

# Evaluation of Different Process Designs for Biobutanol Production from Sugarcane Molasses

*by*

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## **Declaration of Own Work**

I, the undersigned, hereby declare that the work contained in this thesis is my own original work and that I have not previously in its entirety or in part submitted it at any university for a degree.

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A.B. van der Merwe

19 February 2010

## **A Word of Thanks**

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## Abstract

Recently, improved technologies have been developed for the biobutanol fermentation process: higher butanol concentrations and productivities are achieved during fermentation, and separation and purification techniques are less energy intensive. This may result in an economically viable process when compared to the petrochemical pathway for butanol production. The objective of this study is to develop process models to compare different possible process designs for biobutanol production from sugarcane molasses. Some of the best improved strains, which include *Clostridium acetobutylicum* PCSIR-10 and *Clostridium beijerinckii* BA101, produce total solvent concentrations of up to 24 g/L. Among the novel technologies for fermentation and downstream processing, fed-batch fermentation with *in situ* product recovery by gas-stripping, followed by either liquid-liquid extraction or adsorption, appears to be the most promising techniques for current industrial application. Incorporating these technologies into a biorefinery concept will contribute toward the development of an economically viable process. In this study three process routes are developed. The first two process routes incorporate well established industrial technologies: Process Route 1 consist of batch fermentation and steam stripping distillation, while in Process Route 2, some of the distillation columns is replaced with a liquid-liquid extraction column. The third process route incorporates fed-batch fermentation and gas-stripping, an unproven technology on industrial scale. Process modelling in ASPEN PLUS<sup>®</sup> and economic analyses in ASPEN Icarus<sup>®</sup> are performed to determine the economic feasibility of these biobutanol production process designs. Process Route 3 proved to be the only profitable design in current economic conditions. For the latter process, the first order estimate of the total project capital cost is \$187 345 000.00 (IRR: 35.96%). Improved fermentation strains currently available are not sufficient to attain a profitable process design without implementation of advanced processing techniques. Gas stripping is shown to be the single most effective process step (of those evaluated in this study) which can be employed on an industrial scale to improve process economics of biobutanol production.

## Samevatting

Onlangse verbeteringe in die tegnologie vir die vervaardiging van butanol via die fermentasie roete het tot gevolg dat: hoër butanol konsentrasies en produktiwiteit verkry kan word tydens die fermentasie proses, en energie verbruik tydens skeiding-en suiweringsprosesse laer is. Hierdie verbeteringe kan daartoe lei dat biobutanol op 'n ekonomiese vlak kan kompeteer met die petrochemiese vervaardigings proses vir butanol. Die doelwit van die studie is om proses modelle te ontwikkel waarmee verskillende proses ontwerpe vir die vervaardiging van biobutanol vanaf suikerriet melasse vergelyk kan word. Verbeterde fermentasie organismes, wat insluit *Clostridium acetobutylicum* PCSIR-10 en *Clostridium beijerinckii* BA101, het die vermoë om ABE konsentrasies so hoog as 24 g/L te produseer. Wat nuwe tegnologie vir fermentasie en skeidingprosesse behels, wil dit voorkom of wisselvoer fermentasie met gelyktydige verwydering van produkte deur gasstroping, gevolg deur of vloeistof-vloeistof ekstraksie of adsorpsie, van die mees belowende tegnieke is om tans in die nywerheid te implementeer. Deur hierdie tegnologie in 'n bioraffinadery konsep te inkorporeer sal bydra tot die ontwikkeling van 'n ekonomies lewensvatbare proses. Drie prosesserings roetes word in die studie ontwikkel. Die eerste twee maak gebruik van goed gevestigde industriële tegnologie: Proses Roete 1 implementeer enkellading fermentasie en stoom stroping distillasie, terwyl in Proses Roete 2 van die distilasiekolomme vervang word met 'n vloeistof-vloeistof ekstraksiekolom. Die derde proses roete maak gebruik van wisselvoer fermentasie met gelyktydige verwydering van produkte deur gas stroping. Die tegnologie is nog nie in die nywerheid bewys of gevestig nie. Om die ekonomiese uitvoerbaarheid van die proses ontwerpe te bepaal word proses modellering uitgevoer in ASPEN PLUS<sup>®</sup> en ekonomiese analises in ASPEN Icarus<sup>®</sup> gedoen. Proses Roete 3 is die enigste ontwerp wat winsgewend is in huidige ekonomiese toestande. Die eerste orde koste beraming van die laasgenoemde projek se totale kapitale koste is \$187 345 000.00 (opbrengskoers: 35.96%). Die verbeterde fermentasie organismes wat tans beskikbaar is, is nie voldoende om 'n proses winsgewend te maak nie; gevorderde proses tegnologie moet geïmplementeer word. Gasstroping is bewys as die mees effektiewe proses stap (getoets in die studie) wat op industriële skaal geïmplementeer kan word om die winsgewendheid van die biobutanol proses te verbeter.

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## Acronyms

AA	Acetic Acid
BA	Butyric Acid
ABE	Acetone, Butanol and Ethanol
ASPEN	Advanced Simulator for Process Engineering
CEPCI	Chemical Engineering Plant Cost Index
CS	Carbon Steel
CSW	Corn Steep Water
CW	Cooling Water
ER	Energy Ratio
GWH	Giga Watt Hour
GS	Gas Stripping
IRR	Internal Rate of Return
LLE	Liquid-Liquid Extraction
MSECI	Marshall & Swift Equipment Cost Index
NEV	Net Energy Value
NPV	Net Present Value
NREL	National Renewable Energy Laboratory
NRR	Net Rate of Return
P&ID	Piping and Instrument Diagram
PFD	Process Flow Diagram
PI	Profitability Index
PO	Payout Period
ROR	Rate of Return
SS	Stainless Steel
T	Ton
TPCC	Total Project Capital Cost

# 1 Introduction

## 1.1 Background on Biobutanol

### 1.1.1 Overview of Butanol

Butanol is a four carbon alcohol (C<sub>4</sub>H<sub>9</sub>OH). There are four structural isomers of which 1-butanol (n-butanol) is the most important commercial isomer. This isomer occurs in nature and is primarily used industrially as a solvent or component in surface coatings. Butanol can also be used as fuel in internal combustion engines. It is a superior biofuel to ethanol, because the longer hydrocarbon chain causes it to be fairly non-polar. Butanol can be produced from biomass (as "biobutanol") as well as fossil fuels (as "petrobutanol"); biobutanol and petrobutanol have the same chemical properties.

### 1.1.2 Production History

Acetone was produced from wood up to World War 1. The supply of wood became insufficient at the start of the war because acetone demand increased in line with the manufacture of cordite, a cartridge and shell propellant in which acetone was an essential ingredient. The Russian chemist C. Weizmann, later Israeli President, developed the ABE (acetone, butanol, and ethanol) fermentation process at Manchester University. In 1912 he isolated a strain which was later known as *Clostridium acetobutylicum*, and ran the first production plant for acetone production from starch (Dürre P. , 1998). Because of the strategic need for large volumes of acetone, facilities were built in the UK and France using maize starch as a substrate, while rice starch was used at facilities in India (Antoni, et al., 2007). In 1917 large-scale industrial plants were also erected in the USA and Canada (Jones & Woods, 1986). Butanol was an unnecessary by-product during the war, and had no value at the time. The fermentation process was about to be abandoned after the armistice in 1918, seeing that there was no further demand for acetone.

There was, however, an increasing demand for butanol after the war. The rapidly expanding automobile industry required quick-drying lacquer which would give a good finish to car bodies (Jones & Woods, 1986). This resulted in a demand for some suitable solvent and it was found that butanol and its ester, butyl acetate, were ideal solvents for these lacquers. Butanol also found application in the synthetic rubber industry (Antoni, et al., 2007). Between 1924 and 1927 new butanol production plants were built, and the

isolation of molasses-fermenting strains increased plant capacity by 60% (Dürre P. , 1998). By 1936 plants were erected in a number of countries including Japan, India, Australia, South Africa, Egypt, Brazil, and USSR. In 1945 66% of the total butanol and 10% of the total acetone production were obtained by ABE fermentation, making it the largest scale bioindustry ever run second to ethanol fermentation (Dürre P. , 1998).

As the petrochemical industry evolved during the 1960s, the production of acetone and butanol by fermentation had virtually ceased. Cost issues, the relatively low-yield and sluggish fermentations, as well as problems caused by end product inhibition and bacteriophage infections, meant that biobutanol could not compete on a commercial scale with butanol produced synthetically (Brekke, 2007). Moreover, the molasses quality was decreasing due to improved sugar processing technology, and the price of molasses also increased seeing that it was used as a additive animal feeds (Zverlov, et al., 2006). It was only in the USSR, China and South Africa that production continued. The plant in South Africa was closed in 1982 (Jones & Woods, 1986), and as the USSR disintegrated during the 1990s, their biobutanol production stopped (Antoni, et al., 2007). In China, solvent fermentation was stepped down to complete closure only in 2004 (Chiao & Sun, 2007).

Today most n-butanol are produced chemically from petroleum sources by either the oxo process starting from propylene (with H<sub>2</sub> and CO over a rhodium catalyst), or the adol process starting from acetaldehyde (Brekke, 2007).

### **1.1.3 Research and Developments**

There are a number of factors which stimulate the interest and funding for the research and development of biobutanol production. These include the current instability of oil supplies from the Middle East, a readily available supply of renewable agriculturally based biomass, and the call for reduction of greenhouse gas emissions. Ultimately, a revival of the ABE fermentation process is dependent on favourable economic conditions relative to petrochemical-based processes (Ezeji, et al., 2004).

In the early 1970s, the rising cost of petrochemicals combined with the energy crisis resulted in renewed interest in ABE fermentation. During the 1980s and 1990s there were tremendous progress in the development of genetic systems for the solventogenic *Clostridia*, which would allow for the development of strains with improved fermentation characteristics (Ezeji, et al., 2004).

Despite these developments there were still three major drawbacks to overcome before an economically competitive biological process could be reintroduced (Dürre P. , 1998):

- The high cost of the substrate.
- The low product concentration and productivity in fermentation due to end-product inhibition (16-18 g/L due to solvent toxicity).
- The high product recovery cost (product is very dilute and distillation has been used in the past).

During the past decade a hyper-butanol-producing strain has been developed as a result of the application of modern molecular techniques and genetic manipulation to the solventogenic *Clostridia* (Ezeji, et al., 2007). Experimental and computational engineering efforts have also led to improved fermentation techniques, downstream processing, and process integration. All these developments resulted in a significant increase in biobutanol concentration, yield and recovery.

A continuous fermentation pilot plant operating in Austria in the 1990s introduced new technologies and proved economic feasibility with agricultural waste potatoes (Nimcevic & Gapes, 2000). The Austrian plant helped bridge the skill gap between the termination of the US, USSR and South-African production and the recent renewal of production (Antoni, et al., 2007).

In 2005, David Ramey drove a 13-year-old Buick across the United States, fuelled by pure butanol. Compared to gasoline, the consumption increased by 9%, but emissions of CO, hydrocarbons and NO<sub>x</sub> were reduced substantially. His company, Environmental Energy, Inc. (EEI), is planning to produce Butyl Fuel™ via a newly developed fermentation process

involving two *Clostridia* species (Ramey & Yang, 2004). While this is a fairly small enterprise, there is a great market opportunity and larger companies, as well as oil companies, have started developing biobutanol. In 2006, BP and DuPont announced a joint venture to bring to market the next generation in biofuels. The first product will be biobutanol, which was targeted for introduction in 2007 in the United Kingdom (UK) as a gasoline bio-component (DuPont, 2006). They claim that their technology will be competitive as long as the crude oil price remains above \$80 per barrel (Scott & Bryner, 2006). In cooperation with British Sugar, an existing ethanol plant in the UK will be converted into a biotechnological butanol production facility, and a feasibility study is already under way to examine the possibility of constructing larger facilities in the UK (DuPont, 2006). Richard Branson, owner of Virgin Atlantic, is currently in the process of funding his own biomass to butanol fuel production plants (Oceanethanol, 2007). The production of biobutanol from specifically lignocellulosic biomass seems promising and is on the agenda for a number of companies (Antoni, et al, 2007).

Biobutanol fermentation technology has been changing at a rapid pace. It is suggested that future research might focus on the development of second-generation cultures which produce total ABE in the order of 25-33 g/L. Another approach where industrial progress could be made involves the recovery of fermentation by-products (large waste water streams, cell mass, CO<sub>2</sub> and H<sub>2</sub>) for more profits, i.e. development of a biorefinery concept. These advances will help a fermentation-based biobutanol industry compete effectively with petrochemical derived butanol (Ezeji, et al., 2007).

#### **1.1.4 Industrial Importance**

Butanol is an important bulk chemical with a wide range of industrial uses. Most of the worldwide production is converted into methacrylate esters and acrylate. Other main derivatives include glycol ethers and butyl acetate, while derivatives with minor uses are amino resins and n-butylamines. Applications, chemicals and products that use butanol include solvents (for paints, coatings, varnishes, resins, gums, dyes, camphor, vegetable oils, fats, waxes, shellac, rubbers and alkaloids), plasticizers (to improve how plastic material processes), coatings (as a solvent for a variety of applications, such as curable lacquers and cross-linked baking finishes), chemical intermediate or raw material (for

producing many other chemicals and plastics, including safety glass, hydraulic fluids and detergent formulations), textiles (as a swelling agent and manufacturing garments from coated fabric), flotation agents, cleaners, floor polishes, cosmetics (including eye makeup, foundations, lipsticks, nail care products, personal hygiene products and shaving products), drugs and antibiotics, hormones, and vitamins (Dow, 2006).

### 1.1.5 Butanol as a fuel

A relatively new, but very important application is butanol as a biofuel. The latter is the primary drive for current interest and development of biobutanol. Butanol has several advantages over ethanol as a fuel component. It is less hygroscopic; therefore in blends with diesel or petrol, butanol is less likely to separate from this fuel than ethanol if the fuel is contaminated with water. It is also less corrosive and more suitable for distribution through existing pipelines for gasoline. The Reid vapour pressure of butanol is 7.5 times lower than that of ethanol, making it less evaporative/explosive (Bohlmann, 2007). Table 1 compares the properties of common fuels with biobutanol.

**Table 1: Liquid fuel characteristics**

Characteristic	Gasoline	Butanol	Ethanol	Methanol
Formula	C <sub>4</sub> -C <sub>12</sub>	C <sub>4</sub> H <sub>9</sub> OH	CH <sub>3</sub> CH <sub>2</sub> OH	CH <sub>3</sub> OH
Boiling Point (°C)	32-210	118	78	65
Energy Density (MJ/kg)	44.5	33.1	26.9	19.6
Air Fuel Ratio	14.6	11.2	9.0	6.5
Research Octane Number	91-99	96	129	136
Motor Octane Number	81-89	78	102	104
Heat of Vaporisation (MJ/kg)	0.36	0.43	0.92	1.20

Calculated from the difference in energy densities listed above, a gasoline engine will theoretically have about 10% higher fuel consumption when run on biobutanol. However, tests with other alcohol fuels have demonstrated that the effect on fuel economy is not proportional to the change in energy density, and the effect of butanol on fuel consumption is yet to be determined by a scientific study.

Compared to ethanol, butanol can be mixed in higher ratios with gasoline for use in existing cars without the need for retrofit as the air-fuel ratio and energy content are closer to that of gasoline. Alcohol fuels, including butanol and ethanol, are partially oxidized and therefore need to run at richer air mixtures than gasoline. Standard gasoline

engines in cars can adjust the air-fuel ratio to accommodate variations in the fuel, but only within certain limits depending on model of the car. If the limit is exceeded by running the engine on pure butanol or a gasoline blend with a high percentage of butanol, the engine will run lean, a condition which can critically damage components (Smith & Workman, 2007). Butanol is considered substantially similar to gasoline for blending purposes and is certified by the U.S. Environmental Protection Agency as a blending agent up to 11 percent. Environmental Energy, Inc., a U.S. company with a patent for biobutanol production, maintains that butanol can be used as a total replacement for gasoline without any modifications to car engines (Brekke, 2007). In general it is considered that the combustion process of biofuels have zero net carbon emissions due to its production from renewable agricultural feedstocks.

Some disadvantages butanol has compared to ethanol are higher viscosity and a lower octane rating. A fuel with lower octane rating is more prone to knocking (extremely rapid and spontaneous combustion by compression) and will lower efficiency. Knocking can also cause engine damage. Butanol is also more toxic than ethanol.

## **1.2 Research Proposal**

### **1.2.1 Aim**

The aim of this study is to develop conceptual process designs to compare different possible process routes for industrial scale biobutanol production from sugarcane molasses in South Africa. Higher oil price, low feedstock cost (molasses), and improved strains and technology, will facilitate improvement on previous biobutanol production processes, anticipating an economic viable process able to compete with synthetic butanol.

### **1.2.2 Process Designs**

Selection of the final process designs for simulation only commences after a thorough literature study of biobutanol fermentation strains and production technologies (see section 2). Three different process routes are developed with technology (process steps) that can be implemented on industrial scale production (only reliable, tested process technology can be used). From these the final designs are obtained for computer simulation.

*i. Process Route 1*

This process route is the base case and makes use of technology previously used in the industry. It consists of **batch fermentation** followed by **steam stripping distillation**. Three process designs are developed for this process route, each using a different fermentation strain:

- **Process Design 1.1** – *Clostridium acetobutylicum* ATCC824
- **Process Design 1.2** – *Clostridium acetobutylicum* PCSIR-10
- **Process Design 1.3** – *Clostridium beijerinckii* BA101

*ii. Process Route 2*

The process route consists of **batch fermentation**, followed by **centrifugation**, **LLE** (with 2-ethyl-1-hexanol as extractant), and **steam stripping distillation**. This design use *Clostridium acetobutylicum* PCSIR-10 as the fermentation strain, and will be referred to in future as “**Process Design 2**”.

*iii. Process Route 3*

This process route consists of **fed-batch fermentation** with *in situ* product recovery by **gas-stripping**, followed by **LLE** (with 2-ethyl-1-hexanol as extractant), and **steam stripping distillation**. *Clostridium beijerinckii* BA101 is the fermentation strain used in this design, which will be referred to in future as “**Process Design 3**”.

### 1.2.3 Objectives

For the above mentioned process designs, space, equipment, and cost requirements must be determined with computer simulation. The computer simulated process models of the designs are developed sufficiently in order to establish the following main objective:

- i. which process design is most viable in current economic conditions, and what is the first order estimate of its total project capital cost?

Other objectives that must be resolved include:

- ii. are there sufficient information available in literature to develop reliable and robust process models for computer simulation of the process designs?
- iii. which strain (currently available) is the most favourable for biobutanol production, and what is the effect of different fermentation strains on a specific



- process route in terms of biobutanol production, equipment configuration, and equipment cost?
- iv. which process step (or combination of steps) has the largest effect on the overall process design in terms of biobutanol production, energy requirements, and equipment cost?
  - v. a sensitivity analysis to determine what external factor (e.g. molasses price, butanol selling price, utility cost, interest rate, etc.) has the largest influence on the net present value (NPV) and internal rate of return (IRR) of a process design?
  - vi. how do the process designs in this study differ from previously developed process designs in literature that utilize molasses or corn for biobutanol production?

#### **1.2.4 Deliverables**

Deliverables at the end of this research project entails a project report covering the following:

- A detailed literature study on biobutanol production strains, fermentation techniques, and downstream processing technology (see section 2).
- Five conceptual process designs that best satisfy the aim of this project (see sections 4 and 5).
- Interpretation of the results, implications for the industry (more specifically the sugar industry in southern Africa), and future recommendations (see sections 6, 7, and 8).

#### **1.2.5 Significance of Research**

This research is of particular importance to the sugar industry in southern Africa. In a earlier study by Werner Crous (done for the Department of Process Engineering at the University of Stellenbosch), technology and process options were evaluated to add value to waste streams of sugar mills, one of which being molasses. Biobutanol was identified as a potential product in this study. Adding value to sugarcane will also provide diversification, allowing an additional source of income for the sugar industry and reduce market risk linked to sugar production.

In the broader spectrum, this research is also significant in furthering the development of biobutanol in general, and more specifically South Africa. Biobutanol is a very promising

biofuel and with all the recent research and development, the ABE fermentation process might become economically viable again. All the process modelling done for biobutanol thus far is based on the American economy and mostly with corn as substrate, therefore this research will determine whether with improved technology and molasses as substrate the biobutanol industry can be economically viable in South African.

### 1.2.6 Thesis Layout

The approach followed in this thesis is illustrated in Figure 1.

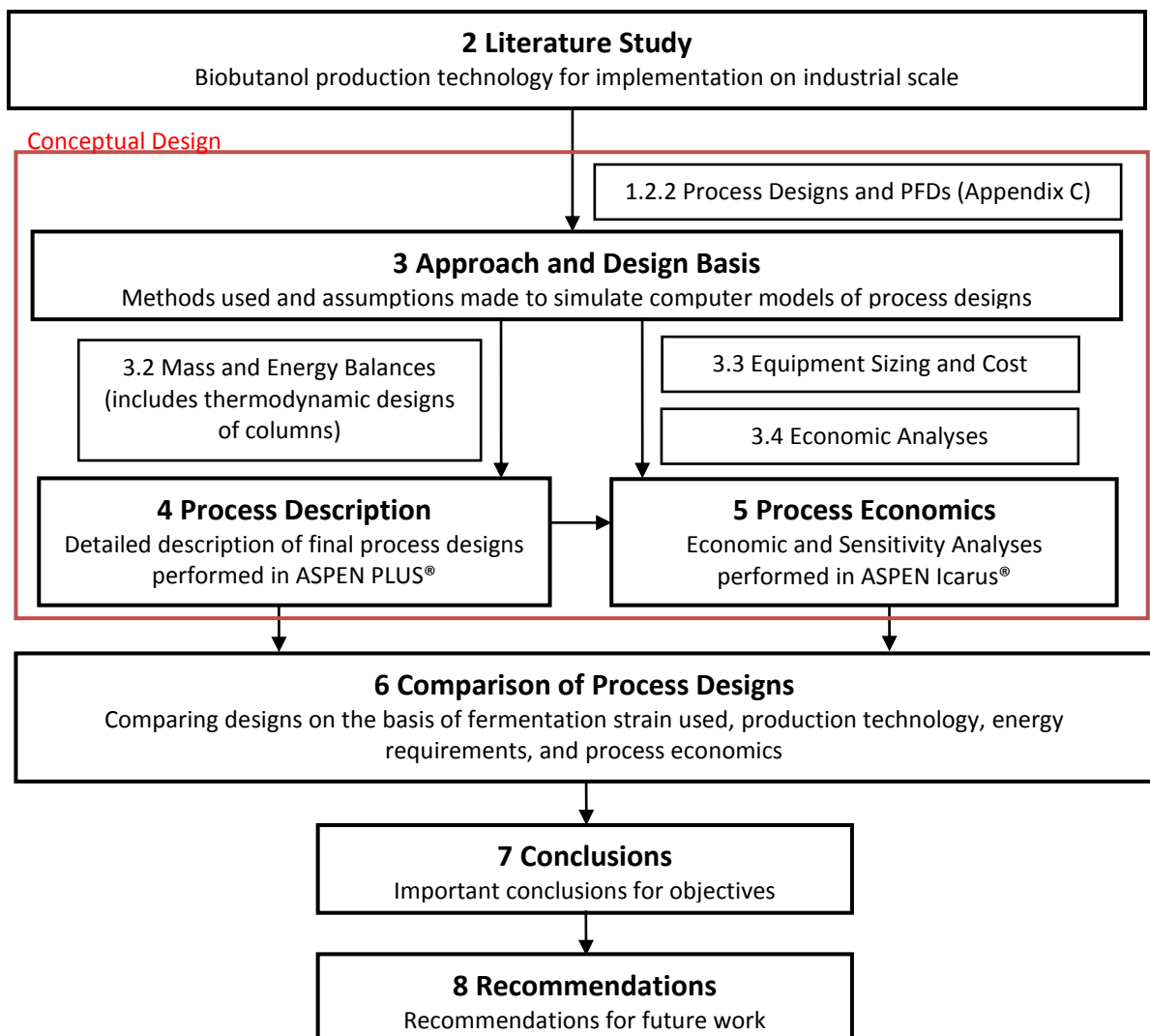


Figure 1: Layout of thesis.

## 2 Literature Study on Fermentative Butanol Production

### 2.1 Substrates and Pre-treatment

Past economic analyses indicate that the fermentation substrate is one of the most important factors that influence the cost of biobutanol (Gapes, 2000; Ezeji, et al., 2004). Corn and molasses were the primary substrates for ABE production before the 1950s. However, in order to make the process more sustainable, and to revert from using food crops as substrates, programs have started developing microorganisms that can efficiently hydrolyze starch and lignocellulosic substrates (Ezeji, et al., 2004).

Lignocellulosic substrates, in particular agricultural wastes, are considered the substrates with the greatest potential for the ABE fermentation due to their wide availability, low price, and sugar composition (Lopez-Contreras, 2003). These substrates are defined as those derived from plant material with major components being lignin and carbohydrate polymers (cellulose and hemicelluloses). Of the aforementioned, cellulose, a linear homopolymer of anhydroglucose residues, is the most abundant organic substrate. Cellulose exists in different forms with varying degrees of polymerisation and molecular weight (Jacques, et al., 2003). Hemicelluloses represent about 20 to 35% of lignocellulosic biomass (Ezeji, et al., 2007). Different from cellulose, hemicelluloses are made up of shorter heteropoly saccharide chains that consist of mixed pentosans and hexosans, which make it more readily soluble, and thus susceptible to enzymatic breakdown. The main components of the arabinoxylan backbone of the hemicelluloses are D-xylose and L-arabinose, and the side chains are primarily composed of D-glucose, D-glucuronic, D-mannose and D-galactose. Glucuroxylan is the major constituent of hardwood hemicellulose, and glucomannan that of softwoods (Jacques, et al., 2003).

The genus *Clostridium*, which is primarily used for fermentative butanol production, can utilise a wide variety of carbohydrates. In a study by Ezeji, et al., (2007), representative sugars present in lignocellulosic biomass were tested to determine their fermentability with *Clostridium beijerinckii* BA101. The sugars that were tested are glucose, xylose, cellobiose, mannose, arabinose, and galactose. Glucose served as the control for the experiment and produced an ABE concentration of 17.8 g/L with a productivity of 0.30

g/L.h. Rapid fermentations were observed with the other sugars as well, with productivities ranging from 0.23-0.32 g/L.h. Results for these fermentations appear in Figure 2. The ability of *Clostridium beijerinckii* BA101 to utilize mixed sugars (hexoses and pentoses) for ABE production was also tested, and it was found that mixed sugars can be metabolized simultaneously, although the rate of sugar utilization is sugar specific. The order of preference for utilization is glucose>xylose>arabinose>mannose. Fermentation time is longer when using mixed sugars as substrate than with pure glucose (productivity decreased to 0.21g/L.h).

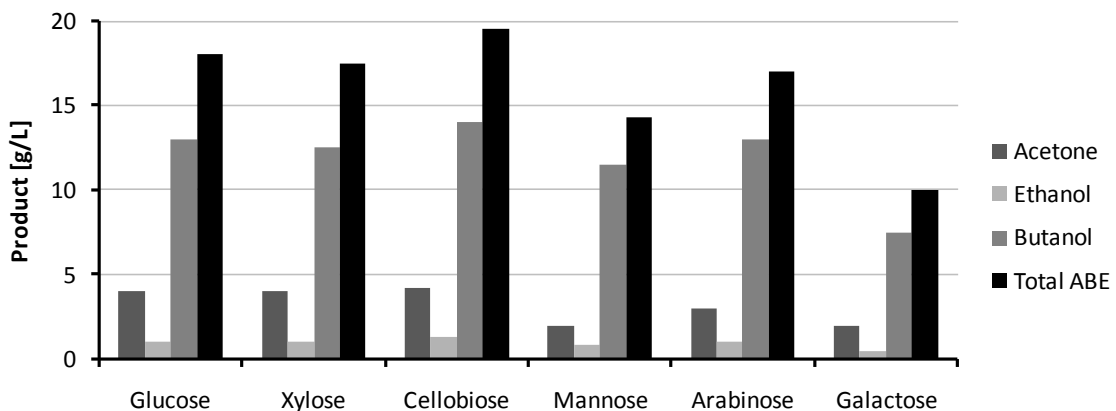


Figure 2: Production of ABE from individual sugars by *Clostridium beijerinckii* BA101 (Ezeji, et al., 2007).

So far, however, *Clostridia* microorganisms have not been shown to directly utilise cellulose or lignocellulosic biomass as carbon source (Ezeji, et al., 2007). Many studies have shown that the hydrolyzates of a variety of lignocellulosic biomass feedstocks are fit for ABE fermentation (Jones & Woods, 1986; Lopez-Contreras, 2003). For the production of hydrolyzates, the lignocellulosic material must first be subjected to pre-treatment, such as steam-explosion or extrusion, in order to expand the polymer fibres and to facilitate their hydrolysis. The hydrolysis can be done chemically (acid hydrolysis) or enzymatically (Lopez-Contreras, 2003). Unfortunately, these treatments can result in the formation of microbial inhibitors that are harmful to the ABE fermentation. Some of these inhibitory compounds include furfural, hydroxymethyl furfural (HMF), and acetic, ferulic, glucuronic,  $\rho$ -coumaric acids, etc. (Ezeji, et al., 2007). In a study by Ezeji, et al. (2007), the effects of these inhibitory compounds on *Clostridium beijerinckii* BA101 was determined: furfural and HMF are not inhibitory (rather it has a stimulatory effect in the microorganism growth and ABE production), but growth and ABE production decreased

significantly in the presence of 0.3 g/L  $p$ -coumaric and ferulic acids. The salts generated during dilute sulphuric acid hydrolysis are also toxic to *C. beijerinckii* BA101. It was concluded that untreated corn fibre hydrolyzate is not suitable for ABE fermentation. A more recent study by Ezeji and Blaschek (2008) was done with different *Clostridia* species (*Clostridium beijerinckii* BA101, *C. acetobutylicum* 260, *C. acetobutylicum* 824, *C. saccharobutylicum* 262, and *C. butylicum* 592) and again it was shown that these species are able to ferment both the pentose and hexose sugars. However, when hydrolysed dried distillers' grains and solubles (DDGS) were tested, the fermentation was unsuccessful. It was concluded that the inhibitors in dilute acid pre-treated DDGS must first be detoxified (Ezeji & Blaschek, 2008).

Physical, chemical, and biological methods can be used for detoxification of lignocellulosic hydrolyzates. It is however difficult to compare different detoxification methods when different lignocellulosic hydrolyzates are used, because the degree of inhibition may vary as well as the tolerance of different microorganisms towards inhibition (Mussatto & Roberto, 2004). All the steps prior to fermentation (pre-treatment, hydrolysis, and detoxification) are thus process specific and will be discussed in more detail if it is implemented.

The Russian plants were the first to implement the use of hydrolyzed agricultural waste (like hemp waste, corncobs, and sunflower shells) for ABE fermentation. These plants were however run on a mixture of agricultural waste, molasses and flour starch. A process to obtain pentose hydrolyzates from hemicellulose was developed by the Russians, because pentoses are largely degraded at high temperatures (160-180<sup>0</sup>C) and with concentrated sulphuric acid, which is the procedure used for complete hydrolysis of lignocellulosic biomass (e.g. wood) to sugars. Pentoses are futile for traditional yeast fermentation to ethanol, but it can be utilized for solvent production by the *Clostridium* genus. The process was as follows: biomass was ground to powder, diluted 1:10 (g/ml) with 1% (v/v) sulphuric acid and heated to 115-125<sup>0</sup>C. Time of hydrolysis ranged between 1.5 to 3 hours, depending on substrate and process temperature. The pentose syrup obtained consisted of mainly xylose and arabinose with traces of glucose and galactose. This partial hydrolyzate containing the pentoses gave better fermentation results than

the complete hydrolyzates using the harsher conditions which contained mostly glucose, but also more toxic by-products. Pentosan hydrolyzates did however decrease the solvent yield and increased the fermentation times when compared with flour starch, but data show that over 70% of the flour starch originally used could be replaced by a mixture of molasses and pentose hydrolyzates with consistent and reliable results in solvent production. The lower cost of the broader substrate basis more than compensated for the slight decrease in production yield (Zverlov, et al., 2006).

The focus of this study will be on biobutanol production from sugar refinery waste streams, therefore, molasses and bagasse as substrates will be discussed in more detail.

### **2.1.1 Molasses**

Sugarcane has very high sucrose content, and is the grass that is harvested for the production of sugar. Molasses is a dark coloured syrupy residue obtained from sugarcane after extraction of all commercially profitable sugar. It is also the principle by-product of a sugar refinery. The composition of molasses from sugarcane varies with the locality, variety of cane, character of soil, climate and the method of processing. Sugar concentration in molasses is about 50-66 wt% (Syed, 1994). The chemical composition of molasses from different sources is shown in Table 2. Seeing that molasses was one of the first substrates to be used for biobutanol production, there is sufficient literature available on fermentation studies with molasses as feed (see section 2.3). The use of this substrate also holds the following economic advantages (Syed, 1994):

- Molasses is one of the cheapest carbon sources in the market.
- It is relatively easy to handle during fermentation (as a liquid, molasses can be pumped).
- The molasses mash is relatively easy to sterilize.

The type of molasses used in this study is C molasses.

**Table 2: Composition of molasses from different sources**

Constituent	Percentage (w/w%)		
	(Roffler, 1987)	(Syed, 1994)	(Crous, 2007)*
Water	15	27.0	37.7
Total Solids	85	73.0	62.3
Total Sugars	55.0	50.2	62.3
Sucrose	n.a.	30.0	25.2
Reducing Sugars	n.a.	20.2	37.1
Fructose	n.a.	13.0	19.2
Glucose	n.a.	7.2	17.9
Ash	n.a.	11.1	n.a.
Nitrogenous substances	n.a.	3.0	n.a.
Free and Combined acids	n.a.	5.0	n.a.

\*Information obtained from personal communication

### 2.1.2 Bagasse

Sugarcane bagasse is a fibrous residue of plant material that remains of sugarcane after undergoing conventional milling. This residue is mostly burned to generate steam power to run the sugar milling process and the unused bagasse is stockpiled (Lee, 2005). Stockpiled bagasse is of low economic value and constitutes an environmental problem to sugar mills and surrounding districts due to the risk of spontaneous combustion occurring within the pile, especially if stockpiled for extended periods (Lavaracka, et al., 2002).

Sugarcane bagasse is a suitable substrate for solvent production: it is composed approximately of 40% cellulose, 24% hemicellulose, and 25% lignin. Its hydrolyzate contains hexose sugars, cellobiose, cellodextrins, and pentoses (all of which can be utilized by solvent-producing *Clostridia*) (Jones & Woods, 1986).

Using bagasse as substrate holds the following advantages (Lee, 2005):

- It does not require a separate harvest (unlike corn stover) – bagasse is collected as part of the sugar production process.
- It is already physically ground as part of the extraction process.
- Bagasse is cheap and readily available.
- It has high carbon content.

Different to molasses, bagasse will need to undergo pre-treatment, hydrolysis and detoxification prior to fermentation. These latter steps mean that the production process will be more complicated and possibly result in a higher process capital cost. The fact that bagasse has a lower market value than molasses might justify these additional costs.

## 2.2 Metabolism

### 2.2.1 Fermentative Metabolism of *Clostridium* Bacteria

The genus *Clostridium* is a heterogeneous collection of gram-positive, obligatory anaerobic, non-sulphate-reducing, spore-forming, rod-shaped bacteria (Montoya, et al., 2001). Solventogenic *Clostridia* have received much attention in recent years, because of their ability to produce industrially relevant chemicals such as butanol and acetone. The *Clostridia* produce several enzymes that bring about the breakdown of polymeric carbohydrates into monomers (Figure 3). These enzymes include  $\alpha$ -amylase,  $\alpha$ -glycosidase,  $\beta$ -amylase,  $\beta$ -glucosidase, glucoamylase, pullulanase, and amylopullulanase (Ezeji, et al., 2007).

During the fermentation of *Clostridia*, two separate growth phases occur: the exponential acidogenic phase and the solventogenic phase. The acidogenic phase is first, with the *Clostridia* performing typical butyrate fermentation when growing on starch or sugars. The major products are butyrate (butyric acid), acetate (acetic acid), carbon dioxide, and hydrogen. Ethanol and acetoin are formed in small volumes. The production of the acids results in a low pH which poses the threat of cell death. Imminent death is evaded by a major metabolic shift that takes place at the end of the exponential growth phase. This also marks the end of the acidogenic phase and the start of the solventogenic phase. The excreted acids are taken up again and are converted into the neutral products, butanol and acetone (in a ratio of typically 2:1). Conversion of butyrate and acetate into solvents increases the pH again, which means the cells can stay metabolically active for a longer time. However, the solvents are also killing the cells, with butanol being the most toxic. Solvents inactivate the membrane proteins and destroy the membranes of the cells. Therefore, there is a limitation to the maximum solvent concentration that can be achieved during fermentation, which is approximately 2 wt% (Dürre P. , 2008).



If there is no excess substrate in the medium and/or there are an excess of nutrients, a state known as acid-crash can occur (Zverlov, et al., 2006). This is a condition where the bacteria do not enter the solventogenic phase and consequently the fermentation ends abruptly due to overproduction of acids.

The solventogenic *Clostridia* have the benefit of producing a variety of fermentation products (acetone, butanol, ethanol, acetic acid, butyric acid, etc.). However, at the same time this can also be an undesirable property seeing that the formation of unwanted by-products results in a loss of available carbon. Evidently, enzyme production and control of electron flow in the glycolytic pathway are very important with regard to the regulation of the butanol fermentation pathways. Ferredoxin is commonly present among the solventogenic *Clostridia*. A change in the type and quantity of fermentation products produced can be achieved with alteration in the direction of electron flow around reduced ferredoxin (Ezeji, et al., 2007). Butanol yield should therefore respond to factors that influence the direction of electron flow and, since the electron flow can be reversed, researchers have tested the effect of numerous reducing compounds. Compounds tested include: carbon dioxide gassing, addition of methyl viologen, and the addition of neutral red into the fermentation medium during the ABE fermentation. In the presence of these electron carriers, butanol and ethanol formation were stimulated at the expense of acetone synthesis (Mitchell, 1998). Scientists continue to study the physiology of the bacterium and associated critical interactions between carbon pathways and electron flow. This research may lead to improved strains and the development of an optimal fermentation medium.

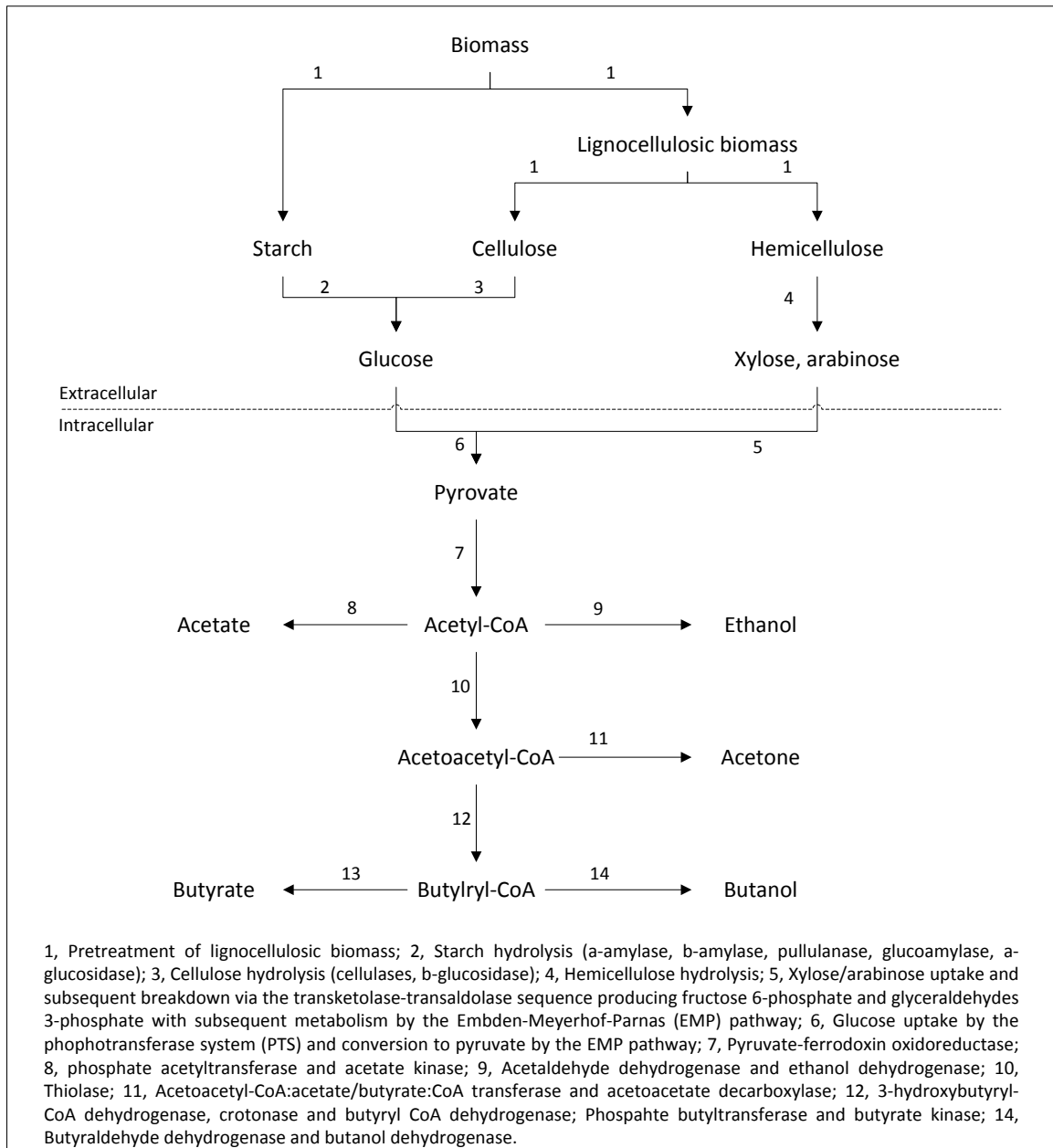


Figure 3: Simplified metabolism of biomass by solventogenic *Clostridia* (Ezeji, et al., 2007).

### 2.2.2 Butanol Producing *Clostridium*

Compared to ethanol production, the yields from glucose are not as impressive since butanol is normally produced together with acetone and ethanol in a ratio of 6:3:1.  $\text{CO}_2$  and  $\text{H}_2$  are major side products of the acid and solvent formation, and are obtained from the fermentors in molar (and volume) ratio of roughly 1.5:1. During fermentation approximately 3 moles of  $\text{CO}_2$  and  $\text{H}_2$  are formed per mole of hexose (glucose); 1.7 T of gasses are formed per T of solvents (97 wt%  $\text{CO}_2$  and 3 wt%  $\text{H}_2$ ) (Zverlov, et al., 2006).

Table 3 shows stoichiometric equations for solvent production from glucose. Using these, together with chemical properties to quantify both the energy and mass yields, Gapes (2000) determined the theoretical limits if the ratio of the products, as stated above, is maintained. A theoretical mass yield of 34%, and theoretical energy yield of 94% was calculated (Gapes, 2000). This, together with the limited solvent concentration of approximately 2%, must be taken into consideration when comparing different strains. Among the first strains to be patented were a number that, under optimal conditions, were able to utilise between 4-6% fermentable sugars producing solvent concentrations of 14-18 g/L with solvent yields from 25-30%. Later, improved strains to be patented were reported to utilise 7.5% fermentable sugars to give reproducible solvent concentrations of 18-23 g/L and yields of 30-33% (Walton & Martin, 1979; Shaheen, et al., 2000).

**Table 3: Stoichiometric Equations for Glucose Fermentation**

Product	Stoichiometric Equation
acetone	$C_6H_{12}O_6 + H_2O \rightarrow C_3H_6O + 3CO_2 + 4H_2$
1-butanol	$C_6H_{12}O_6 \rightarrow C_4H_{10}O + 2CO_2 + H_2O$
ethanol	$C_6H_{12}O_6 \rightarrow 2C_2H_6O + 2CO_2$
butyrate	$C_6H_{12}O_6 \rightarrow C_4H_8O_2 + 2CO_2 + 2H_2$
acetate	$C_6H_{12}O_6 \rightarrow 3C_2H_4O_2$

Environmental factors like substrate medium composition or growth conditions can also greatly influence the composition of the fermentation end products (Montoya, et al., 2001). Therefore, while a particular set of culture conditions utilised for a specific comparative study might be close to optimum for some species and strains, it has to be accepted that it is unlikely that the specific conditions used would be optimal for all strains tested in that study. Also, these culture conditions vary from one study to another, and lastly, when upgrading to industrial-scale fermentations the solvents levels produced will not be comparable to those produced on laboratory-scale fermentations (Shaheen, et al., 2000).

Solvent-producing *Clostridia* are separated into four distinct groups: *Clostridium acetobutylicum*, *C. beijerinckii*, *C. saccharobutylicum*, and *C. saccharoperbutylacetonicum*.

