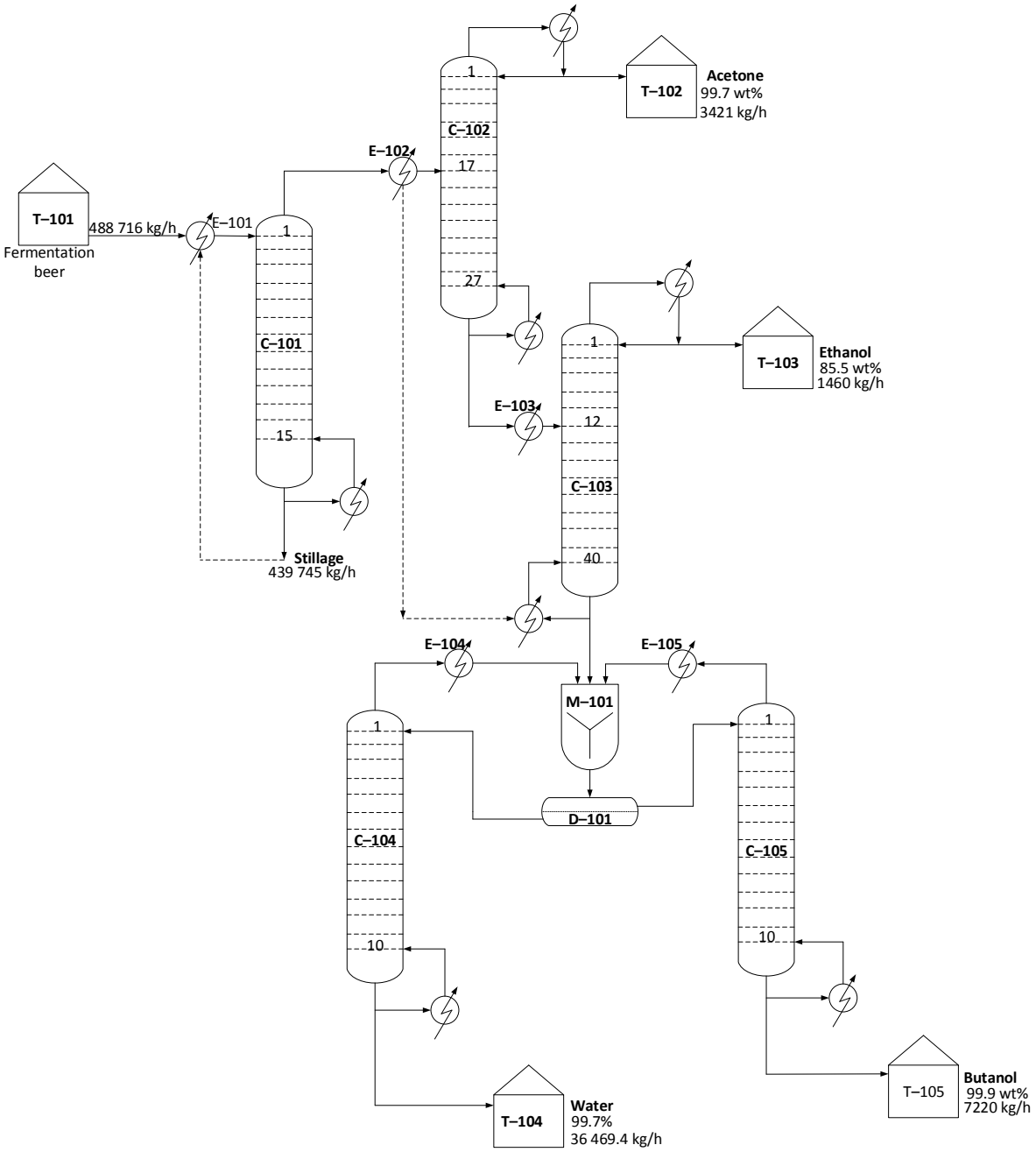
Parameter	Value used	Literature ranges
Fermentation mode	Batch	Batch
Butanol productivity (g/L/h)	0.25	0.18 - 0.60
Product yield $\left(\frac{g\ product}{g\ glucose}\right)$: Acetone	0.10	0.10 – 0.11
Butanol	0.22	0.18 – 0.28
Ethanol	0.04	0.02 – 0.05
Final broth butanol concentration (g/L)	15	5 - 20

A series of five distillation columns was designed and the need and function of each of the columns remains as described in Section 2.1.2 (Conventional Industrial Process). Figure 5-1 shows the distillation trail designed and design parameters for the main equipment, i.e. distillation columns, while Table 5-2 gives the same information including operating pressures and column diameters. The presence of a broth feed tank into which the fermentation products are emptied also ensures that the distillation trail is supplied with a constant and reliable feed.

Table 5-2: Process Scheme 1-Main equipment specifications

Parameter	**C-101 (Beer Stripper)**	**C-102 (Acetone Recovery)**	**C-103 (Ethanol Recovery)**	**C-104 (Water Stripper)**	**C-105 (Butanol Stripper)**
Number of stages	15	27	40	10	10
Feed stage	1	17	12	1	1
Molar Reflux Ratio	-	4	14	-	-
Operating pressure(bar)	1.5	0.7	0.3	1	1
Diameter (m)	4.78	1.82	2.70	1.61	1.28

The beer stripper removes 90% of all the water (and all the carboxylic acids) that is in the fermentation broth and this water leaves as part of the stillage, and the gas stream from the beer stripper is sent to the acetone recovery column. The acetone column produces an acetone product stream with a purity of 99.7 wt. %. The subsequent ethanol column is the biggest, after the beer stripper, (bigger column means higher contribution to the overall fixed capital cost) and most expensive to operate (high reflux ratio) as well. This is the case because very small amounts of ethanol are produced compared to acetone (and butanol) and this is true for most fermentation strains. As mentioned previously, conventional strains produce ABE in the ratio of 3:6:1 by mass (Jones and Woods, 1986). The ethanol column is, therefore, used to recover as much ethanol as possible so that the presence of ethanol in the downstream columns does not affect the purity of the final butanol product. The design dynamics of this column are shown in Figure 5-2. The same relationship can also be shown for the recovery of ethanol in this column.



Key:

Symbol	Description	Symbol	Description	Symbol	Description
T-101	Broth surge tank	E-103	Ethanol column pre-cooler	C-104	Water stripper
E-101	Broth preheater	C-103	Ethanol column	T-104	Waste water tank
C-101	Beer stripper	T-103	Ethanol storage tank	C-105	Butanol stripper
E-102	Stripper gas condenser	E-104/5	Decanter temperature set	T-105	Butanol storage
C-102	Acetone column	M-101	Decanter feed mixer		
T-102	Acetone storage tank	D-101	Decanter		

Figure 5-1: Process Scheme 1-Process flowsheet

Consequentially, the ethanol produced in this process cannot be considered a sellable product but rather a by-product, waste stream. The ethanol stream contains 85.5 wt. % ethanol while the fuel grade ethanol, i.e. the ethanol that is used to blend with gasoline, should have at least 92.1 % (v/v) and less than 1 % (v/v) water (RFA, 2005).

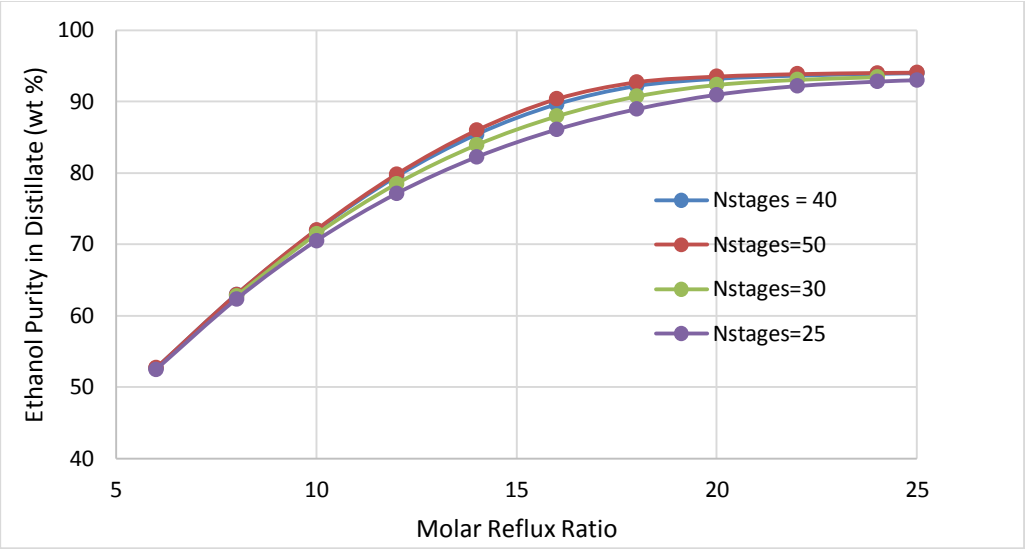


Figure 5-2: Ethanol column (C-103) design dynamics

While Figure 5-2 shows that it is possible to obtain a distillate stream from the ethanol column that has a purity of at least 92 wt. %, it also shows that this requires a very large column that operates at a very high reflux and this is not sustainable considering that there is only up to a maximum of 1.47 t/h ethanol in the whole system. The column size and purity obtained, in the current study is the same as that reported by Mariano et al. (2011) while van der Merwe (2010) only obtained a stream with 42 wt. % ethanol. The treatment of this stream is not considered in the current study. At best it would be sold to some ethanol producers, at a compromise price, who have a system with molecular sieves for complete ethanol dehydration.

The last two columns are for the separation of the butanol-water heterogeneous azeotrope. In the water stripper (C-104), in which the water-rich phase is purified, the top product is a minimum boiling azeotrope of butanol and water while the bottom product is almost pure water. In the decanter, the liquid stream with the azeotropic composition splits into two liquid phases. The aqueous phase is recycled to the water stripper described above while the butanol-rich phase is fed into the butanol stripper (C-105). The butanol-rich phase has a composition higher than the azeotropic concentration and thus, almost pure butanol (99.9

wt. %) is obtained in the bottoms stream. An azeotrope is obtained in the distillate and is recycled back into the decanter.

The final butanol product obtained qualifies to be used as a fuel. Table 5-3 shows the overall compositions of the product streams obtained. For the purposes of the economic analysis, only sales from acetone and butanol were considered for this process scheme.

Table 5-3: Process Scheme 1-Products specifications

Product	Total produced (t/h)	Final Stream Purity (wt %)
Acetone	3.42	99.7
Butanol	7.22	99.9
Ethanol	1.46	85.5

5.1.2. Energy Performance

Based on the utilities that the process requires, Table 5-4 shows the energy performance of Process Scheme 1.

Table 5-4: Process Scheme 1-Energy performance

Parameter	Value
NEV (MJ/kg)	-3.73
Process energy demand (MJ/kg BuOH)	39.73

As expected, the production of biobutanol for fuel use using the conventional distillation process does not make sense from an energy assessment point of view. The energy requirement of the recovery process, per kg of butanol, is higher than the energy content of butanol (36 MJ/kg). These values are in the same range as the values reported in literature. Mariano et al. (2011) predicted the expected energy consumption of the conventional distillation system as a function of the butanol concentration in the fermentation beer. For the range of concentration in the current study, from that reported prediction, distillation would require 41 MJ/kg butanol. Van der Merwe et al. (2013) obtained an energy demand of 38.75 MJ/kg and a NEV of -5.54 MJ/L for the same process scheme. These results from literature served as a validation of the current assessment.

5.1.3. Process Economic Results

Table 5-5 gives a summary of the economic indicators while Figure 5-3 gives the cumulative DCF analysis for a project life of 25 years.

Table 5-5: Process Scheme 1-Main economic analysis results

Parameter	Amount (US$ Million)
Total capital investments	124.85
Total sales	106.11
Total productions costs	102.71
Net present value (NPV)	-3.80

The conventional distillation base case gave a negative NPV of US$3.80 million for a project life of 25 years. From Figure 5-3, it can be seen that the conventional butanol recovery process is not economically viable under the current economic conditions. From Table 5-5, the annual production costs and the sales have almost the same value and this is the same relationship obtained by Lenz and Morelra (1980) for butanol production from molasses. Van der Merwe et al. (2013) and Naleli (2016) also report on this scheme yielding a negative NPV for processes that uses molasses and lignocellulosic biomass as fermentation substrates, respectively.

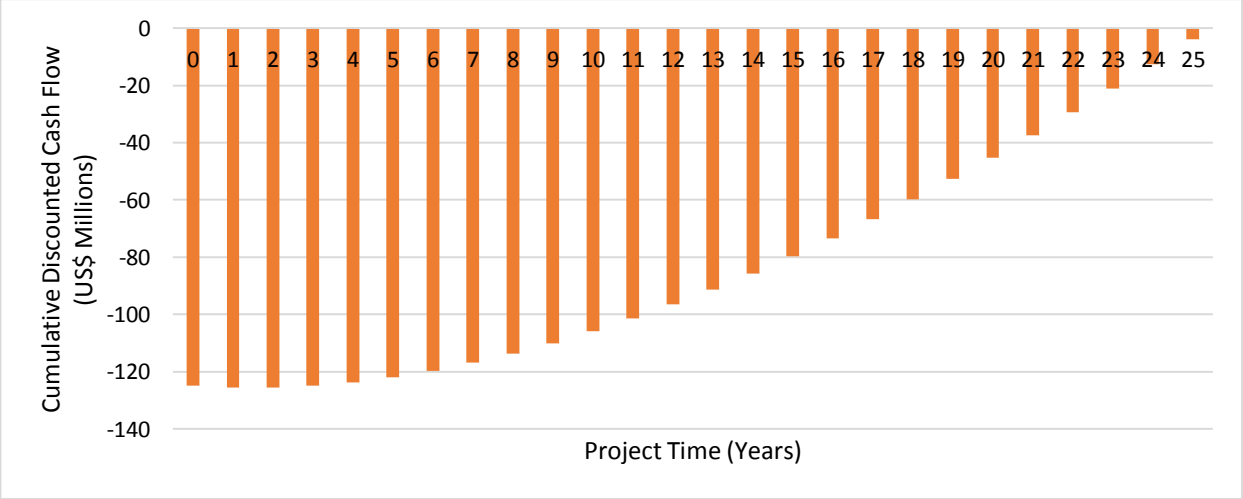


Figure 5-3: Process Scheme 1-Cumulative Discounted Cash Flow Analysis

Figure 5-4 shows how the NPV of the conventional process is affected by various changes in the cost drivers. The centre bars (cost driver = 0) indicates the base case NPV while the bars on the left represent a -15% variance and the bars on the right, a +15% variance.

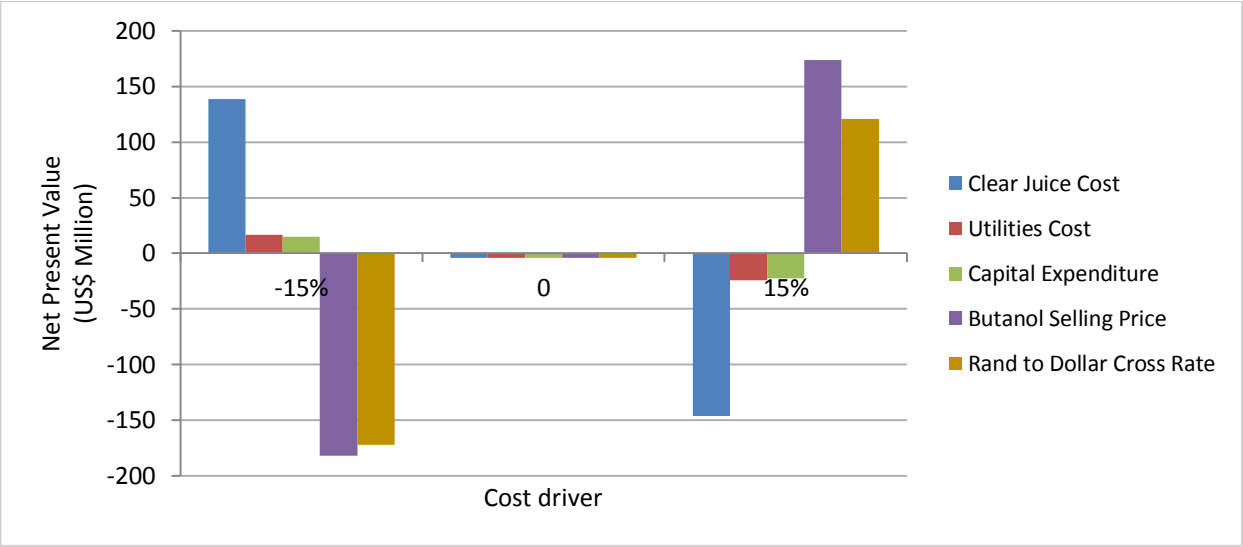


Figure 5-4: Process Scheme 1-NPV sensitivity

Changes in the capital expenditure and the utilities cost exhibit the least influence on the NPV of this process, while the highest influence comes from the butanol selling price. This price, however, is mostly determined by the petrochemical route for butanol production and is unlikely to rise to the levels that will render the conventional biobutanol production process profitable. At least in the short and mid-term, this is yet another motivation towards putting the biobutanol towards a higher value chemical production process where higher selling prices can be realised. The minimum butanol selling price that renders a process profitable has been previously used as a criterion for assessment of the economics of biobutanol production (van der Merwe, 2010, Naleli, 2016).

