Process Modelling In Production of Biobutanol from Lignocellulosic Biomass via ABE Fermentation

by

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Declaration

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Abstract

The interest in production of biobutanol as a fuel has increased significantly in the last two decades. The main reason is that biobutanol is recognised as superior biofuel than ethanol, which is already being blended with gasoline in USA and Brazil. In addition, biofuels have potential to reduce greenhouse gas (GHG) emissions when they are used as replacement of gasoline in transportation industry. A major drawback in Acetone-Butanol-Ethanol (ABE) fermentation is the low final product concentration, due to limited biomass growth and product inhibition. Low concentrations of butanol in the fermentation broth have severe disadvantage of high energy requirement during downstream processing. Fermentation technology improvement like *in situ* gas stripping for butanol recovery during the fermentation has potential to provide a more concentrated feed to downstream purification. For downstream product recovery and purification, alternative methods to double effect distillation (DD), which may be more energy efficient, have been investigated, including liquid-liquid extraction and distillation (LLE&D).

The main objective of this study was to develop six conceptual process model scenarios for production of biobutanol from lignocellulosic biomass, from the literature data available, using ASPEN Plus$^®$ V8.2 software. These include: (1) Batch Simultaneous Saccharification and Fermentation (SSF) integrated with Gas Stripping and double effect distillation used as recovery and purification method(SSF-GS/DD). (2)Batch SSF integrated with Gas Stripping and liquid-liquid extraction and distillation used as recovery and purification method(SSF-GS/LLE&D). (3) Continuous Separate Hydrolysis and Fermentation (SHF) and double effect distillation used as recovery and purification method(CONT-SHF/DD). (4) Continuous SHF and liquid-liquid extraction and distillation used as recovery and purification method(CONT-SHF/LLE&D). (5) Batch SHF and double effect distillation used as recovery and purification method(B-SHF/DD). (6) Batch SHF and liquid-liquid extraction and distillation used as recovery and purification method(B-SHF/LLE&D). The impacts of different fermentation methods, fermentation technology improvements and products recovery/purification methods on the energy demand, energy efficiency and economics of the various process scenarios were investigated. Furthermore, the best performing process scenario was compared to previously process model on

biobutanol production from molasses on the basis of same butanol capacity, in terms of energy demand and efficiency and economic feasibility.

Among the six scenarios modelled for a plant capacity of 1 million dry tonnes feedstock per year, the economic assessment showed that only Batch SSF-GS/DD and SSF-GS/LLE&D scenarios were viable under current market conditions. These scenarios gave net present values (NPV) of US$140million and US$47million and internal rates of return (IRR) of 16% and 11% respectively. Sensitivity analysis showed that change in the feedstock price from US$30/tonne to US$150/tonne has greatest impact in minimum butanol selling price (MBSP) (US$0.41/kg – US$1.76/kg) with the market price at US$0.78/kg. The total capital investment (TCI) of butanol production from molasses (US$187million) was significantly lower than the TCI of US$585million for scaled best performing SSF-GS/DD process scenario; on the basis of equal annual butanol production of 118800 tonnes. The comparison further showed that molasses based butanol had higher IRR and NPV of 36% and US$958million compared to 14% and US$112million of SSF-GS/DD.

With regards to energy demand and efficiency, energy demand was met in all of the scenarios by combustion of solid residues after fermentation-purification together with 10% of the lignocellulose feedstock. Onsite electricity production was in excess to process demands, providing surplus electricity that could be sold for additional revenue. SSF-GS/DD and SSF-GS/LLE&D scenarios gave highest liquid fuel energy efficiencies of 26% and 23% respectively, and overall energy efficiencies of 36% and 30% respectively.Butanol production from lignocellulose required more process energy per unit of butanol produced, compared to butanol production from molasses. This was evidenced by lower energy demand of23MJ/kg for molasses based butanol compared to 58MJ/kg of the best selected scaled up SSF-GS/DD process scenario.

Opsomming

Die belangstelling in die produksie van biobutanol as brandstof het tydens die laaste twee dekades baie vergroot. Die hoofrede hiervoor is dat biobutanol herken word as 'n beter brandstof as etanol wat alreeds in die VSA en Brasilië kombineer word met petrol. Biobrandstowwe het ook die potensiaal om kweekhuisgas-emissies te verminder as dit in plaas van petrol of diesel in die vervoerindustrie gebruik word. 'n nadeel wat betref die fermentasie van Aseton-Butanol-Etanol is die lae konsentrasie van die finale produk weens die beperkte groei van die biomassa en die inhibisie van die produk. Die lae konsentrasie van butanol in die fermentasie vloeistof beteken dat baie energie later in die proses benodig word. Verbeterings in die fermentasie tegnologie soos die *in* situ stroop van gas vir die herwin van butanol het die potensiaal om 'n meer gekonsentreerde voer te verskaf vir latere suiwering. Vir die latere herwinning en suiwering is alternatiewe metodes om die effek van distillasie te verdubbel (DD) ondersoek, sook vloeistof-vloeistof ektraksie en distillasie (LLE&D). Dit mag meer doeltreffend wees.

Die hoofdoel met hierdie studie is om ses konseptuele proses model scenario's vir die produksie van biobutanol vanaf lignosellulose biomassa, in die beskikbare literatuur met die gebruik vanASPEN Plus® V8.2 sagteware, te ondersoek. Die sluit in: (1) Groep Tegelyke Sakkarifikasie en Fermentasie (SSF) geïntergreer met die Stroop van Gas en dubbel-effek distillasie wat gebruik word vir die herwin- en suiwerings metode. (2)Groep SSF geïntergreer met die Stroop van Gas en vloeistof en distillasie wat gebruik word as herwin- en suiwerings metode(SSF-GS/LLE&D). (3) Aanhoudende Aparte Hidrolise en Fermentasie (SHF) en dubbel-effek distillasie gebruik as herwin- en suiweringsmetode(CONT-SHF/DD). (4) Aanhoudend SHF en vloeistof ekstraksie en distillasie gebruik as herwin- en suiweringsmetod(CONT-SHF/LLE&D). (5) Groep (Batch) SHF en dubbel-effek distillasie gebruik as herwin- en suiweringsmetode (B-SHF/DD). (6) Groep (Batch) SHF en die vloeistof-vloeistof ekstraksie en distillasie gebruik as herwings- en suiweringsmetode(B-SHF/LLE&D). Die impakte van die verskillende fermentasie metodes, verbeterings in fermentasie tegnologie en herwin-/suiwerings metodes op die vraag na, doeltreffendheid en ekonomiese scenario's is ondersoek. Die proses wat die beste presteer het is met die proses wat voorheen vir die produksie van biobutanol van molasse gebruik is,

vergelyk wat betef butanol kapasiteit, die energie wat benodig word, die doeltreffendheid en die ekonomiese lewensvatbaarheid. Van die ses scenario's vir 'n aanleg met 'n kapasiteit van 1 miljoen droë ton voer per jaar het die ekonomiese ondersoek bewys dat net die Groep SSF-GS/DD en SSF-GS/LLE&D scenario's onder die huidige marktoestande lewensvatbaar is. Die huidige netto waardes (NPV) is US$140million en US$47million en die interne opbrengs (IRR) is 16% and 11% onderskeidelik.

 Ontledings het getoon dat veranderings in die prys van voer vanaf US$30/tonne na US$150/tonne die grootste impak het op die minimum butanol verkoopprys. (US$0.41/kg – US$1.76/kg) met 'n markprys vant US$0.78/kg. Die totale kapitale belegging van butanol produksie vanaf melasse (US$187miljoen) was heelwat laer as die totale kapitale belegging van US$585miljoen vir die beste SSF-GS/DD proses scenario, op die basis van 'n gelyke jaarlikse butanol produksie van 118800 tonnes. Die vergelyking het verder aangetoon dat die melasse wat op butanol baseer 'n hoër IRR en NPV van of 36% en US$958 miljoen in vergeleke met 14% en US$112 miljoen van SSF-GS/DD, het.

 Wat betref die vraag na krag en die doeltreffendheid, is die vraag na krag in al die scenario's bevredig deur die verbranding van die vaste oorblyfings van die fermentasie-suiwerings proses tesame met 10% van die lignosellulêre voer. Die aanbod van elektriese krag was groter as die vraag daarna en die oortollige krag kon teen 'n wins verkoop word. Die. SSF-GS/DD en SSF-GS/LLE&D scenario's het die beste gevaar wat betref 'n vloeistof/brandstof energie doeltreffendheid van 26% and 23% onderskeidelik, en 'n algehele doeltreffendheid van 36% en 30% onderskeidelik. Butanol wat uit lignosellulose vervaardig is, het meer prosesenergie per eenheid vervaardig, benodig in vergelyking met butanol wat uit melasse vervaardig is. Minder krag 23MJ/kg word vir benodig vir butaneol wat op melasse baseer is as vir die beste geselekteerde opgeskaalde SSF-GSD/DD proses scenario.

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Nomenclature

1G: 1st Generation Feedstock

2G: 2nd Generation Feedstock

ABE: Acetone-Butanol-Ethanol

ASPEN: Advanced Simulator Process Engineering

BFP: Basic Fuel Price

CAPEX: Capital Expenditure

DD: Double effect Distillation

DCF: Discounted Cash Flow

EE: Energy Efficiency

GGE: Gasoline Gallon Equivalence

GHG: Green House Gas

IRR: Internal Rate of Return

LCB: Lignocellulosic Biomass

LLE: Liquid- Liquid Extraction

MBSP: Minimum Butanol Selling Price

GEV: Gross Energy Value

NPV: Net Present Value

NREL: National Renewable Energy Laboratory

OPEX: Operating Expenses

SHF: Separate Hydrolysis and Fermentation

SSF: Simultaneous Saccharification and Fermentation

TCI: Total Capital Investment

1.   Introduction

1.1.   Background to the research problem

Many governments have implemented strategies to advance the use of cleaner and renewable biofuels in transport, to reduce greenhouse gas emissions (GHG) and meet national emission reduction targets(Qureshi and Ezeji 2008; Ezeji et al. 2007; García et al. 2011). The world reserves of fossil fuels are in continuous depletion, which is further triggered by world population growth and usage per capita (Kumar and Gayen 2011; Meech 2010). The transport industry relies heavily on gasoline and diesel produced from coal and crude oil which are non-renewable fossil fuels. These are the major contributors of greenhouse gas emissions such as carbon dioxide (CO_2), methane (CH_4) and nitrogen oxides (NO_x) leading to global warming impacts (García et al. 2011; Raganati et al. 2012). The interest in biofuels production from the renewable lignocellulose biomass (LCB) continues to feature prominently in these discussions, as a preferred alternative to biofuels produced from so-called first generation food crops.

The economic growth for biofuels production is occurring at a fast rate because of government policies. These policies often oblige suppliers of transport fuel to blend their gasoline and diesel with biofuels (Bailey 2013). It is important to note that different countries have different policies with regards to the amount of biofuels blending in fossil fuels (so-called blending ratios). Ethanol is the main biofuel which is being produced in large quantities. South African government, in its biofuel industrial strategy white paper, encourages gasoline blended with bioethanol at 2% ethanol by volume in 2008-2013 DME (2007). However, studies have shown that butanol is a superior biofuel as compared to ethanol (Qureshi and Blaschek 1999; García et al. 2011; Jang et al. 2012; Raganati et al. 2012) and is gaining interest to be blended with gasoline or to use it as a replacement. The USA is the leader in production of biobutanol from corn at commercial scale. It allows blending of butanol to gasoline at 16%Alternative Fuels Data Center(2015). In fact, butanol can fully

replace gasoline as a fuel in gasoline car engines as it has been shown by David Ramey(2005).

Butanol on industrial scale is produced by the Acetone-Butanol-Ethanol (ABE) fermentation of sugarcane molasses, potato starch and maize mash using solventogenic *Clostridia* bacteria (García et al. 2011). Most of the feedstock to the fermentation process comesfrom agricultural food crops such as corn starch, potatoes, sweet sorghum and sugarcane molasses (Jones and Woods 1986; García et al. 2011; Jang et al. 2012). The solventogenic *Clostridia*is used because of its capability to utilize concurrently different types of sugars like hexoses and pentoses as well as starch (Jang et al. 2012; Lee et al. 2008; Qureshi et al. 2008a). With growing world population and global warming affecting food production, food security has caused concern about food versus biofuel production. The International Union of Food Science and Technology (IUFoST) (2010) stated that agricultural land is being used to grow biorefinery feedstocks such as switchgrass and miscanthus rather than to grow food crops. It argued that has pushed up price of starchy food mainly maize in the world market.

The food versus biofuel concern has shifted focus to the use of non-food renewable LCB such as agricultural residues (corn fibre and stover, sugarcane and cassava bagasse, wheat bran and straw, rice bran and straw), forest residues (sawdust, thinning rest) and energy crops (switchgrass and miscanthus) as feedstocks to ABE fermentation process (Ezeji et al. 2007; Jang et al. 2012; Qureshi et al. 2008a). These raw materials are available in abundance and are relatively inexpensive compared to starch and sugars. From South African perspective, there is significant size of marginal land with the potential to produce enough LCB feedstock in the form soft and hardwood from forestry industry (Amigun et al. 2010; Lynd et al. 2003). In addition, there are available million tonnes of invasive alien plants which can be used as LCB feedstock(Amigun et al. 2010; Lynd et al. 2003). Furthermore, the sugar cane industry of South Africa is well developed and it can provide large volumes of crushed sugarcane, from which harvest residues such as tops and trash can be obtained as feedstock. In a study by van der Merwe (2013) sugarcane molasses was used as carbon source for fermentation, to investigate energy efficiency and techno-economics of biobutanol production by building conceptual process models. The

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resulting description of butanol production from molasses will be compared to butanol production from LCB, as modelled in the present study.

The main challenge of ABE fermentation when using LCB as feedstock is the additional costs of sugars production from lignocellulose, compared to molasses or starches. LCB bioconversion requiresthermochemical pretreatment combined with detoxification for removal of inhibitors generated during pretreatment (Ezeji et al. 2007). Another technical challenge with ABE fermentation, which is common to all feedstocks, is product inhibition of butanol on the fermentative activity of microbes, resulting in low fermentation productivity and low final product concentrations, which significantly increase the cost of recovery and separation (Ezeji et al. 2007).

All of these mentioned points make the production of biobutanol expensive (Qureshi et al. 2008c), and selling price per liter to be higher than that of gasoline, hence uncompetitive in the transportation fuels. There is a need for extensive research in the process development models that can be used together with experimental work in investigating ways to reduce costs of biobutanol production.

1.2.   Biobutanol as Fuel and Chemical

The renewed interest in the production of biobutanol from plant biomass has been sparked by benefits associated with its use as biofuels and green chemical. Biobutanol is a 4-carbon alcohol with four isomers namely: n-butanol, sec-butanol, isobutanol and tert-butanol. Among these isomers, n-butanol and isobutanol are the ones mostly produced and applied in the chemical industry. They also have a possibility to be used as gasoline replacement or additive. Both these isomers are produced by fermentation. However, n-butanol is the default alcohol formed in ABE fermentation, while isobutanol is produced by engineered fermentation microorganismsGevo (2014). There are a number of global companies which are pioneering the production of biobutanol with focus on technology improvement, feedstocks and microorganisms. These include Gevo, Butamax, Cobalt Technologies, Green Biologics and Cathy.

i.   Biobutanol as a Fuel

Biobutanol is considered to be a superior biofuel when compared to ethanol and has a larger potential than ethanol for gasoline replacement, due to superior fuel properties(Qureshi and Blaschek 1999; García et al. 2011; Jang et al. 2012; Raganati et al. 2012). From Table 1:1, these properties include an energy content that is closer to gasoline and a lower heat of vaporisation (Dürre 2008; Lee et al. 2008). This means with biobutanol as fuel in car engine, one can travel distance longer than when ethanol is being used as fuel.