*C. acetobutylicum* is a species that is phylogenetically distinct and only very distantly related to the other three solvent-producing *Clostridia*. This strain thrive on starch-based substrates and of the industrial solvent-producing *Clostridia*, all the original starch-fermenting strains belong to this species (Shaheen, et al., 2000). *C. acetobutylicum* is the best-studied solventogenic *clostridium* and many improved strains have been developed of this species (Syed, 1994; Shaheen, et al., 2000; Dürre P. , 1998; Dürre P. , 2008). Shaheen, et al., (2000) performed a comparative fermentation study on solvent-producing *Clostridia*, but none of the three *C. acetobutylicum* strains tested performed well in either of the glucose or molasses media used (see Table 4). The highest solvents concentration was 9.5 g/L, with a yield of 15.8%. These strains did however perform better when it was tested in a maize medium. To date, the best performing *C. acetobutylicum* fermentation, using molasses as substrate, was carried out by Syed (1994). A locally isolated culture of *C. acetobutylicum* PCSIR-5 and its butanol resistant strain *C. acetobutylicum* PCSIR-10 was used (see Table 4). Total solvents concentration reached 19.2 g/L with a yield of 34%.

*C. beijerinckii* is more related to *C. saccharobutylicum* and *C. saccharoperbutylacetonicum*. These three are known as the saccharolytic strains as it contains all the later generation sugar-fermenting industrial strains. The majority of these saccharolytic industrial strains belong to the *C. beijerinckii* species. Although *C. acetobutylicum* is the best-studied solventogenic *clostridium*, it appears that *C. beijerinckii* might have greater potential for the industrial production of biosolvents. *C. beijerinckii* has a wider optimum pH range for growth and solvent production, and the genetic potential to utilise a wider variety of carbohydrates (Ezeji, et al., 2004). Due to the location of the genes in *C. beijerinckii*, it is suggested that this strain is less susceptible to acid crash and therefore more suitable for longer (continuous) fermentations than *C. acetobutylicum* (Grube & Gapes, 2002; Zverlov, et al., 2006). In the comparative study by Shaheen, et al., (2000) the NCP 260 strain performed the best. It consistently produced solvent concentrations above 18 g/L and solvent yields above 30%. The standard industrial fermentation process operated by National Chemical Products (NCP) Ltd. in South Africa, utilised molasses containing around 6.5% fermentable sugars (Spivey, 1978),

therefore when the NCP strain was tested at higher fermentable sugar concentration, better results were obtained (see Table 4). In fact, the solvent concentration continued to increase as the fermentable sugar concentration was increased up to 7.5%, while solvent yields remained fairly constant at 31.5%. The ratio of butanol to acetone did however decrease with this increase in fermentable sugar concentration (Shaheen, et al., 2000). Ezeji, et al., (2004) did extensive studies on *C. beijerinckii* BA101, a mutated strain created by mutagenesis of *C. beijerinckii* NCIMB 8052. This is a very versatile strain that performed well on a variety of substrates giving total ABE concentrations of 14.8-26.1g/L with yields of 37-50% (Ezeji, et al., 2004). Only the results for substrates tested relevant for this study is shown in Table 4.

*C. saccharobutylicum* and *C. saccharoperbutylacetonicum* are strains for which there is not so much literature on fermentation studies available. Shaheen, et al., (2000) included these strains in a comparative fermentation study and found that performance is better on glucose and molasses than on maize. This was to be expected seeing that these strains are also saccharolytic strains. The best fermentation result was obtained with the industrial strain, *C. saccharobutylicum* BAS/B3/SW/336(S), while utilizing molasses as substrate with a fermentable sugar concentration of 6.5%. The average solvent concentration was 19.6g/L with a yield of 30%.

The ultimate goal is to generate strains with a competitive commercial position, which can be used in industrial biobutanol production. The above strains are almost all products of the traditional mutagenesis and selection techniques employed to improve the performance of solventogenic *Clostridia*. Employing recombinant DNA technology, further improvement can be made by modifying targeted metabolic pathways in the *Clostridia*. Although progress has been made, this technology has so far not yielded a hyper-butanol-producing industrial strain (Ezeji, et al., 2007). Given the currently available *Clostridia* strains, it appears that advanced fermentation and recovery techniques (discussed hereafter) are the best short-term solution to improve fermentative butanol production.

**Table 4: Comparative fermentations of *Clostridium* strains**

Strain	Medium/Substrate (6% fermentable sugars)	Total Solvents Conc. (g/L)	Yield (%)	Productivity (g/L.h)	A:B:E
<i>C. acetobutylicum</i>					
PCSIR-10 <sup>b</sup>	Sugarcane Molasses	19.2	34.0	0.42	1.8 : 95.3 : 2.9
PCSIR-5 <sup>b</sup>	Sugarcane Molasses	15.2	30.0	0.24	5.3 : 79 : 15.7
ATCC 4259 <sup>a</sup>	Sugarcane Molasses	9.5	15.8	n.a.	n.a.
ATCC 824 <sup>a</sup>	Sugarcane Molasses	7.8	13.0	n.a.	n.a.
ATCC 824 <sup>d</sup>	Glucose	20.6	42.0	0.58	20.6 : 66.5 : 26.2
<i>C. beijerinckii</i>					
BA 101 <sup>c</sup>	Glucose	24.2	42.0	0.34	17.8 : 81 : 1.2
BA 101 <sup>c</sup>	Soy molasses	22.8	39.0	0.19	18.4 : 80.3 : 1.3
NCP P260 <sup>a</sup>	Sugarcane Molasses*	21.9	33.4	n.a.	n.a.
NCP P260 <sup>a</sup>	Sugarcane Molasses	18.9	31.5	n.a.	n.a.
<i>C. saccharobutylicum</i>					
BAS/B3/SW/336(S) <sup>a</sup>	Sugarcane Molasses*	19.6	30.0	n.a.	n.a.
NCP P108 <sup>a</sup>	Sugarcane Molasses*	18.6	28.6	n.a.	n.a.
NCP P258 <sup>a</sup>	Sugarcane Molasses	18.3	30.5	n.a.	n.a.
<i>C. saccharoperbutylacetonicum</i>					
N1-504 <sup>a</sup>	Sugarcane Molasses	15.6	26.0	n.a.	n.a.
<sup>a</sup> determined by Shaheen <i>et al.</i> (2000)					
<sup>b</sup> determined by Syed (1994)					
<sup>c</sup> determined by Ezeji <i>et al.</i> (2004)					
<sup>d</sup> determined by Roffler <i>et al.</i> (1987)					
* 6.5% fermentable sugars					

## 2.3 Fermentation and Downstream Processing Techniques

### 2.3.1 Commercial Process Technology

Details of the industrial ABE fermentation process have been well documented (Spivey, 1978; Walton & Martin, 1979; Jones & Woods, 1986; Dürre P. , 1998; Jones, 2005; Zverlov, et al., 2006), therefore only a brief summary extracted from these studies is included.

#### *i. Description of Conventional Process*

Batch fermentors, without mechanical agitation systems and ranging in size from 100 to 200 m<sup>3</sup>, were used on industrial scale. Maize mash and molasses were the major substrates used, but the latter had many advantages and superseded maize mash from the mid-1930s onwards. The molasses were sterilized by cooking at 107 to 120°C for 15 to 60 min. For fermentation, the fermentable sugar concentration was diluted between 5.0 and 7.5 wt%. depending on the strain used. Normally the molasses was supplemented with an additional source of organic and inorganic nitrogen, phosphorus,

and a buffering agent. Sometimes distillation slops was used to replace 33% of the makeup water in the fermentation broth. A carbon dioxide blanket covered the broth to help with anaerobic conditions, and often it was also bubbled through the broth before and after inoculation to facilitate mixing. Cultures were normally kept as spores in sterile sand or soil. Inoculum were prepared by heat-activating spores at 65-100°C for 1-3 min, and after two to four build-up stages, the cells were inoculated into the fermenter, either during or just after filling at a concentration of 2-4%. Fermentations using molasses were run at 29-35°C, with 31-32°C being the optimum temperature for many strains. The maize mash fermentations were normally run at higher temperatures (34-39°C) and the Russian fermentations were run at 37°C. Solvent yields based on fermentable sugars were usually in the range of 29-33%, and solvent concentrations of 18-22 g/L were the limit due to the toxicity of the solvents to the cell metabolism; in practice the concentrations obtained were frequently lower. Solvent ratios varied according to the strain and fermentation conditions, but a ratio of 6:3:1 (butanol-acetone-ethanol) was typical. After fermentation, the solvents were separated from the broth by batch or continuous distillation. The liquid effluent after distillation had a total solids content of 40-45% (wt/vol.) and these solids had a fairly high nutritional value (rich in protein and vitamin B). Dried solids was used as animal feed, and in many plants the carbon dioxide and hydrogen produced during fermentation were recovered, separated, and sold to aid in the profitability of the plant.

#### *ii. Limitations to Conventional Process*

The traditional batch fermentation process, followed by distillation, had the following shortcomings (Jones, 2005):

- The synthetic route, using petrochemical feedstock, became more economical than the fermentation route, which utilized renewable carbohydrate substrates (maize and molasses). Improved extraction procedures and applications of molasses also led to lower sugar content and higher market price.
- The toxicity of the butanol to the cells limited the final solvent concentration to 2%. This also made recovery by distillation energy intensive and expensive. At such a low concentration the energy required for butanol separation by

traditional distillation is higher than the energy content of the product itself (Friedl, et al., 1991).

- The fermentation process suffered from intrinsic limitations, which resulted in relatively low solvent yields and production of solvent ratios which were not always desirable.
- Sterile conditions were important, but difficult to maintain in the complex fermentation process. Phage infections were the major contamination problem and decreased productivity.
- The fermentation process produced large volumes of effluent, which required the development of specific processes for handling, treatment, and processing.

### *iii. Improvements Made on Industrial Scale*

After the Second World War, most of the industrial ABE plants in the Western countries were shut down, and consequently development of the ABE fermentation process ceased. In the USSR, however, fermentation and development of process technologies continued well into the 1980s, and the Russian ABE industry accumulated considerable experience with the handling of bacterial strains and with fermentation technology under the guidance of a central research institute run by the Dokshukino plant (Zverlov, et al., 2006). This plant was a full-scale production plant where new technologies were developed and tested, and once successful, the technologies would be integrated into other industrial plants. Research focused on all aspects of the process and included isolation of new strains, the development of more effective substrate preparation, introduction of new substrates, and minimizing bacteriophage infections and foam development during fermentation. Fermentation technology improvements included equipment design, downstream processing of the solvents, and by-product utilization (Zverlov, et al., 2006).

The most significant improvement that was made is the continuous flow process which had major advantages over the batch mode. Batch reactors of 225-275 m<sup>3</sup> (100 m<sup>3</sup> reactors were used in the Western world) were connected in series to form a battery of reactors. To increase overall site production, parallel batteries of reactors connected in series worked on a schedule which used each battery in a sequence and staggered in



time, resulting in a productivity increase of 31% over the batch mode. The plant also made use of a continuous distillation process (Zverlov, et al., 2006).

Other major advantages that the Dokshikino plant had over the ABE fermentation scheme known from the former Western plants, was the replacement of starch and/or molasses by hydrolyzates of agricultural waste material and the use of pentose hydrolyzates in addition to hexoses. A full integration in a biorefinery concept was also made, optimising by-product usage (See section 2.5) (Zverlov, et al., 2006).

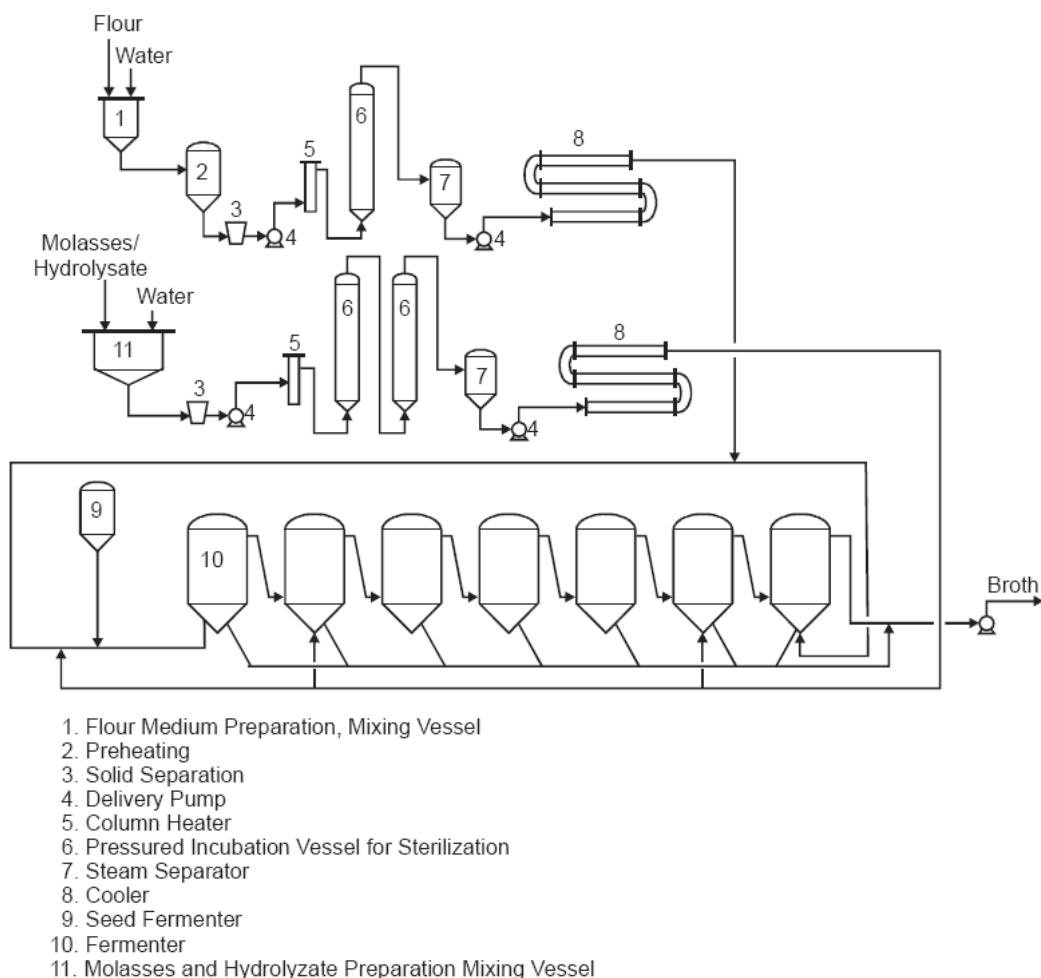


Figure 4: Single battery at the Dokshikino plant (redrawn from Bohlmann, 2007; Zverlov, et al., 2006).

### 2.3.2 Advanced Fermentation and Novel Downstream Processing Techniques

During the past two decades a significant amount of research has been performed on the use of alternative fermentation and product recovery techniques for biobutanol production. These techniques are well documented in literature and patents. Application of the more successful techniques is described below.

#### *i. Fed-batch and Free Cell Continuous Fermentation*

Fed-batch fermentation is used in processes where a high substrate concentration is toxic to the culture. The reactor is started in a batch mode with a low medium volume (usually less than 50% of fermenter volume) and a low substrate concentration (non-inhibitory to the culture). As the substrate is used by the culture, it is replaced by adding a concentrated substrate solution at a slow rate, thereby keeping the substrate concentration in the fermenter below the toxic level for the culture and increasing the culture volume in the reactor over time. Since butanol is toxic to the *Clostridium* cells, the fed-batch fermentation technique cannot be applied unless one of the novel product recovery techniques (discussed hereafter) is applied for simultaneous removal of product. Greater cell growth occurs as result of substrate reduction and reduced product inhibition, which leads to improved reactor productivity (Ezeji, et al., 2004).

Continuous fermentation is another method used to improve reactor productivity. The reactor is initiated in a batch mode and cell growth is allowed until the cells are in the exponential phase. As a precaution, fermentation is not allowed to enter the stationary phase because accumulation of butanol will kill the cells. While cells are in the exponential phase, the reactor volume is kept constant by continuously feeding the medium and withdrawing the product streams at the same flow rate. Downtime is reduced considerably, thereby improving reactor productivity. There is however one mayor drawback to this process: fermentation runs much longer than in a typical batch process which causes the solvent production to fluctuate and ultimately decline with related increase in acid production over time. In a single-stage continuous system, high reactor productivity may be obtained, but this occurs at the expense of low product concentration when compared with that achieved in a batch process (Ezeji, Qureshi, & Blaschek, 2004). A higher solvent concentration can be obtained when two or more

multistage continuous fermentation systems are used (Ramey D. , 1998). This is done by allowing growth, acid production, and solvent production to occur in separate bioreactors. It is reported that a solvent concentration of 18.2 g/L was achieved in a two-stage system, which is comparable to the concentration obtained during batch fermentation, but with the benefit of higher productivity (Ezeji, et al., 2004). Russia was the first to implement multistage fermentation systems on a full scale production plant (Figure 4). Figure 5 is a schematic diagram of patent US5753474 for the two-step continuous fermentation process.

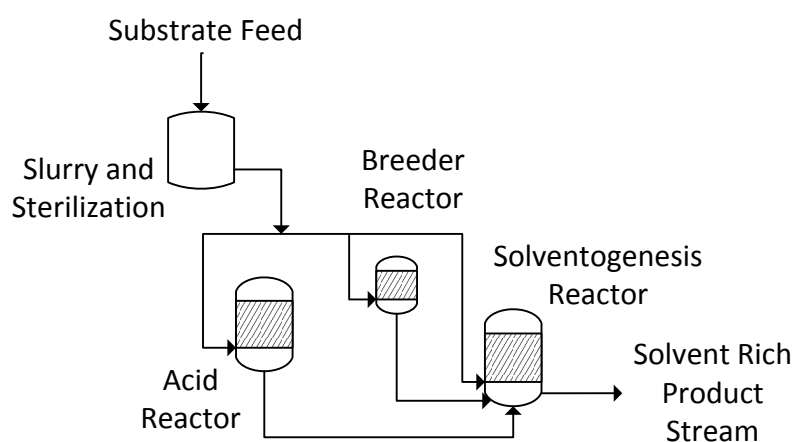


Figure 5: Two-step fermentation process (redrawn from Ramey D. , 1998)

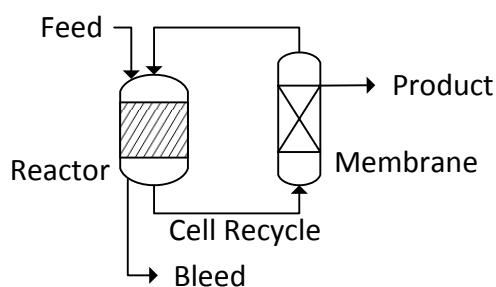
#### ii. Immobilized and Cell Recycle Continuous Reactors

Low cell concentration is one of the factors limiting reactor productivity. In batch reactors a cell concentration of less than 4 g/L is normally achieved. Two techniques have been developed to increase cell concentration in the reactor, namely 'immobilization' and 'cell recycle'.

Qureshi, et al., (2005) explored different cell supports for immobilization of *C. beijerinckii*, and achieved a productivity of 15.8 g/L.h by using clay brick as support in a continuous fermentation. In another approach, Huang, et al., (2004) immobilized cells of *C. acetobutylicum* in a continuous fibrous bed reactor and obtained a productivity of 4.6 g/L.h.

In membrane cell recycle reactors, the reactor is initiated in batch mode and the cells are allowed to grow into the exponential phase. Before the stationary phase is reached, the

cell broth is circulated through the membrane. The membrane allows the aqueous product solution to pass while retaining the cells. This happens in a continuous fermentation process, maintaining a constant level inside the reactor. A schematic diagram of such a system is illustrated in Figure 6.



**Figure 6: Membrane cell recycle reactor (redrawn from Ezeji, et al., 2004).**

In such cell recycle systems it is possible to obtain cell concentrations of over 100 g/L (Ezeji, et al., 2004). A small bleed stream is however included in these systems to keep cells productive. Studies have shown reactor productivity to reach 6.5 g/L.h using this technology (Ezeji T. , et al., 2006). Although superior membranes have been developed, fouling of the membrane with the fermentation broth remains a major obstacle (Ezeji, et al., 2004). With the increase of cell concentration in the reactor, the productivity of the ABE fermentation increased in the order of 10-50 times greater than that obtained during normal batch fermentation, resulting in a major economic advantage.

### *iii. Gas Stripping*

Gas stripping is a simple technique that can be applied for *in situ* butanol recovery during the ABE fermentation (Ezeji, et al, 2006; Ezeji, et al., 2005). It is a process whereby a gas (or gases) is passed through the fermentation broth to capture the solvents. The solvents are recovered from the gas by cooling it off in a condenser, thereby condensing the solvents, where after it is collected in a receiver vessel. The gas is recycled back to the fermenter to capture more solvents. This process continues until all the fermentable sugars are utilized by the culture, or until there is a rapid decrease in productivity. Figure 7 is a schematic diagram of a typical process of solvent removal by gas stripping.

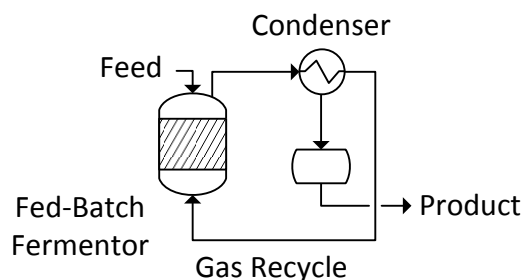


Figure 7: Butanol production and *in situ* recovery by gas stripping (redrawn from Ezeji, et al., 2004).

Nitrogen or the fermentation gasses ( $\text{CO}_2$  and  $\text{H}_2$ ) can be used for recovery, but using the latter will make the process simpler and more economical (Ezeji, et al., 2006; Ezeji, et al., 2005). In some cases a separate stripper can be used to strip off the solvents from the gas (instead of just sending the gas through the condenser), followed by the recycling of the stripper effluent that is low in solvents (Ezeji, et al., 2005). Ezeji, et al., (2005) tested several factors that influence the gas stripping solvent recovery system, and found that the rate of gas recycle and the addition of excessive amounts of antifoam has a significant effect on the system. Fermentation parameters obtained from literature for non-integrated and integrated (with product recovery) batch, fed-batch, and continuous systems are compared in Table 5.

Gas stripping is a simple process with a low chance of clogging or fouling, but it is more energy intensive than membrane recovery techniques (discussed hereafter). It also has a low selectivity resulting in only partial removal of solvents (Dürre P. , 1998).

Table 5: Comparison of novel butanol production systems using culture *C. beijerinckii* BA101 and glucose as substrate (Ezeji, et al., 2007).

Fermentation Process	Sugar Utilized (g/L)	Total ABE Produced (g/L)	Yield	Productivity (g/L.h)	Reference
Batch (Control)	<60	<33	0.38-0.40	0.35	Ezeji, et al. , (2006)
Product Recovery by Gas Stripping					
Batch	161	75.9	0.47	0.61	Ezeji, et al. , (2003)
Fed-batch	500	233	0.47	1.16	Ezeji, et al. , (2004)
Continuous	1163	460	0.40	0.91	Ezeji, et al. , (2005)
Product Recovery by Pervaporation					
Fed-batch	500	165.1	0.33	0.98	Qureshi, et al. , (2000)

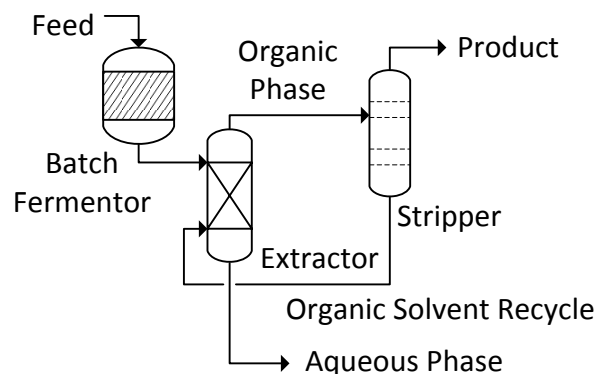
#### iv. Liquid-liquid Extraction

The removal of ABE from the fermentation broth by liquid-liquid extraction (LLE) is considered an important technique (Ezeji, et al., 2007). It can be applied for *in situ*

recovery during fed-batch and continuous fermentation, or as a separate step after fermentation. Extraction is a comprehensive operation and the design of extraction apparatus can be complex (Groot, et al., 1990). In a LLE process, an extractive solvent (usually water-insoluble organic extractant) is mixed with the fermentation broth (Roffler, et al., 1987). ABE is more soluble in the organic phase (extractant) than in the aqueous phase (fermentation broth), therefore ABE selectively concentrates in the organic phase (Ezeji, et al., 2007). It is possible to remove the ABE from the fermentation broth without removing substrates, water, or nutrients (Ezeji, et al., 2007). The ABE is recovered from the organic extractant by either back extraction into another extraction solvent, or by distillation (Roffler, et al., 1987). Figure 8 is a schematic diagram of a typical LLE setup.

The important qualities that are looked for in an extraction solvent are (Ezeji, et al., 2004):

- Non toxic to the production organism
- High partition coefficient for the fermentation products
- Immiscible and non-emulsion forming with the fermentation broth
- Inexpensive and easily available
- Can be sterilized and does not pose health hazards



**Figure 8: Butanol production and recovery by liquid-liquid extraction.**

There have been many reports on the use of numerous extraction solvents for extractive butanol fermentation. Oleyl alcohol has been the subject of a number of investigations since it is relatively non-toxic to the culture, as well as being a good extractant (Roffler, et al., 1987; Roffler, et al., 1988; Qureshi & Maddox, 1995; Chuichulcherm & Chutmanop, 2000). However, most of the extractants that has a relatively high partition coefficient for butanol also has a high toxicity for the culture (Groot, et al., 1990). Therefore, Eckert and

Schugerl (1987) used a microfiltration unit to first separate the butanol producing bacteria from the fermentation broth before extracting the butanol by decanol (which is a toxic extractant). They also made use of a continuous cell recycle system, with which a productivity of 3.08 g/L.h was achieved (Eckert & Schugerl, 1987). This productivity is less than half of that achieved in cell recycle systems without extraction (see section ii), but it is difficult to compare different systems without knowing the biomass concentration and fermentation parameters (Ezeji, et al., 2006). In most studies, 2-ethyl-1-hexanol is the extractant of choice with systems where the culture is first separated before extraction, seeing that 2-ethyl-1-hexanol inhibits the growth of the culture (Chuichulcherm & Chutmanop, 2000; Bohlmann, 2007; Wu, et al., 2007; Dadgar & Foutch, 1988). Dadgar and Foutch (1988) studied the properties of 47 different selected solvents and found that 2-ethyl-1-hexanol has good extractive properties for ABE from water. In another study by Chuichulcherm and Chutmanop (2000), 2-ethyl-1-hexanol proved to be superior to oleyl alcohol and palm oil methyl ester for extraction of ABE from water. Therefore, to conclude, oleyl alcohol is the extractant of choice with *in situ* recovery of ABE from the fermentation broth, and 2-ethyl-1-hexanol is best for when the extraction takes place in a culture free medium.

With an increase in the operating temperature of the extraction process, the volume of butanol extracted increased (Chuichulcherm & Chutmanop, 2000). However, with *in situ* recovery, the maximum operating temperature is 35°C (due to the micro-organism). It was also shown that the amount of salts in a real fermentation broth should not interfere with the butanol extraction capacity (Chuichulcherm & Chutmanop, 2000). The salt actually increased the butanol productivity by 1-2% since the salt increased the ionic strength of the fermentation broth, thereby driving out the polar butanol (Chuichulcherm & Chutmanop, 2000).

LLE is a technique with high capacity and selectivity, with the only major problem being emulsion formation at the extraction interface (Dürre P. , 1998). This process is best performed as a separate step after fermentation in a culture free medium, thereby preventing emulsion formation in the fermenter, and to steer away from the use of membranes (in the case where a toxic extractant is used).

#### *v. Perstraction*

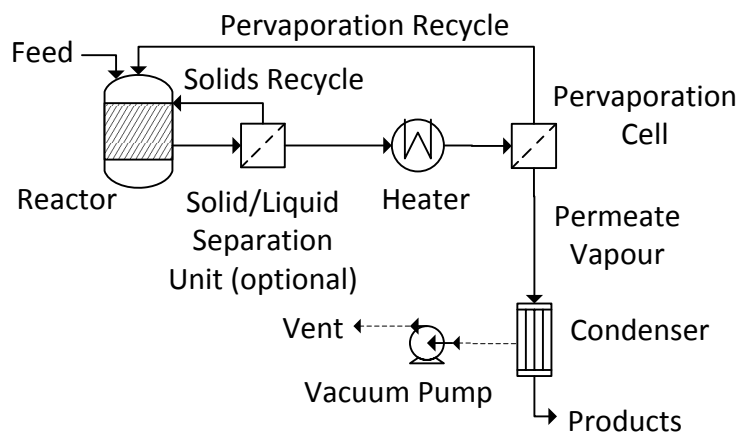
Perstraction is a technique that was developed to overcome problems associated with LLE, such as accumulation and inactivation of cells at the interface, loss of extractant due to incomplete phase separation, extraction of reaction intermediates (e.g. acetic and butyric acids), formation of emulsion which may be difficult to separate, and cell inhibition due to prolonged exposure of cells to extraction solvent (Qureshi & Maddox, 2005). This type of system is similar to LLE, but the fermentation broth and the extractant is separated by a membrane, which provides surface area where the two immiscible phases can exchange butanol. Butanol diffuses preferentially across the membrane, while other components and reaction intermediates are retained in the aqueous phase (Qureshi & Maddox, 2005). There is no direct contact between the two phases, therefore extractant toxicity, emulsion and rag layer formation (i.e. the accumulation of cells at the aqueous-organic interphase) are considerably reduced or eliminated (Ezeji, et al., 2007). In a study by Qureshi, et al., (1992) perstraction yielded superior results to LLE, and productivities similar to that of gas-stripping (performed in the same study) was obtained. The membrane that was used in this study allowed diffusion of butanol into the extractant, but diffusion of acetone was poor (Qureshi, et al., 1992). The productivity of this system depends on the rate of diffusion of fermentation products across the membrane, from the fermentation broth to the organic side. The membrane does, however, present a physical barrier that can limit the rate of extraction (Ezeji, et al., 2007). Therefore a large membrane area is required to achieve a higher productivity. The membrane is also subject to possible clogging and fouling.

#### *vi. Pervaporation*

Membrane separation systems, such as pervaporation and perstraction, have attracted recent attention because of its high selectivity. Pervaporation appears to be particularly promising, since it can accomplish separation and partial concentration of clean products in one step without first recovering the fermentation products from an extractant (Jitesh, et al., 2000). This system is based on the selective permeation of the ABE components through the membrane in preference of water (Liu, et al., 2005). The ABE in the fermentation broth sorbs into/onto the membrane, permeate through the membrane, and evaporate into the vapour phase, where after the vapour is condensed to retrieve the



products. Pervaporation can be coupled with fermentation so that the inhibitory products from the fermentation broth can be removed continuously as soon as they are formed, thereby enhancing the process productivity. A schematic diagram of the pervaporation system is shown in Figure 9.



**Figure 9: Butanol production and *in situ* recovery by pervaporation (redrawn from Vane, 2004).**

A dense non-porous polymeric membrane is used in contact with the fermentation broth on the upstream side, while a vacuum is created on the downstream side in order to induce transport (Jitesh, et al., 2000). An alternative to creating a vacuum, is applying a sweep gas such as nitrogen (Qureshi, et al., 1992). The effectiveness of pervaporation is measured by two parameters: the selectivity (a measure of the selective removal of volatiles) and flux (the rate at which an organic/volatile passes through the membrane per  $\text{m}^2$  membrane area) (Ezeji, et al., 2007). Therefore, the properties of the membrane material dictate the separation and productivity achieved in the process. Several studies have been performed on different membranes and optimal operating conditions (Qureshi, et al., 1992; Qureshi & Blaschek, 1999; Jitesh, et al., 2000; Qureshi & Blaschek, 2000; Vane, 2004). Polydimethylsiloxane (PDMS) appears to be the most widely used organophilic membrane material, and silicalite has been used as filler in the PDMS membranes to improve the membrane selectivity (Liu, et al., 2005). In a study by Jitesh, et al., (2000) the following features of the pervaporation process through dense membranes was summarised:

- Absence of membrane stability problems, unlike liquid membranes or membrane distillation techniques
- Non-porous membrane structure prevents fouling by microorganisms

- Heat from the exothermic bioreactors can be released in the pervaporation unit
- Absence of thermal, chemical, or mechanical stress on the fermentation broth
- Productivity increased through increased substrate consumption and alcohol production

When compared to gas-stripping and perstraction in a study by Qureshi, et al., (1992) the ABE productivity and yield in the pervaporation process was lower than the other techniques. With pervaporation, there were also a lot more acetic and butyric acid present in the product (Qureshi, et al., 1992). However, in a more recent study, productivity closer to that of gas-stripping was achieved, but the yield was still relatively low (Qureshi & Blaschek, 2000). See Table 5 for these results and comparison thereof with other recovery techniques. According to Vane (2004), the following issues must first be addressed for pervaporation to be economically viable, energetically attractive, and implemented on industrial scale for biofuel recovery:

- Increased energy efficiency – improved ethanol-water separation factor and heat integration
- Reduction of capital cost for pervaporation systems – reduction in the membrane/module cost per unit area and increase in membrane flux to reduce required area
- Longer term trials with actual fermentation broths to assess membrane and module stability and fouling behaviour
- Optimized integration of pervaporation with fermenter – filtration to increase cell density in fermenter and allow higher pervaporation temperatures
- Updated economic analyses of pervaporation which provide comparisons to competing technology.

#### *vii. Adsorption*

Adsorption is ubiquitous in the laboratory-scale as well as industrial-scale separation or purification of liquid and gaseous mixtures for the manufacture of a wide variety of chemicals, biochemicals and materials, e.g., fuel-grade ethanol by a biochemical route (Liu, et al., 2006). In a recent study, adsorption has been identified as a simple technique

that can be applied successfully for energy-efficient removal of butanol from fermentation broth (Qureshi, et al., 2005). It was shown that this method requires less energy for butanol separation than any other technique. In addition, a concentrated butanol stream is obtained.

Adsorption can be applied after fermentation or for *in situ* recovery of ABE during fermentation. Although none of the adsorbents tested in literature thus far proved to be toxic to the cultures, it was found that by using a cell-recycle system (applying an ultrafiltration membrane to remove the cells prior to adsorption) greater butanol recovery was achieved as opposed to recovery directly from the fermentation broth (Qureshi, et al., 2005). It is presumed that the cells adhere to the adsorbent if filtration is not used, thus fouling it. Cells can also be removed by centrifugation prior to adsorption, but this will make the process more energy intensive and less attractive (Liu, et al., 2006). Nutrients in the fermentation broth may be adsorbed, which will further reduce fermentability unless additional nutrients are added (adding to the cost of the fermentation) (Qureshi, et al., 2005). Another problem is the adsorption of reaction intermediates (e.g. acetic and butyric acid), which can lead to lower yields and may cause additional problems during concentration and purification. A schematic diagram of ABE separation and concentration from fermentation broth using adsorbent is shown in Figure 10. ABE and a very small amount of water are adsorbed onto the adsorbent and each component is desorbed separately by sequential heat treatment. Qureshi, et al., (2005) removed the adsorbed water from silicate by heating to 40°C, while butanol was removed by heating to 150°C.

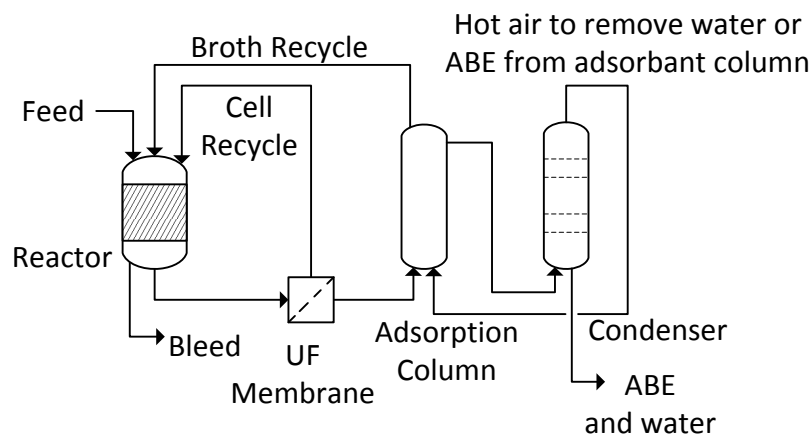


Figure 10: Butanol production and recovery by adsorption (redrawn from Qureshi, et al., 2005).

The general characteristics of an adsorbent should include quick adsorption, high adsorption capacity, low cost, and ease of desorption and regeneration. In a study by Qureshi, et al., (2005) three efficient adsorbents were tested for recovery of ABE from the fermentation broth, namely silicalite, bone charcoal/charcoal, and polyvinylpyridine. Silicalite proved to be the most attractive adsorbent: it can concentrate butanol from dilute solutions (5 to 810 g/L), results in complete desorption, and can be regenerated by heat treatment (Qureshi, et al., 2005). Yang and Tsao (1995) achieved an ABE yield of 0.32 g/g and productivity of 1.33 g/L.h during fed-batch fermentation with cell recycle and polyvinylpyridine as adsorbent.

Adsorption is one of the novel downstream processing techniques with the lowest energy requirements (Qureshi, et al., 2005), but it also has a low capacity, low selectivity, and is subject to fouling (Dürre P. , 1998).

## 2.4 Comparison of different ABE production techniques

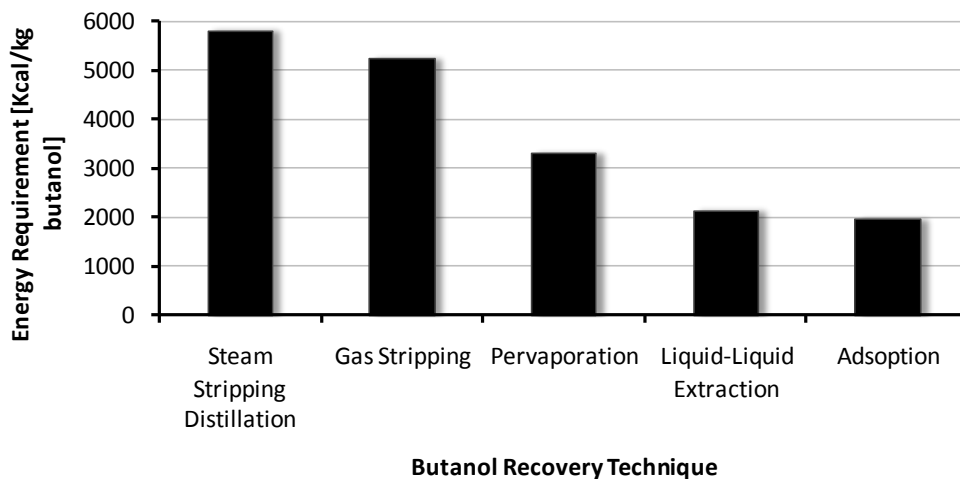
In order to decide upon the best biobutanol production process route to implement on an industrial scale, comparisons of the different fermentation and downstream processing techniques discussed in previous sections, are made. Advantages and disadvantages of the process, energy requirements, and process economics are considered.

From the different fermentation techniques, it is clear that fed-batch and continuous fermentation are vast improvements on batch fermentation. For fed-batch fermentation *in situ* product recovery is required, and continuous fermentation needs multiple reactors to achieve a reasonable product concentration. Another means to improve the continuous fermentation process is to apply cell recycle or immobilization of cells, but none of these technologies have been implemented or proven on industrial scale. Therefore fed-bath fermentation (dependent on the product recovery technique) or even repeated batch fermentation (rendering a continuous process) seems to be the most viable fermentation process options currently available.

Table 6 lists the most important advantages and disadvantages of all the downstream processing techniques discussed in previous sections. There is no clear cut best option. Membrane-based systems show a high selectivity for solvents, but might suffer from clogging and fouling and seem to be more suited for use with immobilized cells. For these reasons membrane techniques are unattractive on industrial scale processes. Adsorption is the technique with the lowest energy requirements, but is also subject to fouling and has a low capacity and selectivity. Gas-stripping is as simple as, or even simpler than, conventional distillation; it does not suffer from particulate substrates or from clogging or fouling by biomass, but no complete removal of solvents from the fermentation broth is achieved (Liu, et al., 2004; Dürre, 1998). Liquid-liquid extraction can be a viable alternative to azeotropic distillation; properly incorporated into the flowsheet, it may eliminate the need for azeotropic distillation (Dadgar & Foutch, 1988). LLE also has a high selectivity, but emulsions might form rendering the process less suitable (Dürre, 1998). In Figure 11 the energy requirements for the different downstream processing techniques are compared.

**Table 6: Comparison of novel downstream processing techniques (adapted from Dürre (1998))**

Method	Principle	Advantage	Disadvantage
Gas Stripping	Heating of effluent, purging with gas, condensation of solvent/water vapours	Simple to perform, low chance of clogging or fouling	Low selectivity, no complete removal of solvents, more energy required compared to membrane-based processes
Liquid-Liquid Extraction	Contact with water-immiscible solvent with fermentation broth, recovery of dissolved solvents by distillation	High capacity, high selectivity, low chance of clogging or fouling	Expensive to perform, possible forming of emulsions
Perstraction	Similar to liquid-liquid extraction, with a membrane separating fermentation broth and extractant	High selectivity, simple to perform	Large membrane area required, possible clogging or fouling
Pervaporation	Selective diffusion of solvents across a non-porous membrane, recovery of evaporated vapours by applying vacuum or sweep gas	High selectivity compared to membrane evaporation, simple to perform	Lower membrane flux compared to membrane evaporation, possible clogging or fouling
Adsorption	Adherence of solvents to e.g. silicate or ion exchange resins, heat regeneration	Lowest energy requirements of all the methods	High price of material, low capacity, low selectivity, possible fouling

**Figure 11: Energy requirements of different downstream processing techniques (Qureshi, et al., 2005).**

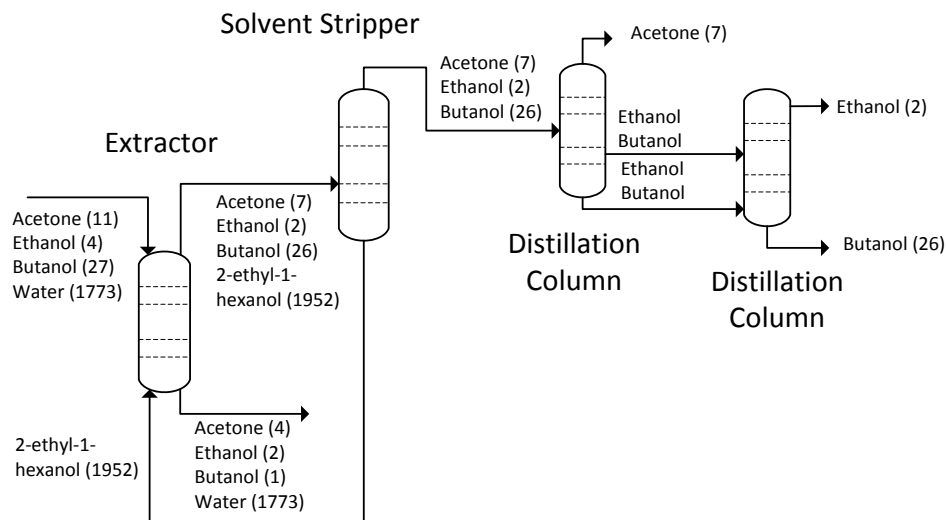
Evaluating from a financial point of view, cost estimates from different studies show that large sterilisable pressure vessels for fermentation are expensive and have a great influence on the total project capital cost (normally in the range of 60% of total equipment cost). However, there are other factors that have equal influence on the total project capital cost (TPCC), e.g. capital cost for product separation is of comparable magnitude (Gapes, 2000). Continuous production has a higher productivity than batch operation and may seem more economic, but there are additional expenditures involved

for not only the installation of dedicated sterilisation equipment, but also to install piping, valves, and other fixtures capable of reliably supporting absolute sterility at all times. Therefore, purely from the investment cost point of view, it is improbable that continuous operation is of great advantage as the requirement for sterility is of dominating importance and governs costs in the plant (Gapes, 2000). The choice of downstream processing technique for product separation also does not have a significant influence on the TPCC. Gas-stripping, liquid-liquid extraction, or even membrane evaporating equipment requires an investment of roughly similar magnitude as traditional distillation columns (Gapes, 2000). Use of low flux, highly selective pervaporation membranes may even require higher investment costs due to large membrane areas required and other operational problems, such as possible capillary blockages and perforation of the membrane, which can cause sterility problems (Gapes, 2000). Therefore, when deciding upon a novel ABE production system the increased productivity must outweigh a greater capital cost to provide an overall viable economic process design.

Researchers have employed computer simulations for process modelling of butanol production processes, including ABE fermentation, and used these simulations to evaluate the process economics. The earliest effort in downstream processing simulation of ABE fermentation was reported by Marlatt and Datta (1986). This study made use of an improved strain in a multistage fermentation process, to manufacture butanol from corn. The conventional distillation process was optimized to minimize energy requirements, but no advanced separation techniques were included. Marlatt and Datta (1986) concluded that improvements had to be made in order to make this process more attractive than the petrochemical route for butanol production.

Studies by Roffler, et al., (1987) and Dadgar and Foutch (1988) followed, which included liquid-liquid extraction. Dadgar and Foutch used the process design of Marlatt and Datta (1986) for the feedstock and fermentation section, and used 2-ethyl-1-hexanol as extractant in LLE. This study showed a 15% reduction in overall cost when compared to the conventional distillation process. Roffler, et al., (1987) made use of fed-batch fermentation, and oleyl alcohol was the extractant of choice. A 20% reduction in TPCC was achieved over the conventional batch fermentation process.