The reduction in the fermentation substrate (clear juice) cost also shows a significant increase in the NPV of this process. The use of cheaper substrates like lignocellulosic biomass has been previously considered, however, it has been shown that it does not improve the economics of the conventional recovery process (Naleli, 2016). This could be due to the extra capital cost incurred in installing a saccharification process infrastructure in which the sugars in the lignocellulosic biomass are made accessible and ready for fermentation. The operating costs of such upstream processes are also a contributor when compared to clear juice which needs at most dilution before introducing it into the fermenters. These costs, possibly, cancel the gains that are obtained from using a cheaper substrate.

Since most of the prices are quoted in US$, the conversion factor to the South African Rand also has an impact on the results obtained. Figure 5-4 also shows a significant increase in NPV once a 15% increase in the Rand to Dollar rate is realised (i.e. from R13.15/US$ to R15.12/US$). In this study, the cross rate mainly affects the operating labour and the RV rate for the clear juice cost. A higher Rand rate indicates a loss in value of the Rand which means that less US$ have to be paid for the same amount of labour and clear juice.

Finally, in Figure 5-4, for all the cases where the change in cost driver factors results in a positive NPV, the resulting IRR is between 1 and 7% which is still insufficient to justify investing in this process scheme. This is considering that the discounting rate used is 10%. The scheme remains unprofitable under the current economic conditions even when either of those changes reflecting a positive NPV is achievable.

5.2. Process Scheme 2: Gas stripping followed by distillation

5.2.1. Process Description

Figure 5-5 shows the process flowsheet for Process Scheme 2 in which the potential advantage of using gas stripping was assessed. The fermenter (R-201) is included only to show how the gas stripping connects to the rest of the flowsheet. The fermentation process was designed to have a sugars utilization rate of 2.49 g L^{-1} h^{-1} and an ABE yield of 0.47. This translated to an ABE productivity of 1.17 g L^{-1} h^{-1} which is well within the reported values in literature (Ezeji et al., 2004, Liu et al., 2009). These fermentation parameters are applicable to all the subsequent processes for they all begin with recovery by gas stripping.

Table 5-6 shows the specifications of the main process equipment. The process still requires a trail of five distillation columns as in the conventional case. This is because the condensate contains 36 wt. % water and that composition does not allow the crossing of distillation boundaries to recover pure products. As mentioned, a disadvantage of gas stripping is that selectivity is low ((Qureshi et al., 2005, Vane, 2008, Xue et al., 2012, Stoffers et al., 2013) and water is carried over with the ABE solvents. The economic gain gas stripping brings is worth investigating.

Table 5-6: Process Scheme 2-Main equipment specifications

Parameter	C-201 (Beer Stripper)	C-202 (Acetone Recovery)	C-203 (Ethanol Recovery)	C-204 (Water Stripper)	C-205 (Butanol Stripper)
Number of stages	15	27	39	10	10
Feed stage	1	21	20	1	1
Molar Reflux Ratio	-	4	14	-	-
Operating pressure(bar)	1.5	0.7	0.3	1	1
Diameter (m)	1.76	1.54	2.37	0.65	1.45

The inclusion of gas stripping does not only reduce the number of fermenters required but also results in smaller (compared to Process Scheme 1) distillation columns in the downstream purification as shown by the smaller column diameters. This is a notable reduction in the capital costs requirements of the process. The beer stripper is the one that is particularly reduced in size as there is an 88% throughput reduction.

Table 5-7 also shows that the inclusion of gas stripping also results in a recovery of the three main products with high purities that are sufficient to sell.

Table 5-7: Process Scheme 2-Product specifications

Product	Total produced (t/h)	Final Stream Purity (wt %)
Acetone	3.53	99.8
Butanol	9.29	99.9
Ethanol	1.41	95.0

Butanol concentration in the condensate stream is 15.5 wt. % compared to 1.5 wt. % in the conventional case. The concentrations of the other organics are also high enough for separation of the ABE solvents in the downstream distillation columns with greater ease than in the conventional case. The feed into the acetone column in Process Scheme 2 has almost the same amounts of ABE organics as in Process Scheme 1, but it has half the concentration of water (35 wt. % compared to 76 wt. %). This results in reduced

contamination of the downstream products with water, especially ethanol, which could not be recovered with high sufficient in Process Scheme 1.

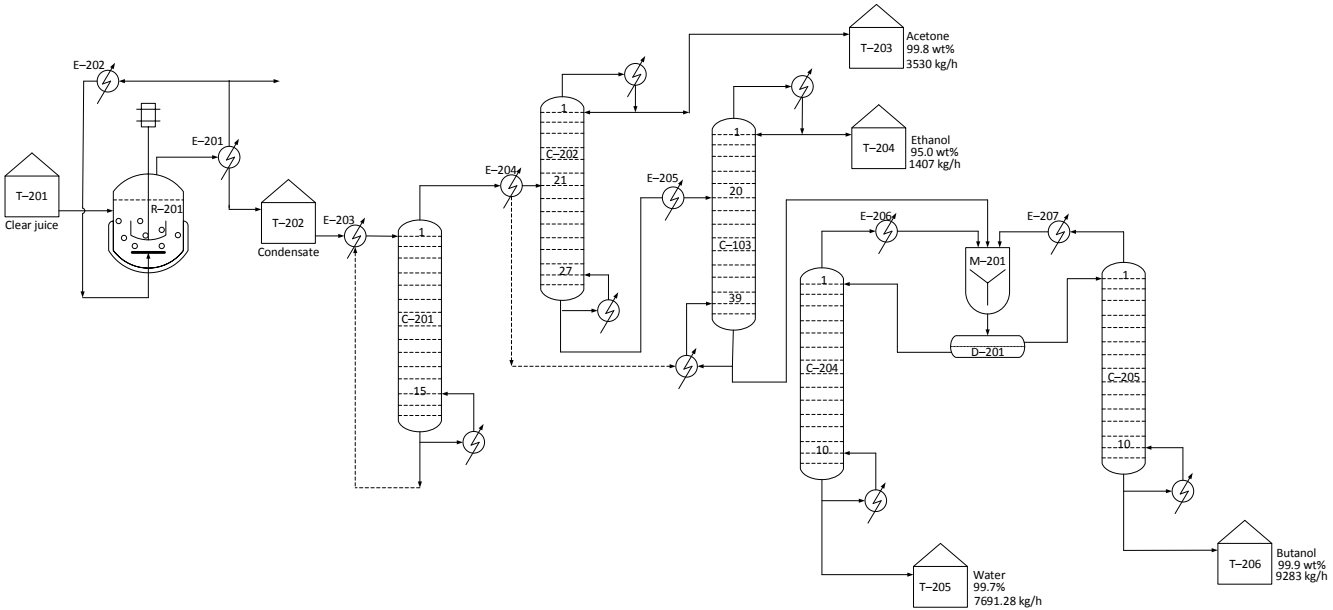
5.2.2. Energy Performance

Table 5-8: Process Scheme 2-Energy performance

Parameter	Value
NEV (MJ/kg)	0.9
Process energy demand (MJ/kg BuOH)	35.1

Table 5-8 shows an improved energy performance due to the incorporation of the gas stripping recovery step to the conventional distillation process. The results, however, show that the energy demand is almost equal to the energy supplied by the fuel butanol. This result, however, should not be overly interpreted at this preliminary stage as not all energy consuming steps have been considered in the same level of detail. The current study focuses more on the recovery stages and thus, the energy demand is likely to increase as the fermentation stage is included in more detail as information becomes available.

The energy performance of this process does, therefore, not indicate an absolute gain in the use of biobutanol as a fuel although it does indicate an improvement when compared to Process Scheme 1.



Symbol	Description	Symbol	Description	Symbol	Description	Symbol	Description
T-201	Clear juice storage	T-202	Condensate surge tank	T-203	Acetone storage	D-201	Decanter
R-201	Fermenter/Stripper	E-203	Condensate heater	E-205	Ethanol column preheater	C-204	Water stripper
E-201	Stripper gas cooler	C-201	Beer stripper	C-103	Ethanol column	C-205	Butanol stripper
E-202	Stripper gas re-heater	E-204	Stripper gas condenser	T-204	Ethanol storage		

Figure 5-5: Process Scheme 2-Flowsheet

5.2.3. Process Economic Results

The economics of Process Scheme 2 benefit and are improved when compared to the conventional case by the significant decrease in the capital cost (46%) and the ability to produce all three products of fermentation at sellable purities. Revenue from sales increase by 27% due to additional sales from ethanol. In addition to the NPV of US$ 505.88 million reported in Table 5-9, the process scheme also realised an IRR value of 31% which renders the process scheme profitable enough under current economic conditions.

Table 5-9: Process Scheme 2-Main economic analysis results

Parameter	Amount (US$ Million)
Total capital investments	67.43
Total sales	134.90
Total productions costs	103.25
Net present value (NPV)	505.88

The higher fermenter productivity that is realised in gas stripping is the major cost driver for the improvement in the economics of the process. This is also true for any other biobutanol recovery technology that improves the productivity. The gain obtained is proportional to the increase in productivity for the same substrate amount and/or the same product amount. Roffler et al. (1987), for example, report that a 29% reduction in purchased equipment cost was realised in an extractive fermentation process compared with the conventional fermentation process. The extractive fermentation process had a productivity of 1.5 g L^{-1} h^{-1} compared to 0.58 g L^{-1} h^{-1} in the conventional case. Green (2011) asserts that if productivity is doubled, capital expenditure can be reduced by approximately 20%, coupled with some reductions in the operating costs. In the current study, the productivity in Process Scheme 2 is a factor of 4 higher than in Process Scheme 1 and this warrants the obtained 46% reduction in capital cost.

The cumulative DCF analysis in Figure 5-6 shows a possible break-even after 3 years of operation based on income projections for the 25 years project life, although this may be rather too optimistic for technology that has not yet been tested and implemented at

practical industrial level. Generally, business ventures reach their break-even after at least five years of operation.

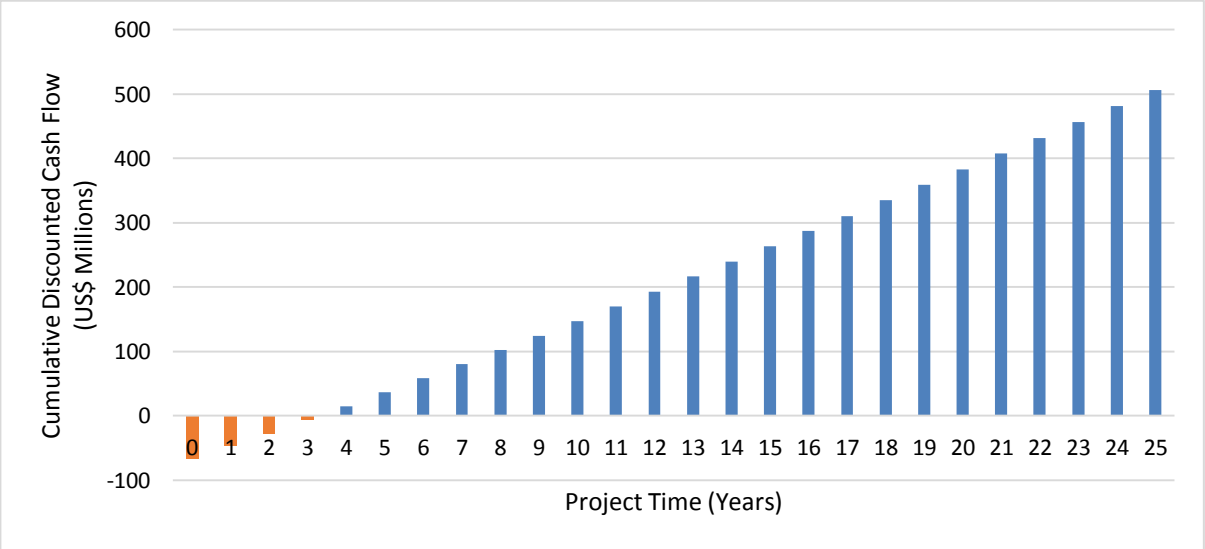


Figure 5-6: Process Scheme 2-Cumulative Discounted Cash Flow Analysis

It is important to note, however, that the factored estimate economic analysis performed in this current study is a preliminary assessment aimed at eliminating unreasonable options from a pool of alternatives. As more information is gathered, changes are made and the analysis becomes more detailed and closer to reality. Figures 5-7 and 5-8 show the sensitivities of the NPV and the IRR to changes in the cost drivers for this process scheme.

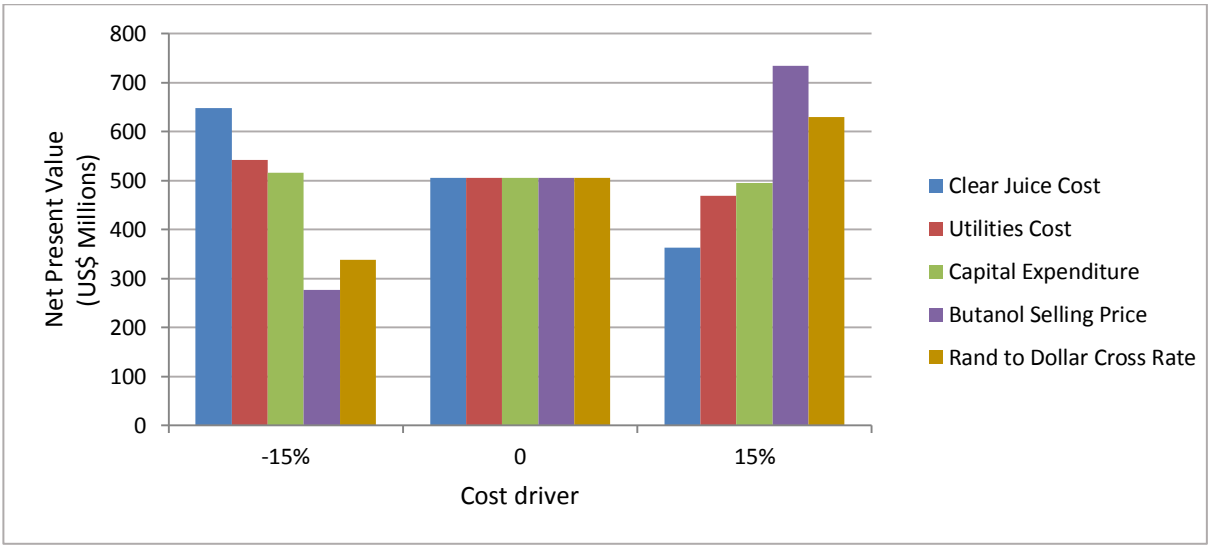


Figure 5-7: Process Scheme 2-NPV sensitivity

As was the case for the conventional process in Process Scheme 1, changes in the utilities costs and capital expenditure have the least bearing on both the NPV and the IRR. The

butanol selling price is the major factor that affects the NPV and IRR. Also important to note is that the different changes in these costs drivers still retain NPV and IRR values that indicates the process' potential profitability under the current economic conditions.

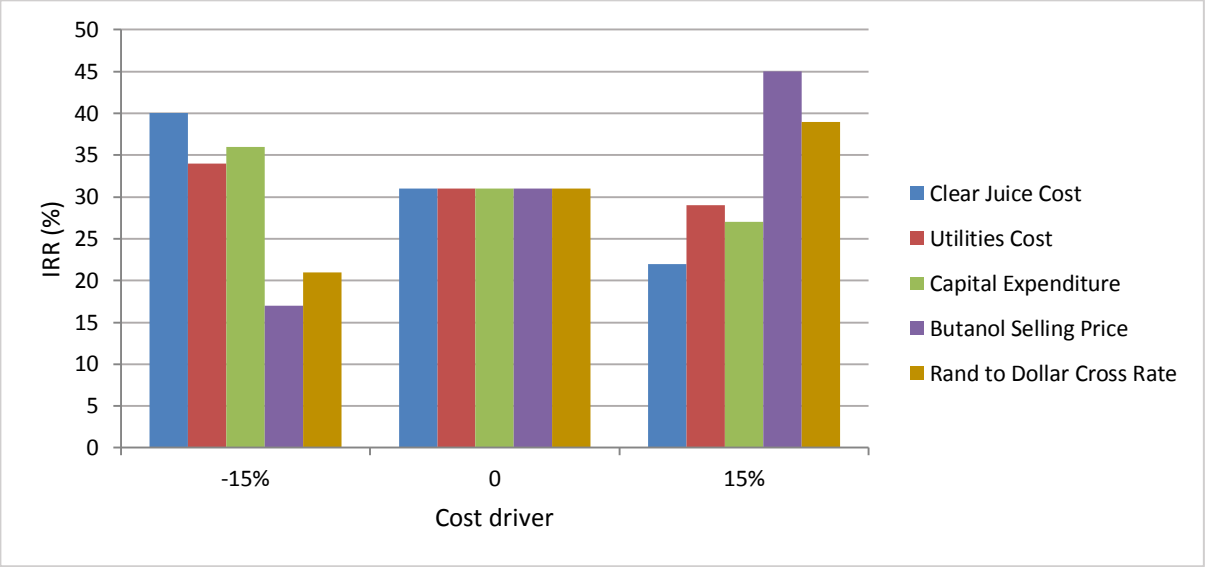


Figure 5-8: Process Scheme 2-IRR sensitivity

Finally, in terms of using butanol as a platform chemical for the production of other chemicals, this process scheme provides more options for possible stream points that can be tapped for that production. Unlike in the conventional case, where butanol of reasonably high concentration is obtained only in the decanter after the ethanol column, the current stream also provided the condensate stream that could be considered for reaction. This is particularly possible if a high concentration that warrants phase separation is obtained as reported by Xue et al. (2012) and Xue et al. (2013).