Table 1:1: Comparison of liquid properties between biobutanol, bioethanol and gasoline (Lee et al. 2008)

Property	Bioethanol	Biobutanol	Gasoline
C-atoms	C2	C4	C4 - C12
Boiling Point (°C)	76	118	32 - 210
Heating Volume (MJ/L)	21	29	32 - 33
Oxygen Content % (w/w)	34.7	21.6	< 2.7
Heat of Vaporisation (MJ/Kg)	0.92	0.43	0.36
Motor Octane Number	89 - 103	78	81 - 89
Research Octane Number	106 - 130	96	91 - 99

These characteristics have advantages from economic point of view because butanol can be processed and transported through the existing gasoline infrastructure and pipeline, without incurring further costs on equipment replacement (Dürre 2008; Lee et al. 2008)unlike ethanol that requires special treatment.

ii.   Biobutanol as a Chemical

Not only can biobutanol be used as a biofuel but it also has a wide industrial application as a solvent and platform chemical (García et al. 2011). According to Natalense and Zouain (2013), the current world supply of butanol and isobutanol is produced from the oxo-process using fossil-fuel-derived propylene, carbon monoxide and hydrogen as reactants in the presence of a catalyst. At the production of about 300 million tonnes per year, the market value was estimated to worth more than USUS$5 billion Cobalt Technologies(2014). As a result, many companies mentioned in section 1.2 are targeting the low volume but high value chemical market for their biobutanol to replace the fossil-based butanol. Some of the current applications of butanolare as solvent in paints, cosmetics and coatings, and as starting material for

butyl acrylate and acetate production(Natalense and Zouain 2013). Furthermore, in the plastic manufacture industry butanol is used as a feedstock and is also used in the food and flavour industryas an extractant (Ezeji et al. 2005). These applications show that there is available market for biobutanol as a green chemical.

1.3.   ProjectMotivation

There is a global drive towards the production ofbiofuels such as biobutanol from second generation (2G) lignocellulosicfeedstocks rather than first generation (1G) starch and sugar feedstocks, both from governments and research groups around the world. 2G feedstocks are non-food materials as compared to starchy and sugar 1G feedstocks. Reports during the last decade on production of alcohol from LCB were largely focused on bioethanol production (Balat 2011; Cheng and Timilsina 2011; Dias et al. 2012; Galbe et al. 2007; Sassner et al. 2008). However, there is increasing interest on butanol product instead because of its value over ethanol.

The high costs incurred during production of biobutanol as ABE fermentation product can substantially be reduced by process optimisations such as energy integration, which is facilitated by process modelling. Descriptive models also allow comparison of alternative process routes to identify those that are preferred based on energy consumption and economics, especially for high-cost processing of LCB in pretreatment and butanol purification in downstream processing (Ezeji et al. 2007); Yang and Wayman 2009). For example, low solids loading in pretreatment leads to high volumes of wastewater generated, which can be costly to remove downstream and treat (Mariano and Filho 2012; Ezeji et al. 2013). Downstream processes of biobutanol recovery and purification are also energy intensive due to low butanol concentrations in the fermentation broth, as a result of butanol product inhibition on the fermentative microbe(Mariano et al. 2011; Mariano and Ezeji 2012; Matsumura et al. 1988). Therefore, process modelling will investigate different processes routes to identify those with lower processing costs, and to minimise production costs by energy integration and improving the efficiency of downstream processing for recovery and separation of ABE products.

1.4.   Aim of the Project

The aim of the project is to develop conceptual process models of alternative process scenarios, which will use literature data for their description and simulation in ASPEN Plus® V8.2 software ASPEN Plus (2013). The mass and energy balances from the ASPENPlus(2013)models will be used to investigate butanol production from LCB through ABE fermentation in terms of energy efficiency and economics. The impacts of different fermentation methods, fermentation technology improvements and solvents recovery and purification methods will be investigated, in terms of process energy demand and efficiency as well as economics. The quantitative descriptions of process scenarios from these models will be compared to similar descriptions and models for butanol production from molasses provided in literature.

In order to achieveproject aim, the following objectives will be addressed:

1.4.1. Objectives of the Project

- To review critically the literature pertaining to production of biobutanol from biomass by ABE fermentation with a focus onLCB as feedstock.

- To collect and refine literature data for biobutanol production and use statistical methods to analyse data. This will form a basis on which the choice of fermentation processes and experimental data for inclusion in process models will be based.

- To develop process flow sheets and use in model development in ASPEN Plus (2013). Validate the models with experimental data in literature, on which the upstream processes are based.

- To determine viable energy integration on different units and streams during fermentation process. The pretreatment and separation processes for butanol productionprovideexit process streams with higher temperatures than subsequent processes, which require heat addition. The heat energy from such streams will be harnessed and be integrated into the process to maximise energy efficiency and environmental sustainability.

- To undertake economic studies by using mass and energy balances results from models to estimate capital and operational costs of butanol production of nth plant. These values will be used for an investment analysis, to determine

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the Net Present Value (NPV) and Internal Rate of Return (IRR) for a typical butanol production plant, for each of the process scenarios.

- To perform sensitivity analysis in order to assess the impact of parameters on minimum butanol selling price for the economic feasibility of the process scenarios.

- To compare the economics of biobutanol production from lignocellulosic to those of butanol production from molasses on the basis of processes having same butanol production capacity.

1.5. Project workflow and deliverables

Precise Problem Statement
Feedstock Cost
Low ButOH Concentration in Broth
Intensive Energy Purification

Initial Exploration
Literature studies and Data collection
Fix Problems with Data
Transform Data

Statistical Data Analysis
Weighted Overall Desirability
Processes and purification Choice

Conceptual Models Development
Flow sheet Development
Models Development
Assess Models (Validation)

Techno-Economic Studies
Models Comparison in terms of Energy Efficiency and Economics
Sensitivity analysis on the process parameters

Conclusions and Recommendations
Important conclusions drawn from techno-economic evaluation
Recommendations for future work

Figure 1-1: The work flow of the project covering all the aspects done

The work done in this project is summarised in Figure 1-1 in order to give a pictorial view that is easier to scan through in a short period of time.

Full thesis report contains the following:

- Detailed literature study on production of biobutanol from LCB from Chapter 2 of the thesis.
- Tools in the form of conceptual process models in ASPEN Plus (2013)that can be used and updated for different LCB to produce biobutanol via ABE fermentation. This will be useful to policy makers for making informed decisions when considering building biorefineries in South Africa to achieve its renewable goals set in its Industrial Biofuel Strategy Document 2007. The description of models is found in Chapters 3 and 4 of the thesis.
- Conclusions based on which different fermentation methods, fermentation improvement technologies and recovery and purification methods are better on improving challenges faced by LCB ABE fermentation.
- Conclusions on whether biobutanol production from LCB feedstock is feasible in terms of energy efficiency and economics as compared to biobutanolproduction from molasses from Chapter 7 of the thesis.

1.6. Project Scope and Limitations

The project will cover conceptual processes for the production of biobutanol via ABE fermentation as well as recovery and purification as a desired product. The processes will include LCB pretreatment, detoxification, enzymatic hydrolysis and fermentation. The downstream processes will involve recovery and purification of fermentation broth to get biobutanol as the final product. The investigations will be based on models simulation developed using ASPEN Plus (2013). Mass and energy balances from the simulations will be used in equipment design and sizing, energy demand and efficiency and economic analysis to compare different process scenarios. Further comparisons will be made with the available models that used molasses as feedstock to produce biobutanol. This comparison will give an indication of how LCB butanol is comparable to malasses based butanol in terms of energy efficiency and economics of the two processes.

The major limitation of the project is obtaining actual plant data from the published literature which will be used to validate the developed models. Currently, the companies producing biobutanol from LCB feedstock are not sharing their data in public domain. As a result, this work will be limited to using only available laboratory scale experimental data, as reported in literature. The limitation with using available experimental data is that what is achieved on commercial scale cannot always reflect the laboratory results especially with processes using microorganisms. The reason is that laboratory results are collected under more conducive conditions than industry, giving better process performance than industrial. However, the laboratory results can be used as maximum target performance that could be reached under industrial conditions, hence still a valid method for comparing alternative process scenarios

Lack of different fermentation processes using the same lignocellulose feedstock presented the major challenge in choosing the representative feedstock for all the process configurations studied. As a result, it was assumed that the unique properties of the specific lignocellulose feedstock used in the individual configurations will have a minimal impact on the performance and economic studies of the processes. It is understood that different feedstocks behave differently to different pretreatment conditions and methods. The sugar yields and generation of inhibitors have been found to be different depending on the feedstock used and pretreatment method (Mosier et al. 2005b). As per literature findings, butanol yields vary with different feedstock, pretreatment conditions, enzymatic hydrolysis and fermentation. Based on available literature, it was only possible to compare process scenarios by assuming that different LCB and their chemical properties will not influence processing conditions and performance significantly. This was because there was no experimental data available for all process scenarios considered using the same feedstock. However, in practice different LCB chemical properties will have differing impacts on the processing (Huang et al. 2009).

Thus, some process parameters with regards to LCB feedstock will be assumed to be identical for all LCBs. For example, an identical LCB feedstock cost will be assumed for all process scenarios. In some studies, a different approach was taken, such as Anex et al.(2010)where the techno-economic comparison of three different processes for conversion of biomass into transportation fuel were all based on corn stover as the most studied feedstock.

Furthermore, some of the process units cannot be investigated directly by ASPEN Plus (2013) simulation because it is a continuous steady state simulation. Most of literature reports on butanol production are for batch production methods, while continuous steady state data is required for process simulations. Batch data was thus converted into estimates for continuous operation, using the same yields and productivities as reported for batch processes. In addition to that, some industrial equipment is not yet available in ASPEN Plus (2013)and to model such equipment in ASPEN Plus (2013)will be a challenge. Galbe et al,(2007)stated that modelling of LCB poses challenges because of three phases involved in the process; gases, liquids and solids. The solid stream involving cellulose, lignin and microorganisms are the ones bringing in challenges as ASPEN Plus (2013) deals mostly with gas and liquid streams.

2.   Literature Review

2.1.   Acetone-Butanol-Ethanol Fermentation History

The history of biobutanol production via biological fermentation dates as far back as 1861 when Louis Pasteur first discovered and isolated a strain capable of producing butyric acid along with biobutanol (Kumar and Gayen 2011; García et al. 2011; Jang et al. 2012; Jones and Woods 1986). Later, Albert Fitz, Martinus Beijerinck, Bredemann, Schardinger and Pringsheim followed the work of Pasteur in developing and improving microorganisms which have the ability to produce biobutanol (Gabriel and Crawford 1930; García et al. 2011). The original aim of ABE fermentation was to produce biobutanol to use it as a precursor for the manufacture of synthetic rubber. Strange and Graham Ltd in Rainham in 1913 erected the first plant, which used potatoes as feedstock and *Fernbach bacillus* as microorganism to produce biobutanol (Gabriel and Crawford 1930).

However, the outbreak of World War shifted the ABE fermentation for the production of acetone that was used as explosive material in artilleries (Kumar and Gayen 2011; Ni and Sun 2009). The Strange-Graham or Fernbach process using potatoes did not yield enough acetone to meet the demand and hence the industrial ABE fermentation process based on Weizmann process which used *Clostridium species* as microorganism and maize as feedstock was put in place in 1916 (Gabriel and Crawford 1930; García et al. 2011). From then, the rollout of plants from England to the rest of the world occurred where two distilleries in Canada were modified; one plant began in India and in the United States (Gabriel and Crawford 1930; García et al. 2011). When the war ended, the need for acetone reduced and the by-products such as biobutanol and ethanol which were produced with acetone were present in large quantities and their use had to be found. Due to the rapidly expanding automobile industry at that period, biobutanol found an application as a rapid agent for car finishing (Gabriel and Crawford 1930; García et al. 2011; Ni and Sun 2009). At that time, the United States invested heavily in the production of biobutanol from maize with acetone being the by-product. However, the fermentation process fell out

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of favour in the US and Europe in the 1950s when the process could no longer compete with their synthetic equivalents on price. Biobutanol production via fermentation continued in China, Russia and South Africa until the early 1980s (Green 2011) while, several other countries produced biobutanol until the mid-1980 with South Africa abandoning production in 1990's due to problems associated with the availability of feedstock.Recently, some of the plants have returned into commercial biobutanol production while others are being revamped to increase capacity mainly in China(Ni and Sun 2009; Zverlov et al. 2006). Companies such as Cathy Industrial Biotech and Laihe Rockly in China started producing biobutanol from corn from 2008. Gevo and Butamax have also made significant strides in the production of biobutanol European Biofuels (2013). It should be noted that these companies are not yet readily sharing their data in public domain.

Even though most of industrial biobutanol production stopped during period 1960 – 1980s, the research in ABE fermentation to find strains of bacteria that can produce biobutanol in high concentrations, to identify better and cheap 2nd generation feedstock, efficient product recovery and enhanced fermentation process continued (Qureshi and Blaschek 2000). The oil crises that hit the world economy in 1970s gave rise to the development of biofuels although the major focus was on ethanol (Jin et al. 2011). The research and interest in biofuels has been on-going ever since that crisis, as it made the countries realise the depletion of oil resources (Qureshi et al. 2008a). Also, with the impacts of global warming being felt of which GHGs are believed to play a major role, there is shift towards the use of renewable fuels (Jin et al. 2011).

There is a renewed interest to revive the ABE fermentation industry. This time around, the main focus is on biobutanol because of its fuel and chemical properties. China leads efforts to re-commercialize the ABE fermentation process. Over US$200 million has been invested in China to install 0.21 million tonnes per annum of solvent capacity with plans to expand to 1 million tonnes per annum (Green 2011). About 6 major plants that produce about 30 000 tonnes biobutanol per annum from corn starch were in operation (Green 2011). The revitalisation of the industry has resulted in significantly more research works aimed at improving the overall performance of the ABE fermentation process. The research is focused on areas such as cheap and

non-food feedstock identification, LCB pretreatment, developing recombinant strains, efficient fermentation technologies and downstream processing.

2.2.   Feedstocks forABE Fermentation

2.2.1. Sugar and Starch Feedstock

The ABE fermentation was traditionally fed with sugar (sugarcane juice, sweet sorghum and sugar beet) and/or starch (barley, cassava, corn, rice, potatoes andwheat) as the carbon sources. Those were generally referred to as 1st Generation (1G) feedstocks(Balat 2011; Jones and Woods 1986; Kumar and Gayen 2011; Jang et al. 2012; Mariano et al. 2013). Those feedstocks were used extensively in ABE fermentation process because of their availability and easy of conversion to desired products by solventogenic bacteria. However, due to growing concern that continual use of 1G feedstock could affect food and feed availability has led to use of LCB as 2G feedstock (Kumar and Gayen 2011).

ABE fermentation using starch and sugar substrates has achieved high yields and productivity due to improved process technologies such as continuous operation, compared to traditional batch fermentation. In traditional batch ABE fermentation was affected by low yields and productivities less than 0.3g/g and 0.5g/lh respectively (Jones and Woods 1986). This was mainly due to sugar inhibition as well as butanol inhibition. Product concentration and yields were improved by implementing techniques which could allow high sugar concentration in fermenter without sugar inhibition (Qureshi et al. 2013).