In a more recent study by Liu, et al., (2004) a variety of technically feasible and cost-effective flow-sheets for downstream processing was generated by incorporating only conventional unit operations. Distillation and extraction were used seeing that these unit operations have been optimised and their cost have been minimised in their long commercial existence (Liu, Fan, & Seib, 2004). The units were simulated in ASPEN PLUS 11.1 and the resultant data loaded and mapped in ASPEN Icarus Process Evaluator 11.1 to evaluate the capital and operating cost. The study showed that the optimal flow sheet (see Figure 12) consists of a liquid-liquid extractor, a solvent stripper, and two distillation columns. The configuration of the two distillation columns is referred to as complex-direct, and 2-ethyl-1-hexanol was used as extractant in LLE (Liu, Fan, & Seib, 2004). It is however very important to take into consideration that in the study by Liu, et al., (2004) it was assumed that, in the extraction unit, all the water is entrained in the raffinate phase and the extractant phase contains no water. Therefore no azeotropes exist in the downstream processing after the extraction unit, making distillation rather simple.



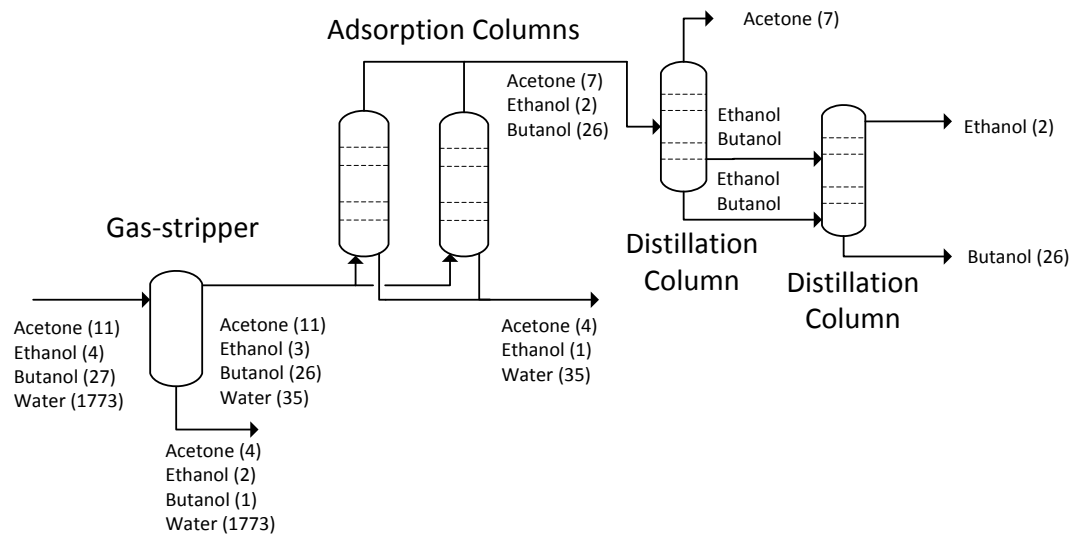
**Figure 12: Optimal flowsheet for downstream processing comprising of conventional separation methods (redrawn from Liu, et al., 2004). Values in brackets are on mass basis.**

An additional study was done by Liu, et al., (2006) to explore the possibility of incorporating both adsorption and the conventional separation methods (various types of distillation, LLE, and gas-stripping) into a plant through synthesizing potentially optimal and near-optimal flowsheets for it. The optimal flowsheet generated in this study consists of a gas-stripper, two adsorption columns, and two distillation columns (see



Figure 13). Different to the adsorption columns as discussed previously in this report (see section 2.3.2), these columns are packed with multiple beds (trays) of thinly-layered molecular sieves. The vapour stream from the gas-stripper is fed to the adsorption columns where essentially all the water is adsorbed onto the adsorbents (Liu, et al., 2006). It must again be taken into consideration that, in this study, it was assumed that the majority of the products are recovered by gas-stripping, and that all the excess water is removed by adsorption.

None of the top 10 flowsheets in the study by Liu, et al., (2006) contains LLE, centrifuging, or azeotropic distillation units. The fact that gas-stripping is used prior to adsorption, means that only a small fraction of the original fermentation broth is fed to the adsorption unit, thereby substantially reducing the equipment size and capital cost. The total cost of this optimal flowsheet is 44% less than that of the optimal flowsheet generated in Liu, et al., (2004).



**Figure 13: Optimal flowsheet for downstream processing incorporating both adsorption and conventional separation methods (redrawn from Liu, et al., 2006). Values in brackets are on mass basis.**

The most recent studies were done by Bohlmann (2007) and Wu, et al., (2007). Bohlmann (2007) did an economic study on the production of ABE from corn: the optimal flowsheet in Figure 12 was used, but an extra gas-stripping step for *in situ* product recovery from fed-batch fermentation was added prior to LLE. The conclusion of the study was that further technical progress must be made in order for biobutanol to be

competitive again (Bohlmann, 2007). Another life-cycle assessment of corn-based butanol was done by Wu, et al., (2007): this study also made use of fed-batch fermentation coupled with *in situ* product recovery by gas-stripping, but it was followed by conventional distillation (two distillation columns: butanol was removed first followed by acetone) and finally adsorption to separate ethanol and water. According to Wu, et al., (2007), this setup is the optimal (most cost-effective) flowsheet. The study showed that, from a liquid fuel production standpoint, the ABE process examined is not as effective as the conventional ethanol production from a corn dry mill (Wu, et al., 2007).

However none of the simulated biobutanol production processes proved to be economically viable when compared with synthetic butanol, Marlatt and Datta (1986) have shown that the production cost for biobutanol would be similar to that of synthetic butanol, if an improved strain, which tolerates slightly higher butanol concentrations, is used and the productivity is increased by about 50%. Woods (1995) stated that if the final solvent concentration can be increased by one-third (*i.e.* to the levels of 22-28 g/L) and if the fermentation time of the batch fermentation of 40-60 hours can be maintained, the ABE fermentation should be industrially viable. Gapes also (2000) concluded in his study that ABE fermentation “appears to be economic if processing low-grade substrates into the chemical market.”

## 2.5 Biorefinery Concept

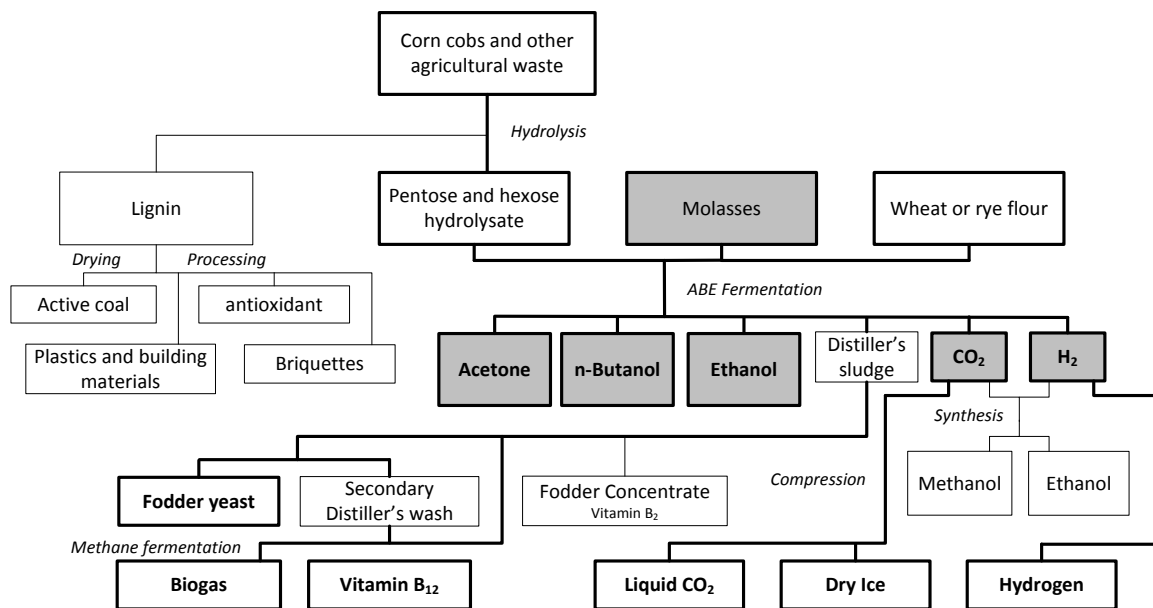
It is envisioned that advanced biorefineries will serve as the foundation of the new bioindustry. The U.S. National Renewable Energy Laboratory (NREL) has defined a biorefinery as a facility that integrates biomass conversion processes and equipment to produce fuels, power and chemicals from biomass (Bohlmann, 2005). Making use of novel chemical, biological and mechanical technologies, biorefineries show potential to significantly increase the use of renewable plant-based materials, and also provide a way for changeover to a more energy efficient and environmentally sustainable chemical and energy economy (Bohlmann, 2005).

According to a study by Lynd, et al., (2005), the advantages of a biorefinery concept as compared to a dedicated production of a single product are:

- Revenues of high-value co-products improve profitability of the primary product.
- Full-size biorefineries provide economies of scale which lowers the processing costs of high-value, low-volume co-products.
- Economies of scale provided by the primary product, means that less fractional market displacement is required for cost-effective production of high-value co-products.
- Biorefineries can utilize most of the component fractions contained in biomass for producing fuel and co-products, thereby maximizing the value generated from the feedstock.
- Common process elements exist for the production of fermentable products, independent of the number of products produced, thus reducing the production cost of co-products.
- Energy requirements can be met by process integration and cogenerated electricity and steam from process residues.

The biorefinery concept of the Russian ABE fermentation plants that operated during the 20<sup>th</sup> century are shown in Figure 14 (only the boxes marked in bold print were realized). The basic outline of the process was gradually modified to optimize the production and to make the overall process more economically viable. This full integration in a biorefinery

concept, making as much use as possible of by-products, is one of the advantages that the Russian plants had over the Western plants operating at that time (Zverlov, et al., 2006). Although only the bold boxes in Figure 14 were realized, it was with the establishment of the yeast production that the overall process reached profitability and at the same time reduced the amount of organic sludge to be disposed. Besides the fermentation gasses, biogas were produced by thermophilic methanogenic fermentation from the fermentation sludge. It was used to provide process heat in sterilization and distillation (Zverlov, et al., 2006).



**Figure 14: Biorefinery concept used for ABE fermentation plants in Russia (redrawn from Zverlov, et al., 2006)).**

This study will focus only on the filled (grey) boxes in Figure 14. This was also the major focus area of most of the studies done by previous researchers on the economics of ABE-production plants, with butanol, ethanol, and acetone being the only major products (Marlatt & Datta, 1986; Woods, 1995; Gapes, 2000; Bohlmann, 2007; Wu, et al., 2007; Roffler, et al., 1987; Dadgar & Foutch, 1988). None of these studies showed positive results for a competitive biobutanol industry. Therefore, it seems that an integrated biorefinery concept might be the only way to achieve a favourable economic condition with the current technology available for ABE fermentation.

### 3 Approach and Design Basis

This section contains the methods used and assumptions made to simulate the process designs (see section 1.2.2) in ASPEN PLUS® and ASPEN Icarus®, and serves as a basis for all the process designs. This section also justifies the reliability and robustness of the computer simulated models, and answers the question of which thermodynamic model should be used to accurately simulate these process designs.

The conceptual designs of multiple processes will be evaluated in this project with the aim of determining the optimum process design for biobutanol production from molasses. Figure 15 illustrates the approach followed for the conceptual designs. The conceptual plans will entail the development of process flow diagrams and configurations for the facilities conceived including any support requirements that must be included for the operations to function. This phase is concluded with order of magnitude estimates that are used to assess the economic viability of the projects. Cost estimates at this level of project design are not very accurate; plus or minus 30% is the norm (Vogel & Tadaro, 1997). The decision whether to go ahead with additional effort to firm up the best project's budget is based on these designs.

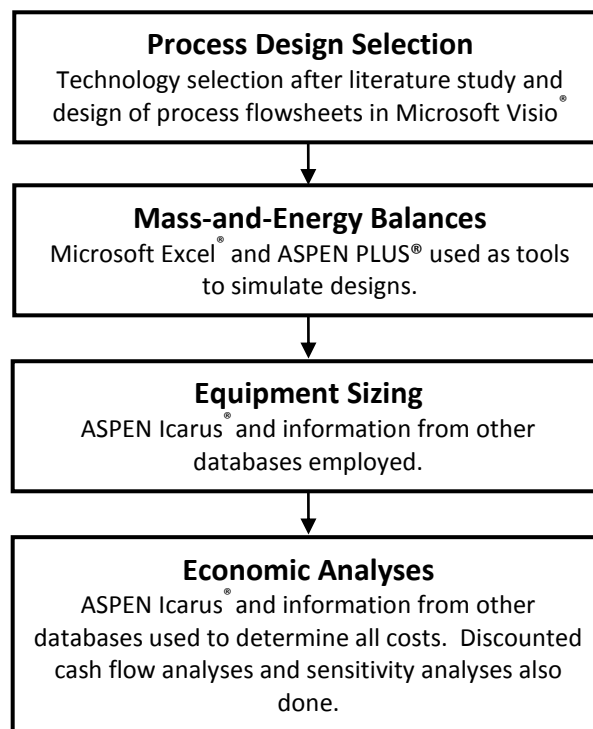


Figure 15: Main steps in conceptual design process

### 3.1 Process Overview

The process being analyzed in this project can be described as: sterilizing molasses from a sugar mill refinery, fermentation of this feedstock to ABE, and purification and separation of the products. The process are designed to be built very close-by, or adjacent to, a sugar mill refinery. It will therefore most likely be an annexed plant built alongside a sugar mill plant. The main objective of the plant will be to produce sugar rather than alcohol, sharing several common systems such as utilities, effluent treatment, and personnel. Therefore facilities to produce utilities at the required capacity, a laboratory, and waste disposal areas are not included in the designs. It is assumed that utilities are available for purchase from the neighbouring sugar refinery and that a waste water treatment facility (or a system for handling the waste) is in place at the sugar refinery and can be used. The process designs do allow for in-process and product storage. All the designs (see section 1.2.2 for the different process designs) consist of the following areas:

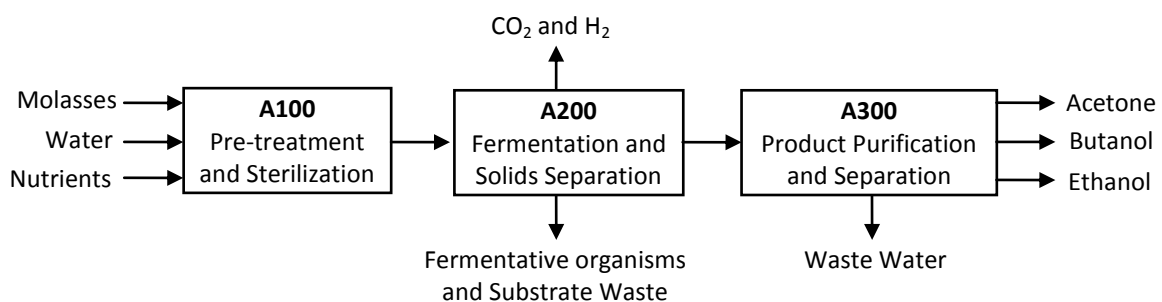


Figure 16: Overall process block flow diagram

### 3.2 Mass-and-Energy Balances

Using the different arrangements of the equipment shown (see Appendix C for PFDs), mass and energy balances for the process designs are developed in Microsoft Excel<sup>®</sup> and ASPEN PLUS<sup>®</sup>. The overall designs are thermodynamically rigorous and use physical properties that are included in the ASPEN PLUS<sup>®</sup> modelling software as well as property data developed by NREL specifically for biochemical processes (Wooley & Putsche, 1996). There are more detail and rigor in some blocks (e.g. distillation columns) than others (e.g. conversion extent in ABE fermentors). Some unit operations, such as solid-liquid separations, are modelled with data from vendor tests for fixed solids removal and liquid retention in the solids stream. The following sub-sections provide details about decisions

and assumptions made prior to simulation of the process designs in ASPEN PLUS® and ASPEN Icarus®, as well as additional techniques used to improve the designs.

### 3.2.1 Physical Properties

High temperature or pressure process steps are not encountered in these designs. However, three different phases of matter (solid phase, gas phase, and liquid phase) are processed and the components present (water, carboxylic acids, alcohols, and gasses above their critical temperatures) make for a highly complex system. This means that no single physical property method is sufficient for accurate simulation of this system. Instead, three different physical property methods are used in ASPEN PLUS® to more accurately simulate the thermodynamic properties of the components. The non-random two-liquid activity coefficient model, using the Hayden-O'Connell model for the vapour phase, (NRTL-HOC) is used throughout most of the process including for alcohol separation calculations. The Hayden-O'Connell equation reliably predicts solvation (cross-association) of polar compounds and dimerization in the vapour phase, as occurs with mixtures containing carboxylic acids (e.g. acetic and butyric acids). A major shortcoming of this property method (NRTL-HOC) is that it does not explicitly account for association (self- and cross-association) in the liquid phase, which generally occurs in systems containing these components. The process also deals with CO<sub>2</sub> and H<sub>2</sub> at temperatures above their critical temperatures. For ASPEN PLUS® to correctly simulate the latter components, they are set to be Henry components. Finally, to more accurately simulate the gas stripping process (where the vapour phase is most important), Soave-Redlich-Kwong equation-of-state (SRK) is used. The latter thermodynamic model also does not explicitly account for association in neither the gas nor liquid phases. See Appendix C for more detail on physical property model selection and binary parameters used.

### 3.2.2 Plant Location, Size and Operation Parameters

The project is designed for location in Africa (more specifically South Africa).

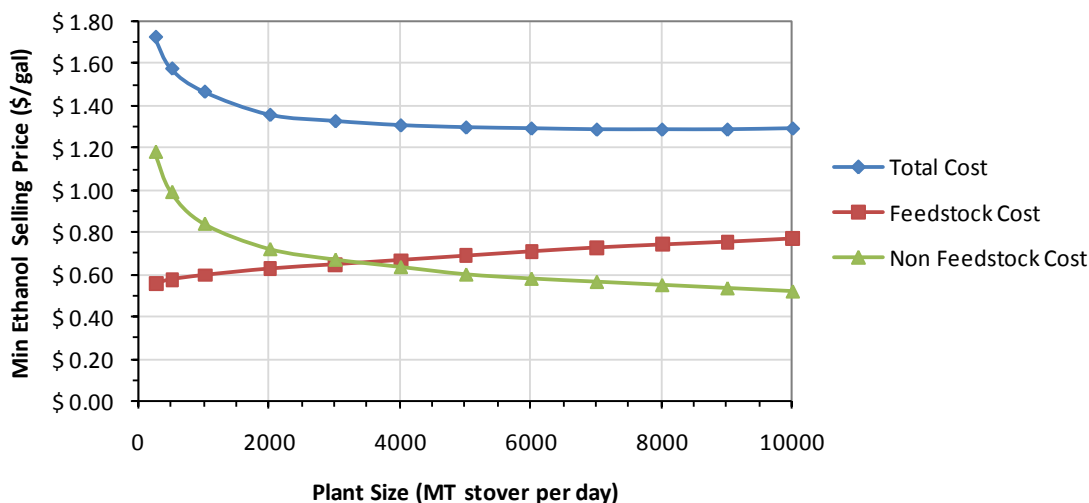
**Table 7: Project information inputs for ASPEN Icarus®**

Project Information	
Project Location	Africa
Project Type	Grass roots/Clear field
Soil Condition Around Site	Gravel

The above table indicate user specified information in ASPEN Icarus®. **Project Location** determines the various location dependent costs based on the actual geographical location of the project site (i.e. freight (domestic and ocean), taxes/duties, wage rates and workforce productivities). Although, as stated in section 3.1, this plant will be located near or adjacent to an existing plant, the **Project Type** is still specified as “Gras roots/Clear field” seeing that this variable determine the configuration of the project’s electrical power distribution and process control systems, and thereby influence the factor used in ASPEN Icarus® for estimation of TPCC (see section 3.4.1) (Aspen Technology, Inc., 2006).

For determining the optimum size of a plant, the effects of a number of tradeoffs must be considered: there are definite savings resulting from economies of scale, but these are offset by the increased feedstock transportation cost resulting from a larger plant (although collection distance for a plant is highly site specific). In understanding both the cost of feedstock transportation and the effect of plant size on capital and fixed operating cost for the plant, an analysis can be done to obtain a plant size for which the overall cost are minimal. Such an analysis does not fall within the scope of this project, but a similar study was done by NREL for an ethanol from corn stover plant (National Renewable Energy Laboratory, 2002). They found that, under assumed conditions, a minimum plant size of 2000 T corn stover per day is a good choice and it is highly unlikely that the maximum plant size will exceed 8000 T per day. It was concluded that a likely range for the designs is between 2000 T and 4000 T corn stover per day. Also, the plant sizes of previous reports on biobutanol process designs are in the range of 3000 T to 7000 T feedstock per day (Bohlmann, 2007; Wu, et al., 2007). The following figure depicts some of the findings of the NREL study:





**Figure 17: Ethanol price as a function of plant size (redrawn from National Renewable Energy Laboratory, 2002).**

For this study, the initial designs in ASPEN PLUS® were done for a molasses feed of 14.7 T/h (322.2 T per day). This was the surplus molasses available from one of the sugar mill refineries in South Africa for the first quarter of 2008. However, final designs cannot be based on this value seeing that it is ever changing. It is assumed that the process economics of the biobutanol industry is roughly similar to that of bioethanol, therefore final designs are scaled up in ASPEN Icarus® to fall within the NREL suggested 2000 T to 4000 T feedstock per day. A constant molasses feed of 147 T/h (3221.9 T per day) are used as preliminary feed size for process designs. This entailed scaling up the original designs with a factor of 10.0144. Only Process Design 3 deviate from this molasses feed stream size and scaling factor. The original ASPEN PLUS® simulated model for Process Design 3 (14.7 T/h) is scaled up with a factor of 2.4 to obtain a molasses feed of 35.28 T/h. This is done in order for Process Design 3 to yield comparable final product mass flowrates to the other simulated processes and to attain equipment that is realistic in size and numbers. Due to the much higher productivity obtained during fed-batch fermentation with *in situ* gas stripping, this feed stream ensure that the final butanol product stream for Process Design 3 (118 800 T per annum) falls within the 118 000 to 167 000 T per annum range obtained for Process Designs 1 and 2. As a reference, earlier process designs ranged in size of annual butanol production between 80 000 and 100 000 ton (Roffler, et al., 1987; Bohlmann, 2005).

The plant on-line time is 8000 hours per year (91.32%), which allows for roughly 4.5 weeks of downtime, and the start-up time is 2 weeks. These assumptions are considered more than reasonable for an “n<sup>th</sup>” operating plant (see section 3.4.1). The following table show the operating parameters specified in ASPEN Icarus®.

**Table 8: Facility operation parameter inputs for ASPEN Icarus®**

Facility Operation Parameters	
Facility Type	Chemical Processing
Operating Mode	Continuous Process
Length of Start-up Period	2 Weeks
Operating Hours per Year	8000
Process Fluids	Liquids, Gases, and Solids

Both **Facility Type** and **Operating Mode** affect the number of operators per shift and maintenance costs of facility equipment. **Process Fluids** indicate the types of fluids involved in the process and affects operating and maintenance costs (see section 3.4.3) (Aspen Technology, Inc., 2006).

### 3.2.3 Feedstock Composition and Preparation

As illustrated in section 2.1.1, the composition of molasses is subject to a number of factors and can vary a great deal. It is assumed that the molasses composition for these process designs is fixed, and the molasses composition as determined by Crous, (2007), is used (refer to Table 2). Due to the lack of availability of different sugar properties in ASPEN PLUS®, it is also assumed that all the sugars in the molasses (i.e. sucrose, glucose and fructose) can be simulated as a glucose concentration. This assumption is validated by the following facts:

- For simulating the fermentation process, data from literature are used and most of these fermentation studies are based on pure glucose (Ezeji, et al., 2004; Liu, et al., 2009).
- Bacteria used for ABE fermentation have been shown to utilize mixed sugars (hexoses and pentoses), therefore, comparison of glucose fermentation with that of molasses (with the same total sugars concentration) are expected to yield similar results (refer to section 2.1). In fact, it has been shown in literature that molasses as feedstock yields improved fermentation results over that of pure

glucose (Shaheen, et al., 2000), therefore, the results achieved in the fermentation process for this study will provide conservative estimates.

- This assumption was also made in multiple literature studies for computer simulated biobutanol process designs (Bohlmann, 2007; Wu, et al., 2007).

The molasses is thus simulated as a glucose stream with a concentration of 623.0 g/L.

#### *i. Diluting Molasses for Fermentation*

The initial sugar concentration for batch fermentation (Process Designs 1 and 2) should not exceed 60g/L seeing that high sugar concentration inhibits the metabolism of the fermenting bacteria. This concentration was determined as the best initial sugar concentration for batch fermentation (Roffler, et al., 1987; Syed, 1994; Ezeji, et al., 2004; Jones, 2005). For fed-batch fermentation (Process Design 3) an improved strain is used and initial sugar concentration for fermentation can be 100 g/L (Ezeji, et al., 2004). To dilute the molasses, it must be taken into consideration that:

- The volume from the prefermenter in the seed train is added to the main production fermenter and will dilute the sugar concentration.
- For batch fermentation the main production fermenter is operated in repeated batch mode, thus it is only emptied completely after every third batch (see section 3.2.4.)
- For fed-batch fermentation an additional undiluted stream (500 g/L) is required for intermittent feed throughout the fermentation.

#### *ii. Molasses Sterilization*

The molasses need to be sterilized to minimize the possibility for bacteriophage infection to occur during fermentation. Sterilization commences batchwise in a pressure heating vessel at 130°C and 3.5 bar for 15 min. Endospores of bacteria are killed above 120°C within 15 min (Jones, 2005). High pressure steam (HPS) is used in the heating jacket of the sterilization vessel to heat the liquid substrate, generating the steam necessary for steam sterilization. It is important to evacuate all the air and other gasses from the vessel seeing that this will increase the lethal effect on the bacteria and also decrease the necessary pressure in the vessel. By leaving the upper point of the reactor open, generated steam will expel the air at around 100°C, where after the vessel can be closed

and pressurized. The temperature of the liquid is controlled and homogeneous conditions achieved by mixing.

### 3.2.4 Fermentation

#### *i. General Parameters*

All fermentations are performed at 33°C and 1atm under anaerobic conditions.

#### *ii. Stoichiometry*

The fermentors could not be modelled with kinetic expressions due to the level of development of the experimental data. It is therefore modelled as experimentally determined conversions of specific reactions. This type of modelling still satisfies the mass and energy balances. The assumption to simulate molasses as a glucose concentration (section 3.2.3) greatly simplifies the stoichiometric equations used to simulate the fermentation process.

**Table 9: Stoichiometric equations for product formation from glucose**

Stoichiometric Reaction Equations	
1	$C_6H_{12}O_6 + H_2O \rightarrow C_3H_6O$ (acetone) + $3CO_2 + 4H_2$
2	$C_6H_{12}O_6 \rightarrow C_4H_{10}O$ (butanol) + $2CO_2 + H_2O$
3	$C_6H_{12}O_6 \rightarrow 2C_2H_6O$ (ethanol) + $2CO_2$
4	$C_6H_{12}O_6 \rightarrow C_4H_8O_2$ (butyric acid) + $2CO_2 + 2H_2$
5	$C_6H_{12}O_6 \rightarrow 3C_2H_4O_2$ (acetic acid)

With a known amount of solvents produced (obtained from literature data) it is possible to assign fractional conversions to stoichiometric reaction equations 1-5 in Table 9.

Due to the lack of sufficient compounds and their properties in ASPEN PLUS®, the bacterial cell growth and cell maintenance reactions are set up with available compounds in the NREL database and structured according to equations used in a NREL process simulation on yeast fermentation (specifically on *Escherichia coli*) (National Renewable Energy Laboratory, 2002). The stoichiometric equations used are very rough estimations, but the best currently available. To more accurately simulate the cell growth and cell maintenance reactions, compounds and properties together with stoichiometric reactions should be developed specifically for the bacteria used in ABE fermentation. This work, however, does not fall within the scope of this project and are recommended for future,

more detailed, designs. Table 10 portray the bacterial cell growth and cell maintenance reactions used:

**Table 10: Stoichiometric equations for cell growth and maintenance from glucose**

Stoichiometric Reaction Equations	
6	$C_6H_{12}O_6 + 6O_2 \rightarrow 6H_2O + 6CO_2$ (cell maintenance)
7	$C_6H_{12}O_6 + 1.1429NH_3 \rightarrow 5.7143ZYMO + 0.2857CO_2 + 2.5714H_2O$ (cell growth)

For reaction 7 in Table 10, ZYMO is the cell biomass. Dry cell weight, or the concentration of cells at the end of fermentation, is obtained from literature. This is then used, together with solvent yield and the total sugar utilization, to assign fractional conversions to reactions 6 and 7 in Table 10. If the cell weight is achieved with reaction 7 but the total sugar utilization (as specified in literature) not met, equation 6 is used to achieve the required sugar utilization. If the total sugar utilization is met before the required cell weight is achieved, additional glucose is added to obtain the cell weight as specified in literature. This additional glucose is just added to achieve the required fractional conversions and is not taken into consideration when cost estimation is done. In both equations 6 and 7 there are compounds needed to satisfy the stoichiometry which is not present in the actual ABE fermentation:  $O_2$  in reaction 6 and  $NH_3$  in reaction 7. These compounds are added to the fermentation broth in the exact amounts to only achieve the required conversions for these reactions. These compounds are therefore completely depleted after fermentation and do not influence downstream processing. The costs of the compounds are not taken into consideration in the economic analyses.

There are still inaccuracies in the simulation of the fermentation process due to limitations in ASPEN PLUS® as well as a lack of fermentation data. The overall fermentation parameters are manipulated to achieve values as close as possible to that of literature. Despite the inaccuracies in the stoichiometric equations, it is believed that a more accurate estimate of sugar utilization, amount of  $CO_2$  and  $H_2$  formed, as well as heat removal requirements for the fermentors are obtained by incorporating the above reactions into the fermentation. None of the previous biobutanol process simulations found in literature took cell growth and cell maintenance into account for the simulation of the fermentation process (Dadgar & Foutch, 1988; Wu, et al., 2007; Bohlmann, 2007).

### iii. Nutrient Requirements and pH Control

Some general nutrient sources to consider for ABE fermentation are nitrogen and phosphorus (as phosphate) which are essential for all metabolic activities in the cell, especially in energy transfer mechanisms like ATP production, substrate activation and phosphorylation. Calcium carbonate is sometimes used as a buffer (Jones, 2005). Molasses are very nutrient rich, and as previously stated, fermentations using molasses yielded improved results over that of glucose (Shaheen, et al., 2000). Jones (2005) also stated that molasses supply nitrogen, phosphorous trace elements, and buffering capacity. Syed (1994) did a study on molasses fermentation testing various nutrients to obtain an optimised nutrient medium for *C. acetobutylicum* strains. In a study by Parekh, et al., (1999) on glucose fermentation, it was found that with a nutrient mixture containing only corn steep water (CSW) and  $7\text{FeSO}_4\cdot\text{H}_2\text{O}$ , similar results were achieved to that of the optimum (but more complex and more expensive) P2 nutrient medium which consists of various compounds and is semi-defined for the ABE fermentation. The latter study was only for strains of *C. beijerinckii*. The nutrient medium with only CSW and  $7\text{FeSO}_4\cdot\text{H}_2\text{O}$  in the Parekh, et al., (1999) study is not the optimum medium for any of the strains used in this project, but it is more economic, industrially viable, and is believed to be sufficient to achieve results similar to that of the optimum nutrient media (especially when used with molasses as feedstock). Consequently, the initial fermentation nutrient concentrations chosen for all the process designs are (Parekh, et al., 1999):

- CSW: 0.125 g/L
- $7\text{FeSO}_4\cdot\text{H}_2\text{O}$ : 0.011 g/L

It is very important to note that these nutrients and their concentrations are only initial estimates. Nutrient selection is process specific and should be optimised for the specific composition of the substrate and the strain used in fermentation. Jones (2005) also found that the composition of molasses from different sugar mills varied considerably and adjustment to nutrients is continuously needed to optimize fermentations. For the ASPEN PLUS® simulations the nutrients are added prior to fermentation and it is assumed that all the nutrients are depleted after fermentation. Seeing that the nutrients do not take part in the stoichiometric reactions for simulation of the fermentation process (see Table 9), it is simply purged after fermentation.

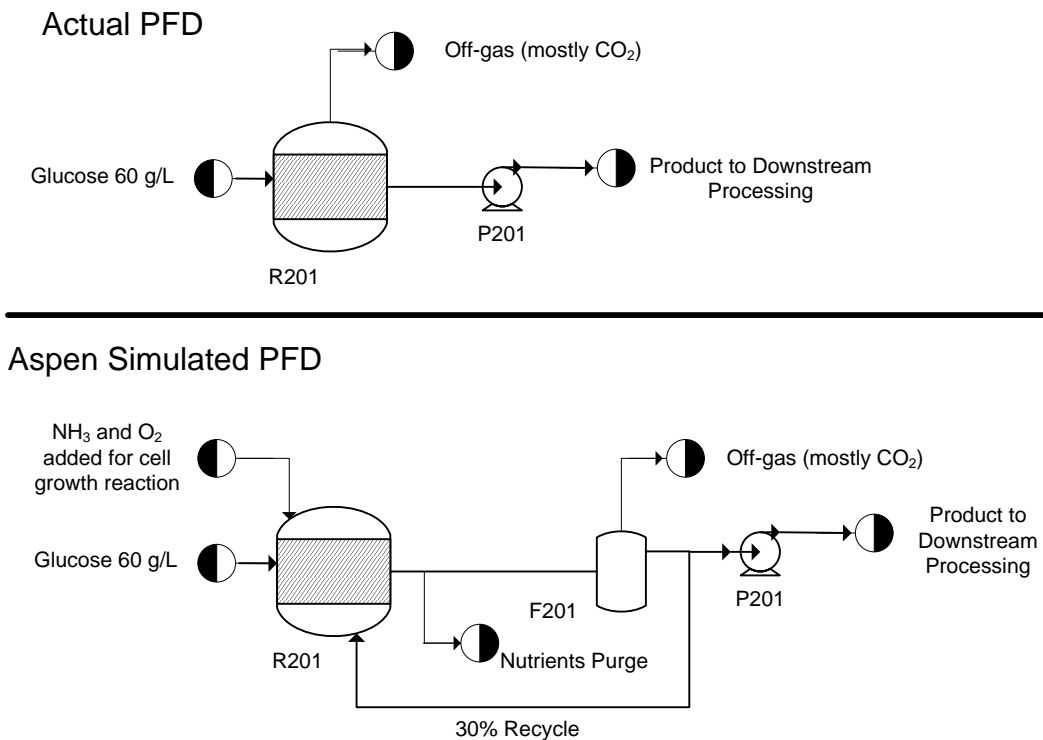
The control of pH is also very process specific and adjustments depend on the fermentation strain, molasses, water, and nutrients added to fermentations. In the study by Jones (2005) on the NCP process that was run in South Africa (biobutanol from molasses), the pH of the water that was added to dilute the molasses, was adjusted to pH 11 with calcium hydroxide. Also, when the pH breakpoint was reached in fermentation, a 25% solution of ammonia liquor was fed into the fermentation vessel. This acted as an additional nitrogen source and was used as a means of pH control (Jones, 2005). The final pH prior to fermentation should be in the range of 5.8-6.3. pH should also be monitored and adjusted continuously. Good mixing is essential, especially in large-scale fermentors, to prevent pH perturbations that may result from intermitted pH-control actions (Doble, 2006). For the level of detail in this study, pH adjustments will not be accounted for, and it is assumed that the pH needs no adjustment before or during fermentation.

#### *iv. Batch Fermentation*

Process Designs 1 and 2 make use of batch fermentation. The batch process is simulated for the case where the main production fermenter is not emptied completely between repeated batch fermentations. Roughly 30% of the final fermentation broth remains in the fermenter (micro-organisms, water, nutrients, solvent products, and unused substrate). It is assumed that there are sufficient bacteria cells in the remaining 30% broth for the next fermentation to proceed, and that all the substrate and nutrients are depleted at the end of fermentation. Therefore, only fresh sterilized diluted molasses medium and nutrients are added before fermentation proceeds. This latter step reduces the downtime between fermentations, thus increasing the productivity of the overall process. After three repeated batch fermentations the productivity of the bacterial cells decreases rapidly. Therefore, after the third fermentation of the cycle, the reactor is emptied completely, sterilized, and new inoculum is added. This repeated batch fermentation is based on the study by Syed, (1994).

The batch fermentation is simulated as a continuous process in ASPEN PLUS® due to limitations in the software. A continuous process can be achieved by using multiple smaller fermentors in a fermentation process schedule (see section 3.3.4iii). In Figure 18

a comparison of the actual batch fermentation process and its simulation in ASPEN PLUS® is illustrated.



**Figure 18: PFD of “actual” and “Aspen simulated” batch fermentation process**

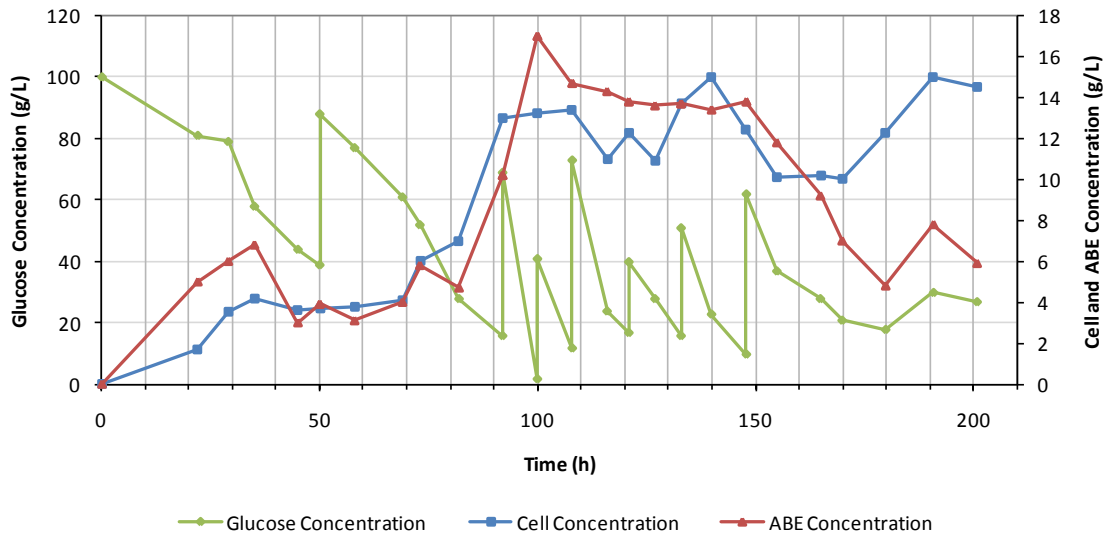
In the simulation, the fermentation productivity and ABE concentrations are the same as the literature values, whereas average rate per hour values are used for the flowrates of glucose, water, nutrients and solvents (average over the duration of fermentation). In ASPEN PLUS® a stream of NH<sub>3</sub> and O<sub>2</sub> are added to the fermentors to obtain an average cell mass per hour (as with the solvents) and assist in cell maintenance, as previously discussed in section ii. After fermentation all the nutrients are purged. The fermentation broth is then fed to a flash drum to simulate the process of gas escaping during fermentation in order to keep the pressure constant. The flash drum is at the same conditions (temperature and pressure) as the fermentors. Lastly, to simulate the repeated batch fermentation cycle, 30% of the product stream is recycled to the fermentors.



v. *Fed-Batch Fermentation with Gas Stripping*

The holding time for fed-batch fermentation with *in situ* gas stripping in Process Design 3 is 180 hours. Gas stripping will commence after 20 hours and continue for the remaining duration of the fermentation. In laboratory fed-batch studies the fermentation duration was 201 hours and gas stripping was started after 15 hours of normal batch fermentation (Ezeji, et al., 2004). From the literature data (Figure 19) it is seen that fermentation productivity is very low during the last 21 hours of the experiment. Therefore, for simulation, the fermentation duration is shortened by 21 hours. Gas stripping is also started 5 hours later than in laboratory experiments to ensure that the ABE concentration is sufficient when gas stripping commence, considering that in larger industrial processes the duration of the lag phase may be longer due to decreased productivity normally experienced relative to laboratory experiments (Doble, 2006). The assumed fermentation and gas stripping durations are conservative estimates for simulating the fed-batch process.

Figure 19 illustrates that the glucose and ABE concentrations fluctuate considerably during fermentation. With proper process control it is expected that a steady state process can be obtained for a large part of the duration of fermentation. For simulation it is therefore assumed that the system is at steady state for the duration of gas stripping: the ABE concentration is constant at 5 g/L and the volume of the fermentation broth is also fixed. The assumed ABE concentration is very low to avoid overestimating this process. From Figure 19 it is evident that for the majority of the fermentation duration the concentration is above 5 g/L. As the solvents are stripped during the gas stripping process, the volume of the fermentation broth decrease, but also, the intermittently fed glucose concentrate will again increase the total volume. There may still be an overall change in fermentation volume seeing that the volumes of the latter two streams are not the same. A practical solution might be to keep the fermentation volume constant by adding waste water from previous fermentations which will reduce extra cost associated with fresh water. Therefore the assumption stands that the fermentation volume is constant for the simulation.



**Figure 19: Fermentation profiles for gas stripping process with *C. beijerinckii* BA101 (redrawn from Ezeji, et al., 2004)**

The fed-batch gas stripping process is simulated in ASPEN PLUS® in the same manner as the batch process, but with a few additions and alterations. See Figure 20 for an illustrated comparison of the actual fed-batch process and its simulation in ASPEN PLUS®. Although this process is continuous for most of the fermentation duration, there is however a lag phase during fermentation, as well as cleaning and loading phases. Therefore, as with the batch process, a schedule is set-up in section 3.3.4iii to render a total continuous process. The fermentation schedule also elucidates what volume of fermentation broth is available for gas stripping at all times from the different fermentors.

The initial concentrated glucose stream (500 g/L) is split in two: a stream which is used for intermitted feed during fed-batch fermentation (500 g/L) and one which is diluted for initial fermenter feed (100 g/L). These streams are simulated as such that the total glucose utilization is the same as that of literature. Additional pure glucose is fed to the fermentation to achieve the values of solvents and cell concentrations as close as possible to those of literature. This latter stream is not included in the cost seeing that it is only used to manipulate the simulated fermentation process (due to the lack of sufficient stoichiometric reactions; see section ii) and in reality it will not exist.

As with the batch fermentation, the overall productivity is maintained in simulation by using average values for flowrates over the total fermentation period. Due to this continuous type of simulation, the volume of the stream that exits the fermenter in ASPEN PLUS® is only 0.556% (1/180) of the total fermentation broth in the actual process, i.e. over a period of 180 hours (fermentation duration) the same amount of glucose and water will have been fed, and the same amount of solvents produced, as in the actual fermentation.

The fermentation product stream that is available from simulation in ASPEN PLUS® has a much smaller volume and lower solvent concentration than that of the actual fermentation process at the start of gas stripping (due to the use of average volumetric productivity in simulation). From the fermentation process schedule (section 3.3.4iii) it is seen that with the use of multiple fermentors, 80% of the total fermentation volume of all the fermentors will be available at all times with an ABE concentration of 5 g/L. Therefore, in the simulation, a stream of water and ABE is added to the fermentation product in order to attain a stream having 80% of the total fermentation volume, and with an ABE concentration of 5 g/L. CO<sub>2</sub> is also added to the fermentation product to obtain a final stream that will resemble the contents of an actual fermenter in the process of gas stripping. Both of these additional streams are only built-in to achieve the design specifications in simulation, and will not be included in the cost.