5.3. Process Scheme 3: Gas stripping followed by liquid-liquid extraction and distillation

5.3.1. Process Description

Table 5-10 gives the main equipment specifications for Process Scheme 3 while Figure 5-9 shows the simplified process flowsheet. Important to note is that this process only produces butanol as a sellable product (8 485 kg/h at 99.99 wt. %). This is a result of sending the condensate of gas stripping into the extraction column where the solvent (2-ethyl-1-hexanol) is preferentially selective to butanol and does not recover as much acetone and ethanol to warrant these to be recovered to pure concentrations in the downstream. This is

a fact for almost all organic solvents-they do not have the extractive properties that are of equal magnitude for all the ABE products.

Table 5-10: Process Scheme 3-Main equipment specification

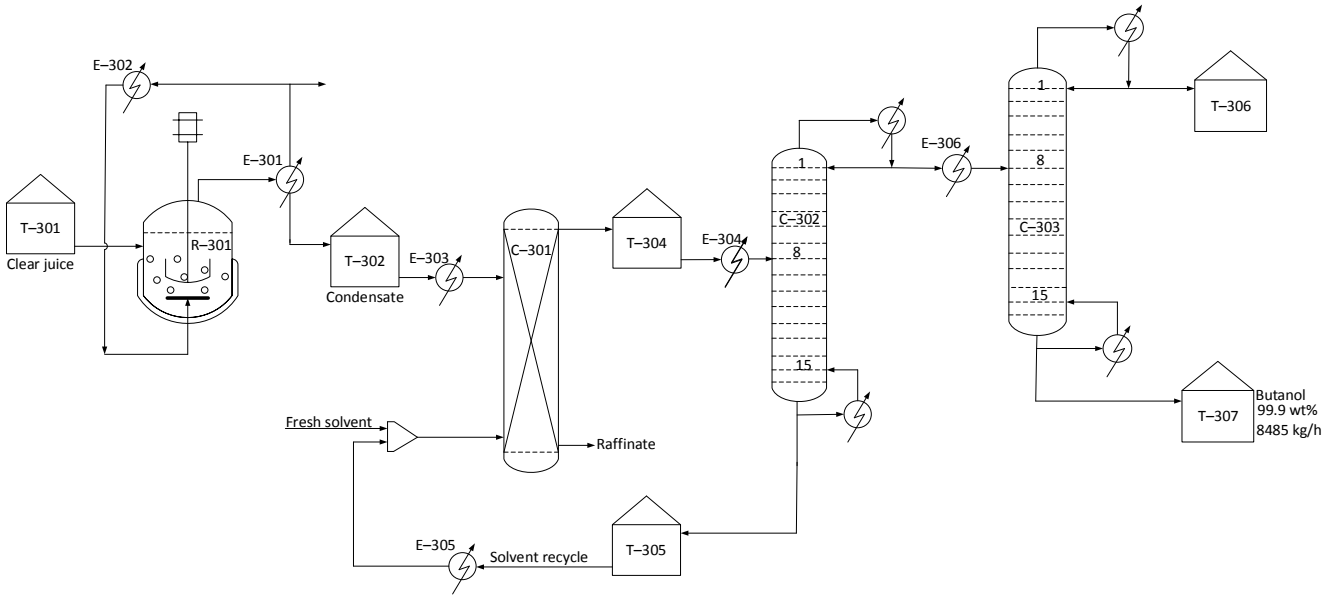
Parameter	**C-301 (Extraction Column)**	**C-302 (Solvent Recovery)**	**C-303 (Butanol Purification)**
Number of stages	30	15	15
Feed stage	1	8	8
Solvent feed stage	30	n/a	n/a
Molar Reflux Ratio	n/a	1.5	3.5
Operating pressure(bar)	1	1	1
Diameter (m)	3.50	2.99	1.76

The high selectivity of the solvent towards butanol compared to other organics would not be such an issue if the fermentation strain produced limited amounts of acetone and ethanol. That way, no potential sale losses would occur. In cases where it is important to recover all the organics one would have to readdress solvent selection, e.g. opt for an ionic liquid.

99% of water in the condensate stream from gas stripping is removed from the process in the raffinate stream of the extraction column. Also lost in the raffinate stream is 67% of the fed acetone and 68% of all the ethanol from the gas stripping. For this reason, only two downstream distillation columns are necessary to purify the extract stream for butanol. Once the solvent is recovered in the solvent recovery column, the feed to the last column contains 81 wt. % butanol and thus, butanol is easily recovered as bottoms stream at a purity of 99.99 wt. %.

The distillate product from the butanol purification column can be considered as waste. The treatment of this stream was not considered in this current study. It is however, important to note that this stream has a total of 3.05 t/h and contains 38 wt. % acetone, 28 wt. % butanol and 15 wt. % ethanol. If such a stream ends up being available in the sugarcane biorefinery, rather than investing into the disposal of this stream as waste, one could think

of what other products could still be possible to make. At the waste case, this stream can be assessed for energy content and be used as fuel in other sections of the biorefinery.



Symbol	Description	Symbol	Description	Symbol	Description	Symbol	Description
T-301	Clear juice storage	T-302	Condensate surge tank	E-304	Solvent preheater	E-306	Butanol preheater
R-301	Fermenter/Stripper	E-303	Condensate heater	T-305	Recycle tank	C-303	Butanol recovery column
E-201	Stripper gas cooler	C-301	Extraction column	E-305	Solvent recycle heater	T-306	A/E waste storage
E-202	Stripped gas re-heater	T-304	Extract-phase surge tank	C-302	Solvent recovery column	T-307	Butanol storage

Figure 5-9: Process Scheme 3-Flowsheet

5.3.2. Energy Performance

A significant energy performance improvement was obtained in Process Scheme 3 as shown in Table 5-11. The inclusion of the extraction column results in a reduced energy use due to fewer distillation columns being required in the downstream purification. The beer strippers in Process Schemes 1 and 2 are the major steam consumers as large amounts of water (and organics) are available in the reboiler. The energy demand of Process Scheme 3, thus, is improved by 56% from the conventional case and by 51% from Process Scheme 2. This ultimately, indicates that liquid-liquid extraction is good technology in improving the energy performance of the biobutanol such that it can be considered to be used as a fuel. Such an improvement in energy performance resulting from the inclusion of the extraction column was also reported on by van der Merwe (2010).

Table 5-11: Process Scheme 3-Energy performance

Parameter	Value
NEV (MJ/kg)	18.67
Process energy demand (MJ/kg BuOH)	17.31

5.3.3. Process Economic Results

Table 5-12: Process Scheme 3-Main economic analysis results

Parameter	Amount (US$ Millions)
Total capital investments	68.99
Total sales	96.99
Total productions costs	91.81
Net present value (NPV)	82.38

Compared to the benchmarking case, capital costs for Process Scheme 3 are reduced not only from using gas stripping but also from reducing the number of downstream columns. Instead of using five distillation columns to purify the condensate stream from the gas stripping (as in Process Scheme 2) only three columns are necessary in this scheme (including the extraction column). Capital costs are almost the same as in Process Scheme 2, however, the absence of sale proceeds from acetone and ethanol reduce the total sales by 34% compared to the same process. The DCF analysis in Figure 5-10 shows that this scheme

economically performs better than the conventional process but not as profitable as Process Scheme 2.

As shown in Table 5-12, the process shows a potential to produce returns as it has a positive NPV of US$ 82.38 million, however, an IRR of 6% was obtained. This IRR is obviously less than the 10% discounting rate that was applied which implies that an investor would rather not consider investing in this process. This process was reported to be profitable using molasses as substrate (van der Merwe, 2010, Van der Merwe et al., 2013) but the current analysis indicates that the same is not true when clear juice is the substrate.

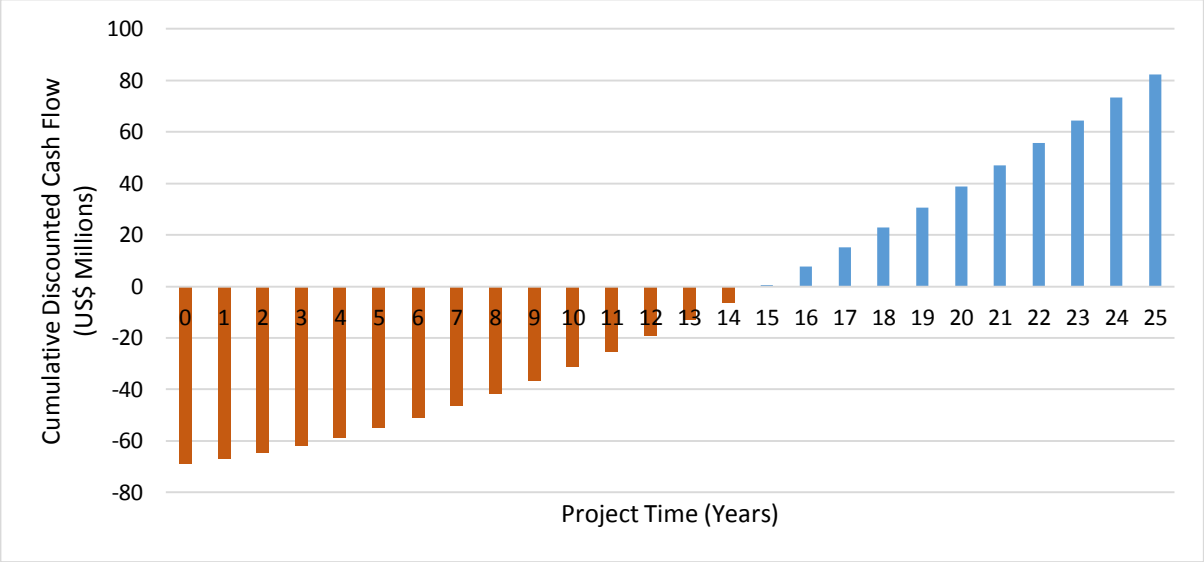


Figure 5-10: Process Scheme 3-Cumulative Discounted Cash Flow Analysis

The sensitivity analysis for the Process Scheme 3 was important in determining the reason for the difference in the results obtained in this current study. Figure 5-11 shows the sensitivity of the NPV to changes in the five factors considered while Table 5-13 shows the IRR sensitivity to the same factors. The 'n/a' in the cells indicates an IRR that is non-existent (negative).

A 15% decrease in the cost of the clear juice cost produces an IRR of 15% coupled with a much higher NPV than the base case. As previously stated, this is the process that was found to be profitable by Van der Merwe et al. (2013) with an IRR of 35.96%. The difference in IRR between the two studies could be due to the fact that Van der Merwe et al. (2013) considered molasses as a substrate which is cheaper than the clear juice used in this current

study. The sensitivity analysis in this study alludes to the cheaper substrate being an effective driver towards profitability.

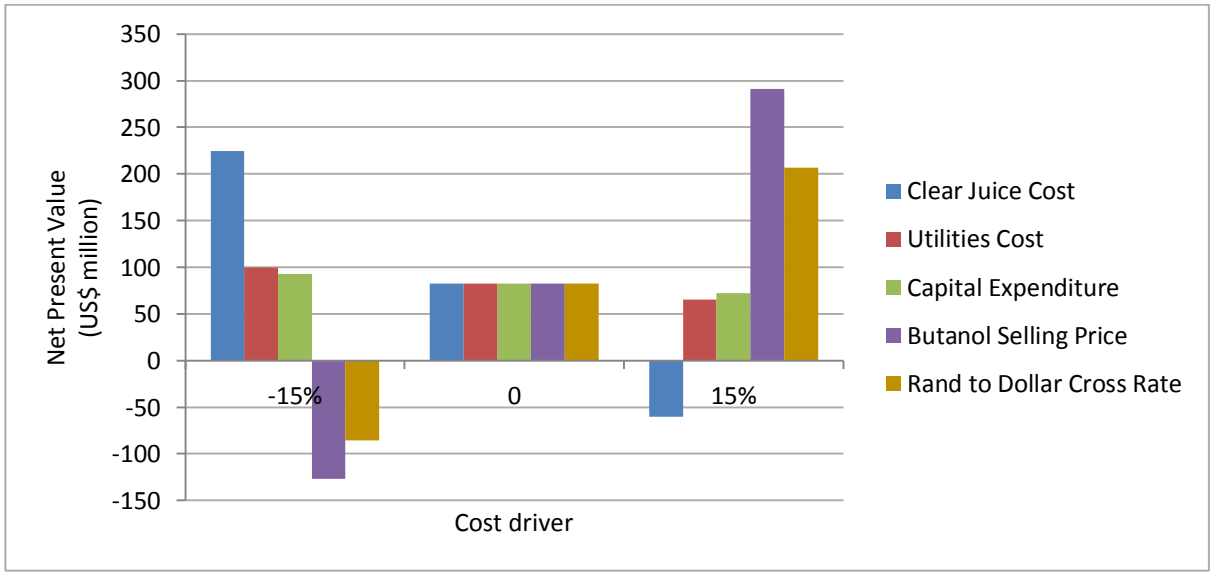


Figure 5-11: Process Scheme 3-NPV sensitivity

An increase in the butanol selling price has the largest potential of producing a profitable process both in terms of the NPV and the IRR while an equivalent decrease takes the process to the most unprofitable end. This should also mean that if another higher value product is found in which butanol is used as a platform chemical, this process scheme could still be considered as a candidate. Just like in Process Schemes 1 and 2, the utilities do not seem to have much an effect on both the NPV and the IRR. This means if a higher value product would require extra process equipment (increase in capital costs), the realised increase in the value from sales could possible produce a profitable process.

Table 5-13: Process Scheme 3-IRR sensitivity

	IRR (%)		
Cost Driver	**-15%**	**0**	**+15%**
Clear juice cost	15	6	n/a
Utilities cost	7	6	5
Capital expenditure	7	6	5
Butanol selling price	n/a	6	18
Rand to dollar cross rate	n/a	6	13

The effect of an increased butanol selling price also indicates than an overall increase in sales would be beneficial, and could be achieved by applying a solvent in the extraction that can extract acetone and ethanol to the same degree it extracts butanol. A tailor-made ionic liquid would a good candidate for such an application as the organic solvents currently reported in literature do not exhibit this property.

5.4. Process Scheme 4: Two-stage gas stripping followed by distillation

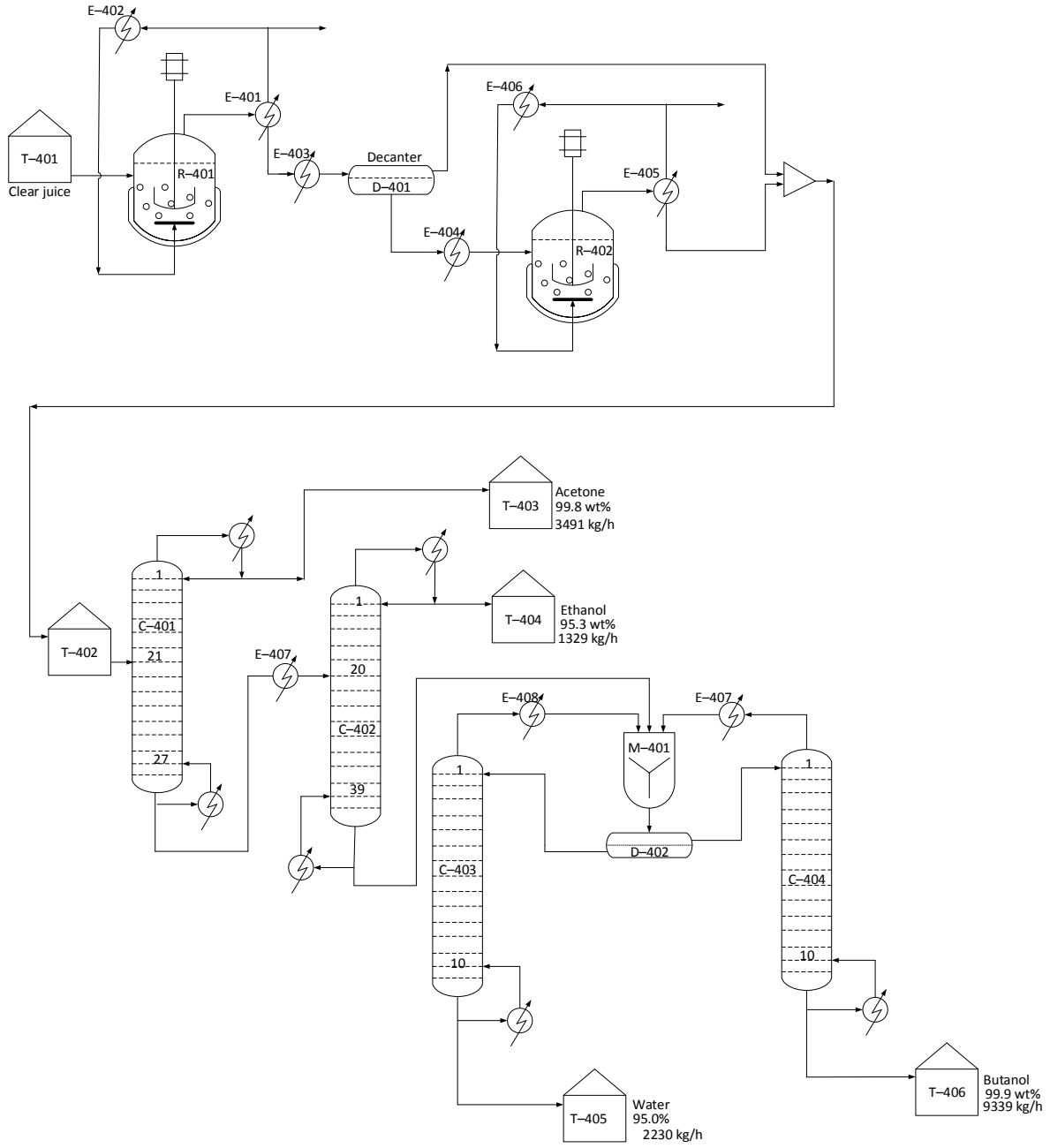
5.4.1. Process Description

In Process Scheme 4, the two-stage gas stripping of Xue et al. (2013) was incorporated into the techno economic analysis of the biobutanol recovery process. The condensate from the first stage gas stripping separates into two phases, the organic and the aqueous phases. The aqueous phase containing about 10 wt. % butanol and 81 wt. % water is heated to 55°C and stripped again with carbon dioxide in the second stage gas stripping. This produces a second condensate stream containing 57 wt. % butanol and 2.5 wt. % water (the rest is acetone and ethanol). The mixture of the organic phase from the first stage gas stripping and the second condensate has a butanol concentration of 72 wt. % and 17 wt. % water. As shown in Figure 5-12, the purification of this mixture requires four distillation columns compared to five required in Process Schemes 1 and 2. The second gas stripping stage enhances the butanol concentration and reduces the water composition such that there is no need for the beer stripper that is designed to remove the bulk of water.