2.2.2. Lignocellulose Feedstock

Theuse of abundant and renewable LCB as feedstock for ABE fermentation is considered as a substitute for sugar and starchy feedstocks(Balat 2011; Kumar and Gayen 2011; Adhami et al. 2009). According to Ni and Sun (2009)the amount of agricultural residues produced in China was 650 megatons per year and the figure was expected to rise to 730 megatons in 2010. In India, it was estimated that over 370 megatons per year of agricultural and forest residues were produced (Kumar and Gayen 2011), while in the United States 68 megatons dry per year of corn stover (cobs, talks and leaves) were available (Petrolia 2008). Some studies have also focused on production of energy crops in high yields such as switchgrass,

Miscanthus and Jerusalem artichoke. Sweet sorghum is also being considered as energy crop for use as feedstock for production of biofuels (Xue et al. 2013).

LCB generally has a composition consisting mainly of cellulose (40 – 45%), hemicelluloses (20 – 30%), lignin (10 – 25%), ash and extractives (Balat 2011; Ezeji et al. 2007; García et al. 2011). The cellulose is mainly found in the secondary wall of plant cell wall and consists of chains of 6-carbon glucose, joined to one another by glycosidic bonds. It has a crystalline structure that makes it insoluble in water (Balat 2011; Ezeji et al. 2007; Rubin 2008). Hemicellulosesare branched heteropolysaccharides with shorter chain lengths and consist mainly of D-xylose with other 5-carbon and 6-carbon monomers (D-galactose, D-glucose, D-mannose and L-arabinoses), which bind to cellulose by H-bonding and inter-link with lignin forming complex bonds to give strong structure (Balat 2011; Ezeji et al. 2007; García et al. 2011; Rubin 2008). Lignin is comprised mainly of six carbon ring phenolic monomers bound onto polymeric structure and it binds to cellulose fibres. It is found mainly in the supporting tissues of cell walls (Balat 2011; Rubin 2008; Ezeji et al. 2007). The pictorial structures of cellulose, hemicellulose and lignin can be seen in Figures 2.1, 2.2 and 2.3 below.
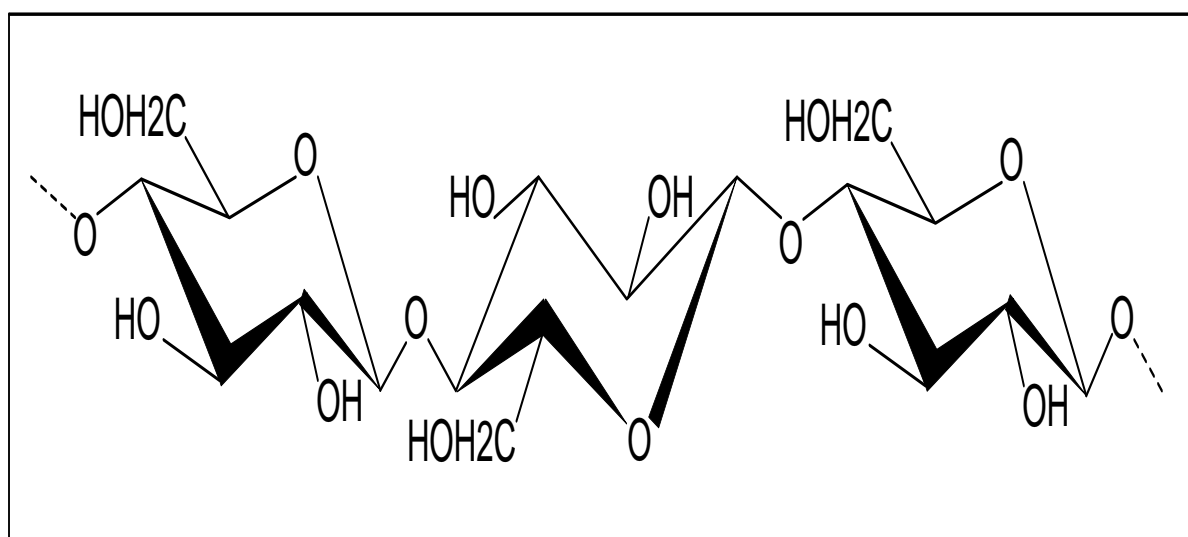
Figure 2-1: The structure of cellulose. Redrawn from: Breaking the Chemical and Engineering Barriers to Lignocellulose Biofuels; Roadmap 2007
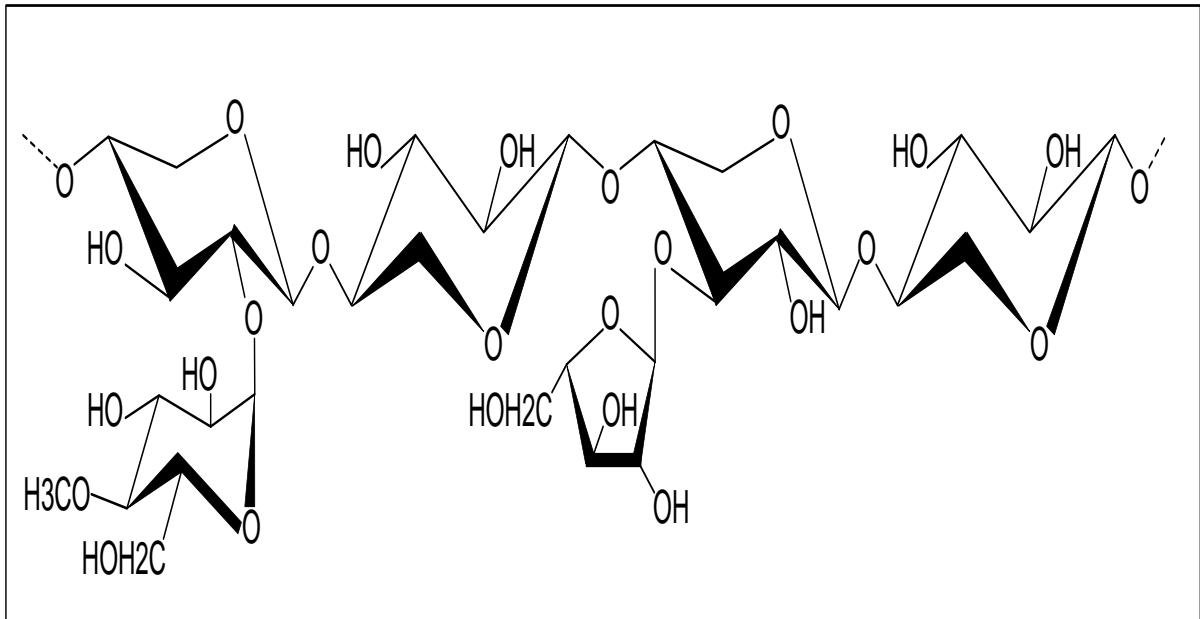
Figure 2-2:The structure of hemicellulose (arabinoglucoxylan). Redrawn from: Breaking the Chemical and Engineering Barriers to Lignocellulose Biofuels; Roadmap 2007
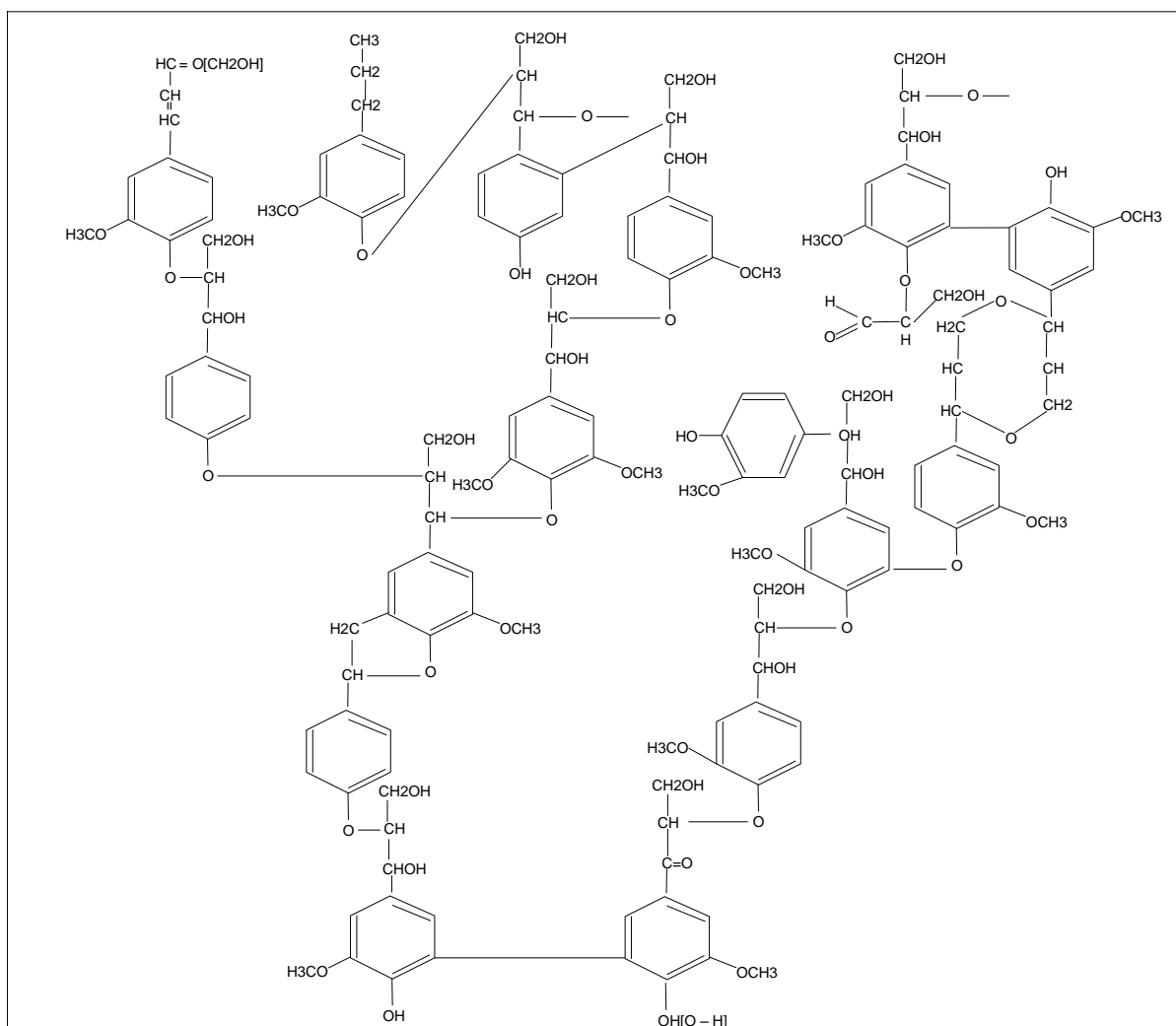
Figure 2-3 : Structure of lignin with its lignols joined to from the lignin polyaromatic structure. Redrawn from: Breaking the Chemical and Engineering Barriers to Lignocellulose Biofuels; Roadmap 2007

The chemical composition of LCB varies within type of the biomassandgeographic area. Overall, the average chemical composition is approximately 48%(w/w) carbon (C), 6% (w/w) Hydrogen (H) and 45% (w/w) Oxygen (O) (Balat 2011).

The value of LCB is their ability to store solar energy in the form of carbon. The energy is retrieved later by different methods such as biochemical conversion to produce biofuels (Rubin 2008). The challenge in obtaining the stored energy from LCB by biochemical conversion is due to its chemical components cellulose and hemicellulose. Cellulose and hemicellulose in LCB cannot be readily fermented to solvents by solventogenic *Clostridia*. LCB has to undergo pretreatment and enzymatic hydrolysis to release the fermentable sugars (Balat 2011; Rubin 2008).

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However, ABE fermenting *Clostridia*are able to concurrently utilize both pentoses and hexoses through glycolysis and the nonoxidative pentose phosphate pathway respectively (Balat 2011; Rubin 2008; García et al. 2011; Jang et al. 2012).

2.3.   Microorganisms and Genetic Strains for ABE Fermentation

ABE fermentation using improved strains of *Clostridia* has the potential to contribute economically to bioprocessing (Papoutsakis 2008; Izák et al. 2008). The solventogenic *Clostridia* are gram-positive, rod-shaped, obligate anaerobic and spore-forming bacteria (Dürre 2008; Kumar and Gayen 2011; Jin et al. 2011). Solventogenic *Clostridia* reported in literature include *Clostridium acetobutylicum*, *Clostridiumbutylicum*, *Clostridiumbeijerenckii*, *Clostridium saccharoperbutylacetonicum,saccharobutylicum* and *Clostridium saccharoacetobutylicum.* These microbeshave metabolic features that result in the solvents being produced in a biphasic fermentation process. The biphasic metabolism of *Clostridia* happen in such a way that during initial acidogenesis, the exponential growing cells produce acetic and butyric acids as well as H_2 and CO_2 gases (Lütke-Eversloh and Bahl 2011; García et al. 2011; Jin et al. 2011). According to Jin et al. (2011); Tashiro et al. (2013), the dramatic change in gene expression in bacteria caused by acidic conditions prompts the shift to solventogenic phase, where acids are re-assimilated and converted to solvents butanol, acetone and ethanol during stationary phase.

The major advantage of solventogenic *Clostridia* is the ability to utilise a variety of carbon substrates toproduce solvents; from momosaccharides, oligosaccharides, polysaccharides, hexoses, pentoses; refined and unrefined starches (Dürre 2008; Ezeji et al. 2007; García et al. 2011; Jang et al. 2012). Some strains contain cellulase and xylanase enzymes which are capable of hydrolysing (pretreated) cellulosic materials for production of hydrolysates (Lütke-Eversloh and Bahl 2011). Among these solventogenic *Clostridia*, *C.acetobutylicum* and *C.beijerenckii*are well studied and have been modified genetically for improved butanol production (Dürre 2008; Papoutsakis 2008). Some research groups have generated strains that can produce 28g/L solvents (butanol 17g/L) (Papoutsakis 2008) and while Ezeji and

Blaschek (2008) developed *C.beijerenckii*BA101 that produced 33g/L solvent from batch fermentation.