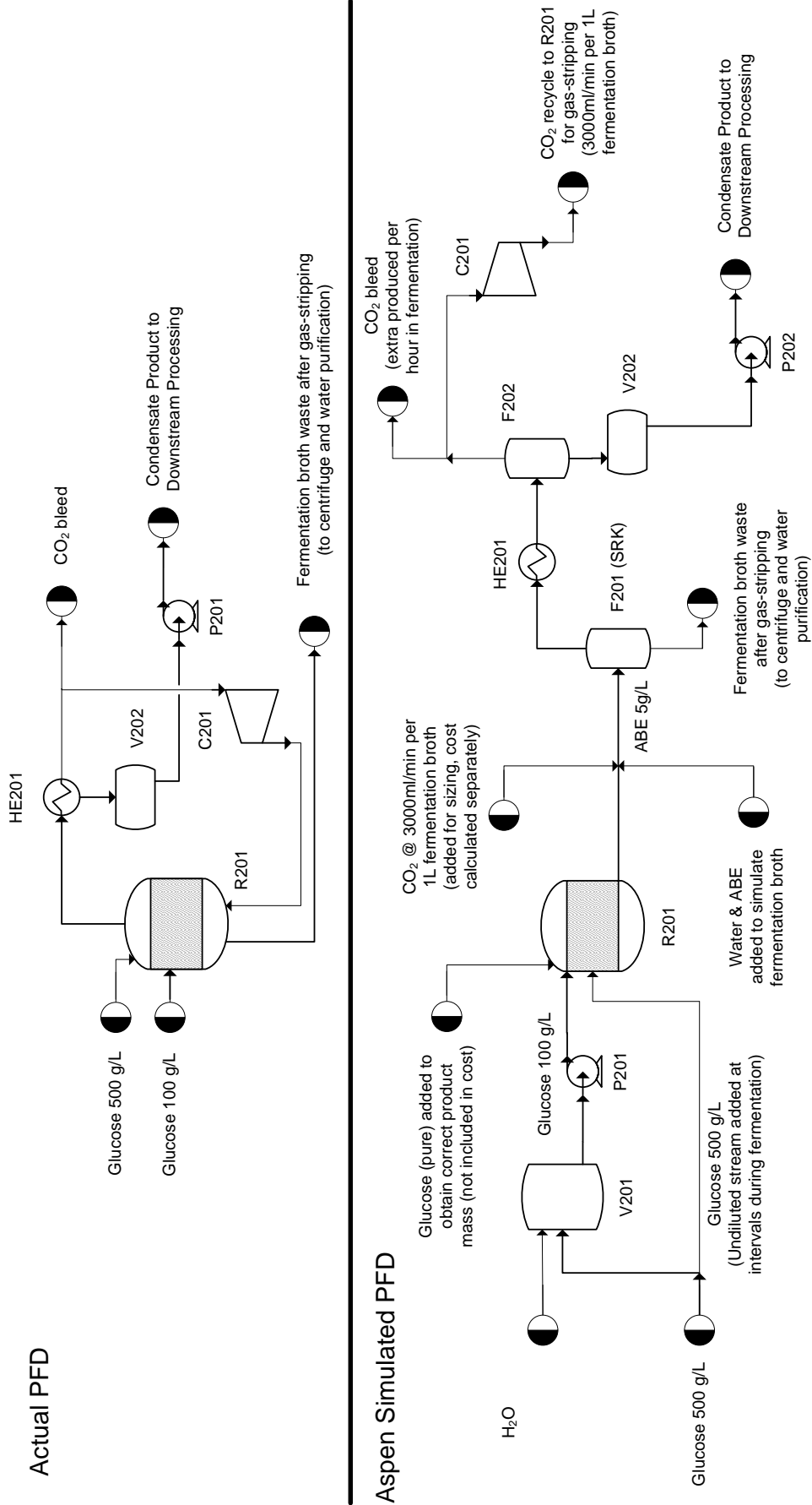


Figure 20: PFD of "actual" and "Aspen simulated" fed-batch fermentation process

The gas stripping process is simulated with a flash drum (F201 in Figure 20) which is at the same conditions as the fermentation. The SRK physical property method is used only for the simulation of this process step (see section 3.2.1). The bottoms product of the flash is waste: water, excess nutrients, carboxylic acids, biomass, and some solvents. The top product, containing most of the solvents, must be condensed and the remaining vapour stream (mostly CO<sub>2</sub>) recycled. The condenser is simulated as a heat exchanger (H201 in Figure 20) and a flash drum (F202 in Figure 20) to facilitate the phase separation. Both H201 and F202 are at the same conditions. A fraction of the top product is bled to obtain the remaining CO<sub>2</sub> flowrate as needed for gas stripping. The CO<sub>2</sub> bled per hour will essentially have the same mass flowrate as CO<sub>2</sub> produced per hour in fermentation. The pressure of the remaining vapour stream is raised in a compressor (see section 3.3.5) and recycled for gas stripping. Enough CO<sub>2</sub> is produced during fermentation to facilitate the gas stripping process, thus there is no need to purchase additional CO<sub>2</sub> (see section 3.4.2iv).

In future, with more detailed designs, this specific process should be optimised with regard to the duration of fermentation and gas stripping, as well as for CO<sub>2</sub> flowrate during gas stripping and intermittent molasses feed. For more details on the fermentation processes of a specific process designs, refer to its subsection in section 4.

### **3.2.5 Solids Removal after Fermentation**

In previous industrial ABE fermentation processes the fermented molasses mash was pumped to beer distillation columns for removal of the stillage slops (mixture of water and cell biomass) (Jones, 2005). This same technique is used for Process Designs 1.1, 1.2, and 1.3. For Process Design 2 a centrifuge is used after fermentation to remove the solids prior to liquid-liquid extraction, thereby preventing clogging in the LLE column. In Process Design 3 the gas-stripping process yields a product stream that is free of solids. All the solids are discarded with the left-over fermentation broth.

### **3.2.6 Liquid-liquid Extraction**

The LLE process in ASPEN PLUS® is simulated as a separation block with specified separation fractions for components, similar to that as used in literature (Dadgar & Foutch, 1988; Liu, et al., 2006; Bohlmann, 2007). This is done due to the lack of sufficient

binary parameters for thermodynamic models in order to accurately simulate the LLE process. For more details on the decision and validation of this process see Appendix A.3.1.

2-Ethyl-1-hexanol is the extractant of choice in all the designs where LLE is performed. The ratio of the fermentation product stream that enters the LLE column, to the extractant is 0.93 (mass basis). This value is the same as used in the studies by Roffler, et al., (1987), and Lynd, (2004). The amount of “fresh” extractant needed per hour is determined by the difference in the required feed to the LLE column and the recycled stream from the solvent recovery column.

### 3.2.7 Distillation

Distillation is used to recover solvents from the fermentation broth and to separate different solvents. This process area presents one of the challenges associated with commercial production of biobutanol due to the potential large energy consumption during separation. There are two azeotropes in the system which complicates the separation process. The possible components in the stream (including the two azeotropes) to be separated by downstream processing are (in descending order of volatilities): acetone, homogeneous ethanol-water azeotrope, ethanol, heterogeneous butanol-water azeotrope, water, and butanol. In industrial ABE fermentation processes, a high boiling fraction containing higher alcohols, esters, and organic acids was also obtained (Jones, 2005). These compounds are not present in the simulations, but must be taken into consideration for the designs.

The distillation process in all the designs is continuous. For each process design a variety of distillation column configurations exist. The optimum configurations, as determined in literature, is mimicked as close as possible (Liu, Fan, & Seib, 2004). However, the final setup is subject to the different products and product ratios. As a starting point (or reference) the distillation columns in the process design of Roffler, et al., (1987) had the following diameters (d) and amount of stages:

- Beer stripper: 2.52 m (d) and 25 plates
- Acetone column : 2.68 m (d) and 50 trays

- Ethanol column: 2.6 m (d) and 58 trays
- Water Stripper: 2.29 m (d) and 20 plates
- Butanol Stripper: 2.41 m (d) and 20 plates

All the distillation columns are simulated in ASPEN PLUS® with the “RadFrac” option. Each column is designed from scratch and optimised as follows:

- Subject to the available utilities (see section 3.2.9), the cooling temperature in the condenser of the column is fixed.
- Design specifications are entered in terms of recovery or purity (mass or mole basis) for a specific compound in either the top or bottoms product.
- For each design specification a design variable, with upper and lower limits, must be specified. Normally distillate rate and reflux ratio are used.
- Number of stages and feed stream stage is specified and manually optimised to obtain better values for design variables (e.g. lower reflux ratio).
- The conversion algorithm is also varied to obtain an optimal design.

This is a tedious process that requires continuous adjustment. If there are any changes in the feed stream of the column, this process must be repeated to re-optimize the column for the new feed.

### 3.2.8 Product Specifications

It is aimed to achieve the following minimum product purities in the simulations:

- Butanol – 99.5 % (wt)
- Acetone – 98.0 % (wt)
- Ethanol – 99.0 % (wt)

The purities are fixed at the same values as used in other computer simulated biobutanol processes from literature (Wu, et al., 2007; Bohlmann, 2007). If for some reason this purity cannot be obtained for a specific product, it will be discarded as waste.

### 3.2.9 Utilities

As mentioned in section 3.1, the utilities are obtained from a neighbouring plant (most likely a sugar mill). For this design report, information on the utilities was obtained directly from Tsb Sugar RSA (Pty) Ltd.. The available utilities and their conditions are:

- Cooling water (CW)

- Available temperature ( $T_{in}$ ): 23.8°C
- Return temperature ( $T_{out}$ ): 35 °C
- Pressure (P): 3.4 atm
- Energy transfer per unit mass: 46.462 kJ/kg
- High pressure steam (HPS)
  - Available temperature ( $T_{in}$ ): 229.2°C
  - Return temperature ( $T_{out}$ ): 229.2°C
  - Pressure (P): 27.22 atm
  - Energy transfer per unit mass: 1 814.963 kJ/kg

The variety of utilities, and conditions at which they are available, put some constraints on the design. An essential utility required for the gas-stripping process, which is not available from the sugar refinery is:

- Refrigerant Freon 12
  - Available temperature ( $T_{in}$ ): -29.8°C
  - Return temperature ( $T_{out}$ ): -29.8°C
  - Pressure (P): 1 atm
  - Energy transfer per unit mass: 164.851 kJ/kg

### 3.2.10 Energy Performance

The net energy value is a key indicator in assessing the energy performance of biobutanol; whether biobutanol production results in a gain or loss of energy. It weighs the energy content of butanol against the energy inputs in the fuel production cycle. Net energy is addressed in the following way (Nguyen, et al., 2008):

- $NEV = \text{energy content of butanol} - \text{Net energy inputs (total fossil fuel and non-fossil energy inputs, excluding energy recovered from the system co-products)}$

The net energy is also displayed in the form of energy ratio:

- $ER = \text{Energy outputs of butanol} / \text{Net energy inputs (utilities and molasses fed)}$
- $ER \text{ (only utility inputs)} = \text{Energy outputs of butanol} / \text{Utility energy inputs}$

For the calculations of the above values and ratios, the value of the energy density for molasses is taken as the value of the glucose stream used in simulation. The energy density of biobutanol appears in Table 1. This latter value is calculated based on the lower heating value of the butanol. The lower heating value, not including the heat



obtained by condensation, is used because the product would be utilized in an internal combustion engine in an automobile that exhausts water vapour produced by combustion without condensing it. All the energy performance calculations are done on per litre of butanol basis.

With the known energy transfer per mass unit of HPS, a total energy value is obtained for both the electricity and the HPS of the production process. The following two ratios are used for the utilities of the production process:

- Total utility energy requirements/Ton of molasses fed
- Total utility energy requirements/Ton of butanol produced

Although energy performance is conventionally considered using NEV, it may be more meaningful to evaluate a biofuel's contribution to fossil energy use reduction. Such an evaluation should address how much energy is gained when non-renewable fossil fuel energy is expended to produce renewable biofuels (Nguyen, et al., 2008):

- $NRnEV = \text{Energy content of butanol} - \text{Fossil energy inputs}$

This latter value will not be calculated in this study seeing that the fossil energy usage for the production process is unknown (it is not specified whether fossil fuel or bagasse will be used to generate steam and electricity).

All the energy values and ratios used in this study to evaluate the energy performance of biobutanol is only for the production process (molasses to butanol) and do not include the whole life cycle of biobutanol (e.g. production of sugarcane, refining in sugar mill, transport costs, etc.). The values obtained are a bit optimistic seeing that for the molasses to ethanol conversion process, the ethanol production process only account for between 60 and 70% of the total life cycle energy consumption (Nguyen, et al., 2008). It is strongly advised that a complete life cycle assessment of biobutanol be done in future studies.

### 3.2.11 Heat Integration

The ASPEN package that is used does not include heat integration tools. Pinch analysis is done in Microsoft Excel® to optimize the energy integration of the process. The findings

are incorporated manually into the ASPEN PLUS® simulated models if applicable. See Appendix B for a discussion on the details of pinch analysis.

### 3.2.12 Additional Design Information

For this project the plant location in terms of specific geographical area, is not specified. The ambient air conditions are assumed to be at 25°C and 1 atm. This is however subject to change depending on the location of the plant and can have a great influence on air coolers and available temperature of cooling water.

## 3.3 Equipment Selection, Sizing, and Cost Estimates

The ASPEN PLUS® simulated models, with complete mass-and-energy balances, are imported into ASPEN Icarus® to generate the final equipment specifications and cost estimates. There is however some equipment types and plant conditions (mostly surrounding bioprocesses) for which ASPEN Icarus® cannot accurately predict size and cost, and these require special consideration (Doble, 2006).

### 3.3.1 General

The size and cost of common process equipment (tanks, pumps, simple heat exchangers, etc.) are accurately predicted using the ASPEN Icarus® software. A report by Loh (2002) contains generic cost curves for several equipment types generated using ASPEN Icarus®. The curves give “purchased equipment cost” as a function of a capacity variable and it aids in the selection and sizing of equipment.

Where needed, quotations for equipment costs are obtained from other studies and/or from vendor quotes, especially for uncommon equipment. If the equipment size changes due to process changes, the equipment is not generally re-costed in detail. The following exponential scaling expression is used to determine the new cost based on the new size or other valid size related characteristics.

$$\text{New Cost} = \text{Original Cost} \left( \frac{\text{New Size}^*}{\text{Original Size}^*} \right)^{\text{exp}} \quad \text{Eq. 1}$$

\* or characteristic linearly related to the size

Information that can be used for scaling includes inlet flow (if the size of the equipment changes linearly with the inlet flow) and heat duty for a heat exchanger (if the log-mean temperature difference is known not to change). Generally these related characteristics are easier to calculate and give the same result as resizing the equipment each time. There is however some equipment for which nothing can be easily related to the size (e.g. heat exchangers with varying temperature profiles), so it must be resized with each process change. For the heat exchanger scenario, the heat exchanger area is calculated each time the simulation is run and the cost is scaled using the ratio of the new and original areas. The scaling exponent (exp) can be obtained from vendor quotes (if multiple quotes are given for different sizes), multiple estimates from ASPEN Icarus<sup>®</sup> at different sizes, or a standard reference (such as Garrett, (1989), Peters and Timmerhaus, (2003), or Perry, et al.,(1997)).

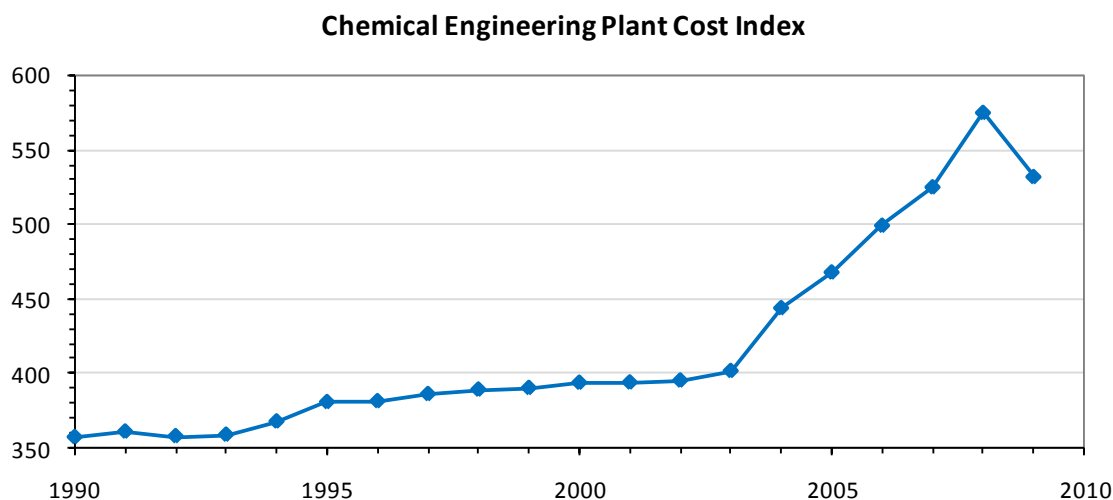
Since a variety of sources are used, the bare equipment costs are derived based upon different cost years. Therefore, all capital costs are adjusted with the Chemical Engineering Plant Cost Index (CEPCI) to a common basis period of February 2009 (Chemical Engineering, 2009).

$$\text{New Cost} = \text{Base Cost} \left( \frac{\text{Cost Index in New Year}}{\text{Cost Index in Base Year}} \right) \quad \text{Eq. 2}$$

The CEPCI indices used in this study are listed in Table 11 and illustrated in Figure 21.

**Table 11: Chemical Engineering Plant Cost Indices**

Year	Index	Year	Index
1990	357.6	2000	394.1
1991	361.3	2001	394.3
1992	358.2	2002	395.6
1993	359.2	2003	402.0
1994	368.1	2004	444.2
1995	381.1	2005	468.2
1996	381.7	2006	499.6
1997	386.5	2007	525.4
1998	389.5	2008	575.4
1999	390.6	Feb 2009	532.3



**Figure 21: Chemical Engineering Plant Cost Indices**

Carbon steel (A285C) is the general construction material for all the equipment. There is equipment in some process areas where acids are present or sterility is important. These require special construction material considerations and are discussed in the following sections.

The final installed capital cost of a process unit (referred to as the “total direct cost”) are developed using general plant-wide factors. The total direct cost incorporates cost contributions for not only the actual installation of the purchased equipment, but also piping, electrical, instrumentation/automation, hidden scope/contingency, escalation, growth in equipment cost, and other minor equipment-related costs, such as paint and insulation. The factors used are dependent on various user defined ASPEN Icarus® inputs (see Table 7 and Table 8). These factors may require revision in more detailed designs, seeing that it was developed for the chemical and petroleum industry, and not specifically for an aqueous-based biotechnology process. Many of the standards for industries handling concentrated chemical and fuels (such as API for refineries and ANSI for chemical plants) are unnecessary for an aqueous-based process (National Renewable Energy Laboratory, 2002).

### **3.3.2 Plant Sterility**

The ABE fermentation process requires sterile operating conditions to avoid the occurrence of bacterial infections. In general, a plant designed for sterile operation is

significantly and unavoidably more expensive to build than a non-sterile plant, such as those used for ethanol fermentation (Gapes, 2000). Additional costs are involved in providing dedicated sterilization equipment, like the very expensive large sterilisable pressure vessels that are required for fermentors. Also adding to the costs are piping, valves, and other fixtures capable of reliably supporting absolute sterility at all times (Jones, 2005). Operating costs are higher due to the need to sterilize the raw materials prior to fermentation, and to run the fermentation under sterile conditions. It is important to sterilize the transfer lines and the holding vessel leading to the fermentors, as well as the fermentors itself. This is done by injecting steam into the pipelines and vessels.

For the conceptual process design sterile conditions are only considered for the major process equipment (discussed in the following sections). Therefore, in future, for more detailed designs, supporting equipment and fixtures required for sterile operation should be incorporated.

### **3.3.3 Molasses Sterilization Vessels**

The vessels in which sterilization of the molasses take place, are simulated as agitated, jacketed vessels with a residence time of 15 min (as specified in section 3.2.3ii). The construction material of the vessels is carbon steel (A285C) while stainless steel cladding (316L) is applied for sterilization purposes.

### **3.3.4 Fermentors**

#### *i. ABE Production Fermentors*

The fermentation process is simulated with a single reactor in ASPEN PLUS®, but when the fermenter is sized it is split up in a number of smaller fermentors to obtain industrially practical fermenter sizes. The multitude of smaller fermentors also makes an overall continuous process possible without relying too much on holding vessels.

All fermentors are designed as agitated, jacketed vessels and constructed from stainless steel (SS304). The main ABE production fermentors are sized in ASPEN Icarus®, but costs are derived from a NREL (2002) report. The reason for this is that large reactor vessels in ASPEN Icarus® are much more expensive than vendor quotes obtained from the NREL

(2002) report for ethanol fermentors of the same size for a specific financial year. Using ASPEN Icarus<sup>®</sup> costing for the main fermentors also resulted in equipment cost for only the fermentors being more than 60% of the total equipment cost of the simulated design. Therefore the vendor costs in the NREL (2002) study is adapted with equations 1 and 2 (section 3.3.1.) to obtain equipment cost for the large fermentors. This is then imported into ASPEN Icarus<sup>®</sup> to determine the total direct cost.

The total volume needed for main production fermentors in a process design is subject to the fermentation inlet streams and fermentation duration (holding time) of the specific strain and process. The batch fermentation holding times for Process Designs 1 and 2 vary between 35 and 70 hours (Roffler, Blanch, & Wilke, 1987; Syed, 1994; Ezeji, Qureshi, & Blaschek, 2004). The holding time for fed-batch fermentation with *in situ* gas stripping in Process Design 3 is 180 hours. Gas stripping will commence after 20 hours and continue for the remaining duration of the fermentation (adapted from Ezeji, et al., (2004); see section 3.2.4v).

The number of fermentors is dependent on specification of individual fermenter size. The size of fermentors, between those previously used in the biobutanol industry to the ones used in computer simulated designs in literature, varies considerably: Zverlov, et al., (2007) report a size of 275 m<sup>3</sup> previously used in the Soviet Union, Roffler, et al.,(1987) used 492 m<sup>3</sup> fermentors, and Bohlmann (2007) 947 m<sup>3</sup>. In this study the size of fermentors varies for the different process designs, but fermentors are not sized larger than 900 m<sup>3</sup>. Also, the number of main fermentors in a specific design is selected in increments of 10. This latter statement is as a result of the fermentation schedules discussed hereafter (see section iii), where it is shown that one train of seed fermentors is required for every 10 main fermentors.

#### *ii. Seed fermentors*

The seed fermentors are sized, and costs are derived, in ASPEN Icarus<sup>®</sup>. Sizes and the number of seed fermentors needed in a seed fermentation train are dependent on the size of the main fermentors. The number of seed trains is subject to the main fermenter residence time as well as the final number of main fermentors in a design. The sizes and

number of seed fermentors in a train are discussed in this section, but the number of trains required can only be determined from a fermentation schedule, which is discussed in the following section.

The seed train is operated in batch mode. Initial seed inoculum is grown in a shake flask in the laboratory, from where it is transferred to the first batch fermenter in the seed train. Each seed batch serves as the inoculum for the next size seed increment. This series of scale-ups is continued until the last step is large enough to support the main fermentation. Syed (1994) experimentally determined that the required inoculum volume for batch fermentation is 3-5% and the holding time of the prefermenter stage was 20 hours (this study was done for *Clostridium acetobutylicum* PCSIR-10). The industrial NCP process used a final inoculation ratio of 1/26 (3.85%) and the fermentation duration of the prefermenter stage in this study was 9 hours (Jones, 2005). Several important advantages can be gained by increasing the inoculum volume, such as shorter fermentation times, increased yields, and reduced risk of bacterial contamination (Jones, 2005). For all the process designs in this study an inoculum volume of 10% is used for every stage of seed fermentation as well as for the main fermentors. The larger volume is chosen as this is the norm in other fermentation industries, and to avoid scale-up underestimations (Doble, 2006). The fermentation time for the prefermenter stage is assumed to be a maximum of 20 hours for any given process design. To make inoculation of the smallest seed fermenter possible with a lab scale bioreactor, four stages (seed fermentors in a train) are required.

The optimum design of the seed train (number of stages, volume of each stage, and fermentation duration) is subject to experimental testing with the specific strain and feedstock used in the process, and should be considered for more detailed design.

### *iii. Fermentation Process Schedule*

To render a continuous process and to increase overall site production, main production fermentors work on a schedule which use each fermenter in sequence and staggered in time. This process is similar to the one used for industrial biobutanol production in the Soviet Union (Zverlov, et al., 2006). Separate preliminary process schedules are created

for batch fermentation (Process Designs 1 & 2) and fed-batch fermentation (Process Design 3).

To avoid overcomplicating the batch fermentation designs, the following assumptions are made to attain one simplified schedule blueprint that is applicable for all the designs of Process Routes 1 and 2:

1. For a main production fermenter with a holding time of 60 hours, 20 hours are sufficient to empty, steam, and refill one of the main fermentors (this is also the maximum residence time of the prefermenter).
2. For the scenario as stated in assumption 1, fresh inoculum for a specific reactor is only needed every 200 hours. The total repeated batch fermentation cycle duration is 180 hours (three batch fermentations per cycle) (see section 3.2.4iv for discussion on repeated batch fermentation).
3. If the main production fermentation time is to change from 60 hours to a new value, all other process times (e.g. “cleaning time” or “total repeated batch fermentation cycle time”) in the schedule will change proportionally. Therefore, the same schedule blueprint is adjusted to incorporate the new fermentation holding time. As a result, only the total duration of the schedule will change.

In previous industrial production of biobutanol, 18 hours were allocated to empty, steam, and refill each fermenter between fermentations (same process steps as in assumption 1) (Jones, 2005). The following batch fermentation schedule is for the scenario where fermentation holding time is 60 hours:

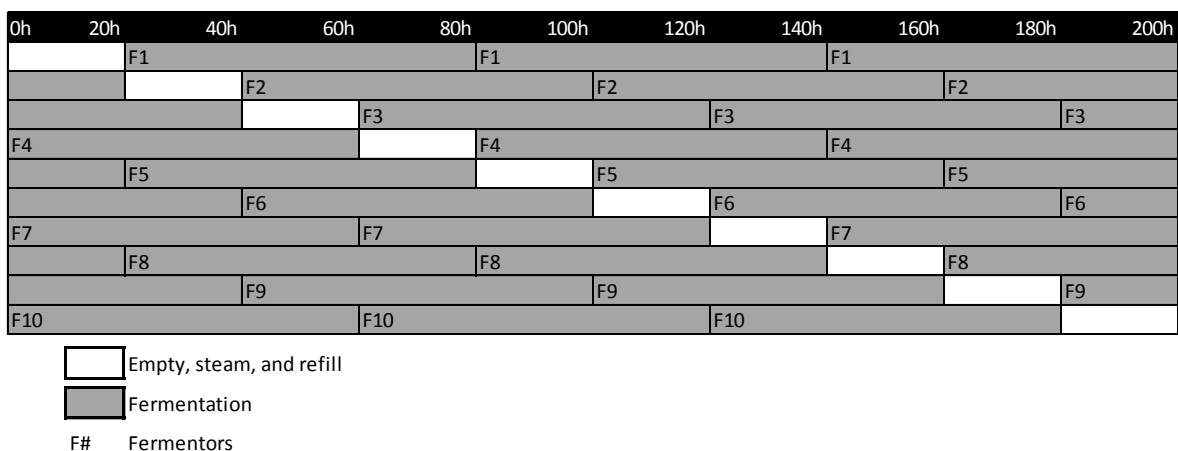
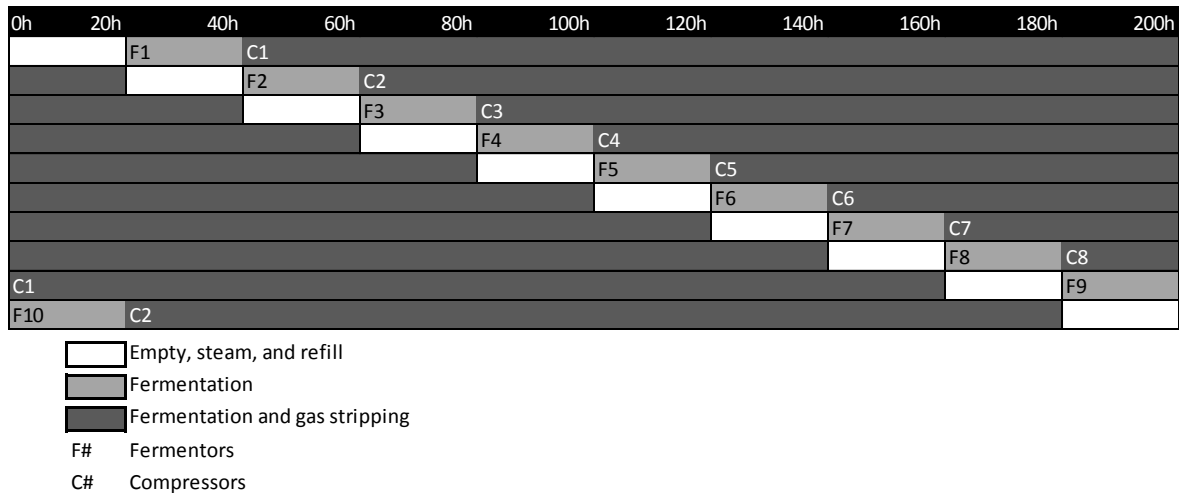


Figure 22: Preliminary batch fermentation process schedule



Process Design 3 is the only design in which fed-batch fermentation is performed. For its fermentation schedule the *in situ* gas stripping process should also be taken into account:



**Figure 23: Preliminary fed-batch fermentation process schedule**

Instead of having the total volume available for 80% of the time (which would be the case if this schedule is replaced with one large fermenter), with this schedule, 80% of the volume is available all of the time, i.e. rendering a continuous process, but keeping the total productivity of the overall process the same.

From both the above fermentation schedules it is evident that for every 10 main ABE production fermentors only one seed fermentation train is needed. Also, for every 10 main fed-batch fermentors (in Process Design 3) 8 compressors are needed for the gas stripping process (see section 3.3.5).

Both blueprint schedules for batch and fed-batch fermentations as presented in this section are greatly simplified and in reality will require some manipulations with holding vessels to render a perfect continuous process. It is however a vast improvement over normal batch fermentation with one large fermenter and also much more practical for industry. On the conceptual design level of this study, it is accepted as sufficient and should be revised in future for more detailed designs.

### 3.3.5 Compressors

Compressors are only used in Process Design 3 to compress the fermentation gasses ( $\text{CO}_2$  and  $\text{H}_2$ ) being recycled for the gas-stripping process. The type of compressor simulated in ASPEN PLUS® is “polytropic using ASME method”. To determine the discharge pressure

needed for compressors, the pressure at the bottom of the main fermentors must be calculated. As an ASPEN Icarus<sup>®</sup> default, all vessels are sized with a height to diameter ratio of 3. Therefore the height of the fermentors used in Process Design 3 is 16.295 m and the minimum required discharge gauge pressure of the compressors is 1.6 bar. With all the design factors taken into account in ASPEN Icarus<sup>®</sup>, the final design discharge gauge pressure of the compressors is 2.437 bar.

Eight compressors are allocated for every ten main fermentors in which gas stripping is performed. This is due to the fact that gas stripping is carried out for 160h of the 180h fermentation (see section 3.3.4i for details and Figure 23 for the preliminary fermentation process schedule). The number of compressors does not influence the total volume of gas that is processed within a certain time period. A multitude of compressors are used to obtain overall less expensive compressors when sizing in ASPEN Icarus<sup>®</sup>. The larger number of compressors will also ensure that the process do not come to a complete standstill in the case of compressor failure.

### **3.3.6 Liquid-liquid Extraction Column**

Due to the fact that this column is simulated with split fractions in ASPEN PLUS<sup>®</sup> (see section 3.2.6), its size and cost could not be estimated in ASPEN Icarus<sup>®</sup>. Therefore it is imported into ASPEN Icarus<sup>®</sup> as a quoted item. All the column details (size and plate count) are adapted with equations 1 and 2 from the study by Dadgar and Foutch (1988) (the same study from which the split fractions for LLE is obtained). An installation factor is added to determine the total direct cost.

### **3.3.7 Distillation Columns**

All the distillation columns are designed with the “Full-Single” configuration in ASPEN Icarus<sup>®</sup>, this entails: the tower, a condenser, a reflux drum (vessel), a reflux pump, an overhead product pump, a reboiler, and a bottoms product pump. All the towers use trays.

### **3.3.8 In-process and Product Storage Vessels**

In-process storage consists of holding vessels between all the major process steps. The residence time for each holding vessel is 2 hours. Prior to final product storage, parallel

holding vessels, each with a residence time of 7 hours, are installed. This is done to avoid final product contamination if a problem is encountered with the product specification. The residence time of a final product storage vessel is 4 days. All the vessels are constructed with carbon steel (A515 or A285C). Only the vessels following molasses sterilization prior to fermentation have cladding of stainless steel (316L) to ensure sterile conditions.

### 3.3.9 Pumps

All the pumps in the designs are simulated as centrifugal pumps and for every pump a spare is fitted and accounted for in cost estimation. In future, for more detailed designs, pumps in areas with hygienic design requirements should be equipped with mechanical seals. Depending on the final construction, either a pump or gravity feed will be used to transfer the seed from one fermenter to the other. If a pump is used it should be a rotary lobe pump to avoid damaging the microorganisms by pump shear. For this design it is assumed that gravity feed is used.

## 3.4 Economic Analyses

The process economics are determined in ASPEN Icarus<sup>®</sup>. For the conceptual designs in this study, an overall estimate accuracy in the range of  $\pm 30\%$  is expected. The cost of butanol production from this estimate can be used to assess its potential in the marketplace, but it is mostly used to evaluate research proposals by comparing relative production costs. Therefore, development of alternative designs, as done in this study, is very useful in evaluating different process design proposals. Using the same discount rate in the discounted cash flow analyses, alternative process designs using different technologies can be compared on the basis of net present value (NPV), internal rate of return (IRR), and payback period.

The total project capital cost (TPCC) is based on total installed equipment cost. The former, together with variable and fixed operating costs, are generated first. Economic viability of the process is then determined with a discounted cash flow analysis and the minimum production cost of butanol is obtained for the scenario where the NPV of the project is zero. Sensitivity analyses are also done to determine the effect of variation in economic parameters and costs.

The currency of all costs in this study is in United State of America dollars (\$). Exchange rates used are averaged values for February 2009 (Tiago Stock Consulting, 2009).

### 3.4.1 Total Project Capital Cost

The project year being considered for estimates is 2009, while the estimated start date of basic engineering is 1 January 2010. Cost estimates are normally approached in two areas: process and architectural (Vogel & Tadaro, 1997). The architectural portion of the estimate, which includes both the building and site costs, will not be covered in detail in this report. Standard costs are taken into account using general factors in ASPEN Icarus<sup>®</sup> to estimate these values. No additional buildings or site developments are included in the designs, as discussed in section 3.1.

Cost estimation of process equipment and its installation are discussed in detail in section 3.3. Factors are added to the total installed equipment cost to attain the TPCC. These factors are process specific and depend on certain user specified inputs. The process economics are based on the assumption that this is the “nth” plant, meaning that several plants using this same technology will have already been built and are operating. This means that additional costs for risk financing, longer start-ups, and other costs associated with first-of-a-kind plants are not included. User defined general plant specifications for ASPEN Icarus<sup>®</sup> appears in Table 12. All these specifications, including those from Table 7 and Table 8, influence the factors that are added to the total installed equipment cost to obtain the final TPCC.

**Table 12: General specification inputs for ASPEN Icarus<sup>®</sup>**

General Specifications	
Process Description	Redesigned Process
Process Complexity	Typical
Process Control	Digital
Contingency Percent	10

**Process Description**, **Process Complexity** and Project Type (see Table 7) combine to generate contingency (as a percent of TPCC). **Process Description** also drives the design allowances for all equipment whose material cost is generated in ASPEN Icarus<sup>®</sup> (Aspen Technology, Inc., 2006).

As mentioned for the estimation of installation costs (section 3.3.1), the factors used in ASPEN Icarus® should be revised for more detailed designs to attain factors that is more specific to aqueous-based biotechnology processes (Aspen Technology, Inc., 2006).

### 3.4.2 Variable Operating Costs

Variable operating costs are incurred only when the process is operating. These costs include raw materials, product credits, utilities, and waste treatment charges.

#### *i. General*

The prices of chemical costs that are from different cost years are adjusted with the Marshall & Swift equipment cost index (MSECI) to a common basis period of 1<sup>st</sup> quarter 2009 (Chemical Engineering, 2009). This index focuses more on the individual process industries and their specific products, and is not so susceptible to the fluctuation in steel price. The MSECI indices used in this study are listed in Table 13.

**Table 13: Marshall & Swift equipment cost indices**

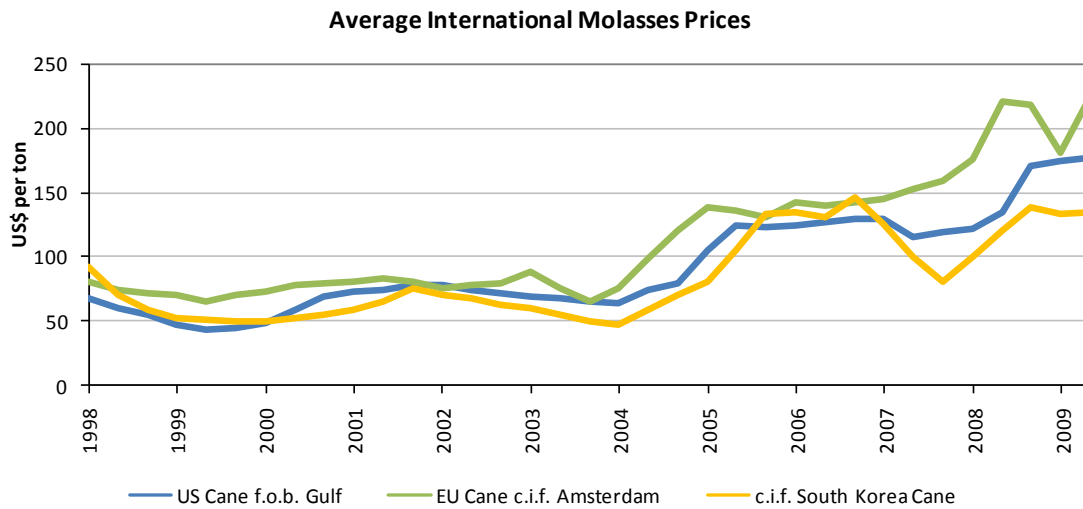
Year	Index	Year	Index
2000	1089.0	2005	1244.5
2001	1093.9	2006	1302.3
2002	1104.2	2007	1373.3
2003	1123.6	2008	1449.3
2004	1178.5	1st Q 2009	1477.7

#### *ii. Raw Materials*

Molasses cost are very dependent on location, composition, and availability. The price of molasses recently spiked due to a worldwide shortage of molasses supply. Over the last 12 months, the US blackstrap cane molasses price (which is considered the global benchmark for the molasses market) has remained at extremely high levels, averaging at around \$ 175 per ton (LMC International, 2009). The price of molasses in South Africa is much cheaper than the values portrayed in Figure 24. However, due to lack of current availability, and to avoid underestimating the cost in the process designs, the molasses price used in this study is **\$ 212.67** per ton. The latter is an average international price for the first quarter of 2009.

The costs of nutrients are adapted from Parekh, et al., (1999) (see section 3.2.4iii):

- CSW – \$ 0.055 per kg
- FeSO<sub>4</sub>.7H<sub>2</sub>O – \$ 0.650 per kg

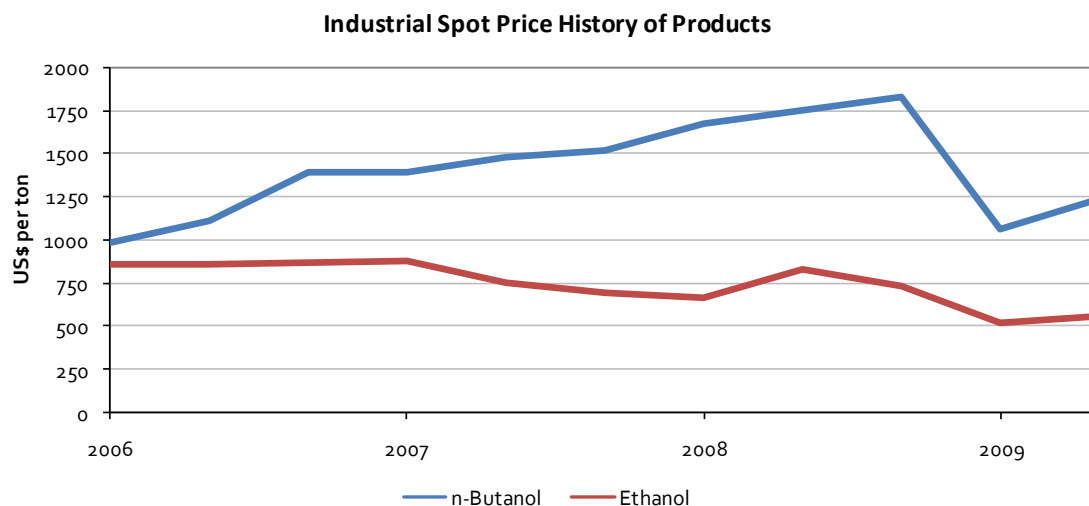


**Figure 24: Average quarterly molasses prices in the US, EU, and South Korea, 1998-2009 (LMC International, 2009).**

### *iii. Products*

Acetone, butanol, and ethanol are the only saleable products in these process designs, with butanol being the most important and abundant. It is thus for butanol that an absolute cost is determined to compare with other fuels. However, it is likely that this cost of butanol may decrease if niche products (normally at small volume) are introduced seeing that these products have significantly higher profit margins than fuel-grade butanol (see section 2.5). In a similar manner, co-location with plants that have an equally synergistic product slate will also likely reduce the cost of butanol.

From the following figure it can be seen that a slump hit the market in October 2008; demand and prices collapsed due to the global credit crisis. There has been some recent recovery, and it is expected that market growth will return to the 2% per year pre-crisis level. If biobutanol were to become a competitive product with petrochemical-based butanol, the former could be a threat to the butanol market in the longer term (ICIS Pricing, 2009).



**Figure 25: Average quarterly industrial spot prices for n-butanol and ethanol (ICIS Pricing, 2009).**

The prices of products used in this study are for February 2009 (ICIS Pricing, 2009):

- Butanol – \$ **1234.5** per ton
- Acetone - \$ **826.73** per ton
- Ethanol - \$ **514.94** per ton

The minimum butanol selling price of a process design is determined in a discounted cash flow analysis. It is the selling price of butanol that makes the net present value zero with a specified desired rate of return and economic project life. See section 3.4.4 for more details.

#### *iv. Utilities*

All utility costs are at industrial rates for the first quarter of 2009 in South Africa, and were obtained from a local sugar mill (personal correspondence with Nico Stolz):

- Cooling and Potable Water – \$ **0.0676** per ton
- High Pressure Steam (HPS) – \$ **4.788** per ton
- Electricity – \$ **0.0759** per kWh
- Freon 12 - \$ **0.250** per ton
- 2-Ethyl-1-hexanol - \$ **1763.70** per ton

Costs are included for a 3% cooling water make-up stream and a 10% potable water make-up stream. In the LLE process, the difference in the required feed and recycled stream of 2-ethyl-1-hexanol is the make-up stream from which costs are determined. CO<sub>2</sub> used for gas stripping is only needed for the very first fed-batch fermentation.

Thereafter, enough CO<sub>2</sub> is generated in all the fermentations to supply the need for gas stripping. Therefore it is assumed that the cost of the initial required CO<sub>2</sub> is negligible.

#### *v. Waste Treatment*

In these process designs, no specific costs are taken into account for waste treatment due to the following reasons:

- There is very little waste and as stated in section 3.1, it is assumed that these process designs will have waste treatment facilities available for waste water treatment and other waste streams at no extra cost.
- Most of the waste streams (like water) are recovered pure enough to be recycled or reused in the system. Allowance is only made for a certain make-up fraction (as previously discussed in section iv).
- Biomass waste and CO<sub>2</sub> off-gas after fermentation are actually by-products and with minor additional capital cost, these streams can be sold for a profit. The profits are not included in the project, but neither are the costs for treating these streams as waste.
- In some of the process designs not all the ABE are recovered to the stringent purities specifications as stated in section 3.2.8. These streams are however very small volume and are assumed to have a negligible cost for waste treatment (it might even be sold for a profit at lower purities).

Waste treatment are however considered and accounted for in the plant contingency (see Table 12), but for more detail designs the above streams should individually be accounted for. Not only cost, but environmental factors also come into play, especially for greenhouse gas emissions and water pollution.

### **3.4.3 Fixed Operating Costs**

Fixed operating costs are generally incurred fully whether or not the plant is producing at full capacity. These costs include labour and various overhead items. For most of the costs (or fractions with which costs are estimated) ASPEN Icarus® defaults are used, although some of the values were obtained via personal communication with Nico Stolz. The parameters specified in ASPEN Icarus® for fixed operating cost appear in the following table.



Table 14: Operating cost parameter inputs for ASPEN Icarus®

Operating Cost Parameters	
General	
Operating Charges	25 (%/year)
Plant Overhead	50 (%/year)
G and A Expenses	8 (%/year)
Labour Unit Costs	
Operator	20 (\$/person/hour)
Supervisor	35 (\$/person/hour)

**Operating Charges** includes operating supplies and laboratory charges and is specified as a percentage of the operating labour costs. **Plant Overhead** consists of charges during production for services, facilities, payroll overhead, etc. This number is specified as a percent of operating labour and maintenance costs. **General and Administrative (G and A) Expenses** are specified as a percentage of subtotal operating costs. It represents general and administrative costs incurred during production such as administrative salaries/expenses, R&D, product distribution and sales costs (Aspen Technology, Inc., 2006). The type of facility, operating mode, operating hours per year, and process fluids (see Table 8) affects the total cost of operating labour and maintenance costs of facility equipment. The total cost of operating labour is calculated by first determining the total number of operators and supervisors necessary to run the facility for a certain number of hours, and adjusting that number for the number of hours the facility operates per period. This number is then multiplied with the respective **Labour Unit Costs** and added together to obtain the total cost of operating labour.

Estimates in this section can vary significantly depending on specific geographical location and will require revision for more detailed designs.