Table 5-14 shows the specifications of the four distillation columns for butanol purification in the downstream of Process Scheme 4. The column specification and sizes are comparable and almost identical to the equivalent columns in Process Scheme 2.

Table 5-14: Process Scheme 4-Main equipment specifications

Parameter	**C-401 (Acetone Recovery)**	**C-402 (Ethanol Recovery)**	**C-403 (Water Stripper)**	**C-404 (Butanol Stripper)**
Number of stages	27	39	10	10
Feed stage	22	20	1	1
Molar Reflux Ratio	4	14	-	-
Operating pressure(bar)	0.7	0.3	1	1
Diameter (m)	1.16	2.30	0.35	1.51



Symbol	Description	Symbol	Description	Symbol	Description
T-401	Clear juice tank	E-404	Second stripper pre-heater	E-407	Ethanol column preheater
R-401	Fermenter/Stripper	R-402	Second stripper	C-402	Ethanol column
E-401	Stripper gas cooler	E-405	Stripped gas cooler	C-403	Water stripper
E-402	Stripper gas re-heater	E-406	Stripper gas re-heater	C-404	Butanol stripper
E-403	Condensate heater	T-402	Distillation feed purge tank	E-407/8	Decanter temperature set
D-401/2	Decanter	C-401	Acetone column	D-402	Decanter
T-403	Acetone storage	T-404	Ethanol storage	T-406	Butanol storage

Figure 5-12: Process Scheme 4-Process flowsheet

The initial consideration was to allow the mixture of the organic phase from the first stage gas stripping and the condensate from the second stage gas stripping to settle and separate into two phases. The aqueous phase would then be sent to an extraction column or adsorption column to remove the water. At the conditions at which the mixture is obtained, no phase separation was predicted and thus, it would not make sense to send the whole stream for extraction. This would require large amounts of extraction solvent, coupled with loss in potential sales from acetone and ethanol as predicted in Process Scheme 3 and hence an alternative design was chosen in which the whole stream is sent to distillation columns.

Table 5-15: Process Scheme 4-Product specifications

Product	**Total produced (t/h)**	**Final Stream Purity (wt %)**
Acetone	3.49	99.8
Butanol	9.34	99.5
Ethanol	1.33	95.3

Table 5-15 gives the products specifications obtained. All the three products are recovered with purity high enough to sell.

5.4.2. Energy Performance

Table 5-16: Process Scheme 4-Energy performance

Parameter	**Value**
NEV (MJ/kg)	20.43
Process energy demand (MJ/kg BuOH)	15.57

Table 5-16 shows an enormous improvement in the energy demand of Process Scheme 4 compared to the conventional case in Process Scheme 1 as well as the incorporation of a single stage gas stripping in Process Scheme 2. The main difference brought about in Process Scheme 4 is the absence of the beer stripper which is the major consumer of steam in the whole recovery trail. This was also alluded to in Process Scheme 3. Both, Process Schemes 3 and 4, benefit from the absence of the high steam-consuming beer strippers as the water concentration is enormously reduced in the downstream purification steps.

It, therefore, makes sense to use biobutanol from this scheme as a fuel source as the energy performance results show a positive NEV, as well as an energy demand less than the energy content of butanol (36 MJ/kg).

5.4.3. Process Economics Results

The economic results of Process Scheme 4 are almost identical to those of Process Scheme 2. Table 5-17 gives the main economic results and these are close to the values in Table 5-9. A NPV value of US$524.09 million and IRR of 32% were obtained and these are in comparison to an NPV of US$ 505.88 million and an IRR of 31% obtained in Process Scheme 2.

Table 5-17: Process Scheme 4-Main economic analysis results

Parameter	Amount (US$ Millions)
Total capital investments	67.81
Total sales	134.92
Total productions costs	102.00
Net present value (NPV)	524.09

The total capital investments of Process Schemes 2 and 4 are almost the same (US$ 67.43 and US$ 67.81 million, respectively). This shows that capital costs of establishing a second stage gas stripping unit almost equals the cost of acquiring a distillation column in the form of a beer stripper in Process Scheme 2. Although steam usage is reduced when a second gas stripping stage is used, there is also no apparent benefit in production costs as there is still need to maintain a cooling system to condense the gases from the second stripper as well as to heat up the feed into the stripper that operates at a temperature of 55°C.

Process Scheme 4 also produces the three products to sellable specifications as the case is in Process Scheme 2. Ultimately, the cumulative DCF analysis in Figure 5-13 is almost identical to that of Process Scheme 2. The process reaches its break even in the fourth year of operation.

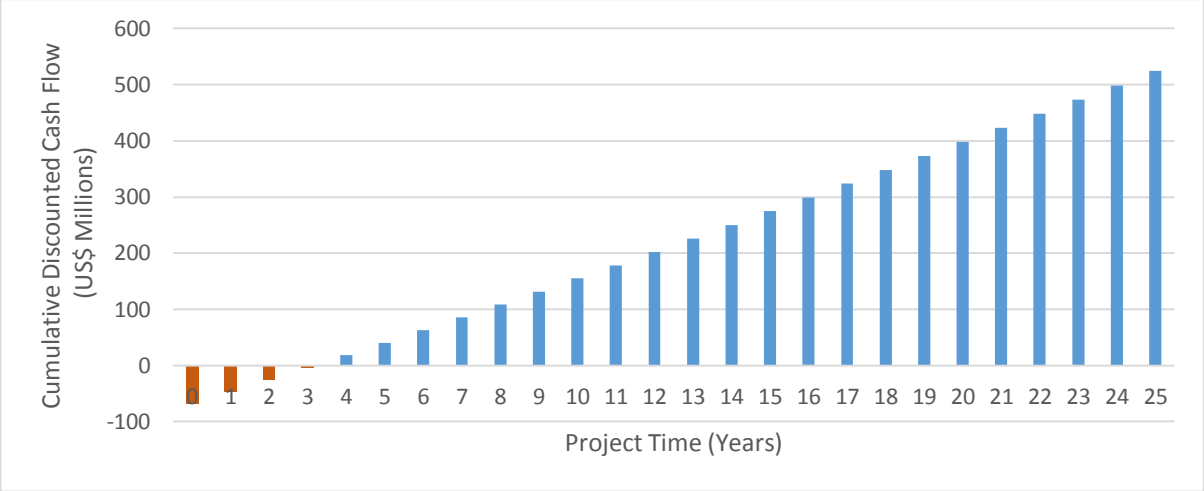


Figure 5-13: Process Scheme 4-Cumulative Discounted Cash Flow Analysis

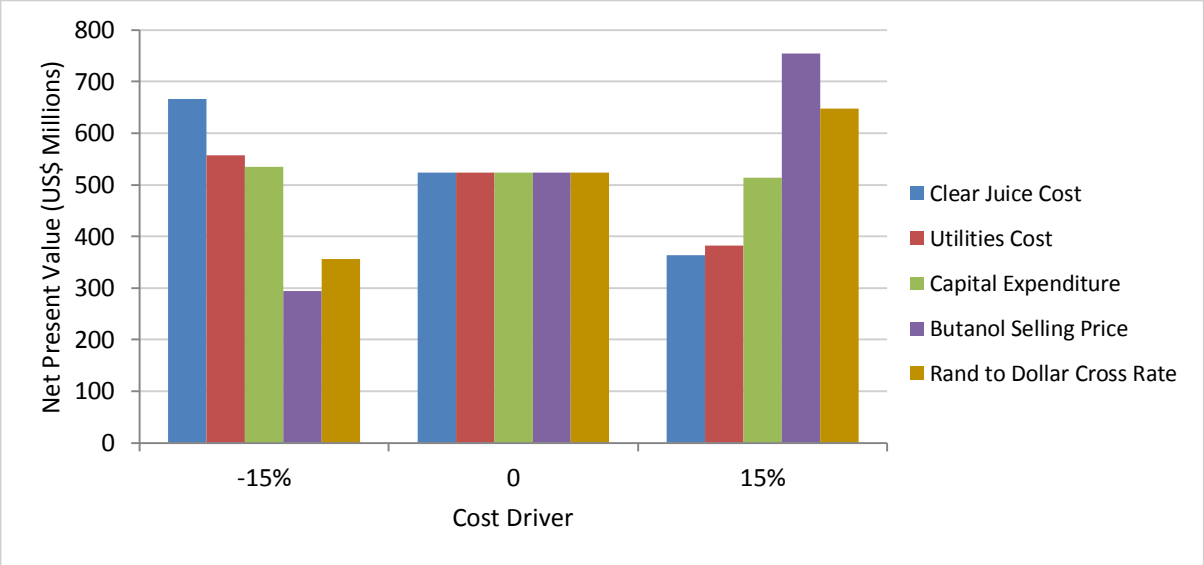


Figure 5-14: Process Scheme 4-NPV sensitivity

The sensitivity analysis is also similar to the results obtained in Process Scheme 2. Figure 5-14 and 5-15 shows the sensitivity of the NPV and IRR, respectively. The NPV of Process Scheme 4 is slightly higher than that of Process Scheme 2 and thus, the IRR in the current case only varies by a unit to that in Process Scheme 2 whenever the different cost drivers are varied up or down.

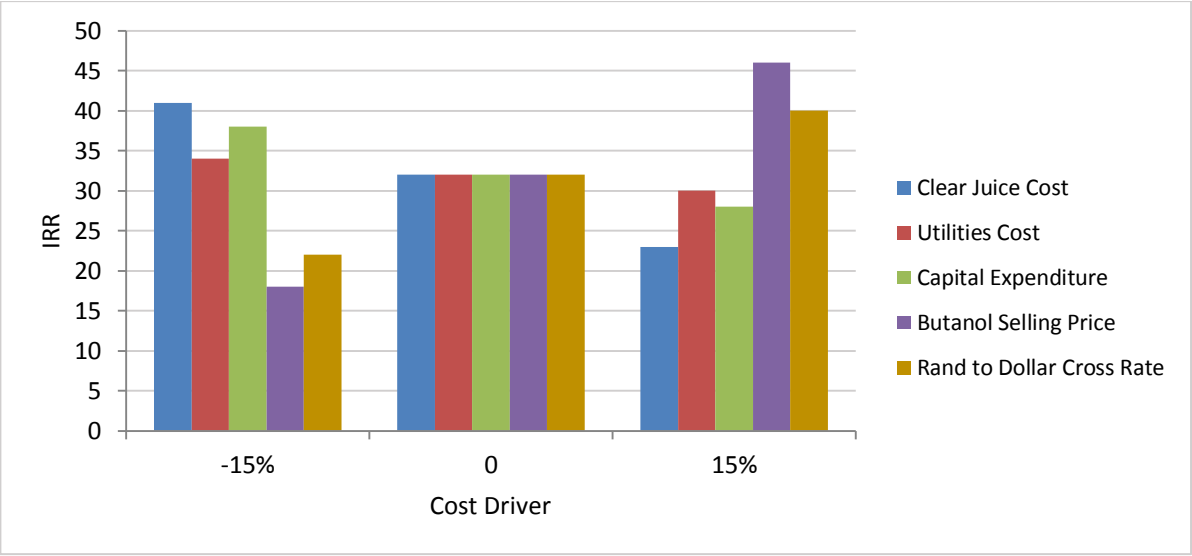


Figure 5-15: Process Scheme 4-IRR Sensitivity

Although from this analysis Process Schemes 2 and 4 seem to have the same variances when parameters are changed, in reality this would not be the same. An example of such circumstances would be when the cost of treatment of the waste streams has to be included into the economic analysis. Depending on which streams are chosen, different costs would be associated with each process which ultimately renders one process better than the other. Additionally, there are current projects on vinasse management whose output will serve as in input in making a decision on waste management and/or value addition.

5.5. Summary and Comparison of Process Schemes 1-4

Table 5-18 is a summary of the output of the analysis of the four Process Schemes that were considered as potential biobutanol recovery routes. The benchmarking case, which is the conventional distillation case, gave a negative NPV showing unfavourable economics under the current economic conditions. Due to the large amount of water in the broth from batch fermentation it is not possible to obtain ethanol at a sellable purity. Sensitivity analysis showed that the economics of Process Scheme 1 would be improved towards a positive NPV if higher butanol selling prices could be realised as well as the use of a cheaper feedstock. The use of cheaper (compared to clear juice) feedstock, like molasses and lignocellulosic material, has already been included in full techno economic analyses using conventional distillation and the process has still been found unprofitable (van der Merwe, 2010, Naleli, 2016).

Table 5-18: Summary and overall comparison of Process Schemes 1-4

Parameter		Process Schemes			
		1	**2**	**3**	**4**
Sellable products (kg/h):	Acetone	3 420	3 529	-	3 491
	Butanol	7 220	9 293	8 485	9 339
	Ethanol	-	1 407	-	1 329
Total capital costs (US$ millions)		124.85	67.43	68.94	67.81
Total sales (US$ millions)/yr.		106.11	134.90	96.99	134.92
Total production costs (US$ millions)/yr.		102.71	103.25	91.81	102.00
NPV (US$ millions)		-3.80	505.88	82.38	524.09
IRR (%)		n/a	31	6	32
NEV (MJ/kg)		-3.73	0.9	18.67	20.43
Process energy demand (MJ/kg BuOH)		39.73	35.10	17.31	15.57

Process Scheme 2 and 4, incorporating single stage and two-stage gas stripping respectively, showed almost identical economics results. The major characteristic of these two schemes is their ability to produce all the ABE products at sellable quality which increases the sales by 27% compared to the conventional case. This increase in sales coupled with the reduced capital costs due to lower fermenter sizes (as productivity is increased) renders the processes profitable with NPV values of at least US$ 500 million and IRR values of 31 and 32%, respectively. This current study is the first to include the two-stage gas stripping of Xue et al. (2013) in a full techno economic analysis and the results showed that such an inclusion removes the need for the beer stripper. The beer stripper is a major steam consumer and thus, Process Scheme 4 showed one of the best energy performance results in the considered processes as shown in Table 5-18.

Process Scheme 3, which incorporates a single gas stripping stage and liquid-liquid extraction, has a positive NPV but an IRR of 6% will not render it worth investing in. The use of an organic solvent for extraction only enables the production of butanol to sellable quality as the solvent is more selective to butanol extraction compared to acetone and

ethanol. To improve on economics of this process, an increase in sales would be the best way which can be achieved by using a solvent which is tailor made to recover acetone and ethanol with comparable capacity to butanol.

It is also important to note that Process Schemes 2, 3 and 4 have approximately the same total capital costs. The difference and similarity in the economic performance of these processes thus, depend on how much sellable products can be made as well as the total production costs. This means that for the same fermenter productivity, the downstream capital costs of purifying the ABE solvents is almost the same, e.g. the cost of establishing the second stage gas stripping in Process Scheme 4 is almost equal to the total cost of the distillation column, in the form of the beer stripper in Process Scheme 2, that it replaces. This fact points the need to optimise the downstream purification steps to reduce energy consumptions while increasing the number and purity of sellable products to improve the overall economics, rather than trying to choose technologies based on the cost of installations.

Overall, Process Scheme 4 can be considered the most economic process as it has the highest NPV and IRR values as well as the lowest process energy demand. Process Scheme 3 is at the boarder of profitability with good energy performance results, and could also be considered when an appropriate solvent is identified.

5.6. Overall Comparison with Other Studies and Limitations of Results

This current study focused on the cost and economics of the ABE products recovery from fermentation but with little detail of the actual fermentation process. As a result the costing of the fermentation process only accounts for the price of fermenters and broth and condensate surge tanks. There are other studies that contain an in-detail costing of the fermentation stage. Lenz and Morelra (1980), for example, account for the molasses cookers that are required before the fermenters for feed sterilization. The sensitivity analysis on the total capital investment performed in this study gives an indication on the possible effects of increasing the capital (which might arise from an increase in the fermentation stage costs) on the obtained NPV and IRR, and this analysis is deemed sufficient to intelligently determine the most economically viable process alternative as intended by the objectives of the study.

In a similar way, the energy demand in this current study is dependent on the butanol recovery and purification steps but does not account for energy that is needed prior to fermentation, e.g. sterilization of equipment and any substrate conditioning. The results obtained correlate well with those reported by Mariano et al. (2011) and van der Merwe (2010) but they significantly differ from results reported by Naleli (2016). This is attributed to a more robust analysis that was performed for steps prior to fermentation which was critical for that study as it considered different lignocellulosic biomasses that require different processing steps and ultimately consume variable energy amounts. In reality, therefore, the energy demands of the processes would be higher than those reported in this preliminary study as more information on the fermentation is gathered and included. The obtained values, however, still report on the need for a paradigm shift from considering biobutanol as an energy fuel but rather as an invaluable sugarcane biorefinery platform chemical as explored in the bigger context of this study (Chapter 6).