Engineering *Clostridia* to improve butanol production is said to have its own challenges because of multiple fermentation pathways and little information about life cycle of the organism (Lütke-Eversloh and Bahl 2011). However, studies for eliminating some reaction pathways and increased overexpression for alcohol production have been on going. For example, the acetone production pathway were reduced or eliminated to in order to produce alcohols (Papoutsakis 2008; Hou et al. 2013). In a study byHou et al. (2013), the effects of inactivating the acetone pathway during ABE fermentation and increasing the alcohol titres were investigated. The two main enzymes in *C.acetobutylicum* ATCC 824 (WT 824) responsible for acetone production are acetoacetate decarboxylase (*AADC*) and coenzyme-A transferase (*CoAT*). The reaction pathways catalysed by the two enzymes with their respective genes; (see Figure 2-4) were repressed. The outcome was production of 14.8 g/Lbutanol after 64 h of fermentation and acetone production was reduced to0.15 g/L in the engineered strain 824. These results showed that metabolic engineering will bring a crucial solution in providing strains that can selectively produce alcohols. This means more substrate will be diverted to alcohols production rather than acetone.
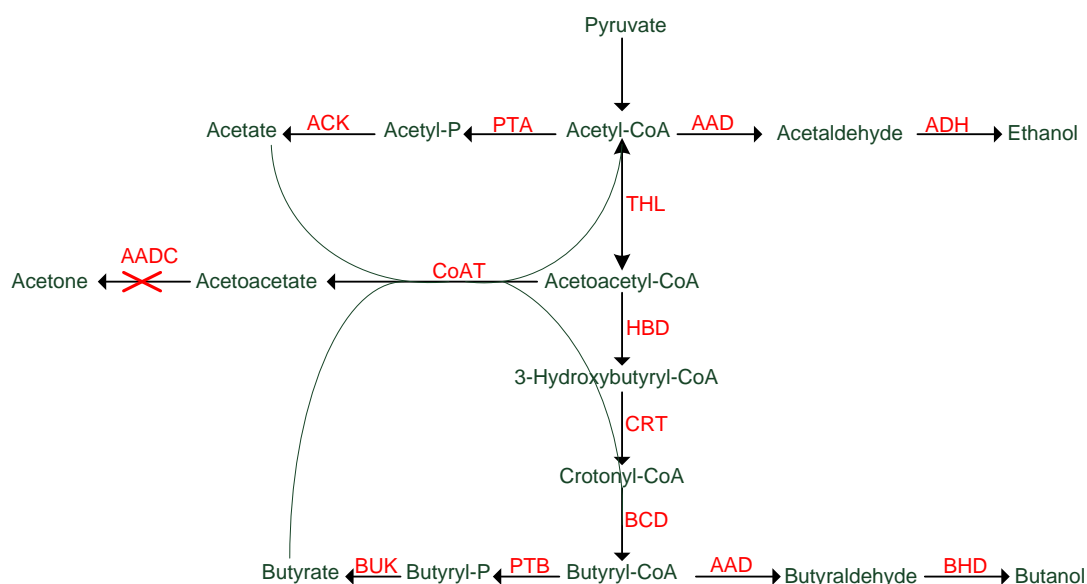
Figure 2-4: The pathways followed for production of solvents during ABE fermentation by solventogenic clostridia with Acetone pathway eliminated. Redrawn from:Hou et al. (2013)

2.4. Lignocellulose Pretreatment

LCBpromises to be available at lower cost than the high substrate cost incurred by 1G ABE fermentation. This is due to their availability in abundance and low value for alternative (non-food) applications.Cellulose and hemicellulose components of LCB are suitable for the extraction of fermentable sugars for ABE fermentation, because *Clostridia* can utilise both hexose and pentose sugars. Residual lignin from LCB after hydrolysis, fermentation and purification can be sent to boilers for generation of steam and electricity or be further processed for industrial chemicals production.

In order to make sugars present in cellulose and hemicellulose components readily available in the form of fermentable hydrolysates, LCB has to undergo pretreatment and subsequent enzymatic hydrolysis (García et al. 2011).During pretreament process, LCB is subjected to harsh conditions in which the structure is changed by destructing and opening up cell wall. The crystalline cellulose is attacked, increasing its porosity such that the surface area for enzymes to act on is exposed, while in some methods, hemicellulose and lignin are removed (Chandra et al. 2007; Elander et al. 2009; García et al. 2011). Pretreatment can be categorised into physical, chemical and biological processes, or a combination of any of the processes.

2.4.1. Physical Pretreatment Method

The physical pretreatment of LCB involves mainly size reduction to make material handling easier (Mosier et al. 2005b). The process of size reduction also destructs the plant cell wall structure; destructing cellulose crystallinity and thus making it more accessible to cellulase attack (Chandra et al. 2007). According to Mosier et al. (2005a) chipping, grinding and milling, or combination of these are done during physical pretreatment method. Soni et al. (1982) used chopping method for bagasse and rice straw before the alkali pretreatment for enzymatic hydrolysis.However, physical pretreatment can be expensive, because the energy cost for size reduction in milling increase exponentially with fine milling. It is therefore advised to reduce feedstock particle size just enough for pretreatment suitability. The other disadvantage is that physical pretreatment does not result in lignin removal which could hamper enzymes efficiency in subsequent enzymatic hydrolysis(Chandra et al. 2007).

2.4.2. Physiochemical Pretreatment Method

The physiochemical pretreatment involves the combination of physical and chemical method to pretreat LCB in which high pressures and temperatures are used. This method has been applied extensively in research in the form of catalysed steam explosion pretreatment (STEX), ammonia fibre explosion (AFEX) and liquid hot water pretreatment (LHWP) as well acid and alkali pretreatment (Chandra et al. 2007).

AFEX pretreatment method uses liquid anhydrous ammonia at moderate temperatures of 60°C to 100°C at high pressure usually 5 bars for 5 minutes, (Teymouri et al. 2005). The prepared biomass is placed in the reactor containing spherical steel pellets that minimises liquid ammonia evaporation. The reactor is tightly closed and exposed to reaction temperature and pressure for desired time; usually 5 minutes. After that time, the reactor is suddenly decompressed creating an explosion. Ammonia vapour destroys the cell wall structure of biomass, reducing the cellulose crystallinity and solubilises the hemicellulose and lignin (Teymouri et al. 2005). This method has minimal degradation of cellulose and hemicellulose sugars to inhibitors. It is also a dry process and therefore there are savings in water usage and it is suitable for high solids loading in pretreatment reactor. Ammonia can be recovered leading to reductions in materials cost (Teymouri et al. 2005).

LHWP involves LCB pretratment using liquid hot water at temperature ranges of 160°C to 230°C. Different reactor configurations such as plug flow reactor (flow-through and/or counter-current) or batch reactor (co-current) are used (Liu and Wyman 2005; Mosier et al. 2005b; Qureshi et al. 2008a). This process maximises the solubilisation of hemicellulose to oligomers with minimisation of monomeric sugars and thus reduces the degradation of monomer sugars to inhibitors (Liu and Wyman 2005; Mosier et al. 2005a). However, the use of large volumes of hot water by this method can have negative impactson the water footprint and energy balances of the process. To minimise water usage, Liu and Wyman(2005)investigated corn stover pretratment in a partial flow pretreatment reactor using LHW. LHW has been used in other studies too. For instance, Mosier et al. (2005a) studied the pretreatment of corn stover, while Qureshi et al. (2008a)pretreated corn fibre using

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LHW at an optimised pH to produce a hydrolysate with low inhibitors' concentration for subsequent processes.

In a study by Ezeji and Blaschek (2008), distiller's dried grains and solubles (DDGS) from grain-ethanol production were subjected to AFEX and LHWP, with subsequent enzymatic hydrolysis to produce hydrolysates from fibrous components, for butanol production by different types of *Clostridia*. These methods produced fermentable sugars in the form of hexoses and pentoses. Their results showed that LHW produced total sum of 48.8 g/l sugars, while AFEX produced 41.4 g/l. ABE fermentation of the hydrolysates was performed and the above mentioned ABE solvents were produced without any inhibition by sugar degradation products. Fermentation stopped because of sugar depletion in the broth. This result was a significant one because the methods showed minimal production of inhibitors due to less severe pretreatment conditions since DDGS had been pre-processed.

Steam Explosion Pretreatment (STEX) method can be done uncatalysed or in the presence of catalyst to enhance hemicelluloses removal. Sulphur dioxide (SO_2) or dilute H_2SO_4 are the common catalysts used for steam explosion. In steam explosion the reactor is decompressed at the end of the reaction time by releasing pressure. The rapid decompression of the reactor contents causes a vigorous explosive shocks and raptures the structure of the biomass. The acetic acid formed during deacetylation of acetyl groups is thought to hydrolyse the hemicelluloses during steam explosion, while water behaves like a weakacid at high temperature (Mosier et al. 2005b). In steam explosion, the hemicellulose solubilisation and cellulose disruption are the main targets as it increases the enzymes accessibility to cellulose.

2.4.3. Chemical Pretreatment Method

The chemical pretreatment method employs the use of either acid or alkali to destroy the structure of LCB by opening up cell wall structure. The crystalline cellulose is attacked, increasing its porosity and the surface area for enzymes to act on is exposed, while hemicellulose and lignin are partially or completely removed (Chandra et al. 2007; García et al. 2011). With either the acid or alkali, the method uses high chemical loading at a lower temperature or low chemical loadings at high temperature. The choice of chemical loading is based on the type of LCB being pretreated, the costs of having process units that can resist extreme conditions used

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and formation of inhibitors during the reaction (Qureshi et al. 2008a). Generally, the high chemical loading method is considered corrosive to equipment. In addition, it requires large amounts of neutralising agent to correct hydrolysate pH and that drives up chemical costs even higher. Furthermore, the recovery of neutralising agent may be necessary and that means extra costs in terms of purchased equipment (Mosier et al. 2005b).

The dilute acid pretreatment is effective in solubilising most of the hemicellulose and part of the lignin during pretreatment. The insolubilized hemicellulose and its oligomers are further converted into xylose during enzymatic hydrolysis process provided the enzyme cocktail has xylanase (Qureshi et al. 2008a). Most common acids used are sulphuric acid (H_2SO_4) and hydrochloric acid (HCl). H_2SO_4 is mostly used in research and industry as compared to HCl because of its strength due to two hydrogen ions and also it's easy of availability. For dilute acid pretreatment, Llyod and Wyman(2005)varied the temperature and acid concentration and they foundthe maximum combined sugars yield was measured at a pretreatment temperature of 180ºC, H_2SO_4concentration of 0.49% (v/v), and pretreatment time of 5 minutes. Their study found more than 90% recovery of the total sugars from corn stover.Liu et al.(2010) used dilute H_2SO_4 0.75%(v/v) to pretreat wheat bran and the resultant hydrolysate had 93% of the sugars initially present in wheat bran.Ting et al.(2013)used 3.6% (w/w) H_2SO_4, temperature of 121ºC for 2.5 hours in corn fibre pretreatment. The dilute acid method is known to produce significant amount of inhibitors such as furfural, 5-hydroxymethylfurfural (HMF) and acetic acids as well as phenolic compounds (Liu and Wyman 2005; Mosier et al. 2005b; Qureshi et al. 2008a; Ting et al. 2013). These inhibitors have negative impact in the hydrolysis and fermentation process because they affect enzymes activities.

Alkali pretreatment is also effective in solubilising most of the hemicellulose and part of lignin during pretreatment. The common bases used in alkali pretreatment process are hydroxides ofcalcium, sodium, potassium and ammonium (Mosier et al. 2005b). The alkali pretreatment employs mild temperatures in the region of (25°C - 60°C) and longer reaction times days to some weeks for its processes (Mosier et al. 2005b). However, higher temperatures such as 120°C can also be used (Ni et al. 2013). The choice for mild or higher temperatures can be selected from energy cost point of view. Kim and Holtzapple (2005)found that the non-oxidative lime pretreatment of

corn stover had higher recovery of glucan and xylan than the oxidative pretreatment. However, the lignin content in the non-oxidative pretreatment was still higher than 50% which had negative impacts on hydrolysis because the cellulase is believed to adsorb irreversibly on lignin surface leaving little to hydrolyse the cellulose. In the 16 weeks of lime pretreatment, the oxidative pretratment removed 87.5% of lignin at 55°C while the non-oxidative removed 47.7%.

2.4.4. Biological Pretreatment Method

Biological pretreatment utilises wood degrading fungi, of the brown, soft and white rot type, to change the chemical composition of LCB. The brown and soft rot fungi are mainly used to solubilise hemicellulose with little attack on lignin, while the white rot fungi can degrade more lignin. Its application has mainly been in pulp and paper processing not in biorefinery (Chandra et al. 2007). This has been due to long residence time required by the fungi to act on LCB. From process engineering perspective, the longer residence time is accompanied with larger reactor vessels and productivity will be low. So, space would be a limiting factor while long residence could affect amount of product produced and have negative impacts in the biorefinery process.

2.5.   Detoxification of Hydrolysates

Pretreatment of LCB is done under harsh conditions to overcome the effect of its recalcitrant structure on bioprocessing. The pretreatment severity, which is the combination of factors used in pretreatment such as temperature, pressure, time of exposure and pH, will determine the yields and concentrations of the inhibitors in the hydrolysates(Lloyd and Wyman 2005). The inhibitors are undesired by-products of pretreatment, which occur as a result of LCB components degradation (Ezeji et al. 2007). They inhibit the activity of microorganisms in the subsequent step of fermentation. For example, in a study by Qureshi et al. (2008a), *C. beijerinckii*BA101 failed to produce solvents in a non-detoxified dilute sulphuric acid hydrolysate of corn fibre, because of severe inhibition to cell growth. By detoxifying hydrolysate prior to fermentation, ABE solvent concentration of 9.3 g/l (butanol 5.7 g/l), was achieved. That was an indication of how significant detoxification of hydrolysates is for fermentation. Furthermore, Ezeji and Blaschek (2008) reported that ABE fermentation using non-detoxified acid pretreated dried distiller's grain and solubles

(DDGS) medium was not able to produce solvents because of inhibitor problems.As a result, inhibitors are usually removed from the hydrolysates and the process of their removal is referred to as detoxification or conditioning. As much as detoxification is important, Ting et al.(2013) warns that it can be difficult to do and also increases production costs.

Detoxification can be done in a number of ways and these are grouped into chemical and physical methods or the combination of the two methods.

2.5.1. Chemical detoxification of hydrolysates

Chemical detoxification of pretreatment hydrolysate involves the addition of chemicals to precipitate and agglomerate the undesired by-products. Overliming is the common method used for conditioning of acid pretreated hydrolysates. This is done by adding either calcium carbonate ($CaCO_3$) or calcium hydroxyde ($Ca(OH)_2$) or sodium hydroxide (NaOH) to the slurry increasing the pH, followed by pH adjustment to neutral by addition of acid. Ezeji and Blaschek(2008)and Liu et al.(2010)detoxified dilute acid pretreated DDGS and dilute sulphuric acid wheat bran hydrolysate by overliming using $Ca(OH)_2$ respectively. Soni et al.(1982)used ammonium sulphate to detoxify alkali pretreated bagasse and rice straw hydrolysates and butanol concentration increased by more than100% for both feedstock.Also, Qureshi et al. (2008a)detoxified barley straw hydrolysate by overliming it with $Ca(OH)_2$ and Na_2SO_3 to pH 10 at 90^oC for 30 minutes, followed by cooling and pH adjustment to 7.0 by concentrated H_2SO_4. This increased ABE concentration by from 7.09g/l to 17.42g/l, which was 146% that of when non-detoxified hydrolysate was used.

2.5.2. Physical Detoxification of hydrolysates

The physical method is can be done in several ways. For instance, adsorption by activated charcoal, ion exchange resin, microporous resin or electrodialysis is widely used. Soni et al.(1982)used activated carbon to detoxify alkali pretreated bagasse and rice straw hydrolysates. This was done after the unconditioned hydrolysates gave poor solvent production. Detoxification resulted in 68% and 70% increase in butanol concentration for bagasse and rice straw hydrolysates respectively. Qureshi et al. (2008a)used XAD-4 resin to remove inhibitors in sulphuric acid corn fibre hydrolysate. Qureshi et al. (2008b)used electrodialysis to remove inhibitors from

alkaline peroxide pretreated wheat straw hydrolysate. The inhibitors removal increased ABE concentration by more than 100% compared to when untreated hydrolysates were used. In some cases, physical pretreatment can bedone by exposing the hydrolysate to vacuum evaporative conditions so that the volatile inhibitory compounds such furfural and acetic acid can evaporate with water. Chen et al.(2010) detoxified the dilute sulphuric acid hydrolysate of corncobs in an evaporator at 70°C under vacuum conditions. This allowed volatile inhibitory compounds such furfural and acetic acid to evaporate with water to produce a concentrated hydrolysate.