#### 3.4.4 Discounted Cash Flow Analyses

A discounted cash flow analysis is used to determine the economic viability of a process design, and to compare different projects on the basis of NPV and IRR for a set desired rate of return and economic project life. The minimum butanol selling price for a project can be determined for the scenario where the NPV are zero. The required specifications for this analysis appear in the following table:

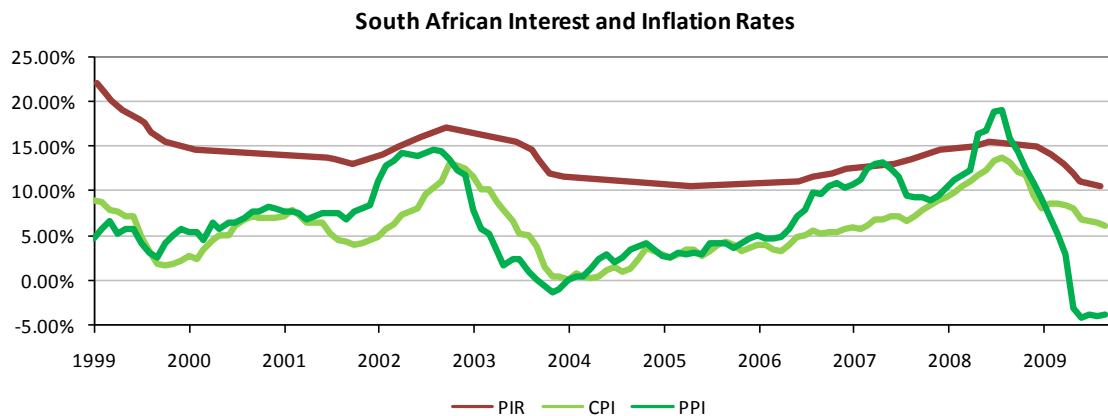
**Table 15: Investment analysis parameter inputs for ASPEN Icarus®**

Investment Analysis Parameters	
Tax Rate	28 (%/year)
Interest Rate/Desired Rate of Return	10 (%/year)
Economic Life of Project	25 years
Salvage Value (% of Initial Capital Cost)	20 %
Depreciation Method	Straight Line
Escalation Parameters	
Project	8 (%/year)
Raw Materials	9 (%/year)
Operating and Maintenance	8 (%/year)
Utilities	8 (%/year)
Project Capital	
Working Capital	5 (%/year)

The **Tax Rate** used is the highest tax rate for companies in South Africa (Price Waterhouse Coopers, 2009). The **Interest Rate** (discount rate) used for analyses is selected based on the recommendation of Short, et al., (1995): "In the absence of statistical data on discount rates used by industrial, transportation, and commercial investors for investments with risks similar to those of conservation and renewable energy investments, it is recommended that an after tax discount rate of 10%... be used." It is assumed that all capital cost is sourced from the bank seeing that no data on shareholders equity is available. The interest rate used is the same as the internal rate of return (IRR) obtained in scenarios where the minimum butanol selling price is determined. If the butanol price is fixed (as specified in section 3.4.2iii) the specified interest rate will yield an IRR which is used to compare different projects. For projects on this conceptual design level, the IRR should be in the region of 30% for the project to be considered for future development by potential investors.

All the other parameters in Table 15 were obtained from industry. The **Working Capital** (expressed as a percentage of total capital expense per year) indicates the amount required to operate the facility until the revenue from product sales is sufficient to cover costs. It includes current assets such as cash, accounts receivable and inventories. When the facility starts producing revenue, this cost item can be covered by the product sales (Aspen Technology, Inc., 2006). The percentage used fall within the range as specified by Garrett, (1989), and is the same as value used by NREL, (2002).

The interest rate and escalation parameters can be compared to the historic trend of interest and inflation rates in South Africa.



**Figure 26: History of South African interest and inflation rates (Statistics South Africa, 2009).**

The prime interest rate (PIR) is a reference interest rate commercial banks use when issuing variable interest rate loans to their customers. In South Africa, the current PIR is 10.5%. The consumer price index, or CPI, is the cost of a 'shopping basket' of goods and services of a typical South African household. The producer price index, or PPI, is the cost of a 'shopping basket' of goods of a typical South African producer of commodities. The PPI inflation rate is thus seen as an early indicator for coming changes in the CPI inflation rate. The inflation target in South Africa is between 3 and 6% (South African Reserve Bank, 2009). All the financial assumptions are subject to change with a specific project and its location.

### 3.4.5 Sensitivity Analyses

Due to uncertainty in some design areas, sensitivity analyses are done to determine the impact of varying factors. The level of uncertainty associated with the cost estimate of core technologies can be decreased with more research. There is however other areas in the designs where there will always be uncertainty and varying costs that are difficult to control. It is important to define the range of variation for the important factors and determine its influence on the economic viability of the project. Historic data and/or predictions from experts are needed to fix the ranges in which to vary factors.

Due to the large number of process designs simulated in this study, sensitivity analyses will only be done on projects profitable under current economic conditions. For process designs that are not profitable, only the maximum molasses price and minimum butanol price, to obtain a NPV of zero, will be determined. This is done due to the fact that non-profitable designs will most likely not be considered for further development. Sensitivity analyses will cover the following varying factors:

- Molasses Price – \$100 to \$300 per ton
- Butanol Price (for fixed interest rate) – \$800 to \$1800 per ton
- Utility Costs (water, steam, electricity) – +20% and +50%
- Capital Expenditure – -10%, and +20%
- Interest Rate – 10%, 20% and 30%

The minimum butanol selling price for a worst case scenario of the above factors will also be determined for designs that are profitable in current economic conditions.

Molasses prices in South Africa are currently cheaper than the international price (as used in this study); therefore cheaper molasses are a possibility. However, global use of molasses as feedstock for biofuels will also contribute to the current shortage of molasses and might further increase the international price. Utility costs in South Africa will most likely only increase in the near future due to the current electricity problems in the country and planned hikes announced by Eskom (the sole electricity provider in South Africa). If this plant is to be built adjacent to a sugar refinery, the utility price hikes of Eskom may be avoided with on-site self-generated electricity and steam by means of bagasse. The influence of higher interest rates will be also determined. For a fixed interest rate of 10%, the butanol price will be varied in the range of recent highs and lows to determine the impact on economic viability. Capital expenditure is most likely to increase, but the effect of a slight decrease will also be determined.

## 4 Process Description

The following section describes in detail the process steps for the molasses-to-butanol based process designs presented in section 1.2.2. The data used in these designs have been demonstrated in either a laboratory, pilot plant, or previously operated full-scale plant. **To avoid redundancy in the description of separate model sub-sections, Process Design 1 is used as basis for all five process designs discussed hereafter. Only changes between this basis and subsequent designs are discussed in the subsections of the altered process design itself.**

Important assumptions made for all the process designs (as stated in section 3.2) include:

- A molasses feed of 147 T/h will be available and that the resulting size of the process designs are optimal for industry.
- Molasses can be simulated as a glucose concentration, and fermentation studies with glucose as substrate can be used to predict the molasses fermentations.
- The NRTL physical property model is sufficient to accurately simulate the thermodynamic properties of the overall system.

Appendix C contains the PFDs of all the process designs.

*The CD attached to this report contains the following on this section: all the ASPEN PLUS® and ASPEN Icarus® simulation models with additional stream and equipment information, as well as Microsoft Excel® spreadsheets used for mass balance calculations. Take note that due to the fact that scaling up of process designs could only be done in ASPEN Icarus®, the stream mass flows and equipment information in ASPEN PLUS® are smaller than in ASPEN Icarus® (see section 3.2.2 for information on initial plant sizes and scale-ups). Only stream data that are not mass dependent (e.g. temperature and pressure) are the same in ASPEN PLUS® and ASPEN Icarus® simulations of a specific process design.*

## 4.1 Process Design 1.1

See Appendix C, PFD Process Design 1.1

### 4.1.1 Process Overview

This design is the base case. It can be described as batch fermentation of molasses by the fermenting organism *Clostridium acetobutylicum* ATCC 824 and product recovery by distillation. Five distillation columns are used: a beer column to remove the fermentation media together with most of the water, a column to recover acetone, a column to remove excess light end waste, and two columns for the separation of water and butanol.

The different process areas are:

- Area 100 – Pre-treatment and sterilization
- Area 200 – Batch fermentation
- Area 300 – Distillation

Both the batch fermentation and overall design of this process is based on the base case process design simulated in the study by Roffler, et al., (1987).

**Table 16: Summary of mass and energy balances for Process Design 1.1**

<b>Molasses</b>	
Mass Flow (T/h)	147.21
Volume Flow (L/h)	118178.49
Energy Density (MJ/L)	1.02
Total Energy (MJ/h)	121022.78
Energy input (MJ/L of butanol)	5.62
<b>Butanol</b>	
Mass Flow (T/h)	14.86
Volume Flow (L/h)	21547.75
Energy Density (MJ/L)	26.81
Total Energy (MJ/h)	577716.77
<b>Steam and Electricity Utilities</b>	
HPS (MJ/h)	508240.55
Electricity (MJ/h)	67766.03
Total Energy (MJ/h)	576006.58
Energy input (MJ/L of butanol)	26.73
<b>Energy Performance</b>	
NEV (MJ/L)	-5.54
ER	0.83
ER (only utility inputs)	1.00
Total utility energy requirements/Molasses (MJ/T)	3912.78
Total utility energy requirements/Butanol (MJ/T)	38749.93

#### 4.1.2 Detail Description

##### *i. Area 100: Pre-treatment and Sterilization*

In this process area the molasses is diluted with water, nutrients are added, and the mixture is sterilized prior to fermentation. The 147 T/h stream of molasses from the sugar refinery, with a sugar concentration of 62.3 wt% (refer to Table 2), is fed into a mixing vessel (V-101). To dilute the molasses, water is added to V-101 in a ratio of roughly 7:1 (see section 3.2.3i for factors to consider when diluting). Water from the water treatment plant is recycled, and it is assumed that it is supplemented with 10% fresh (make-up) water. Also in this step, nutrients needed for fermentation (as specified in section 3.2.4iii) are added to V-101. The diluted molasses and nutrient mixture in V-101 is pumped to a pressure heating vessel for sterilization (A-101). Sterilization will commence batchwise at 130°C and 3.5 bar for 15 min (as specified in section 3.2.3ii). The hot stream from A-101 and the cold stream from V-101 exchange heat in a fixed shell and tube heatexchanger (HE-101). This is mainly done to minimize the energy requirements needed during sterilization. The stream entering A-101 is heated from 25°C to 121.35°C in HE-101. Also, the sterilized stream leading to fermentation is cooled down to 33°C, which is the optimum incubation temperature for fermentation (Syed, 1994; Jones, 2005). The sterilized, cooled down stream enters a holding vessel (V-102), from where separate streams are pumped to the different fermentors.

##### *ii. Area 200: Batch Fermentation*

The diluted sterilized molasses mash from Area 100 is fermented to produce solvents (acetone, butanol, and ethanol) in this area. The simulation of the batch fermentation process and its general parameters are discussed in detail in section 3.2.4. Seed fermentation is covered in section 3.3.4ii. *Clostridium acetobutylicum* ATCC 824 is used as the biocatalyst in this design. It is one of the older strains previously used in industrial biobutanol production and therefore yields less favourable results when compared to the other improved strains used in this study. It does however have a high productivity, but also produces the largest amounts of acetone and ethanol of all the strains used. The main production fermenter is R-202.

**Table 17: Fermentation parameters for Process Design 1.1 (Roffler, et al, 1987)**

Fermentation Parameters		
Final ABE Concentration	20.6	g/L
ABE Productivity	0.58	g/L.h
A:B:E:AA:BA Ratio	25.6 : 64.9 : 7.1 : 0.9 : 1.4	
Solvent Yield	42	% (mole basis)
Sugar Utilization	81	% (mole basis)
Cell Concentration	3	g/L
Fermentation Time	35.5	hours

**Table 18: Stoichiometric reaction parameters for fermentation in Process Design 1.1**

	Stoichiometric Reaction Equations	% Conversion
1	$C_6H_{12}O_6 + H_2O \rightarrow C_3H_6O$ (acetone) + $3CO_2 + 4H_2$	19.55
2	$C_6H_{12}O_6 \rightarrow C_4H_{10}O$ (butanol) + $2CO_2 + H_2O$	38.83
3	$C_6H_{12}O_6 \rightarrow 2C_2H_6O$ (ethanol) + $2CO_2$	3.42
4	$C_6H_{12}O_6 \rightarrow C_4H_8O_2$ (butyric acid) + $2CO_2 + 2H_2$	0.45
5	$C_6H_{12}O_6 \rightarrow 3C_2H_4O_2$ (acetic acid)	0.34
6	$C_6H_{12}O_6 + 6O_2 \rightarrow 6H_2O + 6CO_2$ (cell maintenance)	13.92
7	$C_6H_{12}O_6 + 1.1429NH_3 \rightarrow 5.7143PCSIR-10 + 0.2857CO_2 + 2.5714H_2O$ (cell growth)	4.48

The off-gas stream during fermentation has a mass flow of 56.3 T/h which contains 95 wt% CO<sub>2</sub>. Average cell biomass produced during fermentation is 4.86 T/h. The average fermentation product stream flowrate is 1136.6 T/h. This stream is pumped to holding vessel V-201 prior to distillation.

### *iii. Area 300: Distillation*

In this process area 5 distillation columns are used to recover the solvents from the fermentation broth. See section 3.2.7 for detail description on the distillation process. The fermentation product stream is first sent to a beer column (T-301) to remove most of the water, all the solids (cells, proteins, and unfermentable molasses), and most of the acetic and butyric acids. This column operates at 1.5 atm, has 15 stages with the feed on stage 1, a boilup ratio of 0.1714, and no condenser. The bottoms product has a mass flowrate of 1101.9 T/h with a 0.987 mass fraction H<sub>2</sub>O. Of the ABE in the fermentation product, 3.32 wt% is lost to the bottoms product in T-301. The overhead vapour stream from the beer column is flashed in a flash drum (F-301) at ambient conditions (25°C and 1 atm) to remove excess light end waste products. A 0.987 T/h stream containing 91.6 wt% CO<sub>2</sub> is flashed off. The bottom liquid stream from the flash is pumped to holding vessel V-301.



Table 19: Design information and mass balance for T-301

Beer Column (T-301)					
Design Information		Feed Stream (kg/h)		Top (kg/h)	Bottom (kg/h)
Stages	15	H <sub>2</sub> O	1098669.16	10986.51	1087682.65
Feed Stage	1	Butnanol	15368.36	15357.75	10.61
Reflux Ratio	n/a	Acetone	5752.17	5752.17	0.00
Diameter	7.23 (m)	Ethanol	1673.49	927.18	746.31
		Butyric Acid	215.32	1.77	213.55
		Acetic Acid	334.98	3.81	331.17
		CO <sub>2</sub>	1067.48	1067.48	0.00
		H <sub>2</sub>	0.56	0.56	0.00
		Temp. (°C)	33.01	99.40	111.72
		Pressure (atm)	1.50	1.50	1.50

T-302 is the acetone stripper; it operates at 1.1 atm, has 30 stages with the feed on stage 15, makes use of a partial-vapour condenser, and has a reflux ratio of 6.89. 99.9 wt% of the acetone fed is recovered overhead. The vapour product from the column is sent to a flash drum (F-302), that operates at ambient conditions, to remove light end waste products. The final **acetone product stream** has a flowrate of **5.68 T/h** at a purity of 98.8 wt%. This stream is pumped to product storage (V-304). The bottoms product is cooled to ambient conditions in HE-301 and pumped to holding vessel V-305.

Table 20: Design information and mass balance for T-302

Acetone Recovery (T-302)					
Design Information		Feed Stream (kg/h)		Top (kg/h)	Bottom (kg/h)
Stages	30	H <sub>2</sub> O	10974.60	7.06	10967.54
Feed Stage	15	Butnanol	15350.43	0.00	15350.42
Reflux Ratio	6.89	Acetone	5690.62	5684.93	5.69
Diameter	2.89 (m)	Ethanol	924.78	9.25	915.53
		Butyric Acid	1.77	0.00	1.77
		Acetic Acid	3.81	0.00	3.81
		CO <sub>2</sub>	162.03	162.03	0.00
		H <sub>2</sub>	0.48	0.48	0.00
		Temp. (°C)	25.02	57.86	93.42
		Pressure (atm)	1.10	1.10	1.10

T-303 removes most of the ethanol; it operates at 0.3 atm, has 40 stages with the feed on stage 15, makes use of a total condenser, and has a reflux ratio of 9.75. Vacuum operation reduces the reflux ratio needed to remove 94.0 wt% of the ethanol overhead. Due to the small amount of ethanol produced in fermentation, it is not recovered pure enough to be considered a product. The overhead stream has a flowrate of 2.03 T/h and

contains 42.4 wt% ethanol and 25.0 wt% butanol. The bottoms product is pumped to holding vessel V-306.

**Table 21: Design information and mass balance for T-303**

Ethanol Recovery (T-303)					
Design Information		Feed Stream (kg/h)		Top (kg/h)	Bottom (kg/h)
Stages	40	H <sub>2</sub> O	10967.55	654.80	10312.75
Feed Stage	15	Butnanol	15350.42	506.56	14843.86
Reflux Ratio	9.75	Acetone	5.69	5.69	0.00
Diameter	2.89 (m)	Ethanol	915.53	860.60	54.93
		Butyric Acid	1.77	0.00	1.77
		Acetic Acid	3.81	0.00	3.81
		CO <sub>2</sub>	0.00	0.00	0.00
		H <sub>2</sub>	0.00	0.00	0.00
		<b>Temp. (°C)</b>	25.09	45.73	63.53
		<b>Pressure (atm)</b>	1.10	0.30	0.30

Butanol and water are separated in a setup with two columns and a decanter. The stream from V-306 as well as the overhead streams from the water (T-304) and butanol (T-305) strippers are fed to a decanter (D-301) where a water-rich phase is allowed to separate from a butanol-rich phase. The water-rich phase, containing 9.63 wt% butanol, is refluxed to the water stripper. This column has 10 stages, operates at 0.5 atm with no condenser, and produces a 10.35 T/h water stream with 99.17 wt% purity. The butanol-rich phase, containing 18.53 wt% water, is refluxed to the butanol stripper. This column has 10 stages, operates at 2 atm with no condenser, and produces a final **butanol product stream** of **14.86 T/h** with 99.5 wt% purity. This stream is pumped to product storage (V-309). 96.7 wt% of all the butanol produced in fermentation is recovered.

Table 22: Design information and mass balance for T-304

Water Stripper (T-304)					
Design Information		Feed Stream (kg/h)		Top (kg/h)	Bottom (kg/h)
Stages	10	H <sub>2</sub> O	11569.13	1302.27	10266.86
Feed Stage	1	Butnanol	1257.18	1208.78	48.40
Reflux Ratio	n/a	Acetone	0.00	0.00	0.00
Diameter	1.45 (m)	Ethanol	228.04	192.71	35.33
		Butyric Acid	0.25	0.02	0.24
		Acetic Acid	1.67	0.09	1.58
		CO <sub>2</sub>	0.00	0.00	0.00
		H <sub>2</sub>	0.00	0.00	0.00
		Temp. (°C)	96.85	75.98	80.79
		Pressure (atm)	1.00	0.50	0.50

Table 23: Design information and mass balance for T-304

Butanol Stripper (T-305)					
Design Information		Feed Stream (kg/h)		Top (kg/h)	Bottom (kg/h)
Stages	10	H <sub>2</sub> O	5157.63	5111.73	45.89
Feed Stage	1	Butnanol	21839.28	7043.81	14795.48
Reflux Ratio	n/a	Acetone	0.00	0.00	0.00
Diameter	2.41 (m)	Ethanol	832.27	812.68	19.58
		Butyric Acid	1.60	0.07	1.53
		Acetic Acid	2.58	0.35	2.23
		CO <sub>2</sub>	0.00	0.00	0.00
		H <sub>2</sub>	0.00	0.00	0.00
		Temp. (°C)	96.96	110.75	136.94
		Pressure (atm)	2.00	2.00	2.00

## 4.2 Process Design 1.2

See Appendix C, PFD Process Design 1.2

### 4.2.1 Process Overview

The process design can be described as batch fermentation of molasses by the fermenting organism *Clostridium acetobutylicum* PCSIR-10 and product recovery by distillation. Four distillation columns are used: a beer column to remove the fermentation media together with most of the water, a column to remove the light end waste, and two columns for the separation of water and butanol. The different process areas are:

- Area 100 – Pre-treatment and sterilization
- Area 200 – Batch fermentation
- Area 300 – Distillation

The design of this process is based on the base case process design simulated by Roffler, et al, (1987), and the batch fermentation is based on the laboratory research results by Syed (1994).

**Table 24: Summary of mass and energy balances for Process Design 1.2**

<b>Molasses</b>	
Mass Flow (T/h)	147.21
Volume Flow (L/h)	118178.49
Energy Density (MJ/L)	1.02
Total Energy (MJ/h)	121022.78
Energy input (MJ/L of butanol)	4.51
<b>Butanol</b>	
Mass Flow (T/h)	18.71
Volume Flow (L/h)	26814.31
Energy Density (MJ/L)	26.81
Total Energy (MJ/h)	718918.52
<b>Steam and Electricity Utilities</b>	
HPS (MJ/h)	496230.68
Electricity (MJ/h)	87385.97
Total Energy (MJ/h)	583616.65
Energy input (MJ/L of butanol)	21.77
<b>Energy Performance</b>	
NEV (MJ/L)	0.53
ER	1.02
ER (only utility inputs)	1.23
Total utility energy requirements/Molasses (MJ/T)	3964.47
Total utility energy requirements/Butanol (MJ/T)	31190.44

#### 4.2.2 Detail Description

##### *i. Area 100: Pre-treatment and Sterilization*

Refer to Area 100 of Process Design 1.1 (pg.86), as its process area description is identical to that of this design.

##### *ii. Area 200: Batch Fermentation*

Refer to Area 200 of Process Design 1.1 (pg.86), as its process area description is similar to that of this design. The only difference is in the fermentation parameters seeing that *Clostridium acetobutylicum* PCSIR-10 is used as the biocatalyst in this design. This strain produces the largest fraction of butanol (the smallest combined volume of acetone and ethanol). It does however have a slightly lower total solvents concentration and ABE productivity than the strain used in Process Design 1.1. The residence time for this fermentation is also longer and it produces a lower final cell concentration.

**Table 25: Fermentation parameters for Process Design 1.2 (Syed, 1994)**

Fermentation Parameters		
Final ABE Concentration	19.2	g/L
ABE Productivity	0.42	g/L.h
A:B:E:AA:BA Ratio	1.67 : 88.6 : 2.7 : 3.5 : 3.5	
Solvent Yield	34	% (mole basis)
Sugar Utilization	91	% (mole basis)
Cell Concentration	2.4	g/L
Fermentation Time	45	hours

**Table 26: Stoichiometric reaction parameters for fermentation in Process Design 1.2**

	Stoichiometric Reaction Equations	% Conversion
1	$C_6H_{12}O_6 + H_2O \rightarrow C_3H_6O$ (acetone) + $3CO_2 + 4H_2$	1.24
2	$C_6H_{12}O_6 \rightarrow C_4H_{10}O$ (butanol) + $2CO_2 + H_2O$	51.35
3	$C_6H_{12}O_6 \rightarrow 2C_2H_6O$ (ethanol) + $2CO_2$	1.26
4	$C_6H_{12}O_6 \rightarrow C_4H_8O_2$ (butyric acid) + $2CO_2 + 2H_2$	1.71
5	$C_6H_{12}O_6 \rightarrow 3C_2H_4O_2$ (acetic acid)	0.83
6	$C_6H_{12}O_6 + 6O_2 \rightarrow 6H_2O + 6CO_2$ (cell maintenance)	33.57
7	$C_6H_{12}O_6 + 1.1429NH_3 \rightarrow 5.7143PCSIR-10 + 0.2857CO_2 + 2.5714H_2O$ (cell growth)	3.58

The off-gas stream during fermentation has a mass flow of 72.4 T/h which contains 97.4 wt%  $CO_2$ . Average cell biomass produced during fermentation is 3.74 T/h. The average fermentation product stream flowrate is 1139.6 T/h. This stream is pumped to holding vessel V-201 prior to distillation.

### iii. Area 300: Distillation

In this process area 4 distillation columns are used to recover the solvents from the fermentation broth. See section 3.2.7 for detail description on the distillation process. The fermentation product stream is first sent to a beer column (T-301) to remove most of the water, all the solids (cells, proteins, and unfermentable molasses), and most of the acetic and butyric acids. This column operates at 1.5 atm, has 10 stages with the feed on stage 1, a boilup ratio of 0.1714, and no condenser. The bottoms product has a mass flowrate of 1 101.0 T/h with a 0.992 mass fraction H<sub>2</sub>O. Of the ABE in the fermentation product, 0.05 wt% is lost to the bottoms product in T-301. The overhead vapour stream from the beer column is flashed in a flash drum (F-301) at ambient conditions (25°C and 1 atm) to remove excess light end waste products. A 0.624 T/h stream containing 97.3 wt% CO<sub>2</sub> is flashed off. The bottom liquid stream from the flash is pumped to holding vessel V-301.

**Table 27: Design information and mass balance for T-301**

Beer Column (T-301)					
Design Information		Feed Stream (kg/h)		Top (kg/h)	Bottom (kg/h)
Stages	10	H <sub>2</sub> O	1111951.48	16679.28	1095272.19
Feed Stage	1	Butnanol	19549.82	19549.39	0.43
Reflux Ratio	n/a	Acetone	349.62	349.62	0.00
Diameter	7.23 (m)	Ethanol	593.02	583.00	10.02
		Butyric Acid	779.55	13.07	766.48
		Acetic Acid	778.36	15.22	763.13
		CO <sub>2</sub>	1365.62	1365.62	0.00
		H <sub>2</sub>	0.06	0.06	0.00
		<b>Temp. (°C)</b>	34.12	103.67	111.79
		<b>Pressure (atm)</b>	1.50	1.50	1.50

T-302 is employed to strip all the light end products; it operates at 0.9 atm, has 40 stages with the feed on stage 10, makes use of a partial-vapour condenser, and has a reflux ratio of 5.5. The top product has a mass flowrate of 3.3 T/h and it contains all the acetone and 94.7 wt% ethanol from the feed stream. Due to the very small amounts of acetone and ethanol produced in fermentation, these products could not be recovered pure enough and are considered a waste stream. The bottoms product is cooled to ambient conditions in HE-301 and pumped to holding vessel V-302.

Table 28: Design information and mass balance for T-302

Acetone Recovery (T-302)					
Design Information		Feed Stream (kg/h)		Top (kg/h)	Bottom (kg/h)
Stages	40	H <sub>2</sub> O	16671.55	819.74	15851.81
Feed Stage	10	Butnanol	19543.01	827.46	18715.55
Reflux Ratio	5.5	Acetone	347.51	347.51	0.00
Diameter	2.89 (m)	Ethanol	582.32	551.27	31.05
		Butyric Acid	13.07	0.00	13.07
		Acetic Acid	15.22	0.00	15.22
		CO <sub>2</sub>	758.72	758.72	0.00
		H <sub>2</sub>	0.05	0.05	0.00
		Temp. (°C)	25.02	79.53	88.84
		Pressure (atm)	1.10	0.90	0.90

Butanol and water are separated in a setup with two columns and a decanter. The stream from V-302 as well as the overhead streams from the water (T-303) and butanol (T-304) strippers are fed to a decanter (D-301) where a water-rich phase is allowed to separate from a butanol-rich phase. The water-rich phase, containing 9.40 wt% butanol, is refluxed to the water stripper. This column has 20 stages, operates at 0.5 atm with no condenser, and produces a 15.92 T/h water stream with 99.60 wt% purity. The butanol-rich phase, containing 17.94 wt% water, is refluxed to the butanol stripper. This column has 20 stages, operates at 1.5 atm with no condenser, and produces a final **butanol product stream of 18.71 T/h** with 99.9 wt% purity. This stream is sent to product storage (V-304). 95.6 wt% of all the butanol produced in fermentation is recovered.

Table 29: Design information and mass balance for T-303

Water Stripper (T-303)					
Design Information		Feed Stream (kg/h)		Top (kg/h)	Bottom (kg/h)
Stages	20	H <sub>2</sub> O	17866.72	2014.87	15851.85
Feed Stage	1	Butnanol	1874.90	1852.95	21.95
Reflux Ratio	n/a	Acetone	0.00	0.00	0.00
Diameter	1.45 (m)	Ethanol	217.23	186.24	30.98
		Butyric Acid	2.31	0.25	2.06
		Acetic Acid	10.10	1.58	8.52
		CO <sub>2</sub>	0.00	0.00	0.00
		H <sub>2</sub>	0.00	0.00	0.00
		Temp. (°C)	96.85	76.42	81.27
		Pressure (atm)	1.00	0.50	0.50

Table 30: Design information and mass balance for T-304

Butanol Stripper (T-304)					
Design Information		Feed Stream (kg/h)		Top (kg/h)	Bottom (kg/h)
Stages	20	H <sub>2</sub> O	6060.89	6060.93	0.00
Feed Stage	1	Butnanol	27066.08	8372.48	18693.70
Reflux Ratio	n/a	Acetone	0.00	0.00	0.00
Diameter	2.41 (m)	Ethanol	632.08	632.03	0.00
		Butyric Acid	11.76	0.75	11.01
		Acetic Acid	12.23	5.53	6.69
		CO <sub>2</sub>	0.00	0.00	0.00
		H <sub>2</sub>	0.00	0.00	0.00
		<b>Temp. (°C)</b>	96.91	103.24	129.62
		<b>Pressure (atm)</b>	1.50	1.50	1.50

### 4.3 Process Design 1.3

See Appendix C, PFD Process Design 1.3

#### 4.3.1 Process Overview

The design can be described as batch fermentation of molasses by the fermenting organism *Clostridium beijerinckii* BA101 and product recovery by distillation. Five distillation columns are used: a beer column to remove the fermentation media together with most of the water, a column to recover acetone and ethanol, a column to separate acetone and ethanol, and two columns for the separation of water and butanol. The different process areas are:

- Area 100 – Pre-treatment and sterilization
- Area 200 – Batch fermentation
- Area 300 – Distillation

The design of this process is based on the base case process design simulated in the study by Marlatt and Datta (1987) and the batch fermentation is based on the laboratory research results by Ezeji, et al., (2004).



**Table 31: Summary of mass and energy balances for Process Design 1.3**

<b>Molasses</b>	
Mass Flow (T/h)	147.21
Volume Flow (L/h)	118178.49
Energy Density (MJ/L)	1.02
Total Energy (MJ/h)	121022.78
Energy input (MJ/L of butanol)	4.06
<b>Butanol</b>	
Mass Flow (T/h)	20.83
Volume Flow (L/h)	29821.81
Energy Density (MJ/L)	26.81
Total Energy (MJ/h)	799552.68
<b>Steam and Electricity Utilities</b>	
HPS (MJ/h)	535415.87
Electricity (MJ/h)	126788.02
Total Energy (MJ/h)	662203.89
Energy input (MJ/L of butanol)	22.21
<b>Energy Performance</b>	
NEV (MJ/L)	0.55
ER	1.02
ER (only utility inputs)	1.21
Total utility energy requirements/Molasses (MJ/T)	4498.31
Total utility energy requirements/Butanol (MJ/T)	31797.52

#### 4.3.2 Detail Description

##### *i. Area 100: Pre-treatment and Sterilization*

Refer to *Area 100* of Process Design 1.1 (pg.86), as its process area description is identical to that of this design.

##### *ii. Area 200: Batch Fermentation*

Refer to *Area 200* of Process Design 1.1 (pg.86), as its process area description is similar to that of this design. The only difference is in the fermentation parameters seeing that *Clostridium beijerinckii* BA 101 is used as the biocatalyst in this design. This strain produces the highest ABE concentration and the smallest quantity of ethanol. It does however have the lowest ABE productivity of all the strains used. The residence time for fermentation is the longest, and it also produces the highest final cell concentration, of all the strains.

**Table 32: Fermentation parameters for Process Design 1.3 (Ezeji, et al, 2004)**

Fermentation Parameters		
Final ABE Concentration	24.2	g/L
ABE Productivity	0.34	g/L.h
A:B:E:AA:BA Ratio	16.5 : 75.3 : 1.2 : 3.5 : 3.5	
Solvent Yield	42	% (mole basis)
Sugar Utilization	91	% (mole basis)
Cell Concentration	4.2	g/L
Fermentation Time	70	hours

**Table 33: Stoichiometric reaction parameters for fermentation in Process Design 1.3**

	Stoichiometric Reaction Equations	% Conversion
1	$C_6H_{12}O_6 + H_2O \rightarrow C_3H_6O$ (acetone) + $3CO_2 + 4H_2$	15.54
2	$C_6H_{12}O_6 \rightarrow C_4H_{10}O$ (butanol) + $2CO_2 + H_2O$	55.56
3	$C_6H_{12}O_6 \rightarrow 2C_2H_6O$ (ethanol) + $2CO_2$	0.71
4	$C_6H_{12}O_6 \rightarrow C_4H_8O_2$ (butyric acid) + $2CO_2 + 2H_2$	2.17
5	$C_6H_{12}O_6 \rightarrow 3C_2H_4O_2$ (acetic acid)	1.06
6	$C_6H_{12}O_6 + 6O_2 \rightarrow 6H_2O + 6CO_2$ (cell maintenance)	14.71
7	$C_6H_{12}O_6 + 1.1429NH_3 \rightarrow 5.7143PCSIR-10 + 0.2857CO_2 + 2.5714H_2O$ (cell growth)	6.27

The off-gas stream during fermentation has a mass flow of 59.13 T/h which contains 95.4 wt% CO<sub>2</sub>. Average cell biomass produced during fermentation is 6.50 T/h. The average fermentation product stream flowrate is 1132.3 T/h. This stream is pumped to holding vessel V-201 prior to distillation.

### *iii. Area 300: Distillation*

In this process area 5 distillation columns are used to recover the solvents from the fermentation broth. See section 3.2.7 for detail description on the distillation process. The fermentation product stream is first sent to a beer column (T-301) to remove most of the water, all the solids (cells, proteins, and unfermentable molasses), and most of the acetic and butyric acids. This column operates at 1.5 atm, has 15 stages with the feed on stage 1, a boilup ratio of 0.1769, and no condenser. The bottoms product has a mass flowrate of 1 093.5 T/h with a 0.992 mass fraction H<sub>2</sub>O. Of the ABE in the fermentation product, 0.001 wt% is lost to the bottoms product in T-301. The overhead vapour stream from the beer column is flashed in a flash drum (F-301) at ambient conditions (25°C and 1 atm) to remove excess light end waste products. A 0.974 T/h stream containing 94.1 wt% CO<sub>2</sub> is flashed off. The bottom liquid stream from the flash is pumped to holding vessel V-301.

Table 34: Design information and mass balance for T-301

Beer Column (T-301)					
Design Information		Feed Stream (kg/h)		Top (kg/h)	Bottom (kg/h)
Stages	15	H <sub>2</sub> O	1100986.38	16514.80	1084471.58
Feed Stage	1	Butnanol	20998.64	20998.64	0.00
Reflux Ratio	n/a	Acetone	4367.39	4367.39	0.00
Diameter	7.23 (m)	Ethanol	333.10	332.85	0.25
		Butyric Acid	985.08	15.15	969.93
		Acetic Acid	983.58	18.52	965.07
		CO <sub>2</sub>	1099.10	1099.10	0.00
		H <sub>2</sub>	0.46	0.46	0.00
		Temp. (°C)	34.16	101.94	111.78
		Pressure (atm)	1.50	1.50	1.50

T-302 strips all the light end products; it operates at 1 atm, has 40 stages with the feed on stage 22, makes use of a partial-vapour condenser, and has a reflux ratio of 7.92. The top product has a mass flowrate of 5.3 T/h and it contains all the acetone and 80.0 wt% ethanol from the feed stream. This stream is sent to a flash drum (F-302), that operates at ambient conditions, to remove light end waste products. The bottom liquid stream from the flash is pumped to holding vessel V-302. The bottoms product from T-302 is cooled to ambient conditions in HE-301 and pumped to holding vessel V-306.

Table 35: Design information and mass balance for T-302

Ethanol and Acetone Recovery (T-302)					
Design Information		Feed Stream (kg/h)		Top (kg/h)	Bottom (kg/h)
Stages	40	H <sub>2</sub> O	16502.78	393.73	16109.05
Feed Stage	22	Butnanol	20989.92	160.95	20828.97
Reflux Ratio	7.91	Acetone	4330.96	4330.96	0.00
Diameter	2.89 (m)	Ethanol	332.16	265.69	66.46
		Butyric Acid	15.15	0.00	15.15
		Acetic Acid	18.51	0.00	18.51
		CO <sub>2</sub>	182.89	182.89	0.00
		H <sub>2</sub>	0.43	0.43	0.00
		Temp. (°C)	25.03	64.58	91.69
		Pressure (atm)	1.10	1.00	1.00

T-303 separates the acetone and ethanol in V302; it operates at 1.4 atm, has 20 stages with the feed on stage 10, makes use of a total condenser, and has a reflux ratio of 6.63. Due to the small quantity of ethanol produced in fermentation, it is not recovered pure enough to be considered a product. The bottoms product is a waste stream (consist of a mixture of water, ethanol, butanol and acetone) and has a flowrate of 0.820 T/h. The

overhead stream contains the final **acetone product**; it has a flowrate of **4.31 T/h** at 98.1 wt% purity. This stream is pumped to product storage (V-305).

**Table 36: Design information and mass balance for T-303**

Acetone Recovery (T-303)					
Design Information		Feed Stream (kg/h)		Top (kg/h)	Bottom (kg/h)
Stages	20	H <sub>2</sub> O	392.22	21.20	371.02
Feed Stage	10	Butnanol	160.91	0.00	160.91
Reflux Ratio	6.63	Acetone	4266.76	4224.09	42.67
Diameter	2.41 (m)	Ethanol	264.16	18.75	245.41
		Butyric Acid	0.00	0.00	0.00
		Acetic Acid	0.00	0.00	0.00
		CO <sub>2</sub>	42.13	42.13	0.00
		H <sub>2</sub>	0.02	0.02	0.00
		<b>Temp. (°C)</b>	25.05	29.39	90.94
		<b>Pressure (atm)</b>	1.40	1.40	1.40

Butanol and water are separated in a setup with two columns and a decanter. The stream from V-306 as well as the overhead streams from the water (T-304) and butanol (T-305) strippers are fed to a decanter (D-301) where a water-rich phase is allowed to separate from a butanol-rich phase. The water-rich phase, containing 9.93 wt% butanol, is refluxed to the water stripper. This column has 10 stages, operates at 0.5 atm with no condenser, and produces a 16.21 T/h water stream with 99.29 wt% purity. The butanol-rich phase, containing 19.26 wt% water, is refluxed to the butanol stripper. This column has 10 stages, operates at 1.5 atm with no condenser, and produces a final **butanol product stream** of **20.83 T/h** with 99.8 wt% purity. This stream is pumped to product storage (V-309). 99.0 wt% of all the butanol produced in fermentation is recovered.

Table 37: Design information and mass balance for T-304

Water Stripper (T-304)					
Design Information		Feed Stream (kg/h)		Top (kg/h)	Bottom (kg/h)
Stages	10	H <sub>2</sub> O	18302.82	2205.28	16097.54
Feed Stage	1	Butnanol	2077.27	2029.96	47.30
Reflux Ratio	n/a	Acetone	0.00	0.00	0.00
Diameter	1.45 (m)	Ethanol	528.44	471.03	57.41
		Butyric Acid	2.39	0.16	2.23
		Acetic Acid	8.48	0.47	8.01
		CO <sub>2</sub>	0.00	0.00	0.00
		H <sub>2</sub>	0.00	0.00	0.00
		Temp. (°C)	96.85	75.60	80.96
		Pressure (atm)	1.00	0.50	0.50

Table 38: Design information and mass balance for T-305

Butanol Stripper (T-305)					
Design Information		Feed Stream (kg/h)		Top (kg/h)	Bottom (kg/h)
Stages	10	H <sub>2</sub> O	7870.27	7858.76	11.50
Feed Stage	1	Butnanol	31203.39	10421.73	20781.68
Reflux Ratio	n/a	Acetone	0.00	0.00	0.00
Diameter	2.89 (m)	Ethanol	1755.11	1746.05	9.03
		Butyric Acid	13.49	0.57	12.92
		Acetic Acid	12.19	1.68	10.50
		CO <sub>2</sub>	0.00	0.00	0.00
		H <sub>2</sub>	0.00	0.00	0.00
		Temp. (°C)	96.90	102.29	129.33
		Pressure (atm)	1.50	1.50	1.50

## 4.4 Process Design 2

See Appendix C, PFD Process Design 2

### 4.4.1 Process Overview

The process design can be described as batch fermentation of molasses by the fermenting organism *Clostridium acetobutylicum* PCSIR-10 and product recovery by LLE followed by distillation. Centrifugation is used to remove the fermenting organisms and remaining substrate prior to LLE. The extractant of choice in LLE is 2-ethyl-1-hexanol and three distillation columns are used: first to strip the extractant, then to recover the acetone, followed by simultaneous recovery of ethanol and butanol. The different process areas are:

- Area 100 – Pre-treatment and sterilization

- Area 200 – Batch fermentation and centrifugation
- Area 300 – LLE and distillation

The overall design of this process is based on the Dadgar and Foutch (1988) simulated process. The batch fermentation is based on the laboratory research results by Syed (1994) and the downstream processing design is the same as the optimal flowsheet as proposed by Liu, et al., (2004). The LLE process is based on similar unit operations simulated in process designs by various authors (Dadgar & Foutch, 1988; Liu, Fan, & Seib, 2004; Bohlmann, 2007).

**Table 39: Summary of mass and energy balances for Process Design 2**

<b>Molasses</b>	
Mass Flow (T/h)	147.21
Volume Flow (L/h)	118178.49
Energy Density (MJ/L)	1.02
Total Energy (MJ/h)	121022.78
Energy input (MJ/L of butanol)	4.64
<b>Butanol</b>	
Mass Flow (T/h)	18.60
Volume Flow (L/h)	26108.11
Energy Density (MJ/L)	26.81
Total Energy (MJ/h)	699984.44
<b>Steam and Electricity Utilities</b>	
HPS (MJ/h)	161340.50
Electricity (MJ/h)	89955.56
Total Energy (MJ/h)	251296.06
Energy input (MJ/L of butanol)	9.63
<b>Energy Performance</b>	
NEV (MJ/L)	12.55
ER	1.88
ER (only utility inputs)	2.79
Total utility energy requirements/Molasses (MJ/T)	1707.04
Total utility energy requirements/Butanol (MJ/T)	13513.85

#### 4.4.2 Detail Description

##### *i. Area 100: Pre-treatment and Sterilization*

Refer to *Area 100* of Process Design 1.1 (pg.86), as its process area description is identical to that of this design.

*ii. Area 200: Batch Fermentation and Centrifugation*

Refer to *Area 200* of Process Design 1.2 (pg.92), as its process area description is similar to that of this design. The only difference is that the solids in the fermentation broth must be removed prior to downstream processing seeing that LLE is applied in A300. After holding vessel V-201, a centrifuge (C-201) is used to separate the solids from the fermentation product stream. It is assumed that all the biomass is removed from the product stream and that the bottoms product of the centrifuge is 50% liquid slurry. A small fraction of the solvents are entrained and lost with the bottoms product. The top product that consists of water, acetone, ethanol, butanol, acetic acid, and butyric acid, is pumped to holding vessel V-202.

*iii. Area 300: LLE and Distillation*

In this process area a LLE column and 3 distillation columns are used to recover the solvents from the water. See section 3.2.6 for a description of the LLE process and section 3.2.7 for the distillation process description. First LLE is applied to remove the water from the ABE mixture, thereby removing the azeotropes and simplifying the downstream processing. Only acetone, butanol and ethanol are recovered with the extraction process. 2-Ethyl-1-hexanol is the extractant of choice and has a flowrate of 1220.6 T/h. The LLE column (T-301) operates at ambient conditions and has 6 stages. The product stream from Area 200 is fed at the top stage of the column and the extractant is fed at the bottom stage. All the extractant fed and the following ABE fractions are recovered in the overhead stream: 97 wt% butanol, 63.9 wt% ethanol, 49.3 wt% ethanol. This top product stream is sent to holding vessel V-301. The bottoms product contains all the water and fermentation products not recovered in the top stream. This latter stream has an 1115.7 T/h flowrate and consists of 99.27 wt% water.

Table 40: Design information and mass balance for T-301

LLE Column (T-301)					
Design Information		Feed Stream (kg/h)		Top (kg/h)	Bottom (kg/h)
Stages	6	H <sub>2</sub> O	1100986.38	16514.80	1084471.58
Feed Stage	1	Ethylhexanol			
Reflux Ratio	n/a	Butnanol	20998.64	20998.64	0.00
Diameter	n/a	Acetone	4367.39	4367.39	0.00
		Ethanol	333.10	332.85	0.25
		Butyric Acid	985.08	15.15	969.93
		Acetic Acid	983.58	18.52	965.07
		CO <sub>2</sub>	1099.10	1099.10	0.00
		H <sub>2</sub>	0.46	0.46	0.00
		<b>Temp. (°C)</b>	34.16	101.94	111.78
		<b>Pressure (atm)</b>	1.50	1.50	1.50

The cold stream from V-301 that enters T-302, and the hot bottoms product from T-302, exchange heat in HE-301. The bottoms product from T-302 (which is the recycle stream of 2-ethyl-1-hexanol) is cooled from 184.45°C to 46.05°C, while the feed stream for T-302 is heated to 170°C from ambient conditions. This process reduces utility usage seeing that the 2-ethyl-1-hexanol recycle stream must be cooled down to near ambient conditions prior to LLE.

T-302 is the extractant stripper; it operates at 1 atm, has 15 stages with the feed on stage 8, makes use of a total condenser, and has a reflux ratio of 7.12. The top product has a mass flowrate of 19.0 T/h and it contains all the acetone, ethanol, and 98 wt% butanol from the feed stream. This stream is cooled to ambient conditions in HE-302 and pumped to holding vessel V-303. The bottoms product from T-302 is the 2-ethyl-1-hexanol recycle stream with a 1221.0 T/h flowrate and 99.96 wt% purity.