The use of the US Dollar as a currency of analysis in this study also brings about some limitations. Prices for equipment are mainly from American sources and might not reflect the state in South Africa at this current moment. From the sensitivity analyses reported it can be seen that a 15% decrease in the value of the Rand can render a profitable process unprofitable. With the fluctuations of the Rand in recent times this calls for strict contingencies to be included to account for such fluctuations. The use of local quotes on equipment would also be useful. However, such are not readily available.

Lastly, there are other technologies, like adsorption and pervaporation, which have shown enormous potential in improving the economics and energy performance of the biobutanol recovery process. The inclusion of such in the full techno economic analysis would be good in order to determine the actual potential they offer. Such an inclusion would, however, need properly determined experimental data that will give simulation results that are practically verifiable and can be dependent on. A simulation with predictive abilities is an invaluable resource in determining the economics and feasibility of running different sugarcane biorefinery models as South Africa moves towards the full adoption of this concept.

6

CHAPTER SIX

6. OUTLOOK-REACTIVE EXTRACTION OF BUTANOL USING AN IONIC LIQUID

6.1. Introduction

Reactive extraction is a technique that is widely reported in literature especially in the recovery of carboxylic acids (e.g. lactic acid and propionic acid) from fermentation broth, using amine-based extractants (Järvinen et al., 2000, Hong et al., 2001, Kumar and Babu, 2008). A number of definitions for the term 'reactive extraction' have been proposed but the generally accepted definition represents a combination between chemical (solute and extractant reaction) and physical phenomena (diffusion and solubilisation of the system components) (Hong et al., 2001, Cascaval and Galaction, 2004, Kumar and Babu, 2008). The extractant (also termed "organic phase") reacts with the compound present in the aqueous phase. Whether physical extraction into the organic phase precedes reaction, or whether the reaction takes place in the aqueous phase, followed by extraction, will depend on reaction kinetics and physico-chemical properties of all components involved. In both cases, a biphasic system is obtained (Hong et al., 2001). The extractant could be the extracting solvent itself or could be dissolved in the solvent phase.

There is limited information reported in literature on the use of reactive extraction to recover alcohols from fermentation broth, although some authors suggest that the method could also be applicable (Kumar and Babu, 2008, Hong et al., 2001, Cascaval and Galaction, 2004, Pai et al., 2002).

6.2. Process Description

In this project, it is proposed that an ionic liquid (IL)-based acid (IL-Acid) be used a reactive extractant to recover butanol directly from fermentation broth (or from a concentrated

stream in Process Scheme 4) forming an ester (IL-Ester). The IL-Acid needs to be reactive by design in addition to possessing the properties that a physical extracting solvent for liquid-liquid extraction should have, i.e. low solubility in water, liquid at the reaction temperature etc. The IL-Acid would then be regenerated in a second step by transesterification with a carboxylic acid (e.g. levulinic acid) to produce the final ester product (reactive distillation). The hypothesis is that the esterification would have to be done in two steps because of the effects of water (fermentation broth) on the equilibrium (esterification produces water in a reversible reaction), and solubility issues.

Depending on the physical properties of the final ester product and the IL-Acid, distillation could be used to separate these two to enable the IL-Acid to be recycled to the fermentation broth vessels.

6.3. Process Flow Scheme and Chemistry

Figure 6-1 displays the process scheme and the process chemistry based on a hypothetical IL.

As a starting point, a process scheme derived from a patent by Ayoub (2008) for the reactive extractive extraction of levulinic acid is adapted. Looking at Figure 6-1, the unit operations are the same up to the reactive extraction reactor. However, a transesterification reactor is added for the production of the final ester product and the regeneration of the IL. The filtration unit is for the case when the reactive extraction process is conducted directly using the fermentation broth, otherwise it could be replaced by the first or second stage stripping stage on Process Scheme 4.

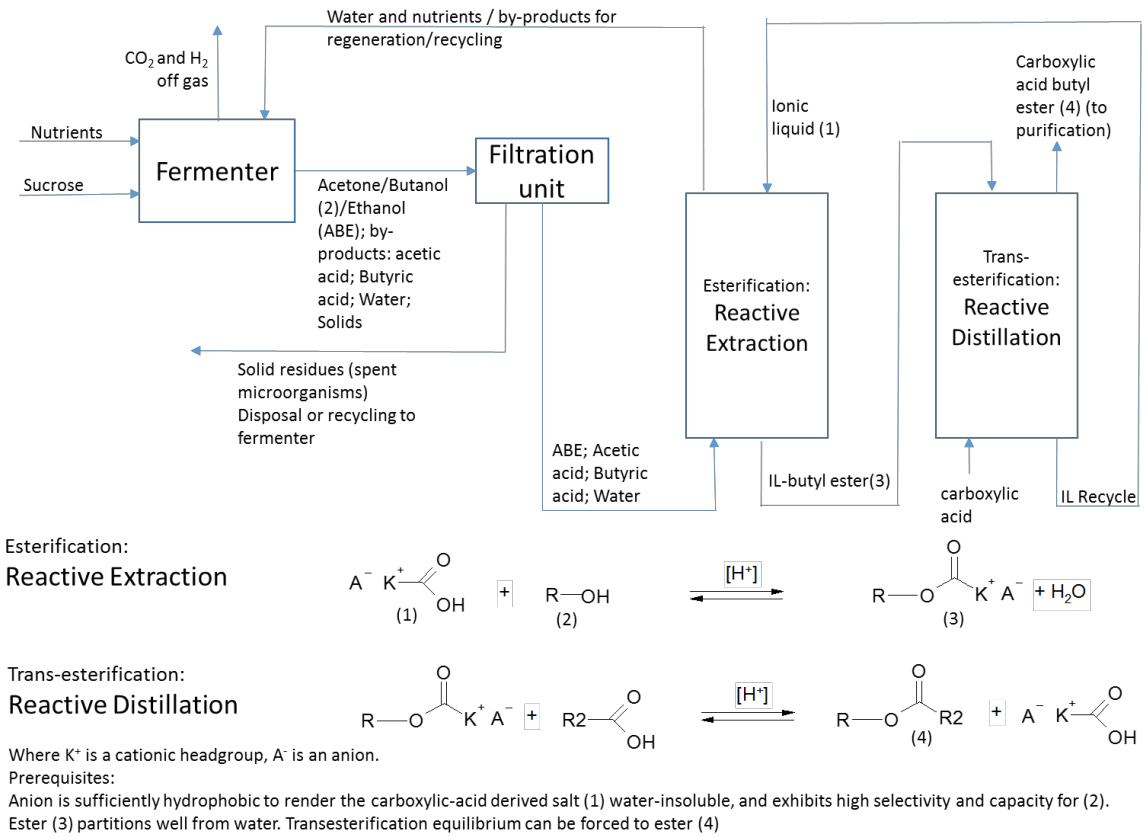


Figure 6-1: Proposed process scheme and chemistry

6.4. Project Deliverables

This section gives an estimated overview and scope of the work that should be covered in this project:

1. The required properties of the IL-Acid have to be first estimated using rule of thumb estimations, literature or any other methods in order to have a starting point for the synthesis of the IL-Acid. These properties include density, viscosity, melting point, solubility in water, reactivity, etc.
2. Synthesis of the IL-Acid. A number of structures can be synthesised in the beginning by varying properties such as the alkyl chain length, the anion or the cationic head group.
3. Reaction kinetics of the IL-Acid and butanol. This can initially be done using pure butanol (and can be extended to include acetone and ethanol). The main property to be varied is temperature, taking into account the obtained conversions as well as the properties of the IL-Acid and the obtained IL-Ester product.

4. Phase equilibria data will then be measured and modelled. This will be LLE for the water-butanol-IL (Acid) and water-butanol-IL (Ester) systems. The results will determine in which phase the broth components and the reaction products will be found after the reactive extraction process comes to completion.
5. A corrective or iterative procedure will then be implemented to devise a structure of an IL-Acid with the best reactive and extractive properties. Results from Steps 3 and 4 above will determine which chemical groups should be added, removed or replaced in the initial proposed IL-Acid based on the general IL synthesis techniques. This iterative process is to be repeated until the IL-Acid with the best properties for the current application is obtained.
6. Design of the extraction equipment based on the kinetics and the LLE data collected with the best synthesised IL-Acid.
7. Design of the transesterification process equipment for the regeneration of the IL-Acid using a biomass-based acid (e.g. levulinic acid) to obtain the final ester product. The acid that will be used in the transesterification will depend on the required properties of the final ester and the identified possible applications of this product.
8. Costing of the production process of the final ester product as well as the estimated selling price. This will give an idea on how this product will perform if included in the mix of products in the sugarcane biorefinery.
9. Inclusion of the ester production into Process Scheme 4 on Aspen Plus® and into the sugar mill model as one of the sugarcane biorefinery model scenarios.

6.5. IL Properties and Structure-Preliminary Investigation

This section reports on the methodology that was applied in order to devise a starting point on the determination of the structure and properties of the IL-Acid for the reactive extraction. The investigation was performed on a preliminary level using group contribution methods on Aspen Plus®.

6.5.1. Approach and Methodology

6.5.1.1. Group Contribution Methods (UNIFAC and modified UNIFAC)

There is an almost infinite number of ILs that can be synthesised depending on the cation and anion combinations. The task of selecting or synthesising an IL which is best suited for a

certain application can, therefore, be made simpler by the application of predictive thermodynamic models. This implies choosing the right combination of the anion, cation and the substituents which gives the required equilibrium behaviour and reactive properties. The UNIversal quasichemical Functional group Activity Coefficients (UNIFAC) and modified UNIFAC (mod. UNIFAC (Dortmund)) are examples of predictive thermodynamic models that have been incorporated in process simulators like Aspen Plus®.

The UNIFAC method was developed by Fredenslund et al. (1975) and various modifications to this method have been proposed including the mod. UNIFAC (Do) (Gmehling et al., 1993). These modifications are meant to improve the applicability range, accuracy and reliability of the predictions. In the mod. UNIFAC (Do) as well as in the original UNIFAC, the activity coefficients (γ_i) are calculated as a sum of a combinatorial (C) and residual part (R) (Gmehling et al., 1993, Kato and Gmehling, 2005):

$$\ln \gamma_i = \ln \gamma_i^C + \ln \gamma_i^R \qquad [6\text{-}1]$$

The residual part is evaluated the same way in the UNIFAC and mod. UNIFAC (Do). However, in the mod. UNIFAC (Do), the combinatorial part was changed in order to make it possible to deal with compounds very different in size (Gmehling et al., 1993). The equations for calculating the combinatorial and residual parts (and their auxiliaries) are well explained in literature for further information (Gmehling et al., 1993).

The group interaction parameters Ψ_{nm} between groups *n* and *m* are calculated using constant temperature (UNIFAC) and temperature dependent group interaction parameters (mod. UNIFAC (Do)). The introduction of the temperature dependent parameters permits for a better description of the real behaviour as a function of temperature (Gmehling et al., 1993, Kato and Gmehling, 2005).

For the original UNIFAC:

$$\Psi_{nm} = \exp\left(-\frac{a_{nm}}{T}\right) \qquad [6\text{-}2]$$

For mod. UNIFAC (Do):

$$\Psi_{nm} = \exp\left(-\frac{a_{nm} + b_{nm}T + c_{nm}T^2}{T}\right) \qquad [6\text{-}3]$$

where T is the absolute temperature, a_{nm}, b_{nm} and c_{nm} are adjustable group interaction parameters of the UNIFAC models.

The successful application of the UNIFAC and mod. UNIFAC (Do) group contribution methods is dependent on the availability of the group volume (R_K), group surface area (Q_k) and group interaction parameters (a_{nm}, b_{nm} and c_{nm}) (Tiegs et al., 1987). There is an extensive matrix of both the UNIFAC and mod. UNIFAC (Do) parameters published. The Dortmund Data Bank (DDB) contains extensive published and unpublished experimental data and its use in the fitting of parameters ensures that the parameters are generally acceptable and the prediction reliable (Tiegs et al., 1987). This work of fitting experimental data continues to improve the accuracy of already published parameters, by including new data, as well as introducing previously unreported on (new) groups.

6.5.1.2. Regression of Parameters

An attempt has been made to use UNIFAC and mod. UNIFAC (Do) models to predict the thermodynamic behaviour for systems involving ionic liquids (ILs) (Kato and Gmehling, 2005). The majority of the ILs reported in literature are based on the imidazolium cation and the common groups of anions include bis(trifluoromethylsulfonyl) amide (BTI), trifluoromethanesulfonate (OTf) and tetrafluoroborate (BF_4). The interaction parameters for these groups have been included in the 2015 UNIFAC consortium version of DDB but are not yet implemented (defined) in Aspen Plus®. In particular, both Aspen Plus® and the 2015 UNIFAC consortium version still miss group interaction parameters between the IL ions and the carboxylic acid (-COO-) and the ester (-CH_2-COO-) groups which are critical for the current application (reactive extraction).

In order to do some predications of the reactive extraction of butanol using an IL-Acid (which is yet unknown), it was therefore, imperative to look into the regression of experimental data to determine the missing interaction parameters. The original UNIFAC utilised vapour-liquid equilibria (VLE) to fit parameters while the mod. UNIFAC (Do) uses LLE, activity coefficient at infinite dilution (γ^{∞}), heats of mixing (h^E), azeotropic data, excess heat capacity (Cp^E) and solid-liquid equilibria (SLE) data (Gmehling et al., 1993). The next step was therefore, to look for such experimental data for systems involving ILs and esters or

carboxylic acids in order to fit the missing parameters. In order estimate with reliable group interaction parameters, there is need for a large data base of experimental data.

As a starting point, ILs containing the imidazolium cation and the BTI anion were chosen to be used. This decision was made due to the fact that BTI-based ILs are in general hydrophobic, i.e. would allow for establishing a binary liquid-liquid system with water. Secondly, dialkylimidazolium-based ionic liquids are the most investigated class of ionic liquids, and hence data exists as starting point for predictions. The volume (R_K) and the surface area (Q_K) contributors of these groups are available and have already been reported on (Kato and Gmehling, 2005). To be able to estimate the group interaction parameters of the imidazolium and BTI ions, data was extracted from DDB and regressed on Aspen Plus®. The regression of UNIFAC and mod. UNIFAC (Do) parameters on Aspen Plus® is a simple procedure already contained in the simulator. Experimental data available on DDB for ionic liquids is, however, often incomplete (sometimes only data point per set) and difficult to regress for reasonable parameters. Furthermore, there is limited data of systems containing ILs with carboxylic acids or esters. Three data sets for the IL 1-octyl-3-methylimidazolium bis(trifluoromethylsulfonyl) amide [OMIM][BTI] were found and used for the regression. The data sets were as follows:

1. γ^{∞} of propionic acid in [OMIM][BTI].
2. γ^{∞} of butyl acetate in [OMIM][BTI].
3. Temperature dependency data for the liquid molar heat capacity of [OMIM][BTI].

Data set 1 and 2 had equal contribution towards the regression while data set 3 had half the weighting compared to the other two. These data sets do not constitute a sufficient base for an accurate regression and thus, still needs to be extended to include more data containing different ILs, carboxylic acids and esters. The regression was done only for mod. UNIFAC (Do) parameters as previously asserted that it is an improvement of the original UNIFAC.

6.5.1.3. IL Definition and Properties

With the group interaction parameters of the imidazolium and BTI ions with the carboxylic acid and ester groups established from the regression, it was now possible to define a new IL that bears a carboxylic acid group (IL-Acid) as well as the ester product of this IL with

butanol (IL-Ester). As a starting point, this IL-Acid was derived directly from [OMIM][BTI] and the structures are shown in Figure 6-2.

Pure IL property and critical data for [OMIM][BTI] were obtained from Valderrama and Rojas (2009) and the defined ILs were made to have these properties as well (as estimates). Also worth noting is that [OMIM][BTI] is not available in Aspen Plus® databases and it also had to be defined by its functional groups, and its properties were incorporated during the regression stage described above.