2.6.   Enzymatic Hydrolysis of Pretreated Solid Residues

Pretreatment plays a major role in ensuring that LCB is partly or fully transformed into monomeric sugars that can be digested by microorganisms during ABE fermentation process (Elander et al. 2009). Enzymatic hydrolysis is done on solid residues stream from the pretreatment process, although there are some exceptions where the whole pretreatment slurry is enzymatically hydrolysed (Humbird et al. 2011). The solid consists mainly of cellulose and small amounts of hemicellulose and lignin. For example, the acid pretreatment will solubilise about 90% of hemicellulose, 45% lignin and 5% cellulose into a liquid hydrolysate (Humbird et al. 2011).

Enzymatic hydrolysis is affected by temperature, enzyme type and loadings, as well as hydrolysis time.Enzymatic hydrolysis takes place at temperatures around 45°C to 50°C and it has been found to be optimum for most of the cellulases (Lloyd and Wyman 2005).Qureshi et al. (2008a; 2008)performs most of enzymatic hydrolysis at 45°C because it has been found to be optimal for high yields. Ezeji and Blaschek (2008) carried out the hydrolysis of pretreated DDGS at 50°C for 72 hours. Some researchers have found that increasing enzyme loading had significant increase in hydrolysis sugars yield. For example, Liao et al.(2005) varied enzyme loading between 650 - 1300 FPU/L for hydrolysis of cow manure fibre. It was found that increasing enzyme loading increased hydrolysis sugar yield. Thus enzyme loadings of 650 FPU/L gave 28% glucose yield and 1300 FPU/L gave 52% glucose yield in 160 hours from the cellulose content. Llyod and Wyman (2005)also found that maximum sugar yield decreased from 93%to 88% when the enzyme loading was

reduced from 60FPU/g to 7 FPU/g in a corn stover study. Therefore, enzyme loading is a parameter that requires to be taken into account in order to achieve high hydrolysis yields.

2.7.   Comparison of Fermentation Process Technologies

TraditionalABE fermentation was carried out batch-wise using starch and sugar from a 1G feedstock. Shifting from use of 1G to 2G feedstock meant that ABE fermentation process has continuously evolved with several methodologies. Recently, ABE fermentation of hydrolysate from 2G feedstock has been carried out in a number of ways. These include separate hydrolysis and fermentation (SHF), simultaneous saccharification and fermentation (SSF) and simultaneous saccharification and co-fermentation (SSCF). Also, future promising processes like consolidated bioprocessing fermentation (CBP) is currently under development. Studies show that it can only come to demonstrations at industrial scale, once the recombinant microorganism that can efficiently hydrolyse and ferment sugars in one vessel to produce solvents is developed (van Zyl et al. 2007).

The SHF method has been studied extensively and has been previously implemented commercially to produce solvents in China and Russia using 1G feedstock. However, the plants were shut down due to competition from petrochemical butanol. Recently, some of the plants have returned into commercial biobutanol production while others are being revamped to increase capacity mainly in China(Ni and Sun 2009; Zverlov et al. 2006). Companies such as Cathy Industrial Biotech and Laihe Rockly in China, currently produce biobutanol from corn. Gevo and Butamax have also made significant strides in the production of biobutanol (European Biofuels 2013). The current research and demonstrations are on how to improve concentration, yields and productivity of solvents during fermentation.

In SHF method, enzyme is first used to hydrolyse cellulosic solid residues from pretreatment process. Subsequently, the resulting hydrolysate is fermented using solvent producing microorganisms(Balat 2011). Fermentation continues until process stops due to either sugar depletion or cell inhibition by biobutanol. There are two main problems associated with this method; first, the glucose produced during enzymatic hydrolysis may become inhibitory to enzymes at high concentration, which will lead to incomplete conversion of cellulose to glucose and/or a higher required

enzyme dosage.Secondly, the biobutanol produced is inhibitory to microbial activities and cell growth at concentrations from 6 g/l and 16 g/l respectively and cause the fermentation to stop (Cheng and Timilsina 2011; Jin et al. 2011; Patakova et al. 2011; Raganati et al. 2012). This means fermentation is restricted to low product concentrations because the cells are inactive even when there is still source of carbon present in SHF batch bioreactor.

Despite the mentioned shortcomings of SHF, it is still the most widely researched method for ABE fermentation. For example, a number of studies by Qureshi and colleagues investigated production of biobutanol from dilute sulphuric acid hydrolysateof barley straw(Qureshi et al. 2010), and dilute acid and liquid hot water treated corn fibre(Qureshi et al. 2008a). In these studies, cellulosic solid residues from acid and liquid hot water pretreatment reaction were enzymatically hydrolysed achieving more than 80% hydrolysis yields. Hydrolysateswere fermented to produce biobutanol in fed-batch fermentation. Qureshi et al.(2008)investigated the production of biobutanol from dilute acid treated wheat straw using *C. beijerinckii* P260 and SHF. The acid treated wheat straw was enzymatically hydrolysed for 72 hours. The hydrolysate was batch fermented at $35^{°}$C. ABE concentration of 13.38 g/l was produced of which 8.09 g/l was biobutanol.

SSF occurs when cellulosic solid residues from pretreatment process are fed into a bioreactor and the enzymes and bacteria are added simultaneously, so that hydrolysis and sugars fermentation happen simultaneously in one bioreactor (Cheng et al. 2012; Qureshi et al. 2008; Qureshi et al. 2008c). This technique is advantageous because glucose concentration does not reach inhibitory level. The reason is that glucose is continually utilised by the microbes as it is released to produce fermentation solvents. It also reduces the equipment costs because one vessel is used for both hydrolysis and fermentation processes instead of two. However, SSF also has its own challenges. One of the challenges is the difference between the optimum temperature requirement for hydrolysis enzymes and fermentation bacteria. Enzymatic hydrolysis is usually done at temperature range of $45^{°}$C to $50^{°}$C for effective activity of enzymes. The bacteria on the other hand require around $35^{°}$C temperature for fermentation, implying lower enzymatic activity(Jones and Woods 1986).Qureshi et al.(2008c; 2008b)investigated production of biobutanol using *C. beijerinckii* P260 by SSF of dilute acid treated wheat straw at $35^{°}$C. In the

process, all wheat straw was hydrolysed in a batch and fed-batch SSF and a total of 378.9g sugar was fed together with 86 g wheat straw. 192 g/l ABE solvent was obtained with a corresponding yield of 0.44g/g sugar. They also found that supplementing wheat straw hydrolysate with sugar increased productivity from 0.31 to 0.36g/l/h. In their previous study where they did not supplement sugar, they found productivity to be low due to limited sugar.

SSCF involves carrying out the cellulosic enzymatic hydrolysis, glucose and pentose fermentation (which comes from the liquid stream of the pretreatment operation) simultaneously in a single bioreactor. The successful operation of this process depends on the ability of the microorganism to simultaneously utilise both hexose and pentose sugars for solvent production during fermentation (Balat 2011). Shah and Lee (1992)investigated the simultaneous saccharification of pretreated hardwood and extractive fermentation in a fed-batch mode at 36°C in a 750mL bioreactor. They achieved extractive recovery of biobutanol of 81.3%, while that of acetone and ethanol were 57.8% and 33.3% respectively.

The actual fermentation can be done in in batch mode, fed-batch mode and continuous mode and each method has its own merits and drawbacks. The batch method is the most practiced method because of its simplicity and lowoperational requirements as compared to fed-batch and continuous. However, the method becomes disadvantaged in ABE fermentation process because of inhibitory conditions created by butanol product accumulation. Also, the fermentation feed sugar is limited to around 60 g/l to avoid high sugar concentration inhibition to cells. In fact Qureshi et al. (2013)found that ABE concentration decreased from 24g/l ABE to less than 20g/l when initial sugar concentration was increased from 63g/l to 125g/l using barley straw and corn stover hydrolysates.

Fed-batch method allows concentrated sugar solutions to be fed slowly into the bioreactorand may be coupled with continuous solvent recovery to keep butanol concentration below inhibitory level. Sugar concentrations of more than 200 g/l have been used in fed-batch operation (Lu et al. 2012; Qureshi et al. 2008). Fed-batch method is started with dilute sugar concentration of 60 g/l, to avoid cell inhibition by concentrated sugars (Qureshi et al. 2008). When butanol concentration reaches

inhibitory level (approximately 6 g/l in the bioreactor (Ezeji et al. 2004)), *in situ* product removal process is initiated together with a continuous and controlled feed of concentrated sugar into the bioreactor (Qureshi et al. 2008).

Continuous method which is most ideal for industrial purposes involves the continual feed of sugars and removal of solvents. This allows steady state conditions to be attained and constant volume in the reactors to occur. Concentrated sugar feeds can be used in continuous process but because of to high dilution rates, it results in dilute solvents (Gapes 2000). Therefore, many bioreactors in series connection have to be used to achieve reasonable solvent concentration. Ni et al. (2013) operated four reactors in series in a continuous fermentation of corn stover hydrolysate. An average productivity of 0.429g/l/h was achieved over a period of 220 days which is higher than most batch and fed-batch fermentations. The major problem arises when contamination occurs due to bacteriophage attack. This attack affecting fermentation microorganism has been reportedat industrial plants, leading to loss of products. However, good hygiene, sterilisation of equipment and disinfection are said to minimise such losses arising from bacteriophage (Zverlov et al. 2006).

New process technologies have been studied and tested on continuous process in order to enhance microorganism performance which can lead to improved solvents production. They include: cell recycling Figure 2-5A and immobilised cell Figure 2-5B.
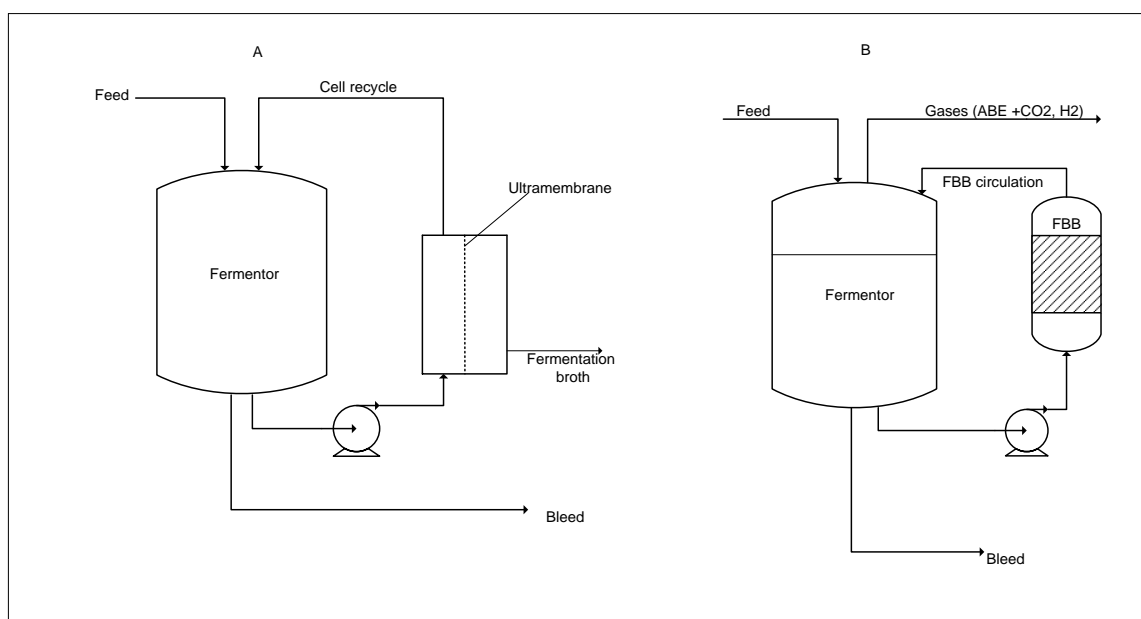
Figure 2-5: A schematic diagram for different ways of cell retaining during ABE fermentation. A: involves cell recycle by ultra-membrane in a separate vessel. B: an immobilised fibrous bed bioreactor (FBB) for cell retention.

In the cell recycle set-up (Figure 2-5A) the bioreactor is coupled with another vessel to retain cells, in order to achieve high cell density at solvent producing state. In cell retaining systems, high productivities can be achieved because of high cell density (Vane 2008). This helps in circumventing the poor cell growth and inhibition by biobutanol, which leads to low solvent productivity in conventional batch bioreactors. As a result, cell recycle configuration techniques have been developed and applied in continuous bioreactors. In this technique, the main bioreactor is connected to another unit of separation, in which a membrane selectively allows the solvent to pass through while retaining the solids with the cells re-circulated back into the fermenter. Fermentation starts in a batch mode during which the cells undergo exponential growth. Later, the fermentation broth is pumped into a connected membrane unit to recover solvents and recycle the cells which are suspended in the broth. This is usually done before the solvent concentration can reach cell growth inhibitory level in the fermenter.

The immobilised cell continuous bioreactor (Figure 2-5B) involves two units where the first is for fermentation process and the second is for cell immobilisation (Lu et al. 2012). Fermentation is initiated in the bioreactor and cell growth monitored. When cell concentration in the bioreactor reaches 4 g/l, at which it normally becomes inhibitory, the pump is switched on to circulate the broth into a packed bed bioreactor for cell immobilisation onto different adsorbent materials, such as clay bricks. In one study, the fibrous bed bioreactor was packed with cotton towel where the *C.beijerinckii* JB 200 cells were adsorbed and grew, achieving cell concentration of around 5 g/l (Lu et al. 2012). The immobilised cells were employed to investigate the production of ABE from a mixture of LCB sugars at different dilution rates. They found that continuous immobilised bioreactor enhanced solvent productivity at high dilution rates

2.8.   Product Recovery Technologies integrated with fermentation

In traditional ABE fermentation process, recovery and separation of ABE solvents into individual products were carried out using conventional distillation. Due to the low concentration of the ABE solvents in the broth, double effect distillationconsumes

a lot of energy and this contributes to high cost of the entire process(Ezeji et al. 2007; Qureshi et al. 2005). Several studies have been conducted to find ways of making recovery/purification more energy efficient, and thus reduce the number of separation steps required. There are two categories of integrated recovery techniques usually researched in the literature. They include: *in situ* product recovery process and *ex situ* product recovery process by gas stripping, liquid-liquid extraction, pervaporation, adsorption, flash and vacuum fermentation (Groot et al. 1992). The advantages and disadvantages of *in situ* and *ex situ* product recovery process are discussed and their types are discussed subsequently.

The *in situ* product recovery process involves the continuous removal of the ABE solvents from the fermentation broth. The distinctive characteristic of this process is that fermentation and removal process take place in one vessel (Vane 2008). This recovery process has a dual advantage of reducing product inhibition by butanol accumulation during fermentation, and increasing the concentration of the solvents for subsequent purification process (Mariano et al. 2012; Mariano and Ezeji 2012; Roffler et al. 1984). The result of these advantages is that energy requirement for downstream purification process is reduced. In addition, reactor productivity is increased because solvents are continuously removed, therebyminimising product inhibition. The disadvantage of *in situ* product recovery process is that some of the processes like liquid-liquid extraction can be toxic to fermentation microorganism, due to extractants used and membrane clogging for techniques like perstraction and pervaporation.