Table 41: Design information and mass balance for T-302

Solvent Recovery (T-302)					
Design Information		Feed Stream (kg/h)		Top (kg/h)	Bottom (kg/h)
Stages	15	H <sub>2</sub> O	0.00	0.00	0.00
Feed Stage	8	Ethylhexanol	1220557.17	12.21	1220544.96
Reflux Ratio	7.12	Butnanol	18882.18	18504.54	377.64
Diameter	7.72 (m)	Acetone	222.60	222.60	0.00
		Ethanol	291.13	291.12	0.00
		Butyric Acid	0.00	0.00	0.00
		Acetic Acid	0.00	0.00	0.00
		CO <sub>2</sub>	0.00	0.00	0.00
		H <sub>2</sub>	0.00	0.00	0.00
		<b>Temp. (°C)</b>	170.00	112.06	184.50
		<b>Pressure (atm)</b>	1.10	1.00	1.00

T-303 is the acetone stripper; it operates at 1 atm, has 25 stages with the feed on stage 5, makes use of a total condenser, and has a reflux ratio of 4.04. Of the acetone fed, 99.999 wt% is recovered overhead. The final **acetone product stream** has a flowrate of **0.227 T/h** at a purity of 98.0 wt%. This stream is pumped to product storage (V-306). The bottoms product is cooled to ambient conditions in HE-303 and pumped to holding vessel V-307.

Table 42: Design information and mass balance for T-303

Acetone Recovery (T-303)					
Design Information		Feed Stream (kg/h)		Top (kg/h)	Bottom (kg/h)
Stages	25	H <sub>2</sub> O	0.00	0.00	0.00
Feed Stage	5	Ethylhexanol	12.21	0.00	12.21
Reflux Ratio	4.04	Butnanol	18504.54	0.22	18504.32
Diameter	2.41 (m)	Acetone	222.60	222.60	0.00
		Ethanol	291.12	4.66	286.47
		Butyric Acid	0.00	0.00	0.00
		Acetic Acid	0.00	0.00	0.00
		CO <sub>2</sub>	0.00	0.00	0.00
		H <sub>2</sub>	0.00	0.00	0.00
		<b>Temp. (°C)</b>	25.00	56.37	115.46
		<b>Pressure (atm)</b>	1.00	1.00	1.00

T-304 is the ethanol stripper; it operates at 1 atm, has 20 stages with the feed on stage 14, makes use of a total condenser, and has a reflux ratio of 4.2. Of the ethanol fed, 71.80 wt% is recovered overhead. The final **ethanol product stream** has a flowrate of **0.208 T/h** at a purity of 99.12 wt%. This stream is pumped to product storage (V-310). The bottoms product is the final **butanol product stream** of **18.50 T/h** with 99.5 wt%

purity; it is pumped to product storage (V-313). 94.7 wt% of all the butanol produced in fermentation is recovered.

**Table 43: Design information and mass balance for T-304**

Butanol Recovery (T-304)					
Design Information		Feed Stream (kg/h)		Top (kg/h)	Bottom (kg/h)
Stages	20	H <sub>2</sub> O	0.00	0.00	0.00
Feed Stage	14	Ethylhexanol	12.21	0.00	12.21
Reflux Ratio	4.2	Butnanol	18504.32	1.85	18502.47
Diameter	1.45 (m)	Acetone	0.00	0.00	0.00
		Ethanol	286.47	205.70	80.77
		Butyric Acid	0.00	0.00	0.00
		Acetic Acid	0.00	0.00	0.00
		CO <sub>2</sub>	0.00	0.00	0.00
		H <sub>2</sub>	0.00	0.00	0.00
		<b>Temp. (°C)</b>	96.90	102.29	129.33
		<b>Pressure (atm)</b>	1.50	1.50	1.50

## 4.5 Process Design 3

See Appendix C, PFD Process Design 3

### 4.5.1 Process Overview

This process design can be described as fed-batch fermentation of molasses by the fermenting organism *Clostridium acetobutylicum* BA-101, and *in situ* product recovery by gas stripping, followed by LLE and distillation. The process of gas stripping yields a concentrated ABE stream, free of solids, which is sent to LLE. The extractant of choice in LLE is 2-ethyl-1-hexanol, and two distillation columns are used to first strip the extractant and then to simultaneously recover the acetone and butanol. The different process areas are:

- Area 100 – Pre-treatment and sterilization
- Area 200 – Fed-batch fermentation with *in situ* gas stripping
- Area 300 – LLE and distillation

The overall design of this process is based on the Bohlmann, (2005), simulated process design. The fed-batch fermentation and *in situ* gas stripping are based on the laboratory research results by Ezeji, et al., (2004) and the downstream processing design is the same as the optimal flowsheet as proposed by Liu, et al., (2004). The LLE process is based on similar unit operations simulated in process designs by various authors (Dadgar & Foutch,

1988; Liu, Fan, & Seib, 2004; Bohlmann, 2007). **It is very important to note that the molasses feed stream for this process design is set at 35.28 T/h** (refer to section 3.2.2).

**Table 44: Summary of mass and energy balances for Process Design 3**

<b>Molasses</b>	
Mass Flow (T/h)	35.28
Volume Flow (L/h)	28322.05
Energy Density (MJ/L)	1.02
Total Energy (MJ/h)	29003.70
Energy input (MJ/L of butanol)	1.39
<b>Butanol</b>	
Mass Flow (T/h)	14.85
Volume Flow (L/h)	20860.10
Energy Density (MJ/L)	26.81
Total Energy (MJ/h)	559280.02
<b>Steam and Electricity Utilities</b>	
HPS (MJ/h)	20782.36
Electricity (MJ/h)	118395.92
Total Energy (MJ/h)	139178.28
Energy input (MJ/L of butanol)	6.67
<b>Energy Performance</b>	
NEV (MJ/L of butanol)	18.75
ER	3.33
ER (only utility inputs)	4.02
Total utility energy requirements/Molasses (MJ/T)	3944.96
Total utility energy requirements/Butanol (MJ/T)	9373.87

#### 4.5.2 Detail Description

##### *i. Area 100: Pre-treatment and Sterilization*

The description of this section is similar to that of *Area 100* for Process Design 1.1 (pg.86) The only difference is the volume of water added to dilute the molasses prior to sterilization. Only 30.66 T/h water is added to 35.28 T/h molasses to obtain a glucose concentration of 500 g/L (see section 3.2.3i).

##### *ii. Area 200: Fed-batch Fermentation with in situ Gas Stripping*

A fraction of the slightly diluted sterilized molasses mash (500 g/L) from Area 100 is diluted further to 100 g/L and used for initial fermentation to produce solvents (acetone, butanol, and ethanol) in this area. The undiluted fraction is used for intermitted feed during the fed-batch fermentation. The extra water needed for dilution is sterilized in a pressure heating vessel (A-201) under similar conditions to that of A-101 (see section

4.1.2i). This is done for the case of using recycled water, but should also be done to assure absolute sterility. The dilution takes place in V-201 and the mixture is cooled in a heat exchanger (HE-201) to 33°C prior to fermentation in R-202. The simulation of the fed-batch fermentation process and its general parameters are discussed in detail in section 3.2.4. Seed fermentation is covered in section 3.3.4ii. *Clostridium beijerinckii* BA 101 is used as the biocatalyst in this design. This is the only strain for which sufficient fed-batch fermentation parameters could be obtained in literature.

**Table 45: Fermentation parameters for Process Design 3 (Ezeji, et al., 2004)**

Fermentation Parameters		
Total ABE Concentration	232.8	g/L
ABE Productivity	1.16	g/L.h
A:B:E:AA:BA Ratio	32.2 : 62.9 : 1.4 : 1.7 : 1.8	
Solvent Yield	47	% (mole basis)
Sugar Utilization	95.1	% (mole basis)
Total Glucose Utilized	500	g/L
Cell Concentration	6	g/L
CO <sub>2</sub> Stripping Rate (per liter of fermentation volume)	180	L/h
Fermentation Time	180	hours

**Table 46: Stoichiometric reaction parameters for fermentation in Process Design 3**

Stoichiometric Reaction Equations		% Conversion
1	$C_6H_{12}O_6 + H_2O \rightarrow C_3H_6O$ (acetone) + 3CO <sub>2</sub> + 4H <sub>2</sub>	36.37
2	$C_6H_{12}O_6 \rightarrow C_4H_{10}O$ (butanol) + 2CO <sub>2</sub> + H <sub>2</sub> O	55.71
3	$C_6H_{12}O_6 \rightarrow 2C_2H_6O$ (ethanol) + 2CO <sub>2</sub>	1.01
4	$C_6H_{12}O_6 \rightarrow C_4H_8O_2$ (butyric acid) + 2CO <sub>2</sub> + 2H <sub>2</sub>	1.30
5	$C_6H_{12}O_6 \rightarrow 3C_2H_4O_2$ (acetic acid)	0.65
6	$C_6H_{12}O_6 + 6O_2 \rightarrow 6H_2O + 6CO_2$ (cell maintenance)	0.00
7	$C_6H_{12}O_6 + 1.1429NH_3 \rightarrow 5.7143PCSIR-10 + 0.2857CO_2 + 2.5714H_2O$ (cell growth)	3.00

This is the only process simulation for which extra glucose (other than specified in literature) were added during fermentation to obtain the product and cell concentrations in simulation, as achieved in literature (see explanation of method in section 3.2.4ii). This is also the reason for no fractional conversion being assigned to equation 6 in Table 46. Average cell biomass produced during fermentation is 0.647 T/h. The condenser for the gas stripping process (HE-202) operates at -2°C. The average condensed product stream after gas stripping has a flowrate of 45.74 T/h and an ABE concentration of 335.8 g/L. This stream is collected in holding vessel V-202 prior to LLE.

Per hour of fermentation, more CO<sub>2</sub> is produced in the fermentation process than is needed for gas stripping, therefore 7.85 T of CO<sub>2</sub> are bled. With the latter stream, small amounts of uncondensed ABE and water also escape. The remaining gas stream is at the literature specified CO<sub>2</sub> flowrate for gas stripping; it is fed to compressors (C-201) to raise the pressure prior to being recycled to the fermentors.

*iii. Area 300: LLE and Distillation*

In this process area a LLE column and 2 distillation columns are used to recover the solvents from the water. See section 3.2.6 for a description of the LLE process and section 3.2.7 for the distillation process description. First LLE is applied to remove the water from the ABE mixture, thereby removing the azeotropes and simplifying the downstream processing. Only acetone, butanol and ethanol are recovered with the extraction process. 2-Ethyl-1-hexanol is the extractant of choice and has a flowrate of 49.2 T/h. The LLE column (T-301) operates at ambient conditions and has 6 stages. The product stream from Area 200 is fed at the top stage of the column and the extractant is fed at the bottom stage. All the extractant fed and the following ABE fractions are recovered in the overhead stream: 97 wt% butanol, 63.9 wt% ethanol, 49.3 wt% ethanol. This top product stream is sent to holding vessel V-301. The bottoms product contains all the water and fermentation products not recovered in the top stream. This latter stream has a 30.112 T/h flowrate and consists of 95.61 wt% water.

**Table 47: Design information and mass balance for T-301**

LLE Column (T-301)					
Design Information		Feed Stream (kg/h)		Top (kg/h)	Bottom (kg/h)
Stages	6	H <sub>2</sub> O	1100986.38	16514.80	1084471.58
Feed Stage	1	Ethylhexanol			
Reflux Ratio	n/a	Butnanol	20998.64	20998.64	0.00
Diameter	n/a	Acetone	4367.39	4367.39	0.00
		Ethanol	333.10	332.85	0.25
		Butyric Acid	985.08	15.15	969.93
		Acetic Acid	983.58	18.52	965.07
		CO <sub>2</sub>	1099.10	1099.10	0.00
		H <sub>2</sub>	0.46	0.46	0.00
		Temp. (°C)	34.16	101.94	111.78
		Pressure (atm)	1.50	1.50	1.50

The cold stream from V-301 that enters T-302, and the hot bottoms product from T-302, exchange heat in HE-301. The bottoms product from T-302 (which is the recycle stream

of 2-ethyl-1-hexanol) is cooled from 184.55°C to 28.95°C, while the feed stream for T-302 is heated to 120°C from ambient conditions. This process reduces utility usage seeing that the 2-ethyl-1-hexanol recycle stream must be cooled down to near ambient conditions prior to LLE.

T-302 is the extractant stripper; it operates at 1 atm, has 15 stages with the feed on stage 8, makes use of a total condenser, and has a reflux ratio of 1.46. The top product has a mass flowrate of 15.63 T/h and it contains all the acetone, ethanol, and 99.99 wt% butanol from the feed stream. This stream is cooled to ambient conditions in HE-302 and pumped to holding vessel V-303. The bottoms product from T-302 is the 2-ethyl-1-hexanol recycle stream with a 49.2 T/h flowrate and 99.99 wt% purity.

**Table 48: Design information and mass balance for T-302**

Solvent Recovery (T-302)						
Design Information		Feed Stream (kg/h)		Top (kg/h)	Bottom (kg/h)	
Stages	15	H <sub>2</sub> O	0.00	0.00	0.00	
Feed Stage	8	Ethylhexanol	255856.38	2.56	255853.82	
Reflux Ratio	1.46	Butnanol	63519.87	63513.52	6.35	
Diameter	8.2 (m)	Acetone	3542.03	3542.03	0.00	
		Ethanol	52.85	52.85	0.00	
		Butyric Acid	0.00	0.00	0.00	
		Acetic Acid	0.00	0.00	0.00	
		CO <sub>2</sub>	0.00	0.00	0.00	
		H <sub>2</sub>	0.00	0.00	0.00	
		<b>Temp. (°C)</b>		120.00	103.37	184.60
		<b>Pressure (atm)</b>		1.10	1.00	1.00

T-303 is the acetone stripper; it operates at 1 atm, has 20 stages with the feed on stage 5, makes use of a total condenser, and has a reflux ratio of 2.72. Of the acetone fed, 99.0 wt% is recovered overhead. The final **acetone product stream** has a flowrate of **0.780 T/h** at a purity of 99.8 wt%. This stream is pumped to product storage (V-306). The bottoms product is the final **butanol product stream** of **14.85 T/h** with 99.88 wt% purity; it is pumped to product storage (V-309). 75.6 wt% of all the butanol produced in fermentation is recovered.

Table 49: Design information and mass balance for T-303

Butanol Recovery (T-303)					
Design Information		Feed Stream (kg/h)		Top (kg/h)	Bottom (kg/h)
Stages	20	H <sub>2</sub> O	0.00	0.00	0.00
Feed Stage	5	Ethylhexanol	2.56	0.00	2.56
Reflux Ratio	2.72	Butnanol	63513.52	3.29	63510.22
Diameter	2.89 (m)	Acetone	3542.03	3506.61	35.42
		Ethanol	52.85	2.11	50.73
		Butyric Acid	0.00	0.00	0.00
		Acetic Acid	0.00	0.00	0.00
		CO <sub>2</sub>	0.00	0.00	0.00
		H <sub>2</sub>	0.00	0.00	0.00
		<b>Temp. (°C)</b>	25.00	56.16	117.41
		<b>Pressure (atm)</b>	1.00	1.00	1.00

## 5 Process Economics

The economic evaluations of all the process designs are done in ASPEN Icarus<sup>®</sup>. Indicators used in this study to evaluate the profitability of a project are defined as follows (Aspen Technology, Inc., 2006):

- Internal Rate of Return (IRR): the rate at which the present value of all cash flows is zero. IRR is the after-tax interest rate at which the organization can borrow funds and break even at the end of the project life. It is an indication of the profitability of the project.
- Net Rate of Return (NRR): the profitability of the project. The net rate of return for each period is calculated by dividing the Net Present Value by the Present Value of Cumulative Outflows and then multiplying the result by 100.
- Payout Period (PO): the expected number of years required to recover the original investment in the project.
- Profitability Index (PI): shows the relative profitability of any project; it shows the present value of the benefits relative to the present value of the costs. For each period, this number is computed by dividing the Present Value of the Cumulative Cash Inflows by the Present Value of the Cumulative Cash Outflows.
- Net Present Value (NPV): the current worth of all the Net Earnings received through period n.

*The CD attached to this report contains the following on this section: all the ASPEN Icarus<sup>®</sup> simulated models and the Microsoft Excel<sup>®</sup> spreadsheets used for cost calculations. A full investment analysis report for every process design is also included.*



## 5.1 Process Design 1.1

### 5.1.1 Project Capital and Operating Cost

**Table 50: Total project capital cost for Process Design 1.1**

Total Project Capital Cost	
Total Installed Cost	\$ 211 730 363.00
Total Installed Equipment Cost	\$ 111 016 800.00
A100 - Pre-treatment and sterilization	\$ 19 845 100.00
A200 - Batch Fermentation	\$ 78 308 300.00
A300 - LLE and distillation	\$ 12 863 400.00
Other (additional expences and support infrastructure)	\$ 100 713 563.00
Indirect Cost	\$ 34 625 680.00
G and A Overheads	\$ 5 229 750.00
Contract Fee	\$ 6 999 930.00
Contingencies	\$ 22 396 000.00
Total Project Cost	\$ 246 356 043.00
Adjusted Total Project Cost	\$ 320 642 000.00

**Table 51: Total variable operating cost for Process Design 1.1**

Total Variable Operating Cost	
Total Raw Material Cost	\$ 250 553 000.00
Total Product Sales	\$ -184 337 300.00
Main Product Sales	\$ -146 805 000.00
By-product Sales	\$ -37 532 300.00
Utility Cost	\$ 22 180 711.99
Electricity	\$ 11 437 400.00
Steam (HPS)	\$ 10 722 231.84
Cooling Water	\$ 21 080.15
Total Variable Operating Cost	\$ 88 396 411.99

**Table 52: Total fixed operating cost for Process Design 1.1**

Total Fixed Operating Cost	
Total Operating Labour and Maintenance Cost	\$ 4 520 000.00
Operating Labour	\$ 960 000.00
Maintenance	\$ 3 280 000.00
Supervision	\$ 280 000.00
Other Operating Cost	\$ 24 804 700.00
Operating Charges	\$ 170 000.00
Plant Overhead	\$ 2 260 000.00
G and A Cost	\$ 22 374 700.00
Total Fixed Operating Cost	\$ 29 324 700.00

### 5.1.2 Discounted Cash Flow and Sensitivity Analyses

Table 53: Profitability indicators for Process Design 1.1

Profitability Indicators		
NPV (Net Present Value)	-\$1 828 670 000.00	end of project life
IRR (Internal Rate of Return)	n/a	percent
NRR (Net Return Rate)	-32.41	percent
PO (Payout Years)	n/a	years
PI (Profitability Index)	0.68	percent

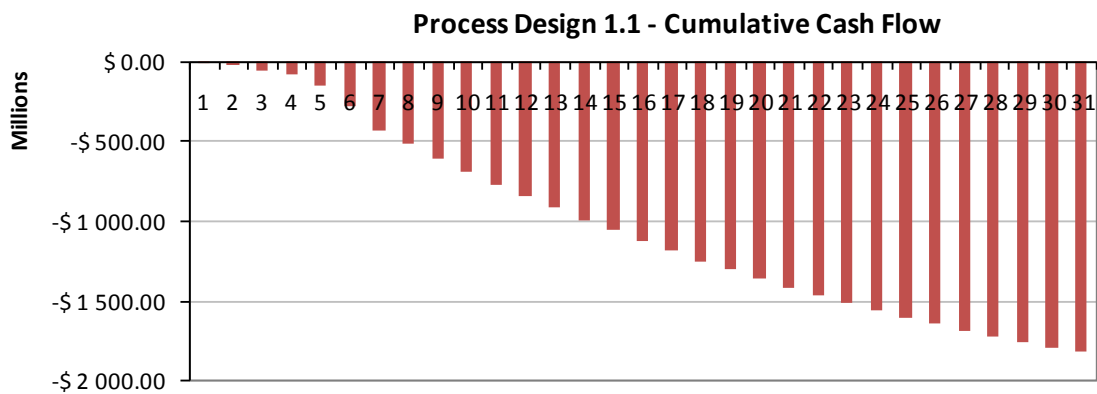


Figure 27: Cumulative cash flow diagram over the life of the project for Process Design 1.1

It is clear that this base case design is not profitable in current economic conditions. Not enough profit is made in order to obtain a positive total variable operating cost (cash inflow). For this process design to break even:

- butanol selling price need to be \$2025 per T (current price \$1234.5 per T)
- or molasses price need to drop to \$126 per T (current price \$212.67 per T)

The minimum required butanol price is higher than the maximum butanol price over the past 5 years (see Figure 25 in section 3.4.2iii ). For molasses, the maximum allowed price is slightly higher than the minimum price over the past 5 years (see Figure 24 in section 3.4.2ii).

## 5.2 Process Design 1.2

### 5.2.1 Project Capital and Operating Cost

**Table 54: Total project capital cost for Process Design 1.2**

Total Project Capital Cost	
Total Installed Cost	\$ 249 175 804.00
Total Installed Equipment Cost	\$ 127 587 500.00
A100 - Pre-treatment and sterilization	\$ 19 845 100.00
A200 - Batch Fermentation	\$ 97 427 300.00
A300 - LLE and distillation	\$ 10 315 100.00
Other (additional expences and support infrastructure)	\$ 121 588 304.00
Indirect Cost	\$ 40 693 770.00
G and A Overheads	\$ 6 060 770.00
Contract Fee	\$ 8 281 200.00
Contingencies	\$ 26 351 800.00
Total Project Cost	\$ 289 869 574.00
Adjusted Total Project Cost	\$ 377 277 000.00

**Table 55: Total variable operating cost for Process Design 1.2**

Total Variable Operating Cost	
Total Raw Material Cost	\$ 250 553 000.00
Total Product Sales	\$ -184 793 000.00
Main Product Sales	\$ -184 793 000.00
By-product Sales	-
Utility Cost	\$ 25 221 249.96
Electricity	\$ 14 739 100.00
Steam (HPS)	\$ 10 468 862.40
Cooling Water	\$ 13 287.56
Total Variable Operating Cost	\$ 90 981 249.96

**Table 56: Total fixed operating cost for Process Design 1.2**

Total Fixed Operating Cost	
Total Operating Labour and Maintenance Cost	\$ 5 140 000.00
Operating Labour	\$ 960 000.00
Maintenance	\$ 3 900 000.00
Supervision	\$ 280 000.00
Other Operating Cost	\$ 25 432 300.00
Operating Charges	\$ 170 000.00
Plant Overhead	\$ 2 570 000.00
G and A Cost	\$ 22 692 300.00
Total Fixed Operating Cost	\$ 30 572 300.00

## 5.2.2 Discounted Cash Flow and Sensitivity Analyses

Table 57: Profitability indicators for Process Design 1.2

Profitability Indicators		
NPV (Net Present Value)	\$-1 858 820 000.00	end of project life
IRR (Internal Rate of Return)	n/a	percent
NRR (Net Return Rate)	-33.07	percent
PO (Payout Years)	n/a	years
PI (Profitability Index)	0.67	percent

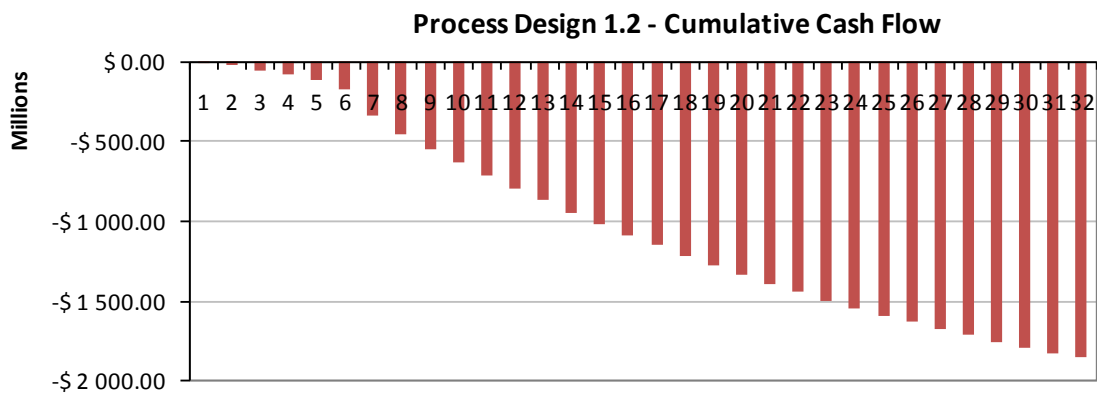


Figure 28: Cumulative cash flow diagram over the life of the project for Process Design 1.2

This design is not profitable in current economic conditions, and economically slightly less viable than Process Design 1.1. Total variable operating cost is a larger negative cash outflow and the TPCC is also more expensive than Process Design 1.1. Break even occurs at:

- a butanol selling price of \$1900 per T (current price \$1234.5 per T)
- or molasses price need to drop to \$120 per T (current price \$212.67 per T)

The minimum required butanol price is higher than the maximum price over the past 5 years, and for molasses, the maximum allowed price is only slightly higher than the minimum price over the past 5 years.

## 5.3 Process Design 1.3

### 5.3.1 Project Capital and Operating Cost

**Table 58: Total project capital cost for Process Design 1.3**

Total Project Capital Cost	
Total Installed Cost	\$ 351 259 162.00
Total Installed Equipment Cost	\$ 176 946 300.00
A100 - Pre-treatment and sterilization	\$ 19 845 100.00
A200 - Batch Fermentation	\$ 143 099 900.00
A300 - LLE and distillation	\$ 14 001 300.00
Other (additional expences and support infrastructure)	\$ 174 312 862.00
Indirect Cost	\$ 57 257 820.00
G and A Overheads	\$ 8 341 320.00
Contract Fee	\$ 11 778 600.00
Contingencies	\$ 37 137 900.00
Total Project Cost	\$ 408 516 982.00
Adjusted Total Project Cost	\$ 531 700 000.00

**Table 59: Total variable operating cost for Process Design 1.3**

Total Variable Operating Cost	
Total Raw Material Cost	\$ 250 553 000.00
Total Product Sales	\$ -234 113 600.00
Main Product Sales	\$ -205 672 000.00
By-product Sales	\$ -28 441 600.00
Utility Cost	\$ 32 718 391.62
Electricity	\$ 21 399 000.00
Steam (HPS)	\$ 11 295 543.20
Cooling Water	\$ 23 848.42
Total Variable Operating Cost	\$ 49 157 791.62

**Table 60: Total fixed operating cost for Process Design 1.3**

Total Fixed Operating Cost	
Total Operating Labour and Maintenance Cost	\$ 6 710 000.00
Operating Labour	\$ 960 000.00
Maintenance	\$ 5 470 000.00
Supervision	\$ 280 000.00
Other Operating Cost	\$ 27 005 500.00
Operating Charges	\$ 170 000.00
Plant Overhead	\$ 3 355 000.00
G and A Cost	\$ 23 480 500.00
Total Fixed Operating Cost	\$ 33 715 500.00

### 5.3.2 Discounted Cash Flow and Sensitivity Analyses

Table 61: Profitability indicators for Process Design 1.3

Profitability Indicators		
NPV (Net Present Value)	\$-1 380 030 000.00	end of project life
IRR (Internal Rate of Return)	n/a	percent
NRR (Net Return Rate)	-22.72	percent
PO (Payout Years)	n/a	years
PI (Profitability Index)	0.77	percent

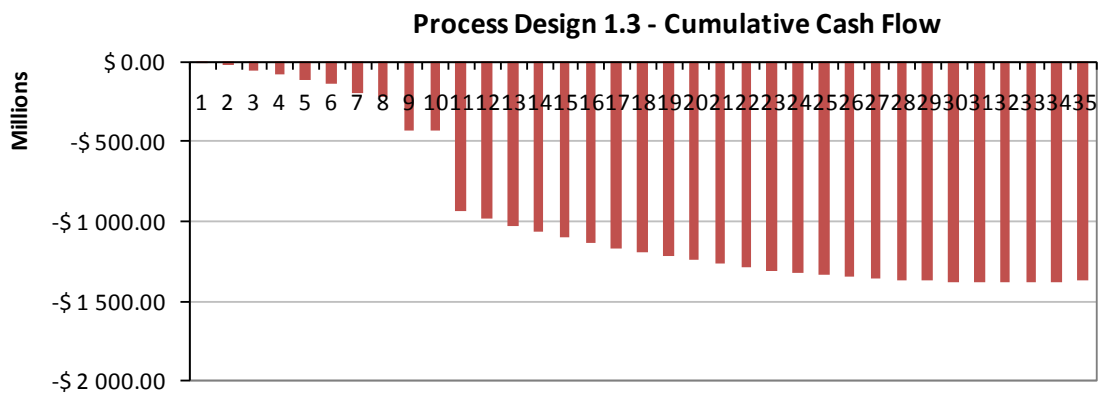


Figure 29: Cumulative cash flow diagram over the life of the project for Process Design 1.3

This design is not profitable in current economic conditions. It is however economically the most viable process design that makes use of previously applied industrial technology (batch fermentation and simple distillation). This design has by far the largest TPCC, but also the largest product sales. Break even occurs at:

- a butanol selling price of \$1750 per T (current price \$1234.5 per T)
- or molasses price need to drop to \$130 per T (current price \$212.67 per T)

Both the these prices fall within the minimum required and maximum allowed price ranges for the specific commodity over the past 5 years, but only just.

## 5.4 Process Design 2

### 5.4.1 Project Capital and Operating Cost

**Table 62: Total project capital cost for Process Design 2**

Total Project Capital Cost	
Total Installed Cost	\$ 281 906 756.00
Total Installed Equipment Cost	\$ 151 172 200.00
A100 - Pre-treatment and sterilization	\$ 19 515 700.00
A200 - Batch Fermentation	\$ 103 901 800.00
A300 - LLE and distillation	\$ 27 754 700.00
Other (additional expences and support infrastructure)	\$ 130 734 556.00
Indirect Cost	\$ 46 139 770.00
G and A Overheads	\$ 6 993 390.00
Contract Fee	\$ 9 323 980.00
Contingencies	\$ 29 822 400.00
Total Project Cost	\$ 328 046 526.00
Adjusted Total Project Cost	\$ 426 965 000.00

**Table 63: Total variable operating cost for Process Design 2**

Total Variable Operating Cost	
Total Raw Material Cost	\$ 250 567 000.00
Total Product Sales	\$ -185 977 600.00
Main Product Sales	\$ -183 649 000.00
By-product Sales	\$ -2 328 600.00
Utility Cost	\$ 18 620 815.21
Electricity	\$ 15 182 500.00
Steam (HPS)	\$ 3 403 762.77
Cooling Water	\$ 34 552.44
Total Variable Operating Cost	\$ 83 210 215.21

**Table 64: Total fixed operating cost for Process Design 2**

Total Fixed Operating Cost	
Total Operating Labour and Maintenance Cost	\$ 5 220 000.00
Operating Labour	\$ 960 000.00
Maintenance	\$ 3 980 000.00
Supervision	\$ 280 000.00
Other Operating Cost	\$ 24 955 000.00
Operating Charges	\$ 170 000.00
Plant Overhead	\$ 2 610 000.00
G and A Cost	\$ 22 175 000.00
Total Fixed Operating Cost	\$ 30 175 000.00

### 5.4.2 Discounted Cash Flow and Sensitivity Analyses

Table 65: Profitability indicators for Process Design 2

Profitability Indicators		
NPV (Net Present Value)	\$-1 747 060 000.00	end of project life
IRR (Internal Rate of Return)	n/a	percent
NRR (Net Return Rate)	-31.76	percent
PO (Payout Years)	n/a	years
PI (Profitability Index)	0.68	percent

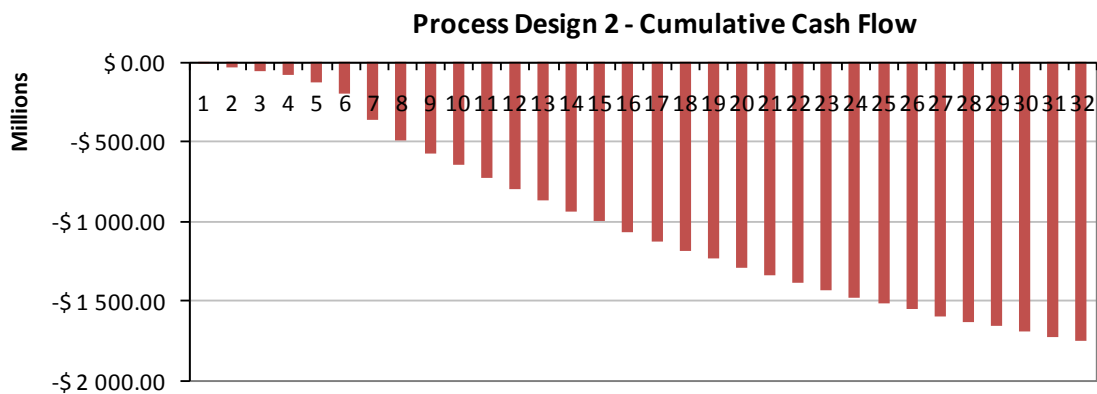


Figure 30: Cumulative cash flow diagram over the life of the project for Process Design 2

This design is not profitable in current economic conditions. The total variable operating cost is a relatively large negative cash outflow and the TPCC is also second most expensive of all the designs. For this process design break even occurs at:

- a butanol selling price of \$1850 per T (current price \$1234.5 per T)
- or molasses price need to drop to \$128 per T (current price \$212.67 per T)

The minimum required butanol price is slightly higher than the maximum price over the past 5 years, and for molasses, the maximum allowed price is somewhat higher than the minimum price over the past 5 years.



## 5.5 Process Design 3

### 5.5.1 Project Capital and Operating Cost

**Table 66: Total project capital cost for Process Design 3**

Total Project Capital Cost	
Total Installed Cost	\$ 123 967 967.00
Total Installed Equipment Cost	\$ 74 390 200.00
A100 - Pre-treatment and sterilization	\$ 1 769 200.00
A200 - Fed-batch fermentation with <i>in situ</i> gas stripping	\$ 66 351 500.00
A300 - LLE and distillation	\$ 6 269 500.00
Other (additional expences and support infrastructure)	\$ 49 577 767.00
Indirect Cost	\$ 19 972 900.00
G and A Overheads	\$ 3 425 740.00
Contract Fee	\$ 3 461 660.00
Contingencies	\$ 13 085 500.00
Total Project Cost	\$ 143 940 867.00
Adjusted Total Project Cost	\$ 187 345 000.00

**Table 67: Total variable operating cost for Process Design 3**

Total Variable Operating Cost	
Total Raw Material Cost	\$ 60 027 000.00
Total Product Sales	\$ -151 767 530.00
Main Product Sales	\$ -146 634 000.00
By-product Sales	\$ -5 133 530.00
Utility Cost	\$ 21 223 480.00
Electricity	\$ 19 982 600.00
Steam (HPS)	\$ 402 979.91
Cooling Water	\$ 12 111.14
Refrigerant Freon 12	\$ 825 788.95
Total Variable Operating Cost	\$ -70 517 050.00

**Table 68: Total fixed operating cost for Process Design 3**

Total Fixed Operating Cost	
Total Operating Labour and Maintenance Cost	\$ 763 000.00
Operating Labour	\$ 320 000.00
Maintenance	\$ 163 000.00
Supervision	\$ 280 000.00
Other Operating Cost	\$ 7 156 700.00
Operating Charges	\$ 170 000.00
Plant Overhead	\$ 381 500.00
G and A Cost	\$ 6 605 200.00
Total Fixed Operating Cost	\$ 7 919 700.00

### 5.5.2 Discounted Cash Flow and Sensitivity Analyses

Table 69: Profitability indicators for Process Design 3

Profitability Indicators		
NPV (Net Present Value)	\$ 958 286 000.00	end of project life
IRR (Internal Rate of Return)	35.96	percent
NRR (Net Return Rate)	41.85	percent
PO (Payout Period)	6.60	years
PI (Profitability Index)	1.42	percent

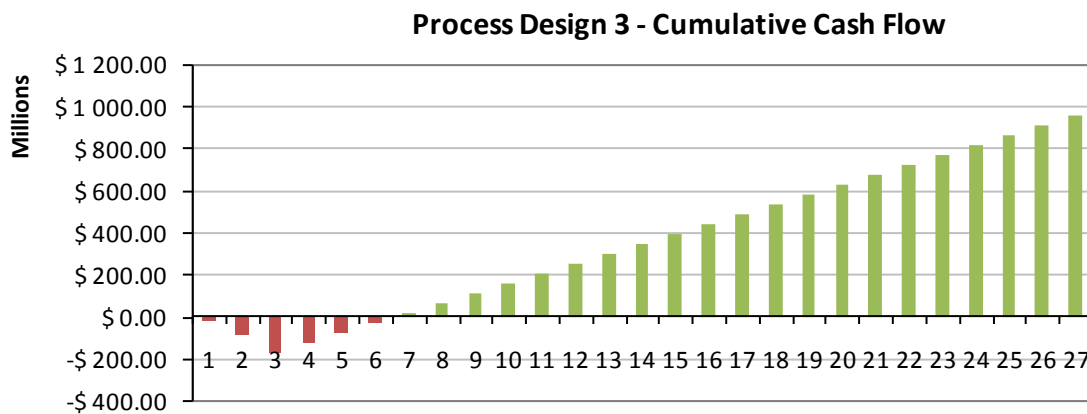


Figure 31: Cumulative cash flow diagram over the life of the project for Process Design 3

This is the only process design in this study that is profitable in current economic conditions. TPCC and raw material cost for this design is the lowest of all the process designs. Break even occurs at the following prices:

- butanol selling price can drop to \$720 per T (current price \$1234.5 per T)
- molasses price must increase to \$440 per T (current price \$212.67 per T)

This butanol price is lower than the minimum price over the past 5 years, and the molasses price is much higher than the maximum value in price history. Fed-batch fermentation with *in situ* gas-stripping greatly increase fermentation productivity and also solvent concentration obtained after the fermentation process. The combined effect of the latter and LLE process have as result smaller, less expensive equipment. Total fixed operating cost is also the lowest of all the process designs due to the smaller equipment. Where in previous designs process area A200 contributed an average of 74% to total installed equipment cost, in this design it is 89% due to the expensive compressors needed for gas-stripping. The compressors also contribute a large fraction to the utility cost (specifically electricity). The TPCC of this process design is very similar to a simulated

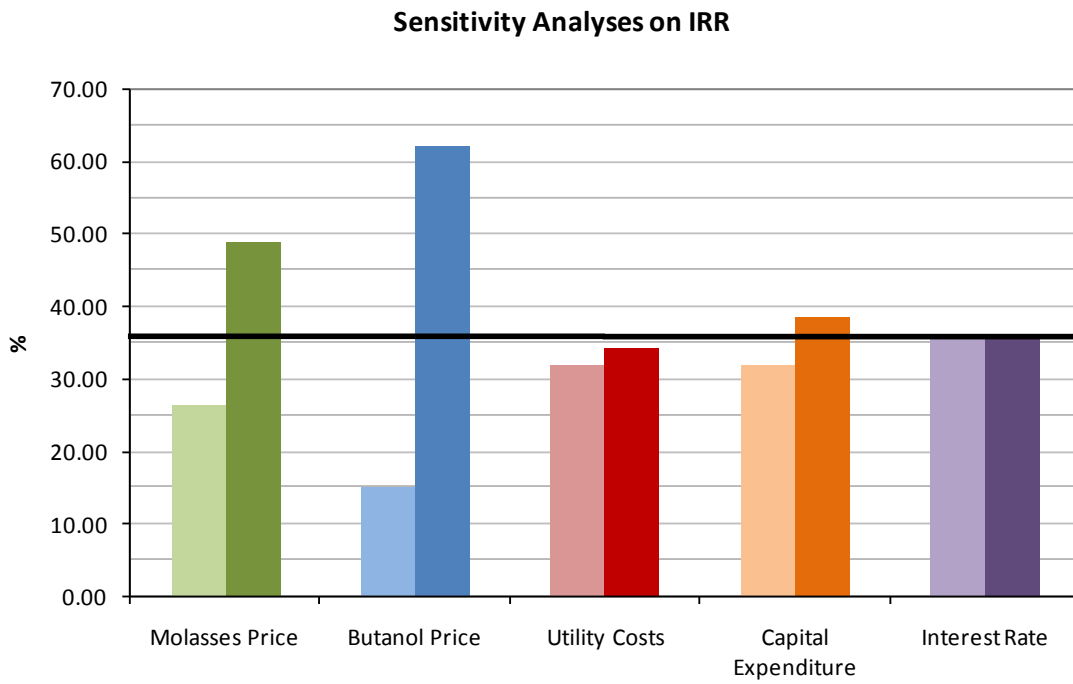
process in literature that use the same technology and produce a similar annual butanol flowrate (Bohlmann, 2007).

The sensitivity analyses proved Process Design 3 to be economically viable over a wide range of various parameters. For the worst case scenario (the combined effect of the worst economic conditions for all the parameters tested in the sensitivity analyses) the break even butanol selling price is \$1490 per T, which is only slightly higher than current market price of \$1234.5 per T.

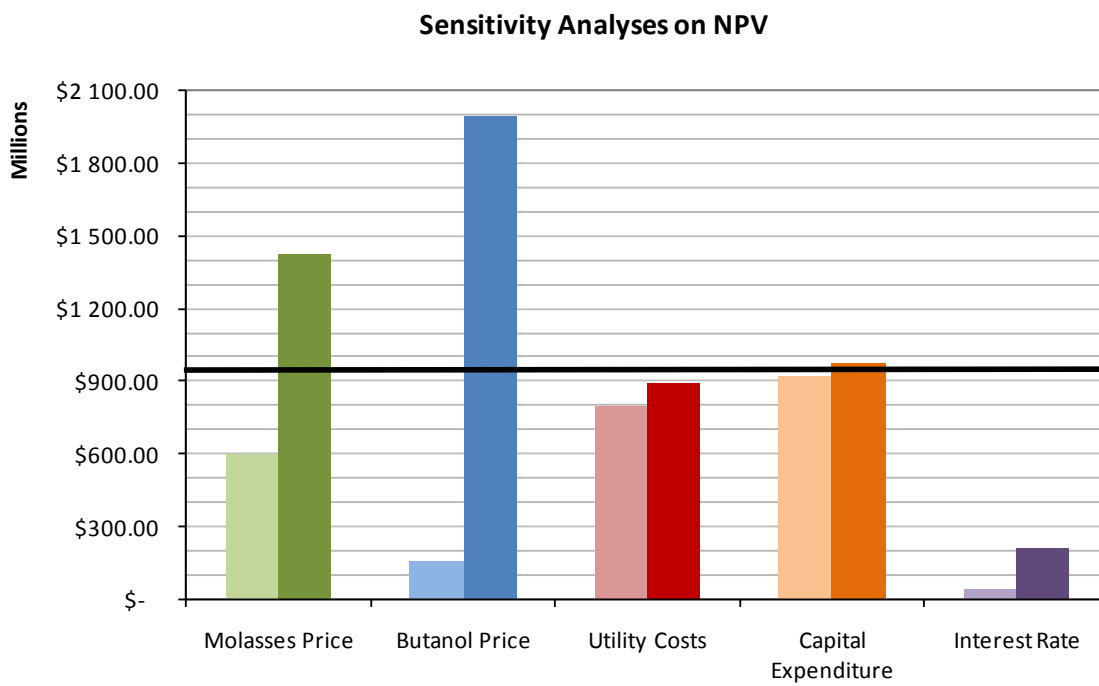
**Table 70: Parameters and results for sensitivity analyses of Process Design 3**

Sensitivity Analyses - NPV (\$) and IRR (%)				
Variable	Scenario 1		Scenario 2	
Molasses Price	\$300/MT		\$100/MT	
	\$ 595 374 000.00	26.30	\$ 1 426 500 000.00	48.87
Butanol Price	\$800/MT		\$1800/MT	
	\$ 156 693 000.00	15.09	\$ 2 001 560 000.00	62.18
Utility Costs	+50%		+20%	
	\$ 801 972 000.00	31.77	\$ 895 761 000.00	34.28
Capital Expenditure	+20%		-10%	
	\$ 924 932 000.00	31.90	\$ 974 964 000.00	38.56
Interest Rate	30%		20%	
	\$ 37 934 400.00	35.96	\$ 209 977 000.00	35.96

It is seen that this design is most sensitive to fluctuation in feedstock and product prices. Although the electricity requirements of this process design are the largest of all the designs, the overall utility requirements are the smallest. Due to this low overall utility requirement of Process Design 3, increasing utility costs have a much smaller influence on NPV and IRR than changes in feedstock and product price. In the following two figures, the thick black line indicates the values obtained for the scenario that was run for current economical conditions. These figures are merely a graphical illustration of Table 70 and all the colours are the same as the values in this table.



**Figure 32: Sensitivity analyses of various factors and its influence on IRR for Process Design 3**



**Figure 33: Sensitivity analyses of various factors and its influence on NPV for Process Design 3**

## 6 Comparison of Process Designs

### 6.1 Basis and Accuracy of Process Designs

To the knowledge of the authors, these process designs, using molasses as feedstock in South Africa, are novel. All the process designs in this study are based on a thorough literature study; designs are similar to previous models (mostly for corn to butanol production processes in USA) and the data of fermentation studies on improved strains are used (mostly for glucose fermentation). Although all the process designs are based on literature data, none of the designs are identical (or directly comparable) to process models from literature.

The simulated process designs are robust and thermodynamically rigorous. NRTL-HOC is the most accurate thermodynamic model available in the ASPEN PLUS® 2006 package that was used for simulation in this study. LLE and gas-stripping are the only process steps where there are uncertainty and more accurate thermodynamic data is needed to better predict the behaviour of the components in this system for these process steps.