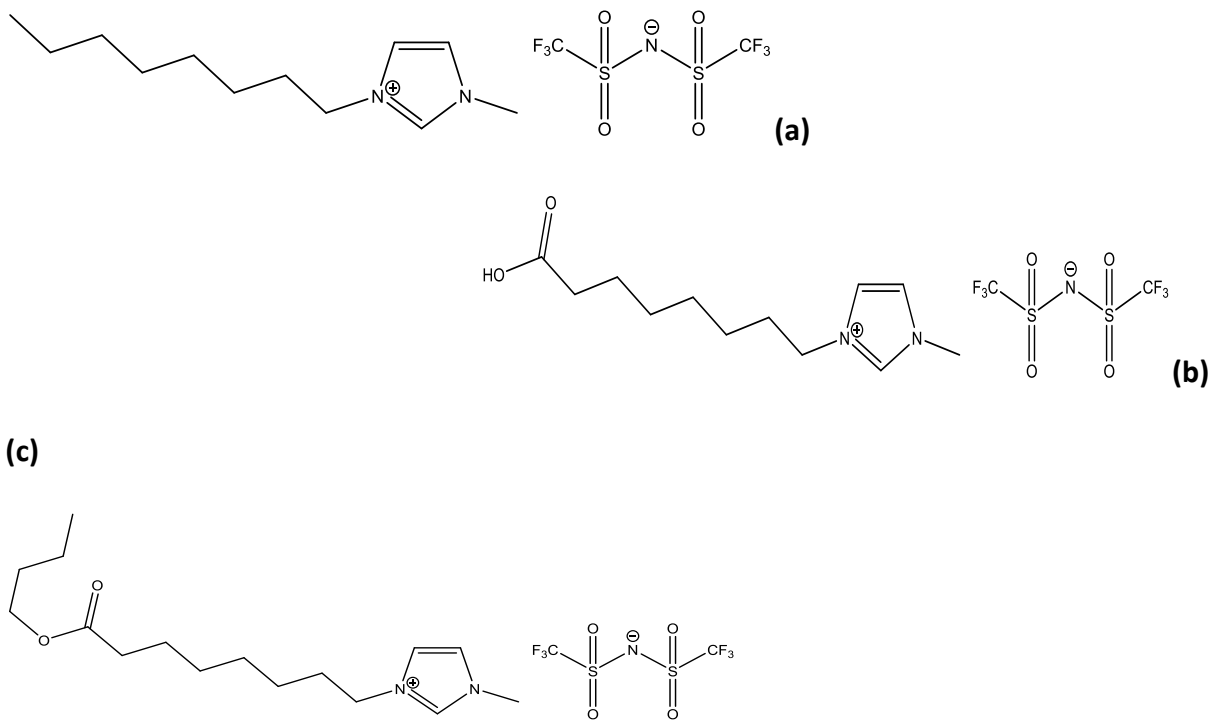


Figure 6-2: Structures for the (a) [OMIM][BTI], (b) IL-Acid and (c) IL-Ester defined on Aspen Plus®

6.5.1.4. Aspen Plus® Simulation

Since all the components that take part in the reactive extraction process had been defined on Aspen Plus® and properties estimated by group contribution methods, it was now possible to simulate the whole process and obtain insights of how the IL-Acid would perform in both extracting butanol and reacting with it. The reactive extraction process has two steps that take place simultaneously i.e. extraction and reaction. The extraction step depends on the equilibrium behaviour between all the reactants and the products (i.e. IL-

Acid, butanol, IL-Ester and water). The equilibrium behaviour was investigated and the results reported ion Section 6.5.2.1.

Figure 6-3 shows a screen shot of the Aspen Plus® simulation of the whole reactive extraction process. The process begins with equal amounts of the fermentation broth being mixed with the IL-Acid (arbitrary basis of 1000 k/hr, each). The fermentation broth is a butanol-water solution just below the solubility limit of butanol. This represents the aqueous phase of the condensate from the gas stripper after phase separation. REACT1 is an equilibrium reactor where esterification reaction between the IL-Acid and the butanol takes place. SPLIT1, before the reactor, is a stream splitter which bypasses 10% of the broth-IL-Acid mixture to simulate an assumed 90% approach to equilibrium in the reactor.

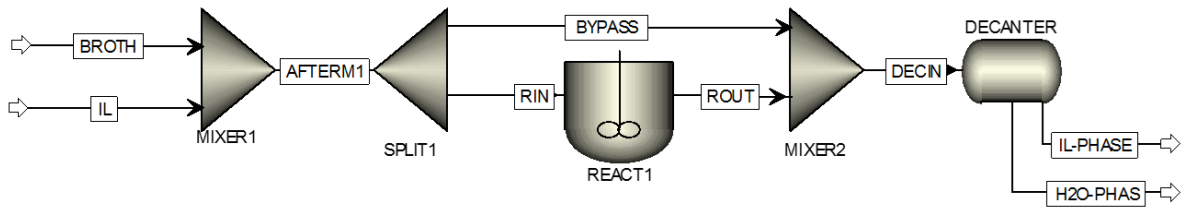
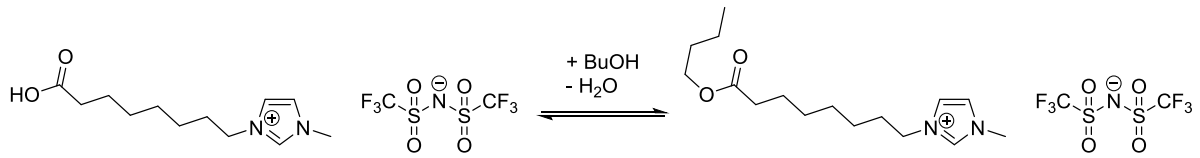
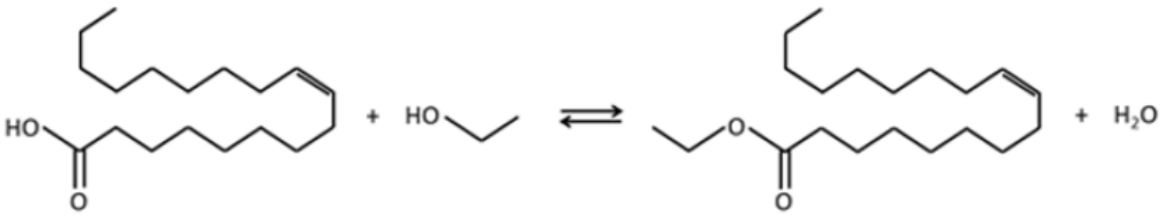


Figure 6-3: Screenshot on the reactive extraction Aspen Plus® simulation

Conversion in the reactor is based on the reaction below:



The prediction of this reaction in the reactor is not possible without some form of reaction kinetics from laboratory experiments. Since the whole point of this preliminary investigation is to find a starting point for synthesis of the IL-Acid by coming up with a plausible structure and possible properties, kinetics for the esterification of fatty acids with alkyl alcohols in the production of biodiesel were used as a first guess to the kinetics in the reactor. The structure and sizes of fatty acids used in biodiesel production are similar to the IL-Acid proposed so far. An example would be the esterification of oleic acid with ethanol to form ethyl oleate and water. Oleic acid is the major fatty acid in waste cooking oil which is a good raw material for biodiesel production (Neumann et al., 2016).



The bulk of the esterification reactions are catalysed by homogenous acid catalysis (e.g. sulphuric acid), however, in this application it is postulated that the reaction can be self-catalysed by the IL-Acid itself. ILs have been used as catalysts for such reactions (Stark, 2011). Since reaction kinetics reported depend on many factors which include the nature of the fatty acids, the alcohol used, catalyst type and amounts, three cases of different kinetics were considered to determine some form of sensitivity of the reactor output to changes in the kinetic parameters used. A fourth case was also included which was just a trial and error input on kinetic parameters that would produce a reaction of the IL-Acid and the butanol in the broth.

The variations of the kinetic parameters was implemented by inputting the expressions for the temperature dependency of the chemical equilibrium constant (K_{eq}) into the reactor model on Aspen Plus®. The chemical equilibrium constant is the ratio of the activities of the products and reactants at equilibrium-esterification reactions are equilibrium reactions. The activity of a component, i, is a product of the activity coefficient, γ_i, and its molar fraction, x_i. In this current state of the study, the activity coefficients were calculated by group contribution methods, i.e. UNIFAC and UNIFAC (Do).

$$a_i = \gamma_i . x_i \qquad [6\text{-}4]$$

The temperature dependency of the equilibrium constant is described by the van't Hoff equation:

$$\frac{d(\ln K_{eq})}{dT} = \left(\frac{\Delta H^{\theta}_{rxn}}{RT^2}\right) \qquad [6\text{-}5]$$

After integration, Equation 6-5 reduces to:

$$\ln(K_{eq}) = A + \frac{B}{T} \qquad [6\text{-}6]$$

Where A and B are constants and A is given by:

$$A = \frac{-\Delta H^{\theta}_{rxn}}{R} \quad [6\text{-}7]$$

By varying these two constants from equation 6-6, a general and rough sense of the kinetics that would make sense for the reactive extraction process was established.

Table 6-1: Fatty acid esterification kinetic parameters

Case	A	B	Esterification details	Reference
1	16.87	-5074.5	Oleic acid + ethanol	Abbas and Abbas (2013)
2	3.43	-941.17	Oleic acid + methanol	Hassan and Vinjamur (2013)
3	42.64	-13064	Jatropha oil + methanol	Neeharika et al. (2017)
4	41.84	-7420.01	Trial and error	-

Finally, the decanter after the reactor on Figure 6-3 is meant to ascertain the phase separation that takes place after the reaction. For an ideal (assumed) IL-Acid used, all the butanol that was originally in the broth would be in the organic phase, either just as unreacted butanol or as the IL-Ester product, and leaving an aqueous phase of almost pure water for possible recycle to the fermenters.

6.5.2. Preliminary Investigation Results

6.5.2.1. LLE Predictions

Table 6-2 shows the binary interaction parameters (in SI units) that were obtained from the regression. These parameters still need to be improved by extending the number of data sets used and that data is currently not available. However, for this preliminary work this was accepted as sufficient.

Table 6-2: Regressed binary interaction parameters

	Imidazolium	BTI	Carboxylic acid	Ester
Imidazolium			-94.3335	-50.3467
BTI			-83.5974	-9.3503
Carboxylic acid	-21.5721	40.6716		
Ester	178.63	6.09021		

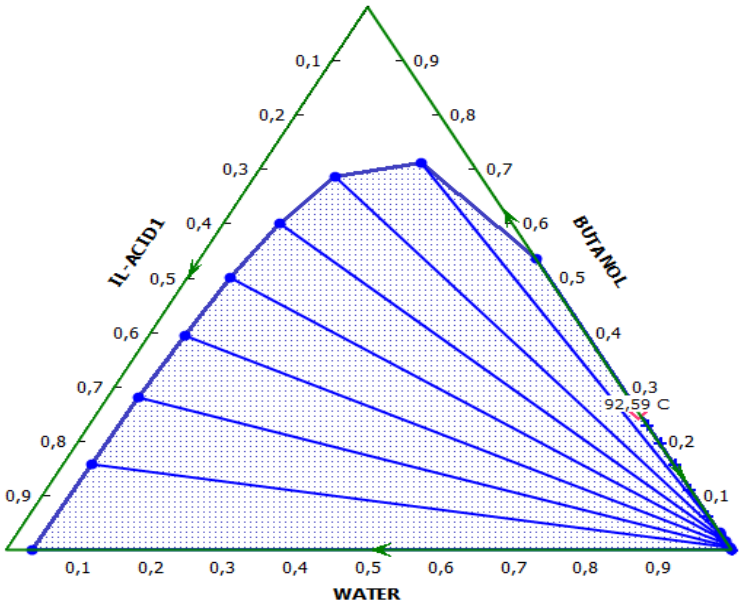


Figure 6-4: Predicted behaviour for IL-Acid + Butanol + Water system

Figures 6-4 and 6-5 below show the predicted LLE behaviour of the IL-Acid + butanol + water and IL-ester + butanol + water systems. In finding the properties of the ideal IL for the reactive extraction, this behaviour becomes critical.

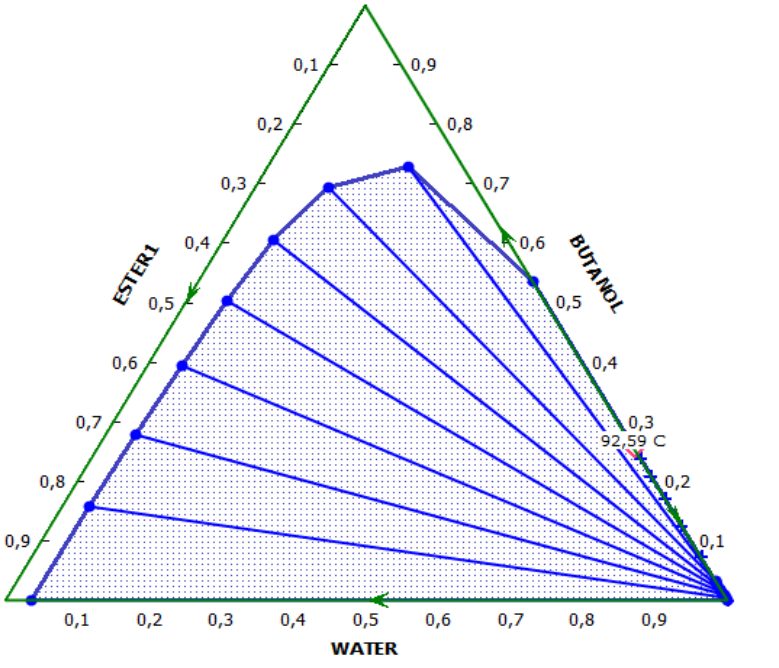


Figure 6-5: LLE behaviour for IL-Ester + butanol + water system

The behaviour displayed above would be ideal for the ideal IL. The two systems indicate the similarity between the IL-Acid and the IL-Ester and the preference of both the butanol and the ester product to remain in the organic phase during the reaction. The low solubility of

both, the ester product and the IL-Acid in water also ensures that at the end of the process, the aqueous phase (with ideally no butanol left) can be recycled back to the fermenters without the risk of harming the microorganisms (e.g. should the IL exhibit toxic properties for the microorganisms).

This also means that in the worst case that no reaction takes place between the IL-Acid and the butanol in the broth, there is still extraction of the butanol from the aqueous phase. This would create an opportunity of first performing a physical extraction in the first step then changing conditions that favour the reaction in a second step.

6.5.2.2. Simulation Results

Table 6-3: Reactive extraction reactor output predictions

Case	Component	Flow in organic phase (kg/h)	Flow in aqueous phase (kg/h)
1	Butanol	43.02	29.90
	Water	1.10	928.92
	IL-Acid	99.43	-
	IL-Ester	0.63	-
2	Butanol	43.02	26.90
	Water	1.10	928.92
	IL-Acid	999.49	-
	IL-Ester	0.56	-
3	Butanol	43.02	26.90
	Water	1.10	928.92
	IL-Acid	999.43	-
	IL-Ester	0.64	-
4	Butanol	0.55	2.93
	Water	4.07	944.76
	IL-Acid	570.28	-
	IL-Ester	477.27	-

Table 6-3 shows the flow results that were obtained in the final organic and aqueous phases on the flowsheet (screen shot) on Figure 6-3 while varying the kinetic parameters according

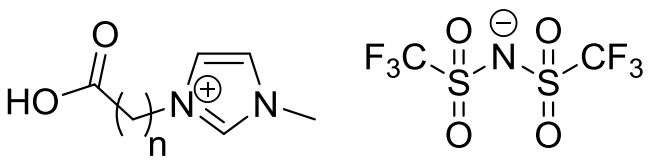
to the values in Table 6-1. In the first three cases that make use of kinetics from fatty acid esterification, no reasonable amounts of the IL-Ester are formed. The bulk of the butanol in the feed is found in the final organic phase, however, around 40% of the butanol is still lost in the aqueous phase.

From the kinetic parameters, the reaction is endothermic and increasing the temperature would, theoretically, yield more ester product. The temperature cannot be too high, for example, at temperatures around and above 100°C water and butanol start to evaporate from the solution. The increase in temperature in this case, still did not yield a significant change in the IL-Ester produced. The reason for this is possibly due to the different conditions that the parameters were obtained to those in the current application. Pure alcohols are used for these parameters while a very dilute butanol solution is used in this case. This means the reaction is marred by equilibrium limitations from the start as there are already large amounts of water in the system.

Case 4 in Table 6-2 shows the output from just arbitrary parameters that were used to effect a reaction in the Aspen Plus® reactive extraction model. It has been reported that ILs can have any desirable properties by changing the cation and anion combinations (Ha et al., 2010, Stark, 2011) and in that case the chemist can look at these parameters and see how that constraint can possibly be met during the synthesis process.

6.6. Conclusions and Framework of Future Work

This preliminary work was an attempt to come up with a starting point of the structure of the IL that is required to carry out the reactive extraction of butanol. From the LLE results from group contribution methods, the first version of the IL of the form shown below can be synthesised:



The chain length variation is important as this determines the solubility properties of the IL. The steps highlighted in Section 6.4 can then be applied from this starting point till the whole scope of the project is fulfilled.

From reading through literature, no publication has reported on such an invention, making this a novel work and thus, this forms a proposal for a degree of Doctor of Philosophy.

7

CHAPTER SEVEN

7. CONCLUSIONS AND RECOMMENDATIONS

7.1. Conclusions

This work represents one of the pioneering projects by the SMRI Sugarcane Biorefinery Research Group in establishing sugarcane biorefinery models that include a number of new products in addition to the products currently produced in South African sugar mills. The study considered four process schemes for biobutanol recovery from the fermentation of clear juice from a South African generic sugar mill. Four process schemes were modelled on Aspen Plus® and techno economic analyses performed. From the techno economic analyses the following can be concluded:

- Process Scheme 1, which is the conventional distillation process, is not profitable under the current economic conditions. An NPV of US$-3.80 million was obtained for this process.
- The incorporation of *in situ* gas stripping in Process Schemes 2, 3 and 4 improves the economics of the recovery process due to the reduction in the fermenter sizes (reduction in capital costs) as well as the reduction in the size of downstream distillation columns.
- Process Scheme 2 consisting of gas stripping and distillation has the potential to be viable under the current conditions. The process is able to yield the three ABE solvents from fermentation to sellable purities which improves the economics significantly with an NPV of US$508.88 million and an IRR of 31%.
- Although a positive NPV of US$82.38 million was obtained for Process Scheme 3, the process cannot be considered worth investing in due to it obtaining an IRR of 6% which is below the discounting rate used (10%). This process, which integrates gas

stripping and extraction, can only deliver butanol to sellable quality due to the action of the solvent used, 2-ethyl hexanol. It can be concluded that the choice of an alternative solvent, which can equally recover acetone and ethanol from an aqueous phase, will lead to an improvement in the IRR of this process.