For *ex situ* recovery process, fermentation takes place in the main fermenter and the fermentation broth is pumped to a recovery unit where the solvent is recovered by any of the methods mentioned earlier (Lu et al. 2012; Mariano and Ezeji 2012; Qureshi and Maddox 1995; Setlhaku et al. 2013).In the recovery vessel, the solvents are recovered and are sent for further purification process to obtain final products. The solvent lean stream is recycled back to the bioreactor and cycle continues until the end of the production process (Vane 2008). The main advantage of this process is that fermentation and recovery can take place at different operating conditions that are suitable for each process (Vane 2008). This can enhance the recovery process which could otherwise be hampered by fermenter conditions. The disadvantage of this method is that it leads to increased process capital costs due to extra process

units. It can also contribute to higher energy costs if the recovery process has to take place at higher temperature and also the pumping costs between the units should be taken into account(Adhami et al. 2009; Ezeji et al. 2004; Ezeji et al. 2005; Huang and Meagher 2001; Izák et al. 2008; Kraemer et al. 2011; Liu et al. 2005; Lu et al. 2012; Mariano et al. 2011; Mariano et al. 2012; Qureshi and Maddox 1995; Setlhaku et al. 2013; Van Hecke et al. 2013).

2.8.1. Gas Stripping Fermentation

Gas stripping has been coupled with batch, fed-batch and continuous fermentation to recover ABE solvents from the fermentation broth hence the term *in situ* product recovery (de Vrije et al. 2013). Its important feature is that fermentation and product recovery take place in one vessel leading to savings in terms of purchased equipment costs and more importantly minimising product inhibition (Qureshi et al. 2008, 2010, 2013). De Vrije et al.(2013) carried out a continuous Isopropanol-Butanol-Ethanol (IBE) fermentation coupled with gas stripping. They found that gas stripping helped to increase the sugar consumption rate to 4.4 g/l/h, butanol concentration to 4.9g/l and productivity to 1.3g/l/h when compared with the control experiment (2.6 g/l/h, 4.3g/l, 0.79g/l/h) at dilution rates of 0.12 h^{-1}. The fact that the technique does not use membrane relieves it from problems of membrane fouling and unlike liquid-liquid extraction; no expensive and harmful extractants are used (Ezeji et al. 2004; 2005; Jang et al. 2012; Lu et al. 2012; Qureshi and Blaschek 2001; Setlhaku et al. 2013).

The fermentation gases (CO_2 and H_2) can be used as an option to inert nitrogen gas leading to reduced costs on gas purchase (Qureshi et al. 2013). The gas is sparged into a bioreactor through a sparger thereby creating bubbles. The formation and breaking of the bubbles inside the bioreactor causes liquid particle vibrations resulting in removal of volatiles from the liquid phase (Ezeji et al. 2005). These gases also act as mixing medium inside the bioreactor. The solvents are condensed from the gas phase in a condenser, collected in a receiver unit and are sent for further separation by distillation, while the stripped gas is returned to the fermenter to recover more solvents (see Figure 2-6).

A number of studies have been done to improve the technique and parameters such as gas recycle rate, gas bubble size, condensation temperature, and so on. The

influence of gas recycle rate, gas bubble size, antifoam addition and presence of ethanol and acetone was investigated by (Ezeji et al. 2005). They found that gas recycle rate and addition of antifoam had the greatest effect on the recovery. They have observed that gas recycle rates of 80 cm^3s^{-1} were sufficientfor keeping the butanol concentration below toxic levels in a 2-L bioreactor. They also noticed that the use of sparger created bubble sizes less than 0.5 mm, which led to the formation of foam and this requires the addition of large volume of antifoam thus affecting ABE production negatively. Ezeji et al.(2013) investigated the impacts of bleed and *in situ* gas stripping product removal from the fermentation using *C.beijerinckii* BA101 and achieved a total solvent concentration of 461.3 g/l ABE from 1,125.0 g/l glucose.

Xue et al.(2012)investigated fermentation by *C.acetobutylicum* JB200 in a fibrous bed bioreactor integrated with a two-stage *in situ* gas stripping for enhanced and energy efficient biobutanol recovery. They produced a final product mixture of 94.0g/l acetone, 420.3g/l biobutanol, 18.0g/l ethanol, and no acid. This process yielded an ABE solvent ratio of 5:23:1, which is better than the 3:6:1 usually obtained in a conventional batch fermentation process. This is a proof on how process engineering of fermentation process configurations helps to enhance ABE fermentation process. Lu et al. (2012)also investigated the fed-batch fermentation for biobutanol production from cassava bagasse hydrolysate in a fibrous bed bioreactor using a high tolerant butanol strain of *C.acetobutylicum* JB200 with continuous gas stripping (Figure 2-6). They found a final concentration of condensed ABE of 108.5g/l. This concentrationis comparable to that of Xue et al. (2012), which could lead to potential energy savings during downstream processing. The aqueous phase can further be subjected to second stage gas stripping to further increase biobutanol concentration and combine the concentrated streams for distillation(Xue et al. 2012).

Although gas stripping process is seen as simple and easy to operate, it should be noted that it can have considerable costs owing to the equipment used to condense the solvents and compression of the gases for recycle into the fermenter. Once the gas strips off the solvents from the fermentation broth, it is cooled to low temperatures in order to condense the solvents out of the gas stream (de Vrije et al. 2013; Lu et al. 2012).When condensing temperatures are lowered below 0°C, there are some energy costs incurred in terms of refrigeration requirements. Another major disadvantage of gas stripping is that of low selectivity and leads to removal of water

and acids together with the desired solvents (Dürre 1998). This has negative impact with regards to energy requirement in the subsequent purification process since water and other impurities still have to be removed. Qureshi et al. (2005) found that energy requirement for fermentation integrated with gas stripping was 21.8MJ/kg butanol. This was the biggest on the recovery technologies investigated.
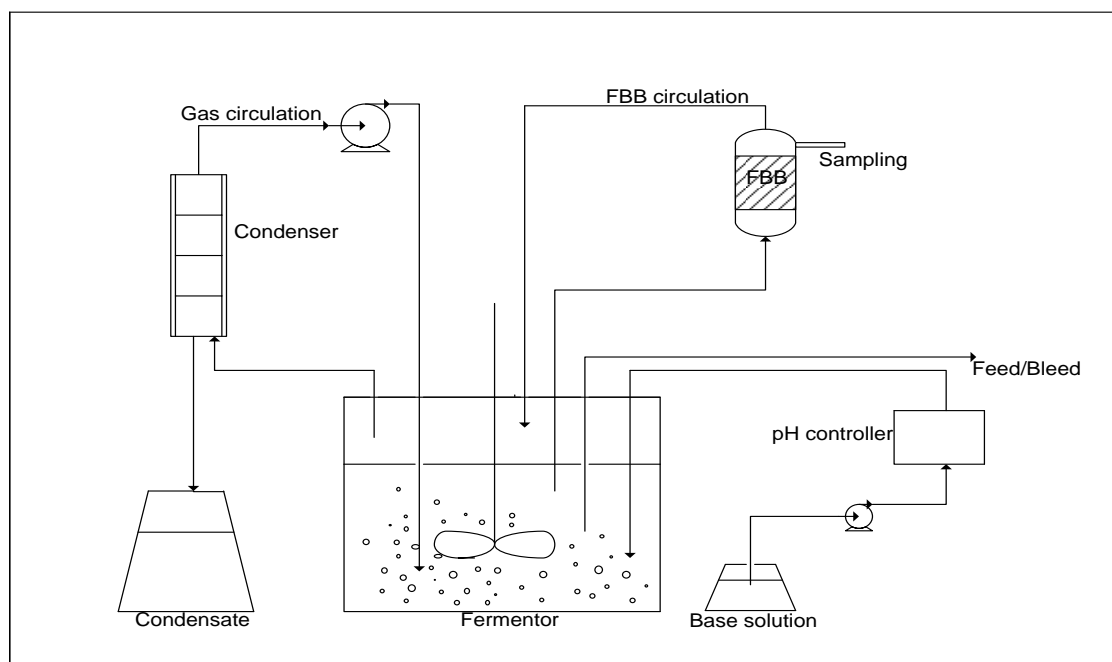
Figure 2-6: A set up for ABE fermentation with Fibrous Bed Bioreactor (FBB) for cell immobilisation integrated with gas stripping redrawn from (Lu et al. 2012)

2.8.2. Flash Fermentation

Flash fermentation allows the bioreactor to be operated at atmospheric pressure, while the broth is circulated to a vacuum reactor causing the solvents to boil off (Mariano et al. 2011; Roffler et al. 1984). By separating the flash tank from the bioreactor, the carbon dioxide from fermentation need not be compressed. This could lead to reduced compressor costs if carbon dioxide is not considered as a secondary product that can be sold in the market and therefore be vented off. Energy demand of this process could be significant due to maintaining the second vessel under vacuum. In addition, the energy requirement for condensation of vapourised solvents should be considered in the overall energy demand of the process (Mariano and Filho 2012). On the other hand, accumulation of the non-

volatile products in the bioreactor will have to be reduced by bleeding some broth (Roffler et al. 1984). Loss of ABE solvents is iGENitable in this case, when there is already low concentration of products in the bioreactor.

2.8.3. Vacuum Fermentation

This fermentation technique involves maintaining the fermenter under the vacuum by using an external pump. The most volatile fermentation products will be removed as they boil off at normal fermentation temperature; around 35°C. A low product concentration is able to be maintained in the fermenter and this significantly contributes to the reduction of product inhibition (Mariano et al. 2012; Mariano and Ezeji 2012; Roffler et al. 1984). It should be noted that only one unit of operation is required with vacuum fermentation because the vacuum is maintained in the fermenter. As a result, the capital cost is not increased as compared with flash fermentation.

Mariano et al. (2012; 2012) investigated the *in situ* recovery of biobutanol by vacuum and cyclic vacuum during ABE fermentation. The former study showed that *in situ* vacuum fermentation improved cell growth that led to complete utilisation of substrate and increase in productivity. Having shown improvements brought by *in situ* vacuum fermentation, they investigated the effects of cyclic vacuum fermentation on the energy requirement of the fermentation process. Two hours' cyclic vacuum fermentation was separated by four hours' fermentation at atmospheric pressure without recovery. During cyclic vacuum fermentation, less water was vapourised as compared to continuous vacuum. This water was correlated with the amount of energy required to compress vapourised ABE solvents. Their analysis showed that cyclic vacuum fermentation led to 39% energy savings. The concentrated stream produced by cyclic vacuum fermentation will also lead to further energy savings in distillation process for further purification.

The disadvantage of vacuum fermentation is that of poor selectivity because all fermentation solvents in the broth are vapourised. As mentioned under flash fermentation, energy requirements will still be present for condensation of vapourised solvents as well as for removal of water in subsequent purification process.

2.8.4. Pervaporation Fermentation

Pervaporation is a technique that allows the selective removal of volatile compounds from fermentation broth using membrane technology (Ezeji et al. 2007; Jin et al. 2011; Qureshi and Blaschek 1999; Van Hecke et al. 2013). The membrane is placed in contact with the fermentation broth and the volatile or organic component selectively diffuses through the membrane as a vapour and is then recovered by condensation. In this process, a phase change occurs from liquid to vapour due to vacuum conditions, maintained on the permeate side of the membrane by continuous suction (Izák et al. 2008). As it is a selective removal process, the desired component requires a heat of vaporization at the feed temperature, which is fermentation temperature (Qureshi and Blaschek 1999). However, when pervaporation is done at higher temperatures, a separate vessel is used. This is to ensure those severe temperatures do not affect that of fermentation process. The effectiveness of pervaporation depends on selectivity of desired solvent and flux through the membrane, which can be a liquid or solid membrane (Jin et al. 2011; Qureshi and Blaschek 1999). Garcia et al. (2011) reviewed the current status of pervaporation as a recovery technique for dilute solutions such as ABE solvents in fermentation broth and found that it could be less energy intensive.

In a study by Izáket al. (2008)the ionic liquid, polydimethylsiloxane, supported by ceramic ultrafiltration membrane was used to selectively recover biobutanol from fermentation broth, and the process achieved a productivity of 2.34 g/l/h. Liu et al. (2005) studied the separation of ABE solvents from the dilute aqueous binary solutions and quaternary solution by pervaporation using poly ether block amide 2533 membrane. The parameters they investigated included membrane thickness, temperature effect and feed concentration. They found that increasing the content of organic compound in the feed increased the permeation flux of the organic compound. An increase in temperature decreased the butanol permeate concentration, due to an increase in water flux and decrease in butanol flux as temperature increased. Huang and Meagher (2001) also found that increase in feed temperature of the ABE broth allowed higher solubility and diffusivity of butanol through a membrane. However, at temperatures greater than 70°C, diffusivity of water increased dramatically at the expense of butanol flux. After 20 hours of

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pervaporation, no acetic and butyric acids were detected in permeate and the membrane showed no signs of fouling by the ABE fermentation broth.

2.8.5. Liquid-Liquid Extraction Fermentation

The liquid- liquid extraction (LLE) technique is one among the recovery techniques to avoid high energy costs associated with conventional distillation. In this method, the fermentation broth is brought into contact with an organic solvent that is insoluble in broth, either *in situ* or in an external vessel (Qureshi et al. 1992).The solvent with high affinity to the extractant migrates from the broth into the extractant forming aqueous and organic phases after which they can be separated easily to get high purity product, while the extractant is recycled (Ezeji et al. 2007; Qureshi and Maddox 1995). Several solvents such as vegetable oils, fatty esters, paraffinic hydrocarbons and primary alcohols are used in LLE to extract dilute concentration of alcohols from dilute fermentation broths. These solvents will need to be non-toxic to fermentation microorganism, have high affinity or selectivity towards desired products and be insoluble in fermentation broth (Roffler et al. 1984).

Adhami et al. (2009) investigated oleyl alcohol and soyabean-derived biodiesel as solvents in extracting butanol from the simulated mixture of ABE fermentation using biodiesel crude glycerol as a medium. They found that biodiesel was very selective to butanol over ethanol and propanediol and was able to extract up to 71% butanol in a two stage extraction process. Oleyl alcohol, which was investigated, achieved 84% butanol extraction. Still with the aim of minimising product inhibition and increasing solvent productivity, Bankar et al. (2012) incorporated *in situ* LLE in their two stage continuous bioreactor fermentation. The inclusion of *in situ* LLE between the stages managed to produce a final solvents concentration of 25.32g/l, solvent productivity of 2.48g/l/h and glucose utilisation of 83.21%.

The important parameter in LLE called partition coefficient,*K*, helps to understand which solvent has a better extraction property than others, for any given solute. It gives the ratio of the concentration of solute (biobutanol in this case) in the extractant to the concentration of solute in aqueous phase (Adhami et al. 2009). The higher the *K* value the better the solvent as an extractant. Shah and Lee (1992) investigated the simultaneous saccharification of pretreated hardwood and extractive fermentation

(SSEF) in a fed-batch mode with a semi-permeable silicone membrane tubing immersed and wound against the bioreactor wall, and connected to external extractant container. Oleyl alcohol was used as an extractant because it is non-toxic to *C. acetobutylicum* and has a high *K* for butanol. The extraction recovery of biobutanol was 81.3%, while that of acetone and ethanol were 57.8% and 33.3% respectively. It was believed that percentage recovery could even be more if the process was continued beyond 428 hours in SSEF in fed-batch process.

Van der Merwe et al. (2013) compared three conceptual process designs in the production of biobutanol from sugarcane molasses. Process design 1 involved batch fermentation with steam stripping distillation as separation technology, Process design 2 consisted of batch fermentation plus centrifugation, LLE and steam stripping distillation and Process design 3 included fed-batch fermentation integrated with gas stripping, LLE and steam stripping distillation. Their major finding was that process design 3 was least demanding in terms of energy for separation and purification of biobutanol as compared to others. The major contribution was attributed to LLE and less to gas stripping. This finding shows that the combination of integrated fermentation and low energy demanding product recovery and separation techniques can bring energy cost down.