It is assumed that the plant sizes of the process designs are optimal for the specific location, but it is strongly recommended that in future an analysis be done to obtain a plant size for which the overall cost are minimal in the specific location. All the process designs have identical molasses feed streams, except for the feed of Process Design 3, which differs from the rest. These feed stream sizes are based on optimal feed stream sizes for corn to ethanol production in USA (National Renewable Energy Laboratory, 2002). Final butanol product streams for all the process designs in this study fall within the range of 118 000 to 167 000 T per annum (see **Figure 34**). Process designs in literature ranged in size of annual butanol production between 80 000 and 100 000 T (Roffler, et al., 1987; Bohlmann, 2005).

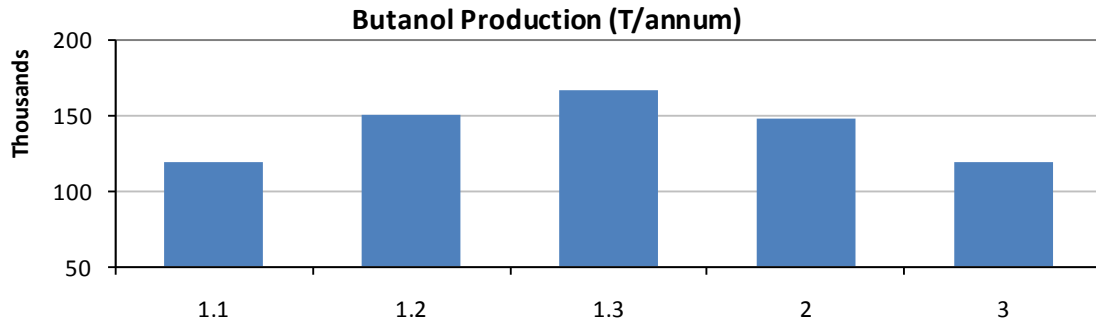


Figure 34: Annual butanol production of all the process designs

## 6.2 Fermentation Strains

Ultimately, the use of improved strains (tested in this study) is not sufficient to attain an economic viable process design for the conditions of this study. This is clear when looked at the process economics of process designs in Process Route 1 (see Figure 36). For the latter, previous industrial technology were implemented (batch fermentation and steam stripping distillation) and only different fermentation strains were used for the various process designs within this process route.

Table 71: Fermentation strains used in process designs

Process Design	Strain	Total Solvents Concentration (g/L)	Yield (%)	Productivity (g/L.h)	A:B:E
	<i>C. acetobutylicum</i>				
1.3 & 2	PC SIR-10 <sup>a</sup>	19.2	34.0	0.42	1.8 : 95.3 : 2.9
1.1	ATCC 824 <sup>b</sup>	20.6	42.0	0.58	26.2 : 66.5 : 7.3
	<i>C. beijerinckii</i>				
1.2 & 3	BA 101 <sup>c</sup>	24.2	42.0	0.34	17.8 : 81 : 1.2

<sup>a</sup> determined by Syed (1994)  
<sup>b</sup> determined by Roffler *et al.* (1987)  
<sup>c</sup> determined by Ezeji *et al.* (2004)

From the process designs it is concluded that designs with low volumetric productivity have a much higher TPCC. With lower volumetric productivity, equipment sizes (specifically fermentors) are larger and much more expensive. Process Design 1.3, using the fermentation strain with the lowest productivity, has by far the largest TPCC of all the process designs.

Higher total solvent concentration in fermentation, even if it comes at a slightly lower productivity, is vital to increase the profitability of biobutanol production. Despite the

fact that Process Design 1.3 has the highest TPCC, it is also the most profitable process of all the designs within Process Route 1. This can be attributed to the fact that the fermentation strain in this design produces the largest total solvent concentration during fermentation which renders the largest butanol product stream of all the designs (see **Figure 34**). This larger butanol stream reduces the variable operating cost of Process Design 1.3 due to the larger volume of products being produced from the same molasses feed stream as the other models in Process Route 1.

There is no advantage in producing higher butanol purity at the expense of lower total solvent concentration and decreased productivity. This conclusion is drawn from comparison of Process Designs 1.1 and 1.2. If butanol is the sole product in the design (as with Process Design 1.2), the downstream processing is less expensive. However, due to the lower productivity the fermentors are more expensive (TPCC is also larger) in Process Design 1.2 and due to the lower total solvent concentration the utility cost is also larger. This design is also more susceptible to fluctuation in butanol selling price than process designs with a wider range of products.

To conclude, for fermentation strains tested in this study it is seen that larger volumetric productivity decreases the TPCC, and larger solvent yield and final ABE concentration have as result a larger butanol product stream and lower utility cost and thus an increase in process profitability. Higher butanol purity and concentration will lower energy requirements for product purification. Gapes (2000) concluded that “if average yields above 33% can be sustained then the economics of the AB-fermentation process will improve slightly, however, it must be noted that even if yields reach their theoretical maximum this alone will not make the process economic. Other factors such as substrate and production costs are much more important”. Marlatt and Datta (1986) have shown that if the volumetric productivity can be increased by 50% and an improved strain which tolerates slightly higher butanol concentrations be used, the production cost of biobutanol will be similar to that of synthetic butanol. Woods (1995) stated that if the final solvent concentration can be increased to the levels of 22-28 g/L and if the batch fermentation time of 40-60 hours (i.e. productivity) can be maintained, the fermentation process should be viable. None of the strains tested in this study performed within the

above mentioned ranges. Lower yields are also expected at a commercial scale than that of the laboratory results used in this study. Nevertheless, both solvent productivity and final solvent concentration can be increased (at least under laboratory conditions) and this can improve the economic feasibility (Gapes, 2000). A more complete understanding of gene expression will also enable the development of improved second-generation strains capable of utilizing mixtures of lignocellulosic-derived sugars and resistant to microbial inhibitors in the lignocellulosic hydrolyzate. (Ezeji, et al., 2004; Ezeji, Qureshi, & Blaschek, 2007).

### **6.3 Process Technology**

The process technology used for previous commercial production of biobutanol (batch fermentation with steam stripping distillation) cannot compete with the petrochemical pathway for butanol production (see Process Route 1). Advanced fermentation and novel downstream processing techniques are needed to render a process economic viable.

#### **6.3.1 Fermentation**

The most effective process step to increase the volumetric productivity of a design is to employ fed-batch fermentation (with *in situ* gas stripping) instead of batch fermentation. Increasing the productivity of a process does not guarantee economic viability seeing that there are extra costs associated with continuous sterile operation of the fermentation process. However, process designs that have low overall process productivity (specifically that using batch fermentation) have much higher TPCC due to the fact that the equipment is larger and more expensive. Large sterilisable pressure vessels for fermentation are very expensive and account for roughly 60-70% of the equipment cost (Gapes, 2000). This effect of batch vs. fed-batch fermentation is clearly seen when comparing Process Routes 1 & 2 (batch fermentation) with Process Route 3 (fed-batch fermentation). The overall productivity of Process Design 3 is the highest, and its TPCC is the lowest of all the designs (see section 6.3.3 for more on the gas stripping process).

#### **6.3.2 Liquid-Liquid Extraction**

The only advantages in employing LLE is lower energy requirements (utility cost) and a wider range of products being recovered. Total equipment cost of a process using LLE (Process Design 2) as apposed to simple distillation (Process Design 1.2) is higher due to



expensive extraction columns and the need for centrifugation prior to LLE. Utility cost for the design using LLE is however much cheaper and product sales are up seeing that a larger volume butanol, as well as acetone and ethanol are recovered. The effect of LLE is apparent when comparing the latter two designs seeing that the same fermentation strain is used for these two process designs. Despite the higher TPCC of Process Design 2, this latter model is only slightly more profitable (2.6% reduction in minimum butanol selling price) than Process Design 1.2 due to the lower utility cost and larger volume products recovered. Dadgar and Foutch (1988) determined that the LLE process can lead to a 15% reduction in butanol production cost. Gapes (2000), however, also established that from an investment cost point of view, the choice of product separation technology for removal of product from the beer is not of deciding importance seeing that most advanced separation technologies incur investments of similar magnitude (some are even more expensive) than distillation columns. None of the LLE process designs simulated in literature proved to be economic viable (Roffler, et al., 1987; Dadgar & Foutch, 1988). Process Design 2 will be less susceptible to increasing energy costs and it is expected that its overall carbon emissions will also be lower due to lower total energy requirements (the energy requirements will be analyzed in more detail in section 6.4).

### 6.3.3 Gas Stripping

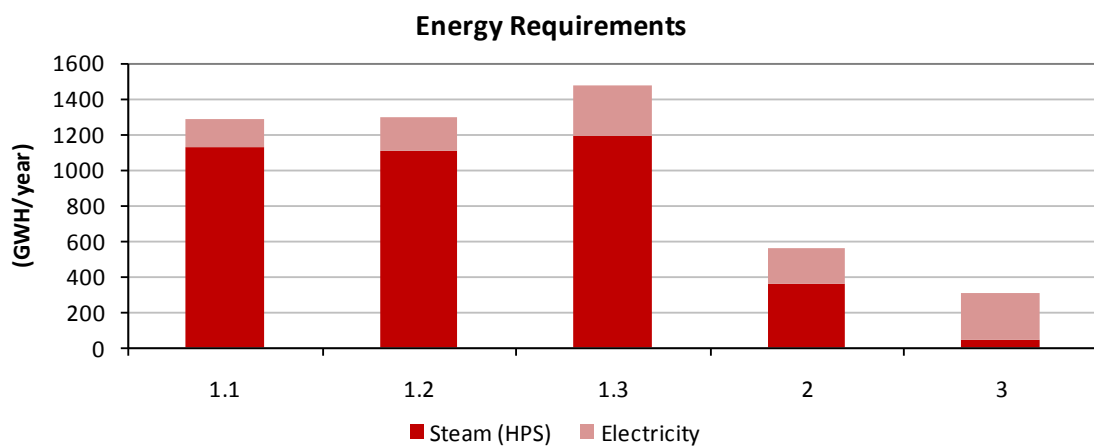
As stated in section 6.3.1, gas stripping (integrated with fed-batch fermentation) is the single most effective process step (tested in this study) that increases the productivity, and thereby the profitability, of the process. The combined effect of gas stripping and LLE is seen from comparison of Process Designs 1.3 and 3 (same fermentation strain used; *C. beijerinckii* BA 101). Relative to the amount of molasses fed, Process Design 3 has by far the largest butanol product stream of all the designs.

The increased productivity and final ABE concentration obtained after fermentation in Process Design 3 are key factors to this design being the only profitable process design in current economic conditions, able to compete with synthetic butanol production. Ezeji, et al., (2004) stated that fed-batch fermentation with integrated gas-stripping dramatically increase the productivity to the point that fermentative-butanol production process is expected to become competitive with petrochemically derived butanol. The

gas stripping process design of Bohlmann (2007), for butanol production from corn, was not able to compete with the petrochemical pathway for butanol production.

#### 6.4 Energy Performance

It is seen from Figure 35 that of all the advance processing techniques tested in this study, LLE is the process step that has the largest effect on reducing energy requirements. The reduction in energy requirements of the processing techniques in this study correlate well with the study of Qureshi, et al., (2005) (see Figure 11). Steam stripping distillation is the most energy intensive (Process Designs 1.1, 1.2 and 1.3), followed by gas stripping, and LLE (Process Design 2). The effect of purely gas stripping could not be determined (seeing that Process Design 3 implement both gas stripping an LLE), but when comparing Process Designs 2 and 3, the biggest difference is the gas stripping process (in Process Design 3). This latter design has the lowest energy requirements, but the reduction in energy requirements due to the LLE process is larger than that of gas stripping.



**Figure 35: Annual energy requirements for steam and electricity of all the process designs**

The total utility cost of Process Design 3 is similar to that of Process Design 1.1 (comparable due to same annual butanol production), but electricity contributes 94% of the utility cost in Process Design 3; cooling water requirements are down 47% and steam 96.3% from that of Process Design 1.1. Due to the need for compressors in the gas stripping process, Process Design 3 has very large electricity requirements.

Energy use is very dependant on the product purity requirements for end use, as well as the composition of product in the fermentation broth. Liu, et al., (2009), concluded that,

given the specific fermentation broth composition, the energy use of the distillation towers can be reduced by as much as 30% if the requirement on the purity of butanol is reduced from 99.5 wt% to 99 wt%. Reducing the purity requirement of ethanol to 96 wt% will also have a result large savings in energy. The development of new fermentation strains, capable of completely eliminating the production of ethanol, will eliminate the ethanol-water azeotrope in the system and result in major reduction of energy requirements.

**Table 72: Summary of energy performance results for all the process designs**

Energy Performance					
Process Design	1.1	1.2	1.3	2	3
NEV (MJ/L of butanol)	-5.54	0.53	0.55	12.55	18.75
ER	0.83	1.02	1.02	1.88	3.33

The NEV result for Process Design 1.1 show that biobutanol in this design requires more energy to make than it is able to produce. This value is much lower than the rest of the designs due to the small volume of butanol being produced. All the other designs show favourable results (NEV is positive and ER larger than 1), but these results are all for conceptual designs of only the production process. It is expected that the values will drop once the entire life cycle of biobutanol is taken into consideration.

Only Process Designs 2 and 3 are considered to be in a favourable energy performance position (taking into account that the energy performance values will drop for more detail designs). Currently the ER values for these two designs show that there is respectively an 88% and 233% gain in energy for all the inputs in these processes. The energy performance values in Table 72 can be compared to the study of Nguyen, et al., (2008) on a complete lifecycle energy analysis of the ethanol production process from molasses. In the latter study NEV values ranged between -5.67 and 13.92, and ER values between 1.39 and 7.22, depending on the different designs considered. Nguyen, et al., (2008) also stated that for each MJ of fossil energy inputs to produce molasses ethanol, there is a 39% energy gain (ER = 1.39) compared to that of gasoline and diesel fuels, where there is a 19.5% and 15.7% energy loss, respectively. These findings highlight the positive effect of renewable fuel production in helping to reduce the dependence on non-renewable energy resources (Nguyen, et al., 2008).

## 6.5 Process Economics

In sections 6.2 and 6.3 the influence of fermentation strains and processing technology on process economics has already been discussed.

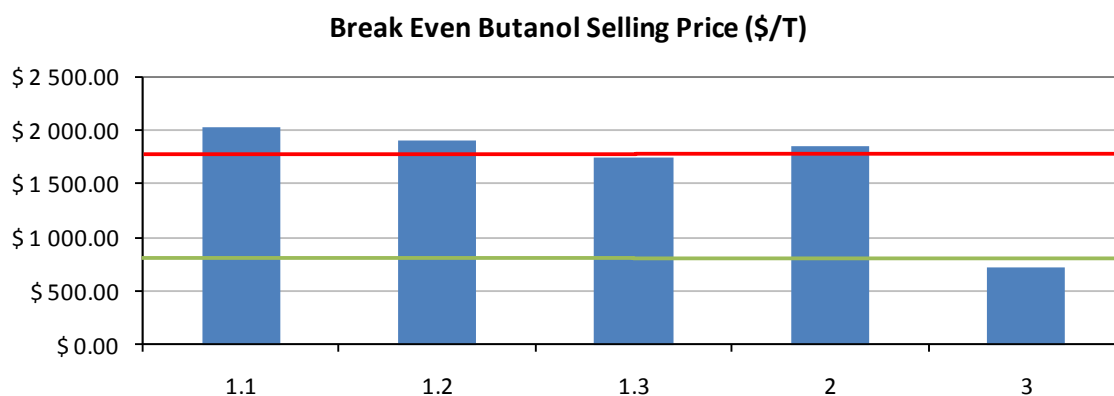
From this study it is seen that Process Design 3 (118 800 T/annum butanol) is the only profitable model and has the lowest TPCC of \$ 187 million. This price is comparable to that of the process design simulation by Bohlmann (2007) for a corn to biobutanol process that also employs fed-batch fermentation with *in situ* gas stripping: over \$ 250 million (2007) for the grass roots plant producing 85 000 T/annum butanol. An amount of \$ 48.3 million (2007) is associated with corn milling prior to the fermentation, which is not necessary for the molasses to butanol process. If the total installed cost (equipment and support infrastructure) of Process Design 3 is compared to the total installed cost of only the fermentation and solvent recovery sections in the Bohlmann (2007) design, Process Design 3 is only 2.5 million less expensive. Therefore these two designs correlate very well if additional equipment associated with corn processing are left out of the equation.

Although some models may be profitable in certain economic conditions, the cost of production and of capital expenditure must also be considered, seeing that this can be a hurdle for investors e.g. of all the designs in Process Route 1, Process Design 1.3 is the most profitable, but also has the highest TPCC (\$532 million). Similarly, when comparing Process Designs 1.2 and 2, the higher investment cost associated with LLE should be weighed against the advantages (e.g. reduction in energy requirements) of this process route. A large capital investment prior to production will greatly reduce the number of possible investors and effectively exclude financially weak consortia, a position which is worsened by the increased risk associated with new and innovative processes (Gapes, 2000). Major reductions in investment costs (as for Process Design 3) will help improve process economics.

As seen in the sensitivity analysis of Process Design 3 (section 5.5.2), feedstock and product price (or volumes) has a major influence on the overall profitability of the process design. For Process Route 1 it was determined that the process designs will be

profitable as long as the molasses price is lower than 120 \$/T. For Process Route 2 this maximum molasses price is 128 \$/T. Process Route 3 is profitable even if the molasses price reach a high of 440 \$/T. Gapes (2000) concluded that above a feedstock price of approximately 93-134 \$/T the fermentative-butanol process cannot be economic unless subsidies or other support measures are available.

Using molasses as feedstock can result in large fluctuations in the biobutanol selling price and influence the viability of the production process. For ethanol production molasses is already a common feedstock, especially in tropical countries. There is however a constant risk of shortage due to high demands for this commodity in both domestic and international markets resulting in large fluctuations in molasses price. Another disadvantage is that molasses is a by-product of the sugar industry; hence its production rates are strongly governed by sugar cane and sugar production conditions (Nguyen, et al., 2008). It is therefore recommended that other feedstocks, like bagasse, be included in the biobutanol production process to minimise the effect of the fluctuation in molasses price.



**Figure 36: Minimum butanol selling price of every process design to break even under current economic conditions (red and green lines indicate past 5 years maximum and minimum butanol market price)**

## 7 Conclusions

The conclusions on the main objectives of this study are:

- Process Design 3, using fermentation strain *Clostridium beijerinckii* BA 101 in fed-batch fermentation with *in situ* gas stripping followed by LLE and steam stripping distillation, is the only profitable process design in current economic conditions.
- The first order estimate of the TPCC for Process Design 3 is \$ 187 345 000.00 (IRR: 35.96%) (118 800 T butanol per annum).

Other important conclusions from this study are:

- There was sufficient information available in literature to develop robust and thermodynamically rigorous process designs for simulation.
- For simulation of the system in this study, NRTL-HOC is the most accurate thermodynamic model available in ASPEN PLUS® 2006 (simulations package used).
- *Clostridium beijerinckii* BA 101 is the strain that yielded the most economic viable process, although improved fermentation strains currently available are not sufficient to attain a profitable process design without implementation of advanced processing techniques.
- The general trend of the fermentation strains are that increasing productivity decreases the TPCC, and increasing solvent yield and final ABE concentration have as result a larger butanol product stream and thus increases the project profitability. Higher butanol purity and concentration will lower energy requirements for product purification.
- Process technology previously used for commercial production of biobutanol (batch fermentation with steam stripping distillation) cannot compete in current economic conditions with the petrochemical pathway for butanol production.
- Fed-batch fermentation with *in situ* gas stripping is the single most effective process step (tested in this study) that increases the productivity, and thereby the profitability, of the process.
- The overall effect of LLE, in terms of profitability of the process design, renders only a slight improvement over basic steam stripping distillation. LLE reduce utility requirements and increase product recovery, but increase the TPCC.

- Of all the process technologies simulated in this study, LLE is the process step with the largest capability for reducing energy requirements in a design.
- The combined effect of fed-batch fermentation and gas stripping renders a very profitable design that can be employed on an industrial scale.
- Only Process Designs 2 and 3 are in favourable energy performance positions (NEV is a large positive and ER are much larger than 1), producing a product with more energy than is required for the production process.
- These models are very sensitive to changes in molasses price and using molasses as feedstock can result in large fluctuations in the biobutanol selling price and influence the viability of the production process.
- Maximum feedstock price for Process Route 1 to be economic viable is 120 \$/T, and for Process Route 2 it is 128 \$/T. Process Route 3 is profitable even if molasses price reach a high of 440 \$/T.

## 8 Recommendations

For improving the exiting process designs it is recommended that:

- Improved physical property methods be used for more accurate simulation of the system (e.g. SAFT), existing interaction parameters be updated, and missing parameters be obtained (either from literature or experimental work). This is very important for the process steps of LLE and gas stripping.
- An analysis is done to determine the optimal plant size for the specific geographical location in order to minimize the overall cost.
- Feedstock composition is updated for simulation to more accurately portray the molasses that will be used in the final design and to improve mass and energy balances. This includes building a database (or updating the existing ASPEN PLUS® database) to include components and properties that are contained in molasses.
- Laboratory experiments are performed with the selected biocatalyst to obtain fermentation parameters that are optimised for the specific feedstock, and to determine the nutrient requirements for final design.
- For simulating the fermentation process, improved stoichiometric reactions must be developed to include all side reaction taking place as well as reactions for sugars that were not included in this design (once these component are developed for simulation). Reaction kinetics can also be included and the process be simulated with more complicated unit options in ASPEN PLUS®. The overall fermentation schedule should be optimized together with the seed fermentation train (sizes and fermentation times).

In addition to these process designs, the following are recommended:

- These designs should be integrated more with the sugar refining process (a sugar mill plant) in order for better energy integration and optimization of waste stream utilization. This will ensure better economics for both sugar refining and biobutanol production.



- A comprehensive energy analysis must be done on the life cycle of the product/biofuel to determine the overall energy requirements (cradle to grave) and to optimise energy integration.
- The biorefinery concept should be developed (e.g. capturing and selling of off-gasses and biomass waste)
- The environmental impact analysis of such a biobutanol plant must be done (e.g. air emissions, greenhouse gasses, water pollution, etc.) and areas identified where improvements to the system must be made to render a more environmental friendly plant.

## 9 References

- Antoni, D., Zverlov, V., & Schwarz, W. (2007). **Biofuels from microbes**. *Appl Microbiol Biotechnol* , 23-35.
- Aspen Technology, Inc. (2006). **Aspen IPE 2006 User Guide**. Cambridge: Aspen Technology, Inc.
- Bamberger, A., & Maurer, G. (2000). **High-pressure (vapour + liquid) equilibria in (carbon dioxide + acetone or 2-propanol) at temperatures from 293 K to 333 K**. *J. Chem. Thermodynamics* , 32: 685–700.
- Bohlmann, G. (2007). **Biobutanol**. California: SRI Consulting.
- Bohlmann, G. (2005, November 11). **Biorefinery Process Economics**. Retrieved May 20, 2008, from redOrbit: [http://www.redorbit.com/news/science/302283/biorefinery\\_process\\_economics/index.html](http://www.redorbit.com/news/science/302283/biorefinery_process_economics/index.html)
- Brekke, K. (2007, March). **Butanol: An Energy Alternative?** *Ethanol Today* , pp. 36-39.
- Carlson, E. (1996). **Don't Gamble With Physical Properties For Simulations**. *Chemical Engineering Progress* , 35-46.
- Chemical Engineering. (2009, June). **Economic Indicators**. Retrieved September 2009, from Chemical Engineering: [http://www.che.com/business\\_and\\_economics/economic\\_indicators.html](http://www.che.com/business_and_economics/economic_indicators.html)
- Chiao, J., & Sun, Z. (2007). **History of the acetone-butanol-ethanol fermentation industry in China: Development of continuous production technology**. *Journal of Molecular Microbiology and Biotechnology* , 12-14.
- Chuichulcherm, S., & Chutmanop, J. (2000). **Butanol separation from ABE model fermentation broth by liquid-liquid extraction**.
- Dadgar, A., & Foutch, G. (1988). **Improving the acetone-butanol fermentation process with liquid-liquid extraction**. *Biotechnology Progress* , 4:36-39.
- Doble, M. (2006). **Avoid the Pitfalls of bioprocess development**. *CEP* , 34-41.
- Dow. (2006, May 2). **Product Safety**. Retrieved August 7, 2008, from DOW: <http://www.dow.com/productsafety/finder/nbut.htm#ProdUses>
- DuPont. (2006, June 20). **News Releases**. Retrieved August 4, 2008, from DuPont: [http://vocuspr.vocus.com/VocusPR30/Newsroom/Query.aspx?SiteName=DupontNew&Entity=PRASSET&SF\\_PRAAsset\\_PRAAssetID\\_EQ=102087&XSL=PressRelease&Cache=False](http://vocuspr.vocus.com/VocusPR30/Newsroom/Query.aspx?SiteName=DupontNew&Entity=PRASSET&SF_PRAAsset_PRAAssetID_EQ=102087&XSL=PressRelease&Cache=False)
- Dürre, P. (2008). **Fermentative Butanol Production**. *Annals of the New York Academy of Sciences* , 353-362.
- Dürre, P. (1998). **New insights and novel developments in clostridial acetone/butanol/isopropanol fermentation**. *Appl Microbiol Biotechnol* , 639-648.
- Eckert, G., & Schugerl, K. (1987). **Continuous acetone-butanol production with direct product removal**. *Appl Microbiol Biotechnol* , 27:221-228.
- El-Zanat, E., Abdel-Hakim, E., El-Ardi, O., & Fahmyb, M. (2006). **Modeling and simulation of butanol separation from aqueous solutions using pervaporation** . *Journal of Membrane Science* , 280:278-283.

- Ezeji, T., & Blaschek, H. (2008). **Fermentation of dried distillers' grains and solubles (DDGS) hydrolysates to solvents and value-added products by solventogenic clostridia.** *Bioresource Technology* , 99:5232–5242.
- Ezeji, T., Karcher, P., Qureshi, N., & Blaschek, H. (2005). **Improving performance of a gas stripping-based recovery system to remove butanol from *Clostridium beijerinckii* fermentation.** *Bioprocess Biosyst Eng* , 27: 207–214.
- Ezeji, T., Qureshi, N., & Blaschek, H. (2005). **Patent No. 60/504,280.** United States of America.
- Ezeji, T., Qureshi, N., & Blaschek, H. (2004). **Acetone-butanol-ethanol production from concentrated substrate: reduction in substrate inhibition by fed-batch technique and product inhibition by gas stripping.** *Appl Microbiol Biotech* , 63:653-659.
- Ezeji, T., Qureshi, N., & Blaschek, H. (2007). **Bioproduction of butanol from biomass: from genes to bioreactors.** *Biotechnology* , 220-227.
- Ezeji, T., Qureshi, N., & Blaschek, H. (2004). **Butanol Fermentation Research: Upstream and Downstream Manipulations .** *The Chemical Record* , 305-314.
- Ezeji, T., Qureshi, N., & Blaschek, H. (2007). **Butanol Production From Agricultural Residues: Impact of Degradation Products on *Clostridium beijerinckii* Growth and Butanol Fermentation.** *Biotechnology and Bioengineering* , 97:1460-1469.
- Ezeji, T., Qureshi, N., & Blaschek, H. (2005). **Industrially relevant fermentations.** In P. Durre, *Handbook on Clostridia* (pp. 797-812). Boca Raton, Florida: CRC Press, Taylor and Francis Group.
- Ezeji, T., Qureshi, N., & Blaschek, H. (2003). **Production of butanol by *Clostridium beijerinckii* BA101 and in-situ recovery by gas stripping.** *World J Microbiol Biotech* , 19:595-603.
- Ezeji, T., Qureshi, N., Karcher, P., & Blaschek, H. (2006). **Butanol production from corn.** *Alcoholic Fuels: Fuels for Today and Tomorrow* , 99-122.
- Friedl, A., Qureshi, N., & Maddox, I. (1991). **Continuous acetone-butanol-ethanol (ABE) fermentation using immobilized cells of *Clostridium acetobutylicum* in a packed bed reactor and integration with product removal by pervaporation.** *Biotechnol Bioeng* , 38:518-527.
- Gamez, S., Gonzalez-Cabriales, J., Ramirez, J., & Garrote, G. (2006). **Study of the hydrolysis of sugar cane bagasse using phosphoric acid.** *Journal of Food Engineering* , 74:78–88.
- Gapes, J. (2000). **The Economics of Acetone-Butanol Fermentation: Theoretical and Market Considerations.** *J. Mol. Microbiol. Biotechnol.* , 2:27-32.
- Garrett, D. (1989). **Chemical Engineering Economics.** New York: Van Nostrand Reinhold.
- Ghanadzadeh, H., & Ghanadzadeh, A. (2003). **(Liquid + liquid) equilibria in (water + ethanol + 2-ethyl-1-hexanol) at T = (298.2, 303.2, 308.2, and 313.2) K.** *J. Chem. Thermodynamics* , 35:1393–1401.
- Ghanadzadeh, H., & Ghanadzadeh, A. (2004). **Liquid-Liquid Equilibria of Water + 1-Butanol + 2-Ethyl-1-hexanol System.** *J. Chem. Eng. Data* , 49:783-786.
- Ghanadzadeh, H., Ghanadzadeh, A., & Alitavoli, M. (2004). **LLE of ternary mixtures of water/acetone/2-ethyl-1-hexanol at different temperatures.** *Fluid Phase Equilibria* , 219:165–169.

- Ghanadzadeh, H., Ghanadzadeh, A., & Sariri, R. (2004). **(Liquid + liquid) equilibria for (water + acetic acid + 2-ethyl-1-hexanol): experimental data and prediction.** *J. Chem. Thermodynamics* , 36:1001–1006.
- Ghanadzadeh, H., Ghanadzadeh, A., Bahrpaima, K., & Saadat, S. (2008). **(Liquid + liquid) equilibria of (water + propionic acid + 2-ethyl-1-hexanol): Experimental data and correlation.** *J. Chem. Thermodynamics* , 40:879–884.
- Groot, W., Soedjak, H., Donck, P., & van tier Lans, R. (1990). **Butanol recovery from fermentations by liquid-liquid extraction and membrane solvent extraction.** *Bioprocess Engineering* , 5:203-216.
- Grube, M., & Gapes, J. (2002). **Application of quantitative IR spectral analysis of bacterial cells to acetone-butanol-ethanol fermentation monitoring.** *Analytica Chimica Acta* , 471:127-133.
- Hallale, N. (2001). **Optimization Application: Pinch Technology Analysis.** *Chem. Eng. Prog.* , 97:414-433.
- Huang, W., Ramey, D., & Yang, S. (2004). **Continuous production of Clostridium acetobutylicum immobilized in a fibrous bed reactor.** *Appl Biochem Biotech* , 113:887-898.
- ICIS Pricing. (2009, March 9-15). **Chemical Profile: N-butanol.** *ICIS Chemical Business* , p. 37.
- Jacques, K., Lyons, T., & Kelsall, D. (2003). **The Alcohol Textbook 4th Edition.** Nottingham: Nottingham University Press.
- Jitesh, K., Pangarkar, V., & Niranjana, K. (2000). **Pervaporative stripping of acetone, butanol and ethanol to improve ABE fermentation.** *Bioseparation* , 9:145-154.
- Jonasson, A., Persson, O., Rasmussen, P., & Soave, G. (1998). **Vapor–liquid equilibria of systems containing acetic acid and gaseous components. Measurements and calculations by a cubic equation of state.** *Fluid Phase Equilibria* , 152: 67–94.
- Jones, D. (2005). **Applied Acetone-Butanol Fermentation.** In P. Durre, *Handbook on Clostridia* (pp. 125-168). Boca Raton, Florida: CRC Press, Taylor & Francis Group.
- Jones, D., & Woods, D. (1986). **Acetone-Butanol fermentation revisited.** *Microbiological Reviews* , 484-524.
- Kneza, Z., Skerget, M., Ili, L., & Lutge, C. (2008). **Vapor–liquid equilibrium of binary CO<sub>2</sub>–organic solvent systems (ethanol, tetrahydrofuran, ortho-xylene, meta-xylene, para-xylene).** *J. of Supercritical Fluids* , 43: 383–389.
- Lavaracka, B., Griffin, G., & Rodman, D. (2002). **The acid hydrolysis of sugarcane bagasse hemicellulose to produce xylose, arabinose, glucose and other products.** *Biomass and Bioenergy* , 23:367-380.
- Lee, Y. (2005). **Oxidation of sugarcane bagasse using a combination of hypochlorite and peroxide.** Louisiana: Louisiana State University.
- Liu, F., Liu, L., & Feng, X. (2005). **Separation of acetone–butanol–ethanol (ABE) from dilute aqueous solutions by pervaporation.** *Separation and Purification Technology* , 42:273–282.
- Liu, J., Fan, L., & Seib, P. (2004). **Downstream Process Synthesis for Biochemical Production of Butanol, Ethanol, and Acetone from Grains: Generation of Optimal and Near-Optimal Flowsheets with Conventional Operating Units.** *Biotechnol. Prog.* , 20:1518-1527.

- Liu, J., Fan, L., Seib, P., Friedler, F., & Bertok, B. (2006). **Holistic Approach to Process Retrofitting: Application to Downstream Process for Biochemical Production of Organics.** *Ind. Eng. Chem. Res.* , 45 (12):4200-4207.
- Liu, J., Wu, M., & Wang, M. (2009). **Simulation of the Process for Producing Butanol from Corn Fermentation.** *Ind. Eng. Chem. Res.* , 48: 5551-5557.
- LMC International. (2009). **Sweetner Analysis: The world molasses market in 2009.** New York: LMC International Ltd.
- Lopez-Contreras, A. (2003). **Utilization of lignocellulosic substrates by solvent-producing Clostridia.** Wageningen: Wageningen University.
- Lynd, L., Wyman, C., & Laser, M. (2005). **Strategic Biorefinery Analysis: Analysis of Biorefineries.** Colorado: National Renewable Energy Laboratory.
- Marlatt, J., & Datta, R. (1986). **Acetone-butanol fermentation process development and economic evaluation.** *Biotechnol. Progress* , 2:23-28.
- Mitchell, W. (1998). **Physiology of carbohydrates to solvent conversion by clostridia.** *Adv Microb Physiol* , 39:31-130.
- Montoya, D., Spitia, S., Silva, E., & Schwarz, W. (2001). **Isolation of mesophilic solvent-producing clostridia from Colombian sources: physiological characterization, solvent production and polysaccharide hydrolysis.** *Journal of Biotechnology* , 79:117-126.
- Mussatto, I., & Roberto, I. (2004). **Alternatives for detoxification of diluted-acid lignocellulosic hydrolyzates for use in fermentative processes: a review.** *Bioresource Technology* , 93:1-10.
- National Renewable Energy Laboratory. (2002). **Lignocellulosic Biomass to Ethanol Process Design and Economics Utilizing Co-Current Dilute Acid Prehydrolysis and Enzymatic Hydrolysis for Corn Stover.** Colorado: National Renewable Energy Laboratory.
- Nguyen, T., Gheewala, S., & Garivait, S. (2008). **Full chain energy analysis of fuel ethanol from cane molasses in Thailand.** *Applied Energy* , 85: 722-734.
- Nimcevic, D., & Gapes, J. (2000). **The acetone-butanol fermentation in pilot plant and pre-industrial scale.** *J. Mol. Microbiol. Biotechnol.* , 15-20.
- Oceanethanol. (2007, February 21). **Oceanethanol.** Retrieved July 28, 2008, from Butanol Jet Fuel: [http://www.oceanethanol.com/CO2/Ocean\\_Ethanol/Entries/2007/2/21\\_Butanol\\_Jet\\_Fuel\\_From\\_CO2.html](http://www.oceanethanol.com/CO2/Ocean_Ethanol/Entries/2007/2/21_Butanol_Jet_Fuel_From_CO2.html)
- Parekh, M., Formanek, J., & Blaschek, H. (1999). **Pilotscale production of butanol by Clostridium beijerinckii BA101 using a low cost fermentation medium based on corn steep water.** *Appl Microbiol Biotechnol* , 51:152-157.
- Perakis, C., Voutsas, E., Magoulas, K., & Tassios, D. (2007). **Thermodynamic Modeling of the Water + Acetic Acid + CO<sub>2</sub> System: The Importance of the Number of Association Sites of Water and of the Nonassociation Contribution for the CPA and SAFT-Type Models.** *Ind. Eng. Chem. Res.* , 46: 932-938.

- Perry, R., Green, D., & Maloney, J. (1997). *Perry's Chemical Engineers' Handbook, 7th ed.* New York: McGraw-Hill.
- Peters, M., & Timmerhaus, K. (2003). *Plant Design and Economics for Chemical Engineers, 5th.* New York: McGraw-Hill.
- Price Waterhouse Coopers. (2009). *Tax Information 2009/2010.* Retrieved from PWC: [http://www.pwc.com/en\\_ZA/za/assets/pdf/pwc-taxcard-09.pdf](http://www.pwc.com/en_ZA/za/assets/pdf/pwc-taxcard-09.pdf)
- Qureshi, N., & Blaschek, H. (2005). **Butanol production from agricultural biomass.** *Food Biotechnology* , 525-551.
- Qureshi, N., & Blaschek, H. (2000). **Butanol Production using clostridium beijerinckii BA101 and recovery by pervaporation.** *Appl Biochem & Biotechnol* , 84:225-230.
- Qureshi, N., & Blaschek, H. (1999). **Butanol recovery from model fermentation broth by pervaporation - evaluation of membrane performance .** *Biomass and Bioenergy* , 17:175-184.
- Qureshi, N., & Blaschek, H. (1999). **Production of Acetone Butanol Ethanol (ABE) by a Hyper-Producing mutant strain of clostridium beijerinckii BA101 and Recovery by pervaporation .** *Biotechnol. Prog.* 1999 , 15:594-602.
- Qureshi, N., & Maddox, I. (1995). **Continuous production of ABE using immobilized cells of clostridium acetobutylicum and integration with product removal by liquid-liquid extraction.** *Journal of Fermentation and Bioengineering* , 2:185-189.
- Qureshi, N., & Maddox, I. (2005). **Reduction in butanol inhibition by perstraction: Utilization of Concentrated Lactose/Whey Permeate by Clostridium acetobutylicum to Enhance Butanol Fermentation Economics.** *Trans IChemE* , 83(C1): 43–52.
- Qureshi, N., Hughes, S., Maddox, I., & Cotta, M. (2005). **Energy-efficient recovery of butanol from model solutions and fermentation broth by adsorption.** *Bioprocess Biosyst Eng* , 27:215-222.
- Qureshi, N., Maddox, I., & Friedl, A. (1992). **Application of Continuous Substrate Feeding to the ABE Fermentation - Relief of product inhibition using extraction, perstraction, stripping and pervaporation.** *Biotechnology Progress* , 8:382-390.
- Ramey, D. (1998). **Patent No. US5753474.** United States of America, Ohio.
- Ramey, D., & Yang, Z. (2004). **Production of Butyric Acid and Butanol from Biomass.** Ohio: Environmental Energy Inc.
- Roffler, S., Blanch, H., & Wilke, C. (1987). **Extractive Fermentation of Acetone and Butanol: Process Design and Economic Evaluation.** *Biotechnology Progress* , 3:131-140.
- Roffler, S., Blanch, H., & Wilke, C. (1988). **In situ extractive fermentation of acetone-butanol.** *Biotechnology and Bioengineering* , 31:135-143.
- Roffler, S., Blanch, H., & Wilke, C. (1987). **In-situ recovery of butanol during fermentation.** *Bioprocess Engineering* , 2:1-12.
- Roffler, S., Blanch, H., & Wilke, C. (1987). **In-situ recovery of butanol during fermentation.** *Bioprocess Engineering* , 2:181-190.

- Scott, A., & Bryner, M. (2006, December 20). **Alternative Fuels Rolling Out Next Generation Technologies.** *Chemical Week* , pp. 17-21.
- Secuianu, C., Feroiu, V., & Geana, D. (2004). **High-Pressure Vapor-Liquid Equilibria in the System Carbon Dioxide + 1-Butanol at Temperatures from (293.15 to 324.15) K.** *J. Chem. Eng. Data* , 49, 1635-1638.
- Shaheen, R., Shirley, M., & Jones, D. (2000). **Comparative fermentation studies of industrial strains belonging to four species of solvent-producing clostridia.** *J. Mol. Microbiol. Biotechnol.* , 2(1):115-124.
- Short, W., Packey, D., & Holt, T. (1995). **A Manual for the Economic Evaluation and Energy Efficiency and Renewable Energy Technologies.** CO: National Renewable Energy Laboratory.
- Smith, J., & Workman, J. (2007, 12 20). **Alcohol for motor fuels.** Retrieved 07 29, 2008, from Colorado State University: <http://www.ext.colostate.edu/PUBS/FARMMGT/05010.html>
- South African Reserve Bank. (2009). Retrieved from **South African Reserve Bank:** <http://www.reservebank.co.za/>
- Spivey, M. (1978). **The acetone/butanol/ethanol fermentation.** *Process Biochem.* , 13:2-5.
- Statistics South Africa. (2009). **Latest key indicators.** Retrieved from StatsOnline: <http://www.statssa.gov.za/keyindicators/keyindicators.asp>
- Syed, Q. (1994). **Biochemical Studies on Anaerobic Fermentation of Molasses by Clostridium Acetobutylicum.** Lahore: University of the Punjab.
- Tiago Stock Consulting. (2009). **American Dollar.** Retrieved from x-rates.com: <http://www.x-rates.com/>
- Vane, L. (2004). **Options for Combining Pervaporation Membrane Systems with Fermentors for Efficient Production of Alcohols from Biomass.** *2004 AIChE Annual Meeting*, (pp. 1-6). Ohio.
- Vogel, H., & Tadaro, C. (1997). **Fermentation Biochemical Engineering Handbook - Principles, Process Design, and Equipment (2nd Edition).** Noyes: William Andrew Publishing.
- Walton, M., & Martin, J. (1979). **Production of butanol-acetone by fermentation.** *Microbial Technology* , 1:187-209.
- Woods, D. (1995). **The genetic engineering of microbial solvent production.** *Trends Biotechnol.* , 13:259-264.
- Wooley, R., & Putsche, V. (1996, April). **Development of an ASPEN PLUS Physical Property Database for Biofuels Components.** *Report MP-425-20685* . NREL.
- Wu, M., Wang, M., Liu, L., & Huo, H. (2007). **Life-cycle assessment of corn-based butanol as a potential transportation fuel.** Chicago: Argonne National Laboratory.
- Yang, X., & Tsao, G. (1995). **Enhanced acetone-butanol fermentation using repeated fed-batch operation coupled with cell recycle by membrane and simultaneous removal of inhibitory products by adsorption.** *Biotechnol Bioeng* , 47:444-450.
- Zverlov, V., Berezina, O., Velikodvorskaya, G., & Schwarz, W. (2006). **Bacterial acetone and butanol production by industrial fermentation in the Soviet Union: Use of hydrolyzed agricultural waste for biorefinery.** *Appl Microbiol Biotechnol* , 587-597.

## **Appendix A – Physical Property Methods**



Physical property methods and parameters are important throughout rigorous mass and energy balance models such as the models used for simulating the process designs in this study. The components present in the simulations (water, carboxylic acids, polar alcohols, and gasses above their critical temperatures) made for a highly complex system. This meant that no single physical property method was sufficient.

### **A.1 Selecting the appropriate physical property methods**

The choice of physical property methods is one of the most important decisions in the design of process models. It affects all subsequent tasks in developing accurate physical properties for simulation. Important factors that should be considered for property method selection are: the composition of the mixture, the temperature and pressure range, and the availability of parameters.

As already mentioned, the composition of the mixture is highly complex. Components, such as water and acetone, have strong dipoles and many of the polar compounds are associative and form complexes. Therefore, it is suggested that equation-of-state models like CPA or SAFT be used as the property method. These models explicitly account for association and will most accurately simulate the thermodynamic properties of these components (Perakis, Voutsas, Magoulas, & Tassios, 2007). However, none of the above mentioned property methods are available in the version of ASPEN that is used for this study. In all the simulations the temperatures and pressures are moderate. Methods that are based on Raoult's law, or that use activity coefficients, are not accurate at high pressure or when the temperature is above the critical temperature of a component. Henry's law is used when there are light gases in subcritical solvents (e.g. CO<sub>2</sub> and H<sub>2</sub>, which are above their critical temperatures in the simulations).

The availability of pure-component and binary parameters is a very important factor for calculating pure-component or mixture properties. ASPEN has many databanks that contain properties for components and binary parameters for different property methods. The choice of property method is highly dependant on the availability of binary parameters in ASPEN, seeing that obtaining of experimental data and regression thereof

are not in the scope of this project. Where available, data are supplemented with literature data (see the following section for parameters used in this project).

The following diagram illustrates the decision making process which were followed in choosing the property methods used in simulations. Light blocks indicate decisions made (i.e. system and component characteristics and properties) and dark blocks specify the final options for possible property methods. Almost all the property methods available in ASPEN are illustrated in this diagram.