- The most profitable process was Process Scheme 4 which incorporates two-stage gas stripping and distillation. An NPV of US$529.09 million and an IRR of 32% was realised for this process. Although slightly more profitable, this process showed very similar economics to Process Scheme 2, which showed that the cost of establishing and operating a second state gas stripping unit is almost the same as the cost for a distillation column, in both respects, that is used as a water stripper of the condensate from the first stage stripper
- From the sensitivity analyses it can be concluded that the substrate cost and the butanol selling prices have the major effects on the profitability of the processes evaluated in terms of the NPV and the IRR

Finally, the preliminary work performed on the reactive extraction process, using group contribution methods) led to the conclusion that an IL that is made up of the imidazolium ion and the BTI anion and functionalised with a carboxylic acid group, could prove to be a good reactive extraction reactant for converting butanol into a higher value ester product.

7.2. Recommendations

To bring some improvements to the work reported in this study as well as to make the study more practical and beneficial to the South African sugar industry, the following aspects are recommended:

- Making use of the optimised fermentation modules and simulations from the STEP-Bio collaborators (UCT) in simulating the fermentation process. It is recommended that the fermentation studies be specifically based on actual streams from the South African sugar mills. The fermentation process is the link between the process identified as the most economic and the generic sugar mill Aspen Plus® model.
- The inclusion of the best performing process into the Aspen Plus® generic sugar mill would be the next stage in making a detailed benefit of producing biobutanol (and ultimately the higher value ester) in addition to sucrose. It is, however, recognised

that it may be difficult to integrate extensively given the requirement of the process design of ABE to be intrinsically safe. Large diameter pipes for vapour and large lengths may be required between ABE process and the sugar mill.

- Since the cost of the substrate has a major impact on the profitability of the best performing process, it is recommended that the study continues to investigate the use of different streams in the sugar mill as carbon sources in the fermentation and downstream chemical production.
- There are other promising technologies that have not been included in this analysis. The use of other technologies such as pervaporation and adsorption could possibly be beneficial in some situations in the biorefinery models and thus, should not be ruled out

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APPENDICES

APPENDIX A: GAS STRIPPING AND EXTRACTION EXPERIMENTS

Appendix A1: Gas Stripping Experiments

The following are the calibration curves used in the gas stripping experiments.

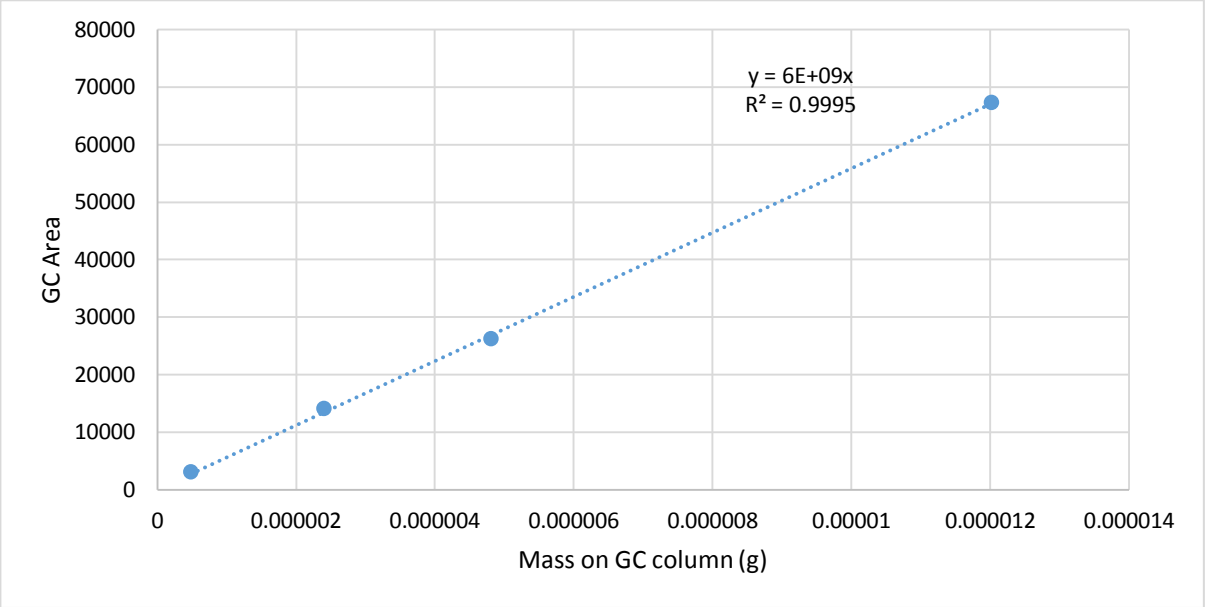

Figure A-1: Acetone calibration curve

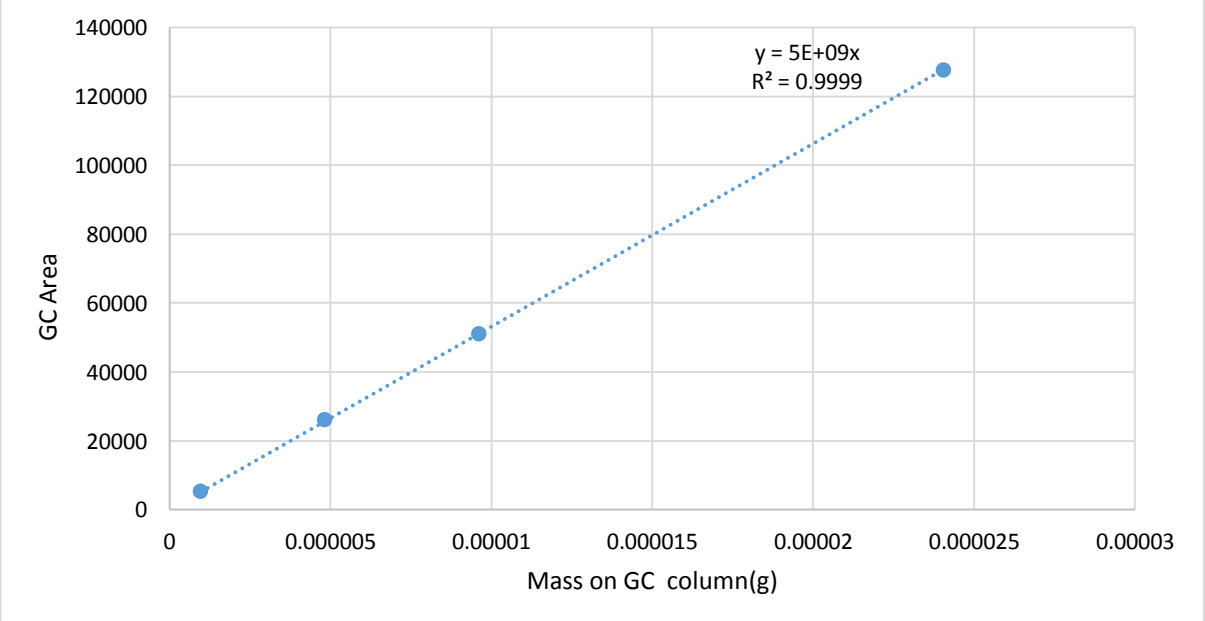

Figure A-2: Butanol calibration curve

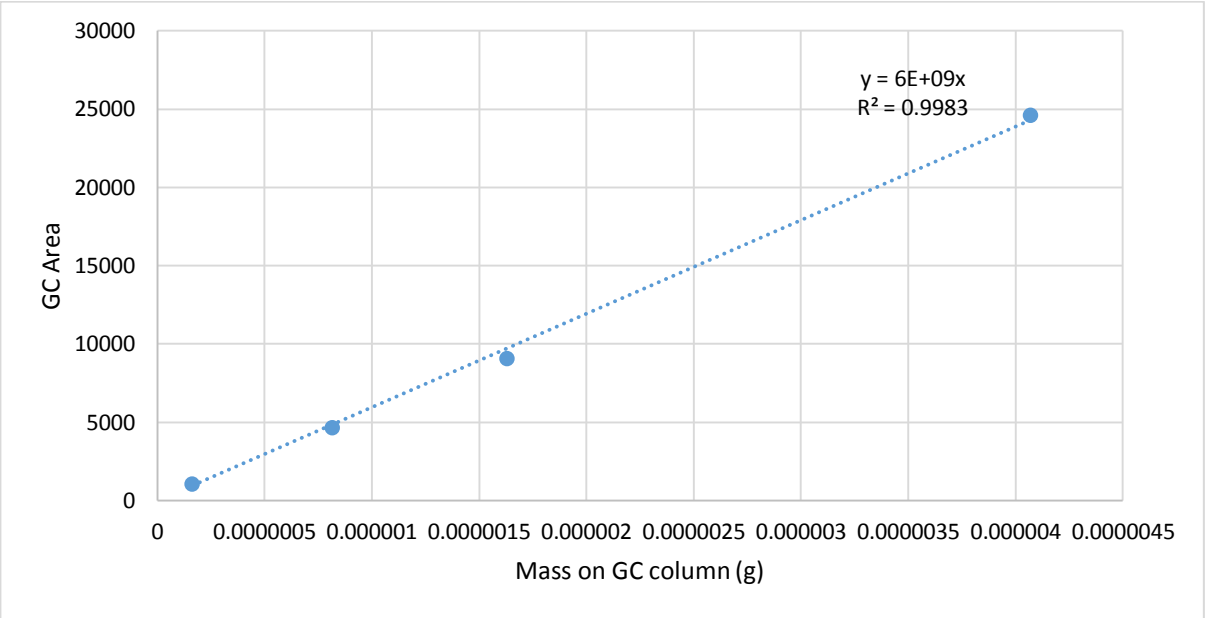

Figure A-3: Ethanol calibration Curve

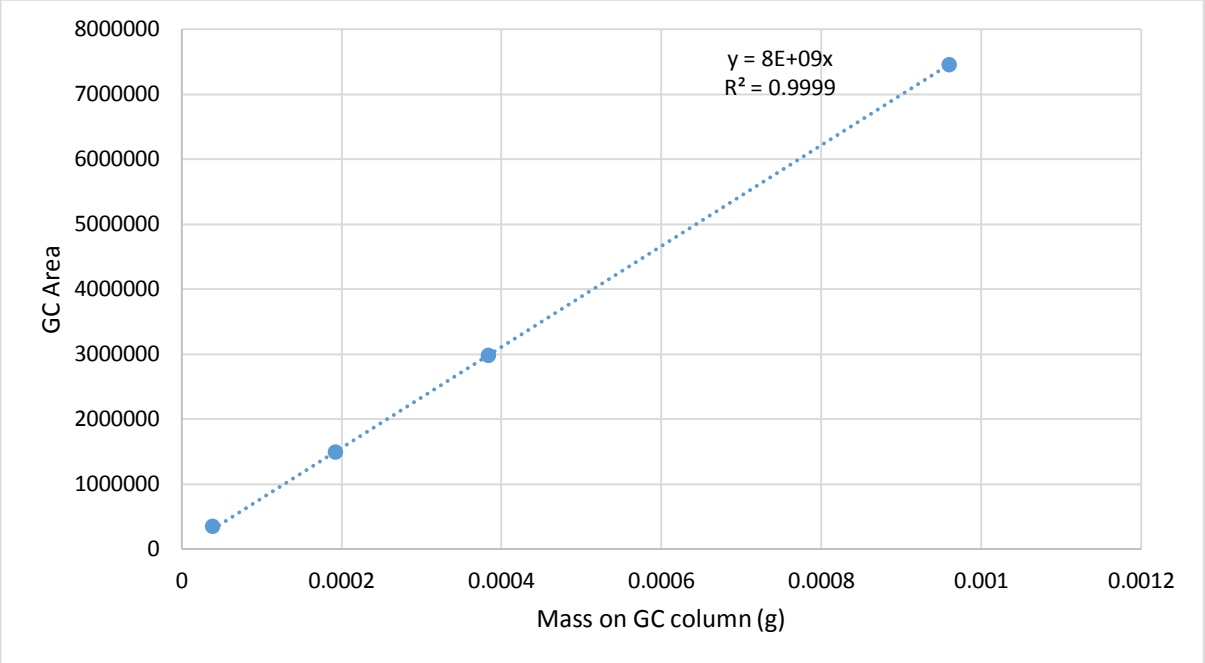

Figure A-4: Water calibration curve

Appendix A2: Extraction Experiments

The GC calibration followed the area ratio method proposed by (Raal and Mühlbauer, 1998). This method has been extensively used in LLE measurements (e.g. Narasigadu (2006)). Standard samples of butanol-water solutions were prepared to cover the whole composition span from the starting aqueous phase to the raffinate phase that remains after extraction.

Generally, the peak area that is obtained from the chromatogram, A_i is directly proportional to the number of moles, n_i, passing through the GC detector. This can be formulated into Equation A-1, where F_i is the response factor which is a proportionality constant.

$$n_i = A_i F_i \qquad \text{[A-1]}$$

In the case of a binary mixture being injected, the use of the following ratios is suggested:

$$\frac{n_1}{n_2} = \left(\frac{F_1}{F_2}\right)\left(\frac{A_1}{A_2}\right) = \frac{x_1}{x_2} \qquad \text{[A-2]}$$

When the response factor ratio, $\left(\frac{A_1}{A_2}\right)$, is plotted against the mole fraction ratio, $\left(\frac{x_1}{x_2}\right)$, the response factor ratio, $\left(\frac{F_1}{F_2}\right)$, is given by the gradient of the slope. Equation A-2 implies that the area factor ratio is a constant.

Table A1 gives the raw data used to calculate the distribution coefficients and selectivities reported in Section 3.2.5. The symbols are as defined in equations 2-8 and 2-9. The butanol and water concentrations are reported as mass fractions.

Table A-1: Extraction experiments raw data at 30°C

Solvent	$[BuOH]_{aq}$	$[H_2O]_{aq}$	**Organic phase water content (wt. %)**	V_0 **(mL)**	V_{aq} **(mL)**	V_{org} **(mL)**
Oleyl alcohol	0.0021	0.9979	1.6351	2.50	2.50	2.80
	0.0022	0.9978	1.6630			
	0.0020	0.9980	1.6282			
2-ethyl-hexanol	0.0017	0.9983	3.9031	2.50	2.40	2.00
	0.0015	0.9985	4.0326			
	0.0015	0.9985	4.1433			
1-Octanol	0.0018	0.9982	6.4989	2.50	2.40	2.00
	0.0021	0.9979	6.3682			
	0.0019	0.9981	6.2272			
Hexyl acetate	0.0029	0.9971	0.9578	2.45	2.40	2.00
	0.0029	0.9971	0.9034			
	0.0029	0.9971	1.0451			
Diethyl carbonate	0.0019	0.9981	1.7443	2.50	2.50	2.00
	0.0024	0.9976	1.5192			
	0.0017	0.9983	1.4112			

APPENDIX B: SIMULATION METHODS AND ECONOMIC ANALYSIS APPROACH

Appendix B1: Distillation Column Design

B1-1: Optimal Column Sequence

For a multicomponent system, the following heuristics as discussed by Seider et al. (2009) are useful in determining the optimal column sequence from possible alternatives:

1. Remove unstable, corrosive, or chemically reactive components early in the sequence
2. Remove final products one by one as overhead distillates
3. Remove, early in the sequence, those components of greatest molar percentage in the feed
4. Make the most difficult separations in the absence of the other components
5. Leave for later in the sequence that favours near-equimolar amounts of overhead and bottoms in each column

B1-2: Residue Curve Maps

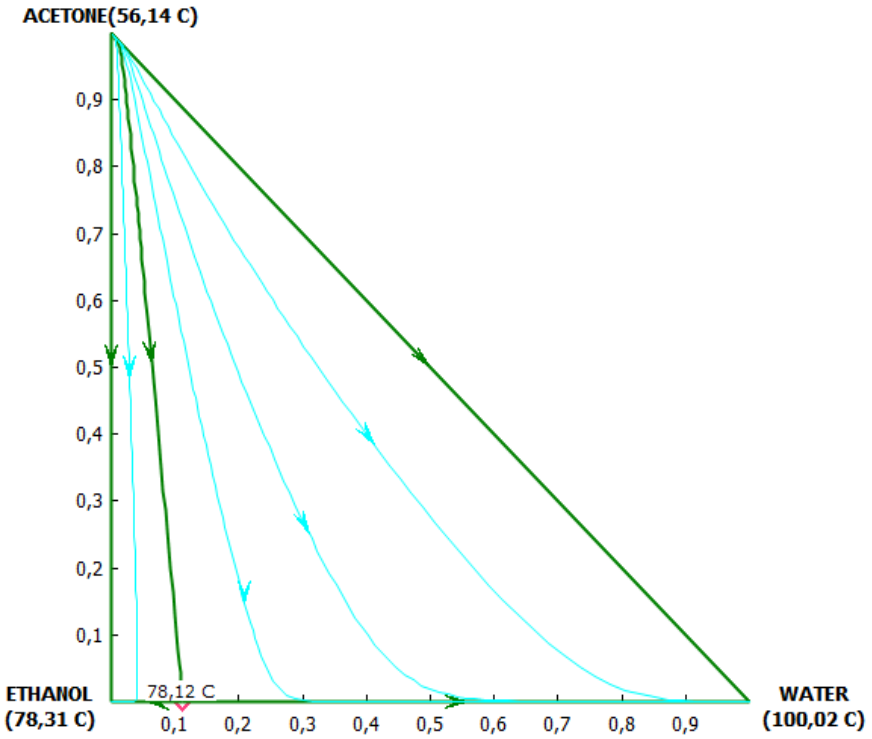

Figure B-1: Acetone-Ethanol-Water residues curves

Table B-1: Classification of nodes on Water-Acetone-Ethanol residue curves

Component	Temperature (°C)	Classification
Water	100.02	Stable
Acetone	56.14	Unstable
Ethanol	78.31	Saddle