2.8.6. Adsorption

This technique uses solid, porous adsorbents with large surface areas for recovery of ABE solvents from the fermentation broth. The adsorbents can be in the form of activated carbon and polymeric resins. The adsorbents can be added into the fermenter or placed in a separate vessel where broth is circulated (Roffler et al. 1984). Liu et al. (2014) performed several studies in which they compared batch, fed-batch and continuous fermentation coupled with product recovery by adsorption on KA-I resins. The biofilm reactor was made by fixed-bed adsorbents of KA-I resins and it is reported that 1.51g/l/h solvent productivity and 0.33g/g solvent yield were obtained in fed-batch fermentation. Another significant increase in volumetric productivity of 1.69g/l/h was obtained in a repeated fed-batch fermentation coupled with cell recycle and product recovery by adsorption on polyvinylpyridine (Yang and Tsao 2004). Adsorption was reported to reduce solvents inhibition on microorganism,

while cell recycle ensured prolonged operation due to high cell density available. It is interesting to note that adsorption, when simultaneously used with fed-batch fermentation, produces significant improvements in the process in terms of product concentration and productivity.As a result, the energy demand for this recovery process is low(Dürre 1998). Qureshi et al. (2005) found that energy requirement for fermentation integrated with adsorption was 8.2MJ/kg butanol. This is the lowest on the recovery technologies investigated.

2.9.   Thermodynamics of the Butanol-Water mixture

The thermodynamic behaviour of butanol-water mixture is very complex because of differing chemical properties of butanol and water. Firstly, butanol boiling point is 117°C and that of water is 100°C(Seader et al. 1997). As a result of these boiling points, water is expected to be more volatile than butanol. When distillation is used to separate the mixture, the difference in relative volatility between the components is used. Normally, the more volatile component boils off first and it is obtained as the distillate while the less volatile component is collected as the bottoms(Seader et al. 1997). Therefore, during distillation water will be expected to vapourise more easily than butanol. However, that is not the case because of vapour pressures of these components. Butanol has a vapour pressure of 605.2 Pa and that of water is 2337.7 Pa at standard conditions(Seader et al. 1997). These vapour pressures change the whole behaviour during distillation and pure components are not obtained. Butanol-water mixture is even made complex for distillation by presence of azeotrope which is discussed subsequently.

From Figure 2-7, the left side of the azeotrope point finds application in processes where butanol of highest purity is not required. It is only important for conditions of pre-concentration of butanol. As it has been mentioned that butanol has lower vapour pressure than water, it is more volatile to the left of the azeotrope. As a result, this behaviour has been manipulated in fermentation improvement technologies such as gas stripping. Gas stripping is done at conditions of fermentation which are normally 35 - 37°C and 1atm(de Vrije et al. 2013; Lu et al. 2012).

Thebinary system of butanol-water is known to form minimum boiling point azeotrope (also known as heterogeneous azeotrope) at atmospheric conditions(Seader et al.

1997). Therefore, when distillation is used to separate the mixture, 100% pure butanol and water cannot be obtained in one column because of the azeotrope. The azeotrope boils at 92.8°C, which is lower than boiling point of butanol orwater (see Figure 2-7). At point of azeotrope, the boiling point composition and vapour-liquid equilibrium diagrams are shown in Figure 2-7 and Figure 2-8. It can be seen that azeotrope contains 24.5% mole butanol. In order to obtain butanol of highest purity, distillation has to be done to the right of azeotrope point (Figure 2-7). That can be achieved by two distillation columns and a decanter (Luyben 2008, Vane 2008, Mariano and Filho 2012, Heitmann et al. 2013, Stoffers et al. 2013). In a decanter, the azeotropic composition of butanol-water mixture is able to separate into two phases. The top phase is butanol rich phase and the bottom phase is lean in butanol and is referred to as aqueous phase. This phase separation occurs because butanol at a concentration of 7.8% weight separate into two phases due to butanol being slightly soluble in water (Mariano and Filho 2012).

The organic phase rich in butanol is pumped in second column. In this column, butanol of highest purity is obtained at the bottoms, while the azeotrope composition of butanol-water is obtained as the distillate(Seader et al. 1997). The distillate is sent through a heat exchanger, where it is condensed and pumped back into the decanter again. The aqueous phase from the decanter is pumped into first column where it is purified to water of high purity to the bottoms(Seader et al. 1997). The azeotrope composition of butanol-water is obtained as the distillate. It is condensed and pumped back into the decanter to effect phase separation again. The discussed set-up is able to achieve butanol of high purity with the use of external components such as entrainers.
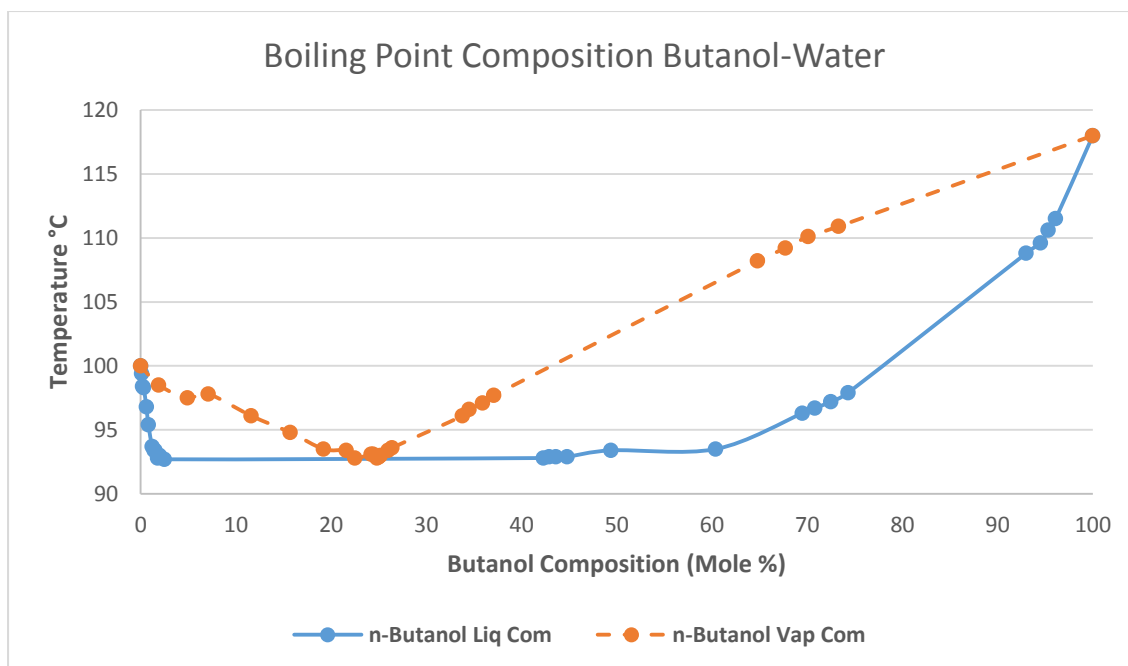
Figure 2-7: Temperature-XY diagram for butanol-water binary mixture at atmospheric pressure (redrawn from Stockhardt and Hull 1931)
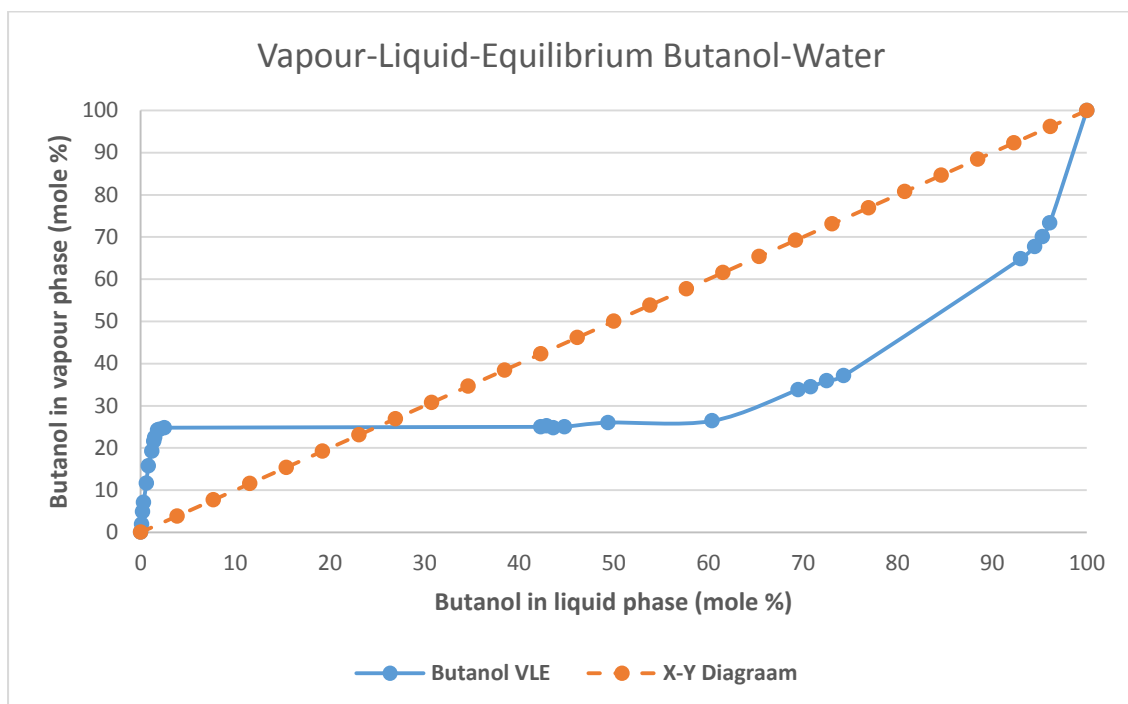
Figure 2-8: Vapour-Liquid Equilibrium diagram for butanol-water binary mixture at atmospheric pressure (redrawn from Stockhardt and Hull 1931)

Thermodynamic equation of states used in ASPEN Plus (2013) to validate the experimental data to produce butanol-water XY-diagram was reviewed, as discussed below. This was done to ensure that the behaviour exhibited by the experimental data agreed with what the models showed(van der Merwe 2010). It is important to choose the appropriate property method for developing models because they have effect on the results of mass and energy. These are ultimately used in the subsequent steps of the study such as equipment design and sizing as well as economics of the process.

For instance, van der Merwe (2013)has done a detailed analysis of choice and validation of different equation of states used for different processes within the whole model. It was found that different property methods using Raoult's Law and activity coefficients could not be accurate at pressures and temperatures greater than the critical temperature of present components. As a result, a different property method hadto be chosen for a particular process and it has to be accurate at the conditions of operation for such unit. For simulation of distillation columns for validating the butanol-water binary mixture vapour-liquid equilibrium XY-diagram, it was found that UNIQUAC physical property in ASPEN Plus (2013)is used (Luyben 2008, Mariano and Filho 2012, Mariano et al. 2011). In some studies,Non-Random Two Liquid(NRTL)activity coefficient property method was used to adequately describe vapour-liquid equilibrium as well as liquid –liquid equilibrium (Stoffers et al. 2013, Heitmann et al. 2013). This property method was also used by Pucci et al. (1986) in a three phase distillation to calculate both VLE and liquid-liquid equilibrium. It can be concluded that the choice of property method to use is dependent on the composition of the mixture and operation conditions.

2.10. ABE Recovery and Purification Technologies

2.10.1.   Double effect Distillation

Traditionally, ABE fermentation solvents were refined by double effect distillation(DD). However, the presence of multiple components in ABE solvents meant that refining of these solvents into individual desired products was challenging. Firstly, the process is energy intensive because of large volume of water

present in the fermentation mixture, which needs to be vapourised(Qureshi et al. 2005; Mariano and Filho 2012). Secondly, DD is made even complex by the presence of azeotropes that forms between ethanol-water and butanol-water. To get products of high purity in the presence of azeotrope, requires special treatment of such mixtures. In DD the set-up of the purification consists of five distillation columns namely beer column, acetone column, ethanol column,butanol column and water column integrated with a decanter (Mariano and Filho 2012; Mariano et al. 2011, 2013; van der Merwe 2013) (see Figure 2-9). Each of these columns performs a particular duty and in some cases a column or two are connected to fulfil their function.
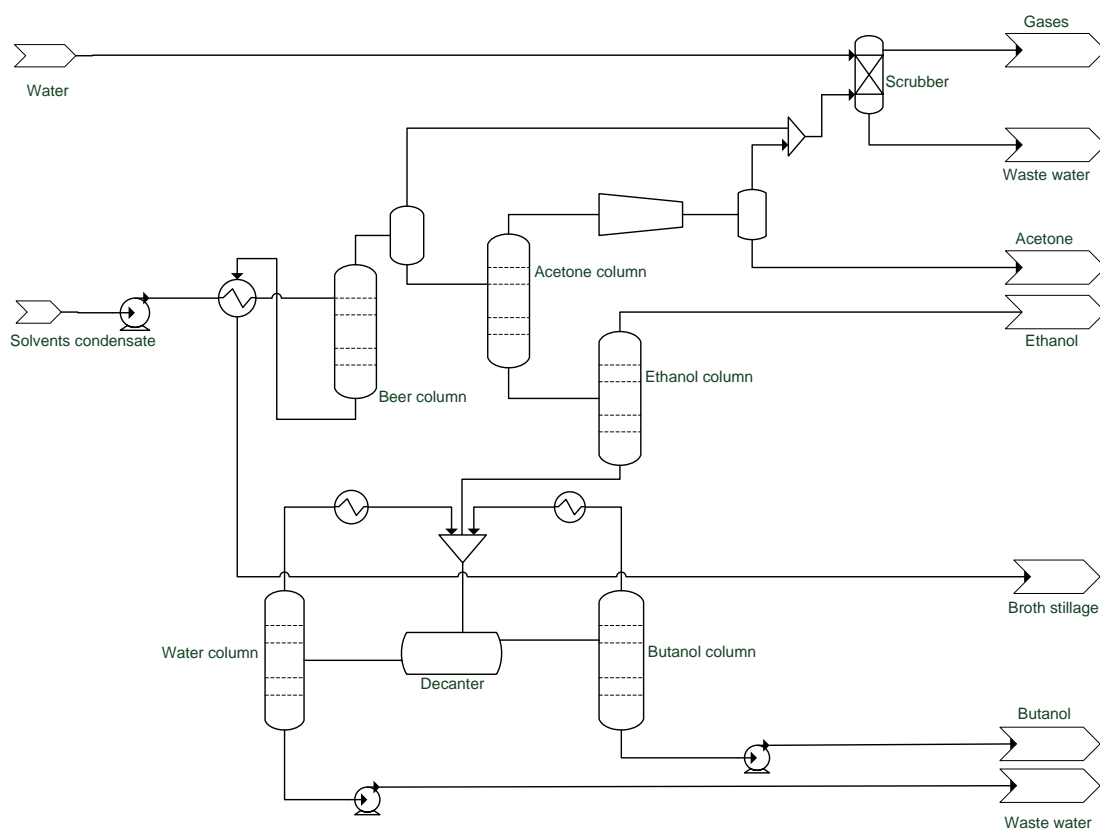
Figure 2-9: Process Flow Diagram for Double effect distillationto obtain ABE as final products. The main equipment's are five columns, Scrubber and a Decanter

Double effect distillationhas both advantages and disadvantages as ABE solvents purification technique. The main advantage of DD is that it has been used in the industry intensively (Mariano et al. 2011). As a result, it is well understood method of

purificationand it has all the available tools to improve its efficiency. In addition, DD allows the feed of multicomponent to be separated into individual components of high purity(Vane 2008). Although DD has these advantages, its main weakness is that of high energy consumption when separating the feed into its purest components(Qureshi et al. 2005; Mariano and Filho 2012). The energy requirement is in the reboilers of the main columns, which provide heating to the stripping section of the column. Studies have shown that when DD is used for butanol production, the energy requirement for refining is greater than the energy content of produced butanol(Mariano and Filho 2012). From energy efficiency perspective, that result is not favourable. Furthermore, the large number of columns presents significant cost to the overall total capital cost and running cost of the plant.