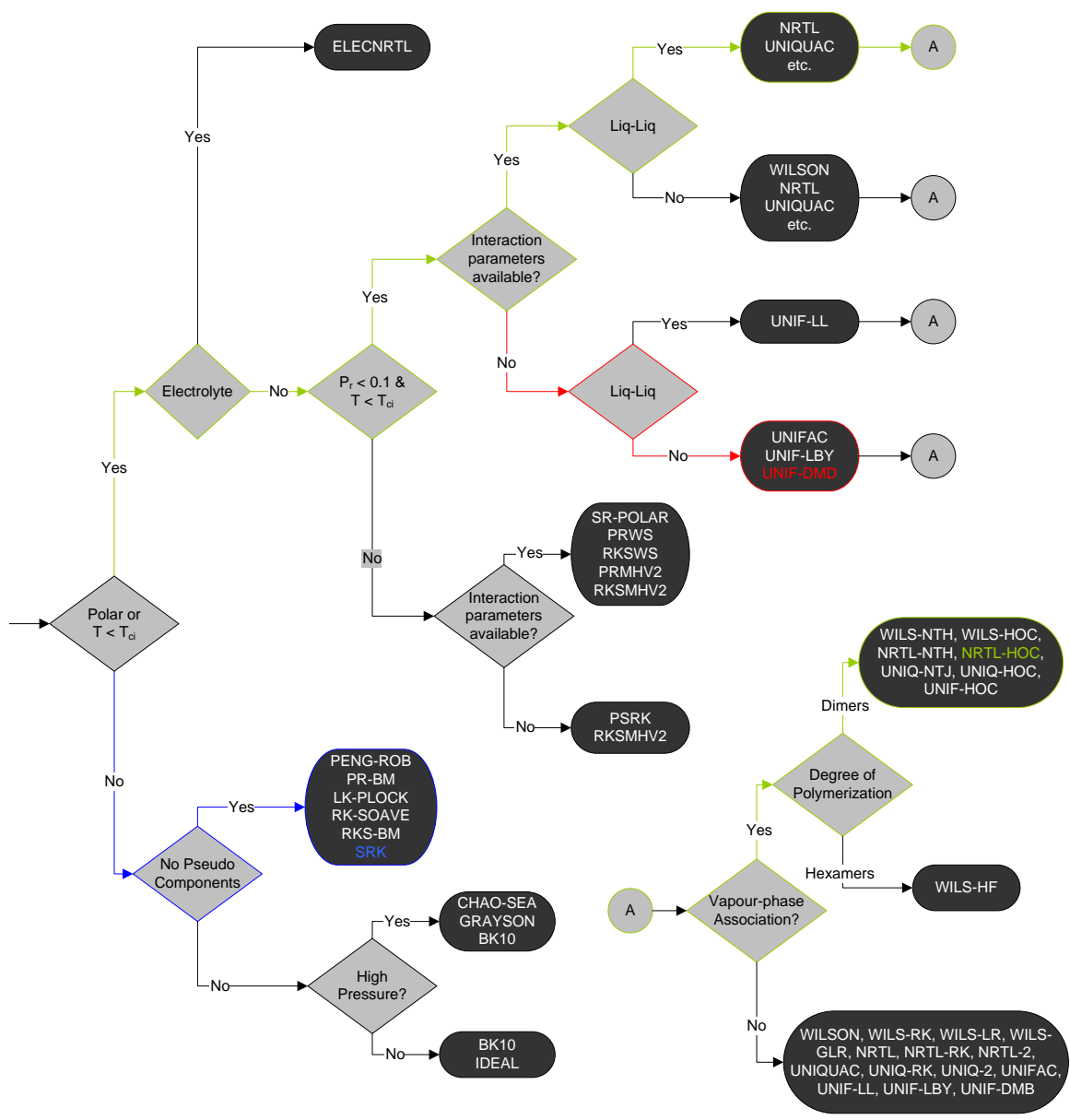


Figure 37: Property methods decision diagram

The green path is followed for the overall property method used in all the simulations (see Figure 37). This resulted in choosing the non-random two-liquid activity coefficient model using the Hayden-O'Connell vapour phase model (NRTL-HOC) option. The reasoning behind this is that, of all the models in the final block (of the green path), the NRTL-HOC model is most commonly used and many binary parameters are available for this model in ASPEN databases (same number of binary parameters as for normal NRTL). The Hayden-O'Connell equation also reliably predicts solvation of polar compounds and dimerization in the vapour phase, as occurs with mixtures containing carboxylic acids (e.g. acetic and butyric acids). There are however some missing interaction parameters. The red path is followed for these missing component pairs, seeing that no experimental or literature data were available. Of the four UNIFAC parameter estimation methods, the Dortmund method (UNIF-DMD) gives the most accurate estimate of infinite-dilution activity coefficients.

Specifically for the process step of gas stripping, the blue path is followed in order to obtain a property method that renders results similar to those obtained in literature of laboratory experiments (Ezeji, Qureshi, & Blaschek, 2004). Soave-Redlich-Kwong equation-of-state (SRK) is chosen this reason. Also, seeing that the most important phase in the gas stripping process is the vapour phase, and that the mole fraction of CO<sub>2</sub> (above its critical temperature) is larger than 0.9 in the vapour phase, it is reasoned that an equation-of-state method would more accurately simulate the vapour phase. The equation-of-state method also is more consistent in the critical region than an activity coefficient model. However, for this method (and all the other equation-of-state methods available in ASPEN), there were no binary parameters available in ASPEN or literature of the components used at the specific conditions. SRK is also the only equation-of-state method for which ASPEN can estimate missing property parameters. Therefore, the UNIF-DMD method is again used to estimate temperature dependant parameters.

## A.2 Parameters Used

Property parameters for most of the components in the system are obtained from ASPEN. Components and their parameters that are not in the ASPEN databanks are obtained

from property data developed by NREL specifically for biochemical processes (Wooley & Putsche, 1996). Components used from the NREL databank are glucose and zymo. In molasses, sucrose is present in larger quantities than glucose, but seeing that glucose is the only sugar available in this database, all the different sugars in molasses is simulated as a glucose concentration. Zymo has a chemical formula of  $\text{CH}_{1.8}\text{O}_{0.5}\text{N}_{0.2}$  and was developed to simulate *Escherichia coli* microorganisms in ethanol process designs. This component with its physical properties is used in this project to simulate the bacteria used during fermentation seeing that it is the best approximation currently available.

The binary interaction parameters for the property methods chosen in the previous section, is either obtained from an ASPEN databank or estimated using UNIF-DMD (see section C.1). As already mentioned, for the SRK method, all the binary interaction parameters are estimated. Therefore, in the following table (Table 73) only the sources of binary interaction parameters for the NRTL-HOC method and Henry components are presented. In this table, the components are ranked and grouped in order of priorities in the system. Also shown is the temperature range for each parameter.

The databanks, VLE-HOC and HENRY, were developed by AspenTech using binary vapour-liquid equilibrium (VLE) data from the Dortmund databank. To the extent possible, only thermodynamically consistent data are used. In addition to the parameter values, the databanks in ASPEN contain the temperature, pressure, and composition limits of the data and the quality of the fits, such as average and maximum deviations. Therefore, for these databank parameters, it is assumed that Aspen can simulate the binary vapour-liquid systems involved in our process and data regression analyses are not done. It is also assumed, for parameters that do not fall within the temperature range as it is used in the simulations, that these parameters are sufficient for their priority in the system (and better than estimated parameters).

All the parameters from the R-PCES source in Table 73 are estimated with the UNIF-DMD method. UNIFAC-estimated binary parameters usually do not provide enough accuracy and, so, only are recommended for early stages of physical property data investigation

and to “fill in the blanks” for components with medium or low priorities (Carlson, 1996). The only high priority parameter pairs that are estimated are that of ethanol and acetone with 2-ethyl-1-hexanol (the extractant used in LLE). In the simulations however, these parameters are not used, seeing that insufficient results are obtained when LLE is simulated with any of the property methods and parameters available (or estimated) in ASPEN. Other estimated parameters are those of some of the pairs with butyric acid. These pairs are however not seen as high priority.

**Table 73: Source and temperature range for binary parameters used in NRTL-HOC method**

High/High Priority					High/Low Priority				
Comp <i>i</i>	Comp <i>j</i>	Source/Databank	Temp Range		Comp <i>i</i>	Comp <i>j</i>	Source/Databank	Temp Range	
H <sub>2</sub> O	Butanol	VLE-HOC	292.32	464.95	H <sub>2</sub> O	CO <sub>2</sub>	HENRY	273.35	347.85
H <sub>2</sub> O	Acetone	VLE-HOC	293.15	503.15	H <sub>2</sub> O	H <sub>2</sub>	HENRY	273.15	344.85
H <sub>2</sub> O	Ethanol	VLE-HOC	298.14	408.65	Butanol	CO <sub>2</sub>	HENRY	298.15	298.15
H <sub>2</sub> O	2-Ethyl-1-hexanol	VLE-HOC	293.15	333.15	Butanol	H <sub>2</sub>	HENRY	213.15	298.15
Butanol	Acetone	VLE-HOC	331.25	388.15	Acetone	CO <sub>2</sub>	HENRY	200.01	307.15
Butanol	Ethanol	VLE-HOC	343.15	384.1	Acetone	H <sub>2</sub>	HENRY	191.25	313.15
Butanol	2-Ethyl-1-hexanol	VLE-HOC	358.03	415.32	Ethanol	CO <sub>2</sub>	HENRY	283.15	313.15
Acetone	Ethanol	VLE-HOC	298.15	372.7	Ethanol	H <sub>2</sub>	HENRY	213.15	323.15
Acetone	2-Ethyl-1-hexanol	R-PCES	298.15	298.15	2-Ethyl-1-hexanol	CO <sub>2</sub>	R-PCES	298.15	298.15
Ethanol	2-Ethyl-1-hexanol	R-PCES	298.15	298.15	2-Ethyl-1-hexanol	H <sub>2</sub>	R-PCES	298.15	298.15
High/Medium Priority					Medium/Low Priority				
Comp <i>i</i>	Comp <i>j</i>	Source/Databank	Temp Range		Comp <i>i</i>	Comp <i>j</i>	Source/Databank	Temp Range	
H <sub>2</sub> O	Butyric Acid	VLE-HOC	324.55	437.05	Butyric Acid	CO <sub>2</sub>	HENRY	273.15	313.15
H <sub>2</sub> O	Acetic Acid	VLE-HOC	293.15	502.9	Butyric Acid	H <sub>2</sub>	R-PCES	298.15	298.15
Butanol	Butyric Acid	R-PCES	298.15	298.15	Acetic Acid	CO <sub>2</sub>	HENRY	291.15	309.15
Butanol	Acetic Acid	VLE-HOC	388.85	395.75	Acetic Acid	H <sub>2</sub>	HENRY	291.75	347.95
Acetone	Butyric Acid	R-PCES	298.15	298.15					
Acetone	Acetic Acid	VLE-HOC	328.75	391.25					
Ethanol	Butyric Acid	R-PCES	298.15	298.15					
Ethanol	Acetic Acid	VLE-HOC	308.15	388.95					
2-Ethyl-1-hexanol	Butyric Acid	R-PCES	298.15	298.15					
2-Ethyl-1-hexanol	Acetic Acid	VLE-HOC	331.7	364.75					
Medium/Medium Priority					Low/Low Priority				
Comp <i>i</i>	Comp <i>j</i>	Source/Databank	Temp Range		Comp <i>i</i>	Comp <i>j</i>	Source/Databank	Temp Range	
Butyric Acid	Acetic Acid	VLE-HOC	391.25	437.05	CO <sub>2</sub>	H <sub>2</sub>	n/a		

### A.3 Validation of Physical Properties

As mentioned in the section C.2, parameters obtained from ASPEN databases won't be validated. Only high priority estimated parameters are of concern. Liquid-liquid extraction and gas-stripping are two specific process steps in the simulations that used property methods with high priority estimated binary interaction parameters, and needs validation.

### A.3.1 Liquid-Liquid Extraction

For the LLE process to be considered for industrial application it should extract most of the solvents from the product stream and almost no water, thereby reducing the energy requirements needed for downstream processing and eliminating the separation problems encountered with the azeotropes involved. Several literature studies simply assume/claim that 100% of the water in the fermentation product stream remains in the raffinate phase after LLE (Dadgar & Foutch, 1988; Liu, Fan, & Seib, 2004; Wu, Wang, Liu, & Huo, 2007). In a study by Chuichulcherm and Chutmanop, (2000), they conclude that 2-ethyl-1-hexanol has the best solvent extraction capabilities for ABE from the fermentation broth, but do not indicate the water concentration in the extracted product. There is also no liquid-liquid equilibrium data available for ABE at such low concentrations in 2-ethyl-1-hexanol (extractant) and water. Therefore, numerous experiments were performed at the University of Stellenbosch to determine the capability of 2-ethyl-1-hexanol to extract such low solvent concentrations from a water-solvent mixture. Also of interest were to determine the amount of water in the extracted product phase. The experiments performed were very basic (only single stage) and did not yield positive results. It is suggested that these experiments be repeated in a multistage extraction column to obtain better/usable results. Due to time constraints for this project, these experiments were not performed.

For the LLE process simulated in ASPEN, various property methods and binary interaction parameter databanks were tried and tested, but none gave results that mimic the literature suggested values. Extractant flowrates and number of column stages were also optimized to obtain favourable results. Most of the solvents (ABE) are extracted, but not 100% of the water remains in the raffinate phase. This might be contributed to the fact that there are some missing binary interaction parameters for the property methods used (these are again estimated using UNIF-DMD method). In Table 74 the results of the best performing systems are shown along with the property methods and databanks used (the latter appear in brackets).

**Table 74: LLE results for different property methods in ASPEN (values in kg/h).**

NRTL-HOC (VLE-HOC)					UNIQU-2 (LLE-LIT)				
Components	Extractant	Feed	Product	Raffinate	Components	Extractant	Feed	Product	Raffinate
H <sub>2</sub> O	0.000	4.265	1.074	3.190	H <sub>2</sub> O	0.000	4.265	0.212	4.053
Ethylhexanol	10.000	0.000	9.999	0.001	Ethylhexanol	10.000	0.000	9.999	0.001
Butanol	0.000	0.514	0.514	0.000	Butanol	0.000	0.514	0.514	0.000
Acetone	0.000	0.018	0.018	0.000	Acetone	0.000	0.018	0.018	0.000
Ethanol	0.000	0.001	0.001	0.000	Ethanol	0.000	0.001	0.000	0.000
Butyric Acid	0.000	0.016	0.016	0.000	Butyric Acid	0.000	0.016	0.016	0.000
Acetic Acid	0.000	0.001	0.001	0.000	Acetic Acid	0.000	0.001	0.001	0.000
CO <sub>2</sub>	0.000	0.020	0.020	0.000	CO <sub>2</sub>	0.000	0.020	0.020	0.000

Even the best performing system (using UNIQU-2(LLE-LIT) method) still contains too much water in the extracted product phase. This makes for a process design that cannot compete economically with older designs relying on beer columns for post-fermentation water removal. Therefore, the use of these property methods and parameters in the LLE process cannot be justified. As a result of this, the LLE process in ASPEN is simulated as a separation block with specified separation fractions for components, similar to that as used in literature (see Table 75). From Table 75 the results of Lui, et al., (2004) are chosen to simulate LLE for this project.

**Table 75: LLE results from different literature sources and ASPEN.**

Component	(Dadgar and Fouch, 1988)	(Liu, et al., 2004)	(Bohlmann, 2007)	ASPEN UNIQU-2 (LLE-LIT)
Initial ABE (g/L)	23.0	23.0	312.3	23
Butanol Recovery (wt%)	97.0	96.3	99.8	100
Acetone Recovery (wt%)	63.9	63.6	98.7	100
Ethanol Recovery (wt%)	49.3	50.0	84.8	9.8
Water Recovery (wt%)	0.0	0.0	0.0	4.9
2-Ethyl-1-hexanol Recovery (wt%)	100.0	100.0	100.0	99.9
Feed:Solvent Flow Ratio	0.93	0.93	0.063	0.48

There are thus still uncertainty regarding the simulation of the LLE process and the validity of the results. It is strongly recommended that data from larger scale experiments be obtained and regressed to determine process specific interaction parameters. This will enable more accurate simulation of the LLE process and make the overall simulated process design more rigorous.

### A.3.2 Gas Stripping

In the gas stripping process it is important that sufficient amounts of solvents (ABE) be taken up in the gas phase (mostly CO<sub>2</sub>) which is circulated through the fermentation broth. For the components, at the concentrations and conditions in this system, there were very little VLE data available in literature. Also, this is a very complex system and

only validating the binary VLE data are not sufficient. Therefore the best way in which to validate the property method and binary interaction parameters used is to compare the ASPEN simulation results with experimental laboratory results from literature. The fermentation data as well as the conditions for gas stripping (product concentration, component mass fractions and CO<sub>2</sub> flowrate) are the same in ASPEN as in the literature. Only slightly different total mass of streams are used.

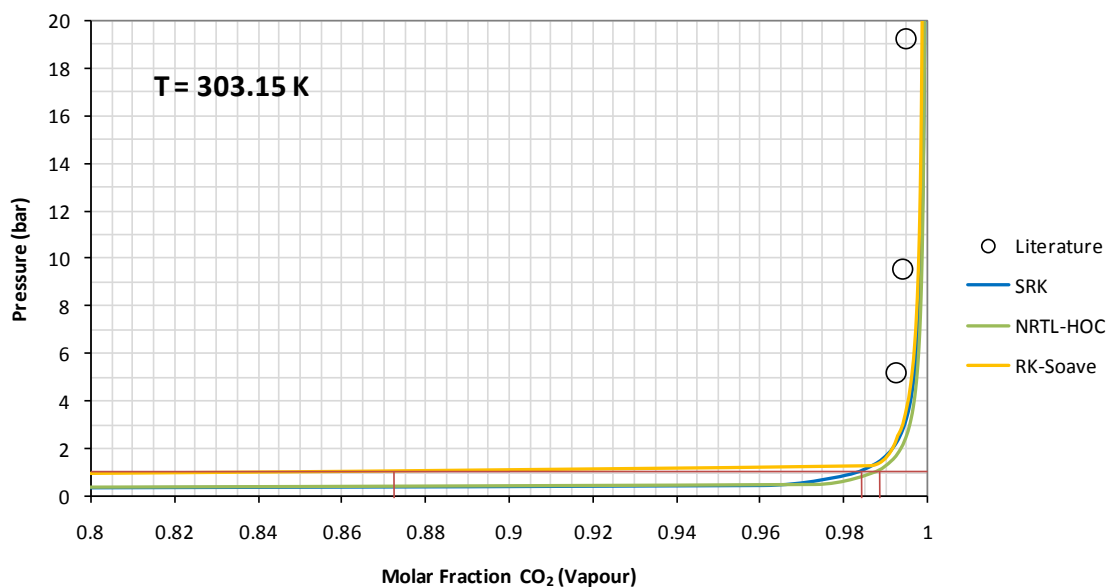
**Table 76: Literature and ASPEN data for gas stripping product streams**

Final Product Stream after Gas Stripping		
Component	(Bohlmann, 2007)	ASPEN
Butanol (wt%)	22.04	33.77
Acetone (wt%)	11.29	2.70
Ethanol (wt%)	0.49	0.05
Water (wt%)	66.18	63.48
Total Mass (kg)	49040	56538
Total Volume (L)	53115	61436
ABE Concentration (g/L)	312	336

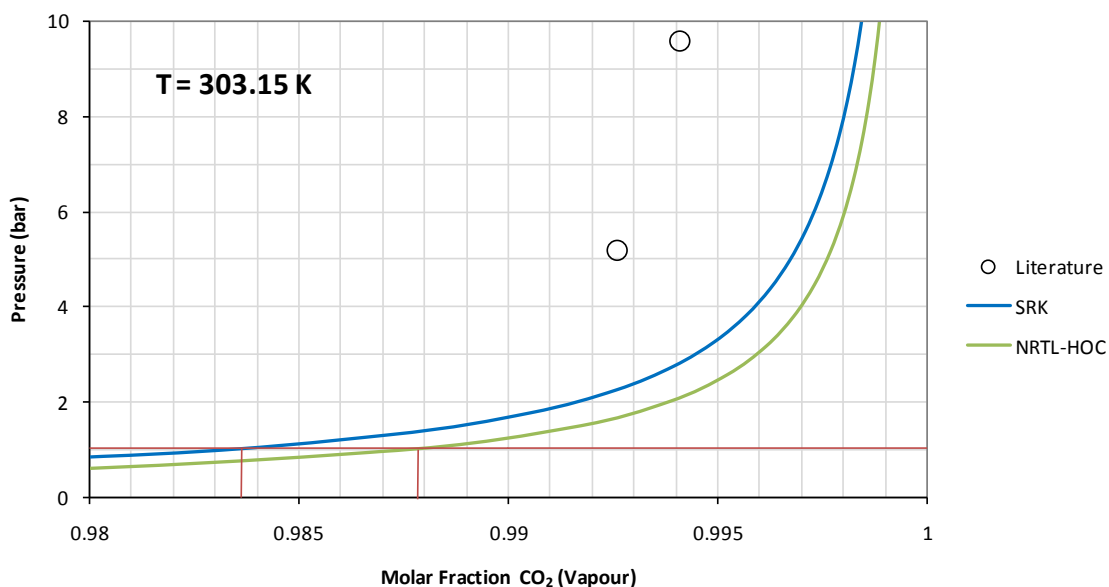
From the above table it is clear that the SRK model with the estimated interaction parameters (as used in ASPEN) do not render results exactly the same as in literature. The product ratios differ, and the amounts of acetone and ethanol are much less. However, the final product concentration is more or less the same and therefore the SRK model were chosen above the other models available in ASPEN seeing that it gave results closest to that obtained in literature. Although this property model is the most accurate (given the models and properties available in ASPEN), it is strongly recommended that data from larger scale experiments be obtained and regressed to determine process specific interaction parameters, thereby enabling more accurate simulation of the gas stripping process and making the overall simulated process design more rigorous.

To explain the difference in simulated results obtained when using different property methods, binary VLE data and fitted models for butanol and CO<sub>2</sub> are considered. This is done because the vapour phase, and specifically the butanol-CO<sub>2</sub> interaction, is most important in gas stripping. The only available literature data are for high pressure conditions.





**Figure 38:** Experimental and predicted VLE for CO<sub>2</sub> and 1-butanol system. Experimental data taken from Secuianu, et al., (2004). Predictions performed using various models in Aspen.



**Figure 39:** Experimental and predicted VLE for CO<sub>2</sub> and 1-butanol system. Experimental data taken from Secuianu, et al., (2004). Predictions performed using various models in Aspen.

The red lines on both of the graphs indicate the conditions where gas stripping commences. From the first graph it is clear the RK-Soave property method (for which no binary interaction parameters are available) predicted the most extreme values, and therefore this model is not considered further. The second graph indicates a small difference between the SRK and NRTL-HOC property methods. Due to the low butanol

concentration in the fermentation broth, this small difference has a large effect on the overall butanol recovery from the broth. This effect is clearer in the following table.

For different property methods evaluated, the following table shows the best results obtained from a single stage flash vessel which is used to simulate the gas stripping process. The CO<sub>2</sub> flowrate and the total input stream volume are kept constant, while the solvent concentration is varied. The gas stripping process commences at the concentration of 5 g/L; the other concentrations are only simulated to show the behaviour of the model at higher concentrations. The results from this table clearly illustrates that the SRK property method produces the most desirable results, seeing that more solvents are recovered. The latter also produce results closest to that of literature obtained values.

For completeness, the binary VLE data and fitted models for CO<sub>2</sub> with some of the other components in the system are also illustrated. As for previous plots, only data at high pressure conditions are available in literature.

SRK						NRTL-HOC					
ABE (g/L)	Feed		Top Product			ABE (g/L)	Feed		Top Product		
	Mass (kg)	Mole Frac	Mass (kg)	Mole Frac	% recovery		Mass (kg)	Mole Frac	Mass (kg)	Mole Frac	% recovery
5						5					
Water	3115950	0.88035	16034	0.01610	0.51	Water	3115950	0.88035	22222	0.05044	0.71
Butanol	10220	0.00070	8462	0.00850	82.79	Butanol	10220	0.00070	571	0.00032	5.59
Acetone	5228	0.00046	1435	0.00144	27.44	Acetone	5228	0.00046	1321	0.00093	25.26
Ethanol	229	0.00003	15	0.00002	6.56	Ethanol	229	0.00003	18	0.00002	7.64
CO <sub>2</sub>	1019988	0.11796	969459	0.97369	95.05	CO <sub>2</sub>	1019988	0.11796	1016384	0.94443	99.65
12						12					
Water	3088610	0.87795	16171	0.03842	0.52	Water	3088610	0.87795	22226	0.05037	0.72
Butanol	24528	0.00169	20249	0.01169	82.55	Butanol	24528	0.00169	1356	0.00075	5.53
Acetone	12547	0.00111	3445	0.00254	27.46	Acetone	12547	0.00111	3167	0.00223	25.24
Ethanol	550	0.00006	36	0.00003	6.60	Ethanol	550	0.00006	42	0.00004	7.61
CO <sub>2</sub>	1019988	0.11868	969958	0.94324	95.10	CO <sub>2</sub>	1019988	0.11868	1016335	0.94276	99.64
100						100					
Water	2744902	0.84508	16375	0.03816	0.60	Water	2744902	0.84508	22252	0.04941	0.81
Butanol	204401	0.01529	25406	0.01439	12.43	Butanol	204401	0.01529	9712	0.00524	4.75
Acetone	104560	0.00999	27030	0.01954	25.85	Acetone	104560	0.00999	26078	0.01796	24.94
Ethanol	4587	0.00055	288	0.00026	6.28	Ethanol	4587	0.00055	329	0.00029	7.17
CO <sub>2</sub>	1019988	0.12855	968226	0.92367	94.93	CO <sub>2</sub>	1019988	0.12855	1015898	0.92332	99.60

Table 77: Comparison of thermodynamic models for the gas stripping process

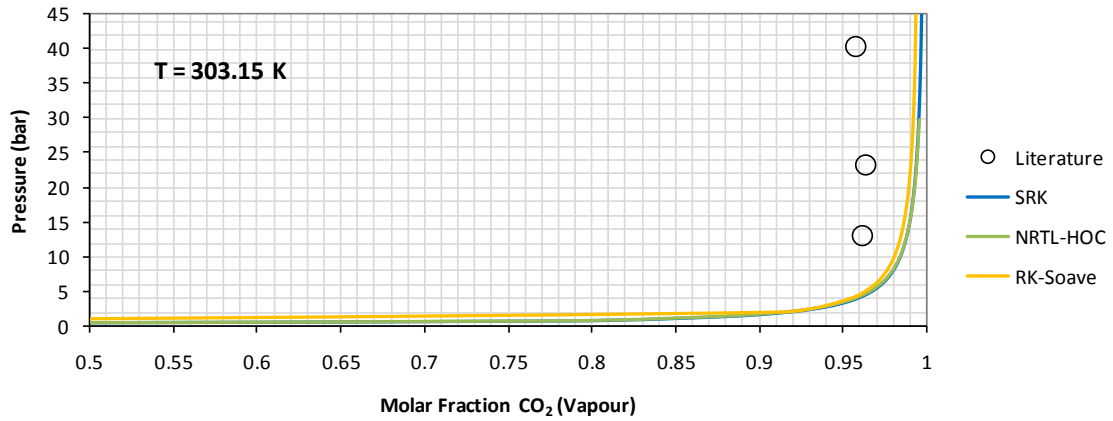


Figure 40: Experimental and predicted VLE for  $\text{CO}_2$  and ethanol system. Experimental data taken from Knez, et al., (2008). Predictions performed using various models in Aspen.

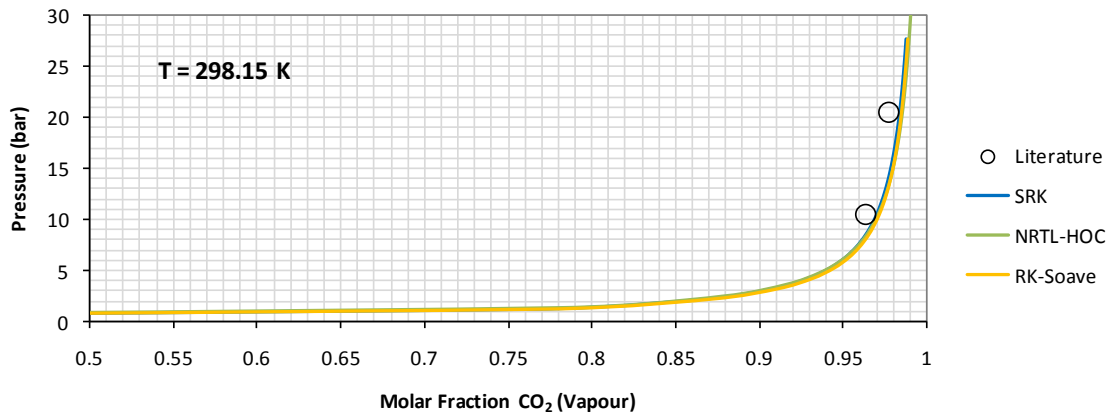


Figure 41: Experimental and predicted VLE for  $\text{CO}_2$  and acetone system. Experimental data taken from Bamberger and Maurer, (2000). Predictions performed using various models in Aspen.

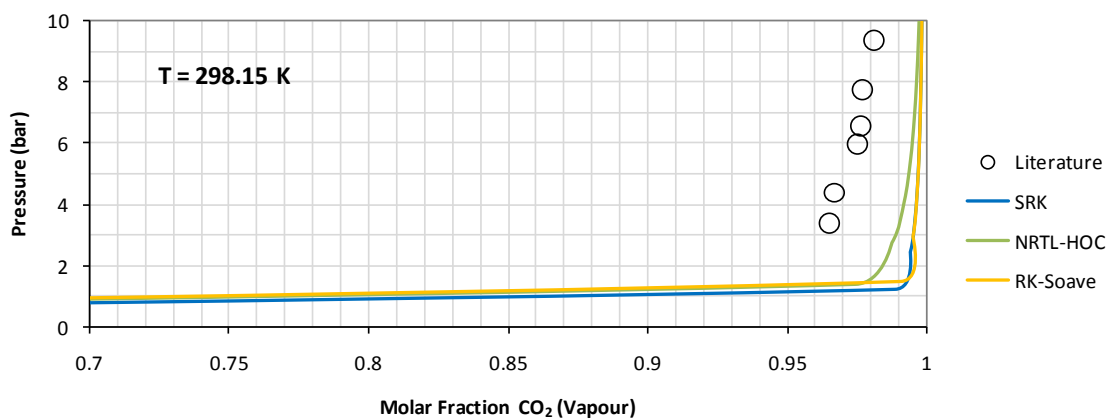
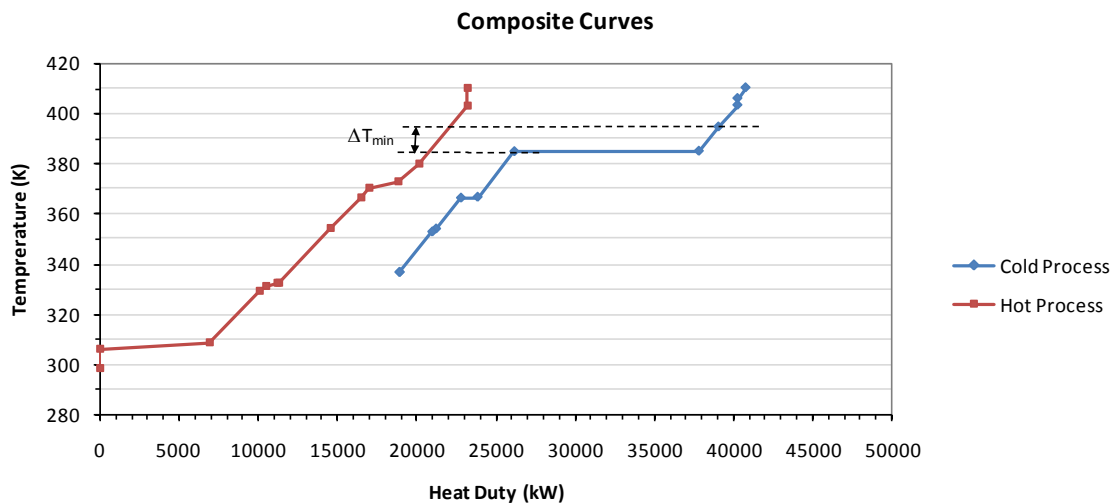


Figure 42: Experimental and predicted VLE for  $\text{CO}_2$  and acetic acid system. Experimental data taken from Jonasson, et al., (1998). Predictions performed using various models in Aspen.

## Appendix B – Pinch Analysis

Pinch technology offers a systematic approach to optimum energy integration of the process. This technique offers improvements in the overall process without making use of advanced unit operations, but by the generation of a heat integration scheme. The principle objective of this technology is to minimize the demands for externally supplied utilities by matching the cold and hot process streams with a network of exchangers. Ultimately, the best design for an energy-efficient heat exchanger network will result in a trade-off between the energy recovered and the capital cost involved in this energy recovery (Hallale, 2001).

The pinch point separates the overall operating temperature region observed in the process into two temperature regions: heat from external sources must be supplied from only at temperatures above the pinch, and removed from the process by cooling media only at temperatures below the pinch. The starting point is to gather temperature and enthalpy data for the “hot” process streams (i.e., those that must be cooled) and “cold” process streams (i.e., those that must be heated). The minimum approach temperature for this system was set at 10 K. A temperature versus enthalpy graph (the “composite curve”) is constructed from the hot and cold process stream data. From this figure the optimum heat exchanger network for a system can be determined.



**Figure 43: Pinch analysis composite curve for Process Design 1.1.**

The above figure is for Process Design 1.1 with a molasses feed of 14.7 T/h. From this figure it is determined that the minimum heating utility needed is 17 513.72 kW, while the minimum cooling utility is 18 911.62 kW.

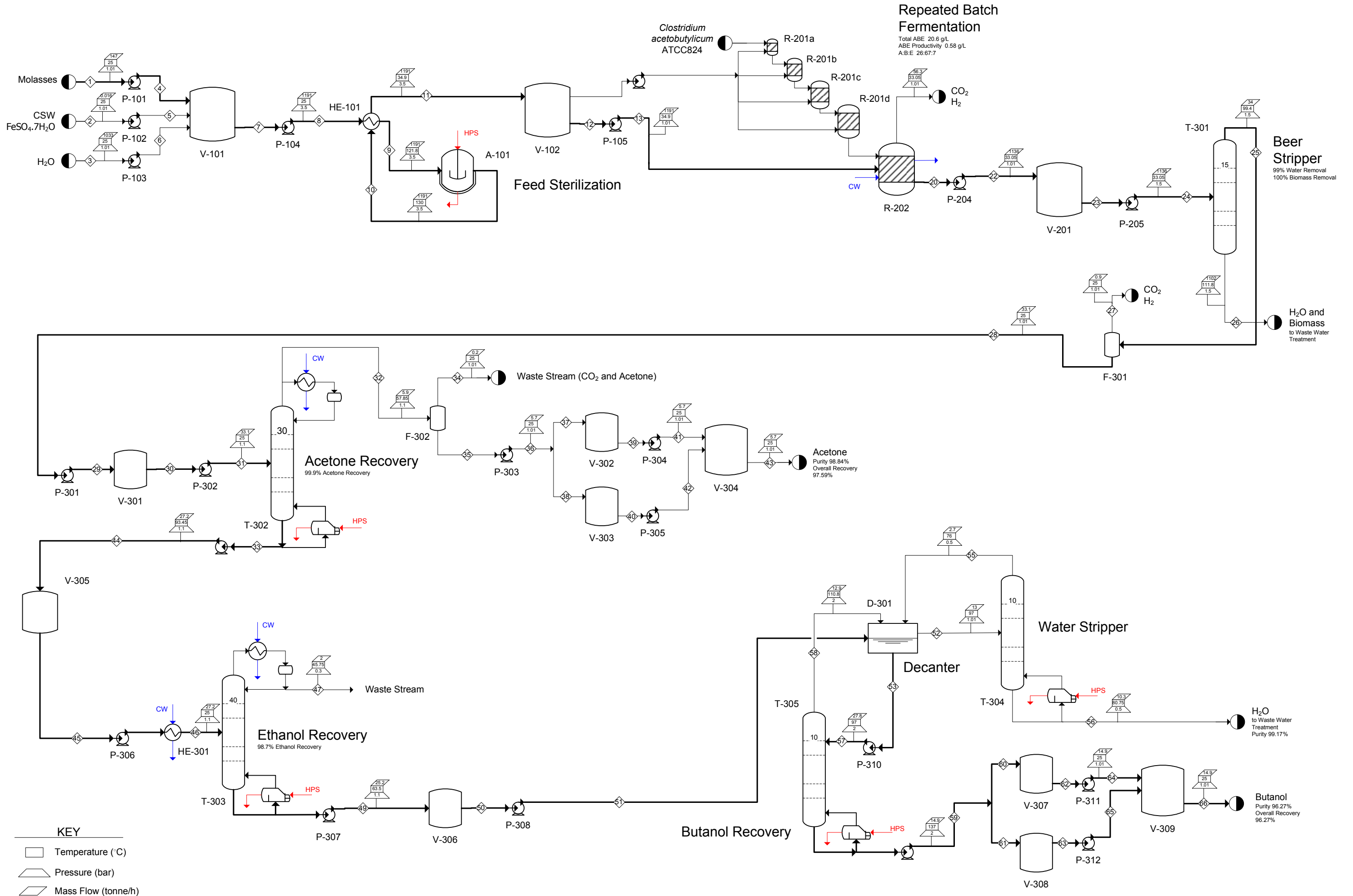
In this study, pinch technology is only used on one of the first process design to illustrate the energy saving possibilities and to identify streams that can easily be integrated for heat exchange. Detailed analyses, determining the energy recovered versus the capital cost involved, are not done for the process designs in this study, but is recommended for more detailed designs in the future.

*The Microsoft Excel® spreadsheet containing the data from the pinch analysis is on the attached CD.*

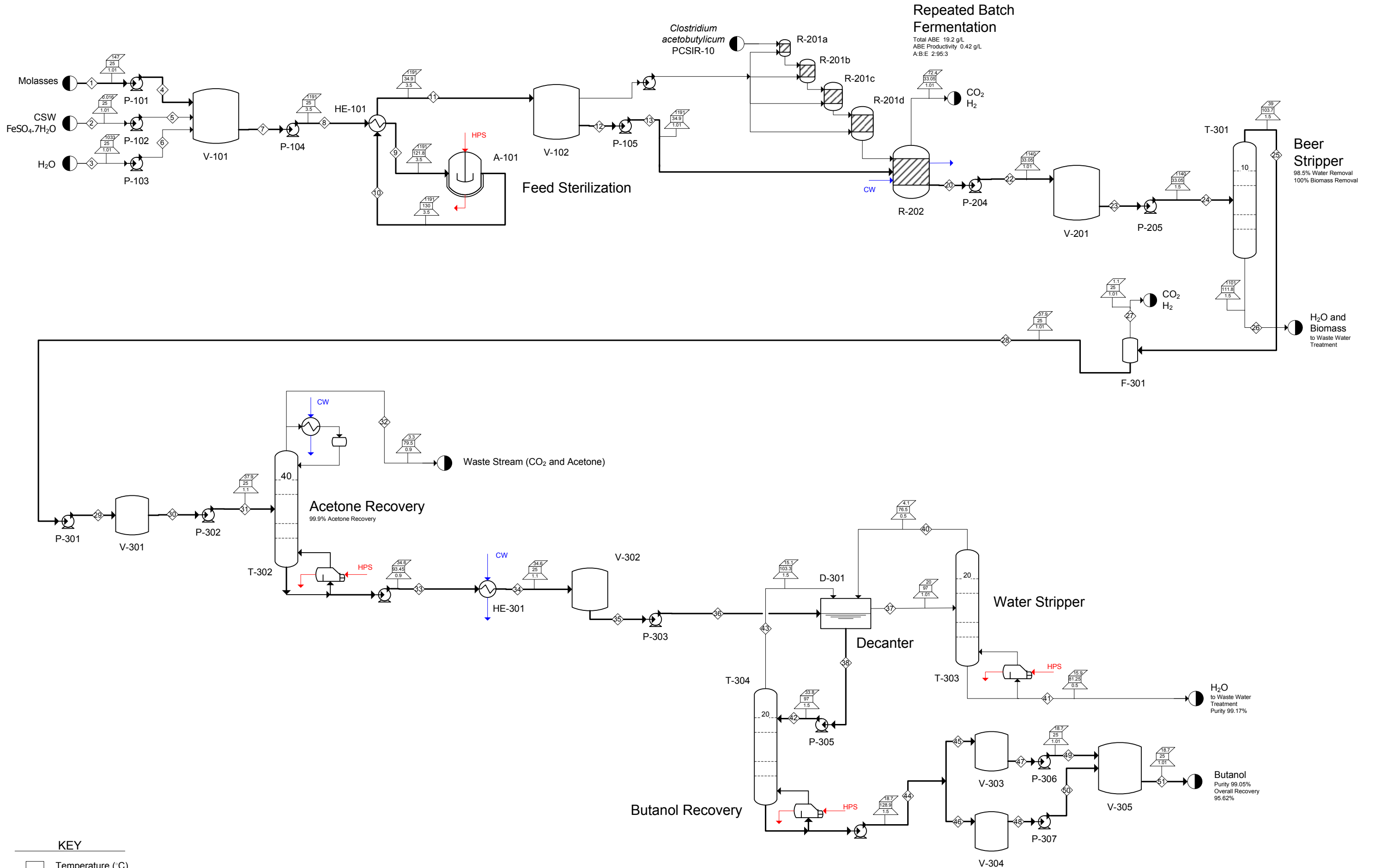
**Appendix C – Process Flow Diagrams**



# Process Design 1.1



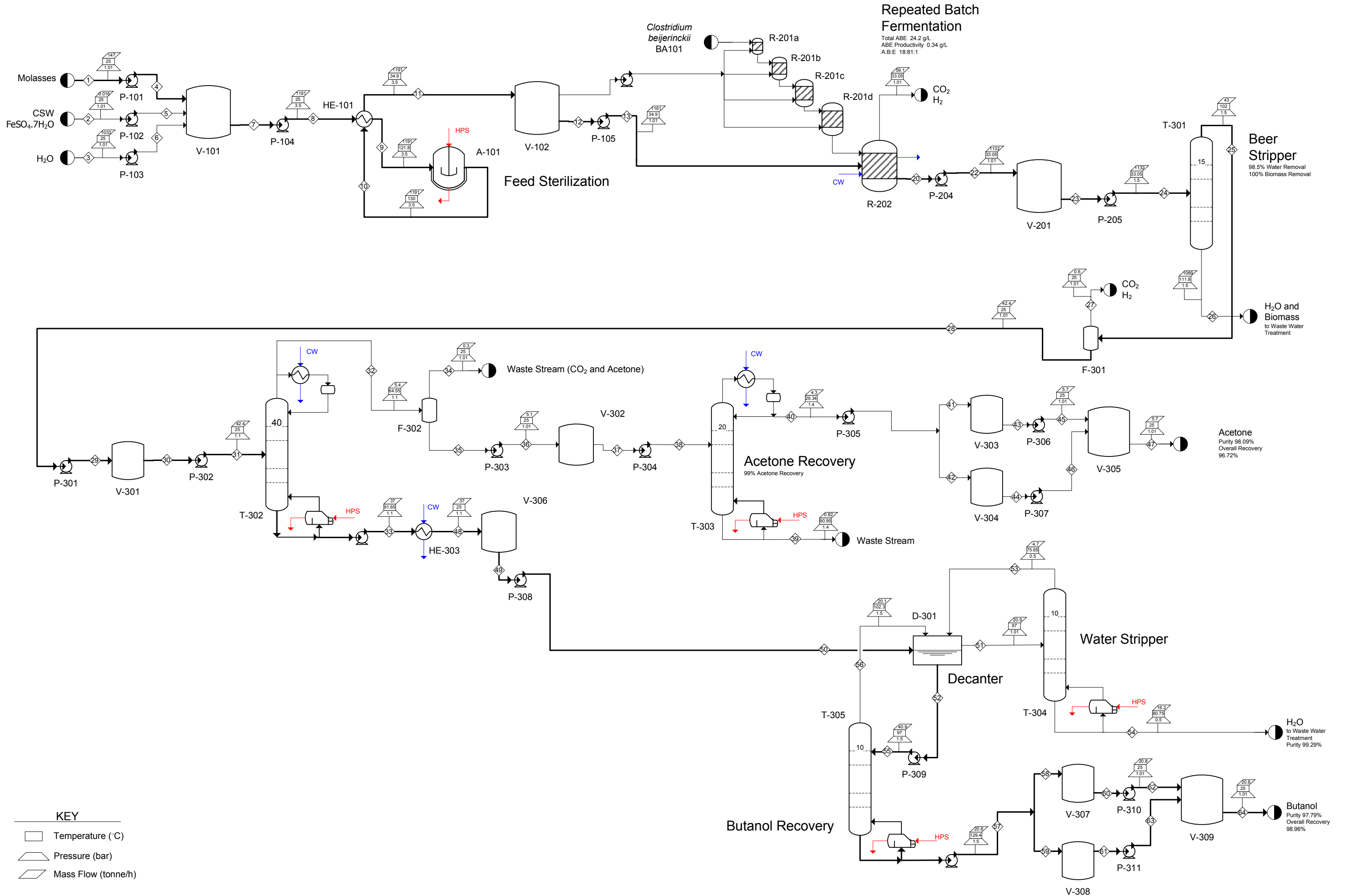
# Process Design 1.2



## KEY

- Temperature (°C)
- Pressure (bar)
- Mass Flow (tonne/h)

# Process Design 1.3



**KEY**

- Temperature (°C)
- Pressure (bar)
- Mass Flow (tonne/h)

# Process Design 2