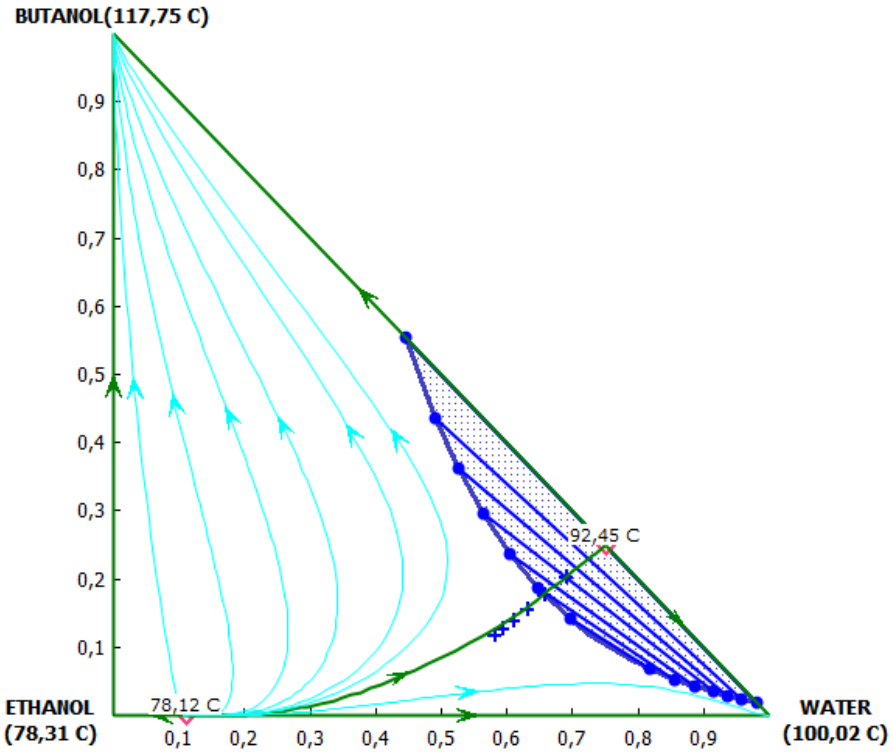

Figure B-2: Ethanol-Water-Butanol residue curves

Table B-2: Classification of nodes in the Ethanol-Water-Butanol Residue Curves

Component	Temperature (°C)	Classification
Water	100.02	Stable
Butanol	117.75	Stable
Ethanol	78.31	Saddle

Appendix B2: Costing of the Clear Juice

The payment of cane in South Africa is based on the Recoverable Value (RV) content. The RV measures the value of sugar and molasses that will be recovered from the cane that is delivered to the sugar mill for processing.

According to the SASA website[7] on cane testing, the RV % is given by the following equation:

$$RV\ \% = S - dN - cF \qquad \text{[B-1]}$$

S, N and F are the sucrose, non-sucrose and the fibre compositions (%) in the cane, respectively. d is the relative value of sucrose which each unit of non-sucrose diverts from sugar production to molasses while c is the loss of sucrose from sugar production per unit of fibre. d and c currently stand at 0.4 and 0.02, respectively, and they are calculated for each season.

Currently, the cane payment system only allows for the costing of cane delivered to the mill by making use of the RV system. The current study attempts to extend the system to the costing of the other streams in the sugar mill in such a way that the opportunity cost of using these streams in making other products in the sugarcane biorefinery can be assessed based on the base case (i.e. raw sugar production). The RV rate, therefore, has to increase from the base case (cane) to the different streams in the mill indicating a value addition that takes place as the cane is processed.

According to the South African Sugar Industry Directory[8], for the 2015/2016 milling season, the RV rate was R 3 979.22 /t cane (to be paid to the farmer). From the raw sugar and molasses sales the RV rate is calculated as 64.3675% of the total proceeds being distributed to the farmer, while the other 35.6325% go to the miller to cater for the operating costs. From these percentages, the overall operating costs to produce sugar and molasses can be estimated to be R 2 202.81 /t cane.

By looking at the raw sugar mill process depicted in Figure 4-1, it was assumed that the extraction and clarification stages account for 25% of the operating costs while evaporation and crystallisation used the rest. Evaporation and crystallisation stages uses up large

[7] http://www.sasa.org.za/divisions/CaneTestingService.aspx
[8] http://www.sasa.org.za/Files/Sugar%20Industry%20Directory%202016.pdf

amounts of steam. With this assumption it, therefore, means for the clear juice stream the RV rate would be R 3 979.22 + (0.25*R 2 202.81) = **R 4 529.92 /t RV**.

From the clear juice compositions reported in Table 4-1 and applying equation C-1 one gets a RV % of 11.09% and multiplying by the amount of clear juice stream available and the RV rate gives the total cost of the juice stream.

Finally, it is important to note that the accuracy of this calculation depends on the how close the 25% operating cost apportionment is close to reality. Additionally, the RV rate calculated is only a reflection of the opportunity cost of using the clear juice to produce biobutanol as opposed to producing raw sugar and molasses. In the actual fermentation process even the non-sugars (fructose etc.) are fermented to produce ABE.

Appendix B3: Costing of High Pressure Steam (HPS)

HPS being generated in the sugar mill model is at 31 bar and superheated to 390°C.

Boiler feed water is available at 100°C with enthalpy = 419.1 kJ/kg.

From steam tables (Felder and Rousseau, 1986), steam at 31 bar and 390°C has an enthalpy of 3 205.15 kJ/kg.

Therefore, to generate this HPS:

Heat duty = 3 205.15 – 419.1 = 2786.05 kJ/kg

Finally, assuming a generation efficiency of 85% and a distribution losses of 10% and considering coal (energy value 27 000 kJ/kg) costs US$44.09/t

Cost of HPS = US$ 6.07/t

APPENDIX C: ECONOMIC RESULT TABLES

Appendix C1: Process Scheme 1-Economic Results Tables

Table C-1: Process Scheme 1-Purchased Equipment Costs

Item	Cost (US$ Thousands)
Storage (1 week):	
Clear juice	3 276
Acetone (T-102)	113
Butanol (T-105)	215
Ethanol (T-103)	54
	3 657
Fermentation:	
Fermenters	19 736
Broth surge tank (T-101)	1 446
	21 182
Product Recovery:	
Broth preheater (E-101)	58
Beer stripper (C-101) tower	570
Beer stripper (C-101) reboiler	204
Stripper gas condenser (E-102)	523
Acetone column (C-102) tower	275
Acetone column (C-102) reboiler	26
Acetone column (C-102) condenser	43
Acetone column (C-102) reflux drum	14
Acetone column (C-102) reflux pump	4
Ethanol column pre-cooler (E-103)	75
Ethanol column (C-103) tower	614
Ethanol column (C-103) reboiler	29
Ethanol column (C-103) condenser	77
Ethanol column (C-103) reflux drum	14
Ethanol column (C-103) reflux pump	4
Decanter (D-101)	18
Water stripper (C-104) tower	97
Water stripper (C-104) reboiler	28
Decanter temperature set (E-104)	27
Butanol stripper (C-105) tower	116
Butanol stripper (C-105) reboiler	32
Decanter temperature set (E-105)	16
	2 864
Stillage handling:	
Stillage handling equipment (50% of fermenter cost)	**10 591**
Total	**38 294**

Table C-2: Process Scheme 1-Total Capital Investment (TCI)

Item	Cost (US$ Thousands)
Direct costs:	
Purchased equipment	38 294
Equipment installation	7 659
Instrumentation and controls	3 063
Piping	7 659
Electrical	3 829
Buildings	6 893
Yard improvements	2 681
Service facilities	9 573
Land	957
	80 608
Indirect costs:	
Engineering and supervision	8 042
Construction expenses	6 127
Contractor's fee	2 681
Contingency	11 105
	27 954
Working Capital:	
Working capital (15% of the fixed capital cost)	**16 284**
Total Capital Investment	**124 847**

Table C-3: Process Scheme 1-Manufacturing Costs

Item	Cost in the first year (US$ Thousands)
Direct costs	
Raw materials (clear juice)	65 080
Operating labour	141
Direct supervisory and clerical labour	21
Utilities	9 359
Maintenance and repairs	6 514
Operating supplies	977
Laboratory charges	14
Patents and royalties	1 061
Fixed charges:	
Insurance	1 086
Local taxes	1 086
Plant overhead costs	3 672
Total Manufacturing Costs	**89 011**

Table C-4: Process Scheme 1-General Expenses

Item	Cost in the first year (US$ Thousands)
Administration costs	28
Distribution and selling	4 244
Research and development	3 183
Financing	6 242
Total General Expenses	**13 698**

Appendix C2: Process Scheme 2-Economic Results Tables

Table C-5: Process Scheme 2-Purchased Equipment Costs

Item	**Cost (US$ Thousands)**
Storage (1 week):	
Clear juice (T-201)	3 276
Acetone (T-203)	115
Butanol (T-206)	254
Ethanol (T-204)	53
	3 698
Fermentation:	
Fermenters	9 272
Condensate tank (T-202)	361
	9 633
Product Recovery:	
Stripped gas condenser (E-201)	626
Stripping gas re-heater (E-202)	177
Condensate preheater (E-203)	14
Beer stripper (C-201) tower	170
Beer stripper (C-201) reboiler	53
Stripper gas condenser (E-204)	182
Acetone column (C-202) tower	253
Acetone column (C-202) reboiler	26
Acetone column (C-202) condenser	43
Acetone column (C-202) reflux drum	14
Acetone column (C-202) reflux pump	4
Ethanol column pre-cooler (E-205)	65
Ethanol column (C-203) tower	528
Ethanol column (C-203) reboiler	30
Ethanol column (C-203) condenser	70
Ethanol column (C-203) reflux drum	14
Ethanol column (C-203) reflux pump	4
Decanter (D-201)	21
Water stripper (C-204) tower	58
Water stripper (C-204) reboiler	14
Decanter temperature set (E-204)	12
Butanol stripper (C-205) tower	106
Butanol stripper (C-205) reboiler	32
Decanter temperature set (E-205)	19
	2 535
Stillage handling:	
Stillage handling equipment (50% of fermenter cost)	**4 817**
Total	**20 683**

Table C-6: Process Scheme 2-Total Capital Investment (TCI)

Item	Cost (US$ Thousands)
Direct costs:	
Purchased equipment	20 683
Equipment installation	4 137
Instrumentation and controls	1 655
Piping	4 137
Electrical	2 068
Buildings	3 723
Yard improvements	1 448
Service facilities	5 171
Land	517
	43 539
Indirect costs:	
Engineering and supervision	4 344
Construction expenses	3 309
Contractor's fee	1 448
Contingency	5 998
	15 099
Working Capital:	
Working capital (15% of the fixed capital cost)	**8 796**
Total Capital Investment	**67 433**

Table C-7: Process Scheme 2-Manufacturing Costs

Item	Cost in the first year (US$ Thousands)
Direct costs	
Raw materials (clear juice)	65 080
Operating labour	106
Direct supervisory and clerical labour	16
Utilities	16 635
Maintenance and repairs	3 518
Operating supplies	528
Laboratory charges	11
Patents and royalties	1 349
Fixed charges:	
Insurance	586
Local taxes	586
Plant overhead costs	2 002
Total Manufacturing Costs	**90 417**

Table C-8: Process Scheme 2-General Expenses

Item	Cost in the first year (US$ Thousands)
Administration costs	22
Distribution and selling	5 396
Research and development	4 047
Financing	3 372
Total General Expenses	**12 836**

Appendix C3: Process Scheme 3-Economic Results Tables

Table C-9: Process Scheme 3-Purchases Equipment Cost

Item	Cost (US$ Thousands)
Storage (1 week):	
Clear juice (T-301)	3 276
Acetone/Ethanol waste (T-306)	104
Butanol (T-307)	234
	3 614
Fermentation:	
Fermenters	9 272
Condensate tank (T-302)	361
	9 633
Product Recovery:	
Stripped gas condenser (E-301)	626
Stripping gas re-heater (E-302)	177
Condensate pre-heater (E-303)	12
Extraction column (C-301)	278
Extract-phase surge tank (T-304)	95
Solvent recovery column (C-302) tower	278
Solvent recovery column (C-302) reflux pump	4
Solvent recovery column (C-302) reboiler	91
Solvent recovery column (C-302) condenser	27
Solvent recovery column (C-302) reflux drum	14
Solvent recovery pre-heater (E-304)	7
Solvent recycle heater (E-103)	27
Regenerated solvent surge tank (T-305)	95
Butanol recovery column preheater (E-306)	38
Butanol recovery column (C-303) tower	163
Butanol recovery column (C-303) reflux pump	4
Butanol recovery column (C-303) reflux drum	14
Butanol recovery column (C-303) reboiler	41
Butanol recovery column (C-303) condenser	26
	2 017
Stillage handling:	
Stillage handling equipment (50% of fermenter cost)	**4 817**
Total	**20 082**

Table C-10: Process Scheme 3-Total Capital Investment (TCI)

Item	Cost (US$ Thousands)
Direct costs:	
Purchased equipment	20 082
Equipment installation	3 615
Instrumentation and controls	1 607
Piping	3 614
Electrical	2 008
Buildings	3 615
Yard improvements	1 406
Service facilities	4 820
Land	502
	41 268
Indirect costs:	
Engineering and supervision	4 016
Construction expenses	3 213
Contractor's fee	1 406
Contingency	10 041
	18 676
Working Capital:	
Working capital (15% of the fixed capital cost)	**8 992**
Total Capital Investment	**68 936**

Table C-11: Process Scheme 3-Manufacturing Costs

Item	Cost in the first year (US$ Thousands)
Direct costs	
Raw materials (clear juice)	65 080
Operating labour	132
Direct supervisory and clerical labour	20
Utilities	7 934
Maintenance and repairs	3 597
Operating supplies	540
Laboratory charges	13
Patents and royalties	970
Fixed charges:	
Insurance	600
Local taxes	600
Plant overhead costs	2 062
Total Manufacturing Costs	**81 546**

Table C-12: Process Scheme 3-General Expenses

Item	Cost in the first year (US$ Thousands)
Administration costs	26
Distribution and selling	3 880
Research and development	2 910
Financing	3 447
Total General Expenses	**10 263**

Appendix C4: Process Scheme 4-Economic Results Tables

Table C-13: Process Scheme 4-Purchased Equipment Cost

Item	Cost (US$ Thousands)
Storage (1 week):	
Clear juice (T-401)	3 276
Acetone (T-403)	115
Butanol (T-406)	254
Ethanol (T-404)	53
	3 698
Fermentation:	
Fermenters	9 272
Condensate tank (T-402)	361
	9 633
Product Recovery:	
Stripped gas condenser (E-401)	626
Stripping gas re-heater (E-402)	177
Condensate preheater (E-403)	12
First stage gas stripping decanter (D-401)	17
Aqueous phase heater (E-404)	10
Second stage gas stripper (R-402)	331
Second stage stripped gas condenser (E-405)	25
Second stage gas recycle re-heater (E-406)	7
Distillation feed tank	209
Acetone column (C-401) tower	231
Acetone column (C-401) condenser	43
Acetone column (C-401) reboiler	25
Acetone column (C-401) reflux pump	14
Acetone column (C-401) reflux drum	4
Ethanol column pre-cooler (E-407)	43
Ethanol column (C-402) tower	528
Ethanol column (C-402) reboiler	29
Ethanol column (C-402) condenser	67
Ethanol column (C-402) reflux drum	14
Ethanol column (C-402) reflux pump	4
Decanter (D-201)	21
Water stripper (C-403) tower	34
Water stripper (C-403) reboiler	11
Decanter temperature set (E-408)	9
Butanol stripper (C-404) tower	106
Butanol stripper (C-404) reboiler	33
Decanter temperature set (E-409)	22
	2 650

Stillage handling:	
Stillage handling equipment (50% of fermenter cost)	**4 817**
Total	**20 799**

Table C-14: Process Scheme 4-Total Capital Investment (TCI)

Item	**Cost (US$ Thousands)**
Direct costs:	
Purchased equipment	20 799
Equipment installation	4 160
Instrumentation and controls	1 664
Piping	4 160
Electrical	2 080
Buildings	3 744
Yard improvements	1 456
Service facilities	5 200
Land	520
	43 781
Indirect costs:	
Engineering and supervision	4 368
Construction expenses	3 328
Contractor's fee	1 456
Contingency	6 032
	15 183
Working Capital:	
Working capital (15% of the fixed capital cost)	**8 845**
Total Capital Investment	**67 809**

Table C-15: Process Scheme 4-Manufacturing Costs

Item	Cost in the first year (US$ Thousands)
Direct costs	
Raw materials (clear juice)	65 080
Operating labour	106
Direct supervisory and clerical labour	16
Utilities	15 347
Maintenance and repairs	3 538
Operating supplies	531
Laboratory charges	11
Patents and royalties	1 349
Fixed charges:	
Insurance	590
Local taxes	590
Plant overhead costs	2 013
Total Manufacturing Costs	**89 169**

Table C-16: Process Scheme 4-General Expenses

Item	Cost in the first year (US$ Thousands)
Administration costs	21
Distribution and selling	5 397
Research and development	4 048
Financing	3 390
Total General Expenses	**12 856**