2.10.2.   LLE as a Downstream Recovery and Purification Technique

Due to the discussed disadvantages of DD, other purification techniques have been investigated in order to reduce the hurdles of DD. Liquid-liquid extraction is one of the methods which can be used as an alternative to DD. In ABE fermentation, studies which have used LLE have used it as fermentation improvement technology. In that case, it is used integrated with fermentation in either *in situ* or *ex situ* process (section 2.8.5). It should be noted that here LLE integrated with distillation is used as a refining technique and as an alternative to DD. This alternative has not been extensively studied, and there is limited literature where it was used as a refining technique (Kraemer et al. 2011; Heitmann et al. 2013; Stoffers et al. 2013; van der Merwe et al. 2013). The advantage of this LLE integrated with distillation is that the extractant used is more selective towards butanol. This means from the extraction column, water leaves with the raffinate as the bottoms. Butanol leaves with the extractant and it is separated in the subsequent columns. Because of varying boiling points between butanol and extractant used, it is easier to separate butanol and recycle the extractant into the extraction column. The process flow diagram for LLE and distillation is shown in Figure 2-10.
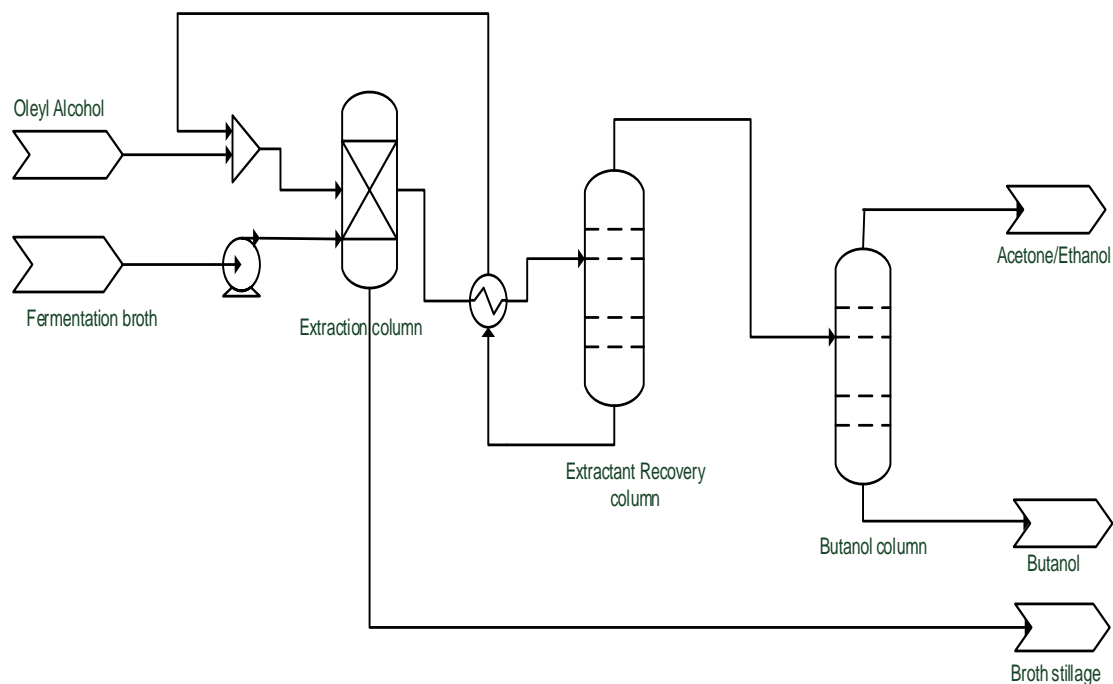
Figure 2-10: Process Flow Diagram for Liquid-Liquid Extraction and Distillation. The main equipment's are extraction column, extractant recovery column and a butanol and acetone/ethanol column

Several extractants can be used here and the advantage is that only selectivity and distribution coefficient towards butanol are the main concern. Unlike when LLE is integrated with fermentation, LLE integrated with distillation does not take into account whether the extractant will be toxic to fermentation microorganism because it does not come into contact with fermenter at all. As a result, an extractant can be chosen from wide ranges which have been investigated. Therefore, the choice of extractant was based on its high selectivity and distribution coefficients towards butanol. In addition, cost and availability was also considered. Several groups of extractants have been studied, including oils, alcohols, alkanes and ionic liquids. Of these groups, ionic liquids are expensive and have lower selectivity and distribution coefficient (Fadeev and Meagher 2001). The oils were found to have moderate selectivity,while alkanes to have high selectivity. However, both of their distribution coefficients were less than 1(Groot et al. 1990). The alcohols were left as the group of choice especially oleyl alcohol, which has been found to have both high selectivity (195) and distribution coefficient (3) towards butanol (Shah and Lee 1992, Kraemer et al. 2011).

2.11. Techno-Economic Studies on Butanol Production

This section gives a brief review on the techno-economic studies in production of biobutanol from both 1G and 2G feedstock available in literature. The achievements contributed by these studies in the field of biobutanol and the challenges that are still present will be discussed. Then conclusions on how well techno-economic studies tie with experimental data available will be summarised. Due to limited commercial plant data available in the literature domain, there is limited number of techno-economic studies available for production of biobutanol. Of those that are there, the data used was from laboratory scale results, which has usually been refined to assume commercial scale. For instance Tao et al. (2011) changed their solids loading in pretreatment to higher than the one used in laboratory scale in order to mimic commercial scale production. The challenge of scaling up microbiological processes to commercial plant scale is that performance is seldom that of laboratory scale (Pfromm et al. 2010). In some cases; pilot plant data could be used, provided it is available. This could give more reliable results since a pilot plant in some cases is a tenth of commercial scale.

Glucose is the main sugar preferred by ABE fermentation microorganism, even though pentoses are consumed. It has been shown experimentally that in a hydrolysate containing all C5 and C6 sugars, glucose is depleted first and is followed by pentoses(Ezeji and Blaschek 2008). As a result, most techno-economic studies used glucose as carbon source in fermentation. Mariano et al. (2013) used sugarcane juice which contains mainly glucose and sucrose as their feedstock for butanol production. The economics of the study from sensitivity targeting butanol production showed that increase in ABE yield from 0.2 to 0.32 by using *C.beijerenckii*BA101 could increase the total revenue of biorefinery by 4.8%. Furthermore, the revenue could be improved by using more energy efficient recovery and purification processes than conventional distillation. Another study by van der Merwe (2013) used sugarcane molasses as carbon source for fermentation studies to investigate biobutanol production energy efficiency and techno-economics from conceptual process models. According to their study, the main sugar component in molasses was glucose even though fructose and sucrose are present in molasses. The economics of the study showed that the use of fermentation improvement techniques such as gas stripping and different separation process like liquid-liquid

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extraction together with improved fermentation strain contributed lowest capital investment of US$187million for Process Design 3. This translated to investment savings of 42% compared to Process Design 1.1 with capital investment of US$321million and did not use any improved fermentation strain and techniques.

Another study which used corn as feedstock for fermentation in a techno-economic study was by Qureshi and Blaschek(2000). When corn is used as feedstock the main carbohydrate is starch which gets converted to glucose during saccharification. However, no saccharification was done as bacterium *C.beijerenckii*BA101 used could ferment starch. They performed sensitivity analysis on a number of parameters and found the price of butanol is affected by corn price, ABE yield in the fermenter and by-product credits such as acetone, ethanol and CO_2 sales. When ABE yield was varied between 0.32g/g to 0.45g/g; butanol production cost reduced by 30% from US$0.73/kg to US$0.51/kg. This meant that the use of mutant strain of *C.beijerenckii*produced high concentration of butanol during fermentation, leading to higher yields, which results in reduced production cost. In another study Mesfun et al. (2014) found from sensitivity analysis that selling of lignin as a co-product decreased butanol production cost by at least 35%. It was further shown that if the other products such as fermentation gases (CO_2 and H_2) and co-products acetone and ethanol can be sold as chemical products, cost for butanol production would be lowered even further.

A series of techno-economic studies by Dias et al. (2014) and Pereira et al. (2014)have shown that production of butanol from ethanol within a sugarcane distillery and selling it as a chemical was more attractive than selling it as a biofuel. The IRR was 13.3% compared to 9.2% with the revenues of US$78.9compared to US$65.7 per tonne of processed sugarcane for chemical market sales and biofuel sales respectively. This was from the plant of same capacity. Since butanol has application both as a chemical product and biofuel, normally it is sold in the chemical market for higher profit margins as was shown by the results. Another important factor is that of butanol quality, where the stringent purity is required in chemical market and thus making its total investment cost to be higher than that when it is sold as a biofuel. It should be noted that from that study butanol was not produced from fermentation route but from ethanol through catalysis route, therefore costs could have been driven up by type and amount of catalyst used in the process.

A techno-economic study by Tao et al. (2013) was conducted using 1G and 2G feedstocks in the form of corn grain and corn stover respectively. However, with corn stover only glucose and xylose were considered for fermentation reactions. They made an assumption that other sugars were available in minor quantities in the hydrolysate and therefore their contribution to solvents was not that significant. It has to be pointed out that the assumed conversion of 24%, 54% and 4.5% to acetone, butanol and ethanol of glucose and xylose to solvents is uncertain. This problem is common in all the modelling studies, because it is unknown how much sugar conversion goes to particular solvents. From the comparison of butanol production form 1G and 2G feedstock, the study found that total capital investment for 2G was greater than that of 1G by 29.7%. It was further found that minimum butanol selling price for 2G feedstock was greater than that of 1G by 30.6%. The study concluded that 2G butanol production was still expensive as compared to 1G due to several factors such as complex process and lower fermentation yields.

In summary, the review of techno-economic studies on butanol production showed that there were several parameters which could be varied in order to bring down the cost of production. Most important was the yield increase in fermentation, which was obtained by use of mutant strain of microorganisms. Furthermore, it was found that *in situ* product removal by techniques like gas stripping helped to reduce inhibition by butanol. Also, sale of other fermentation products like acetone and ethanol and fermentation gases could increase revenues of biorefineries and therefore make the processes more competitive. On the other hand, the major drawback found was that lack of commercial scale data was one of the hurdles in carrying out techno-economics.

3.   Research Design and Methodology

Experiments done in laboratories and pilot plants provided primary data that was used during models validation. Pertinent to this study, experiments play a crucial role because ABE fermentation involves enzymes during enzymatic hydrolysis and microorganisms during fermentation. Modelling cannot give the exact concentration at which butanol becomes inhibitory to the strains during fermentation, but only through experiments can such information be available. This shows how crucial experiment results are for process modelling to be undertaken. From this perspective, process modelling was used to validate feasibility of laboratory scale processes at commercial scale.

The study has three major components which are sequential and are described in detail in the next section. Firstly, an in-depth literature review on the production of biobutanol via fermentation process was done. Data collection from the review was done and compiled in Excel spread sheet. During this process, no specific routes were targeted because a reasonable knowledge had to be gained from both 1G and 2G production of biobutanol. The achievements and the challenges in ABE fermentation were reviewed in detail. Once this was done, more focus was shifted into biobutanol production via ABE fermentation using 2G feedstock. Secondly, statistical methods were done on collected data in order to identify the processes with superior performance, which were selected for subsequent modelling. Process flow sheets of the selected processes were developed and the modelled in ASPEN Plus (2013)software. Lastly, material and energy balance results from ASPEN Plus (2013)were used for equipment sizing, evaluation of processes energy demand, energy efficiency and economics.

3.1.   Data collection from literature studies

For data collection, production of butanol from LCB was captured in Excel spread sheet from journal papers of the original research work. The spread sheet had the

rows as the number of papers reviewed while the columns were used to enter production process parameters. The processing sequence of experimental studies that were considered had included pretreatment, enzymatic hydrolysis and fermentation processes, and in each process, sub process parameters were also captured. For pretreatment, the reaction conditions were chosen based on sugar yields, inhibitors generation and digestibility (Chandra et al. 2007; Elander et al. 2009; García et al. 2011).

 For enzymatic hydrolysis, enzyme and solid loadings were noted because they have effects on the sugar yield as well as operating costs during economic analysis of the process(Lloyd and Wyman 2005; Liao et al. 2005). Hydrolysate conditioning process, which is referred to as detoxification, is considered as one of the key challenges in the ABE process (see section 2.5). Hence, the method of detoxification was also noted. Fermentation was given the major attention, as maximum inputs for the models were obtained from it. The fermentation data included solvents' concentrations, yields, productivities, sugars consumed and residual sugars, acids concentrations and fermentation microorganisms. In addition, fermentation process parameters such as temperature, pH, agitation, and bioreactor size and fermentation time were also captured.

There were challenges encountered when collecting data. This was found in journal papers where data reported was not presented in tabular form. In those cases, data was estimated from figures such as scatter or bar graphs presented within the source literature. In some instances, data was reported in the format that could not be used directly in ASPEN Plus (2013) models. For example, when ABE productivity was reported as an instantaneous one during the course of fermentation, an average productivity was calculated by dividing the total solvent concentration by the total time it took for fermentation to reach completion. Once the spread sheet was populated with data, the columns lacking some data were eliminated. The main data that was needed were inhibitor concentration, butanol yield and concentration, solvents productivity, utilised sugars and feedstock mass used in the process. When elimination has been done on collected data, statistical analysis was done on the data and it is described in the next section.

3.2.   Statistical Analysis of Literature Data

Statistical methods are applied in various fields in science and engineering to have an understanding of input factors affecting the response variables. Optimisation of the significant factors is carried in order to obtain the desired response variable by use of desirability function (Meyers and Montgomery 2002; Costa et al. 2011). In this project, no experimental work was done to obtain data, but data was collected from literature, as explained in section 3.1. Statistical data analysis was done to select the processes that were modelled in ASPEN Plus (2013). In addition, it was done to corroborate the factors affecting response variables namely; solvents concentration, yield and productivity in the production of biobutanol from LCB using desirability function. There are several factors affecting the response variables in the fermentative production of biobutanol which can be classified into controlled and uncontrolled factors (see Table 3:1).

Table 3:1: Category of selected factors affecting response variables in ABE fermentation

Controlled Factors	Uncontrolled Factors
Biomass Pretreatment severity	Utilised sugar concentration
Solids and Enzyme loading	Inhibitors concentration

According to Costa et al. (2011); Islam et al.(2009); Mourabet et al. (2012),desirability function requires two steps: (i) finding levels of independent variables that produce the most desirable predicted responses on the dependent variable at the same time. (ii) Maximising the overall desirability with respect to the controllable factors. From the two steps, it is clear that desirability functions are used to obtain qualitative and quantitative responses by conversion of several responses to a single measurement.

The approach taken in this present study was to convert the responses to individual desirability function (d_i) that ranged from 0 to 1; where 0 was the lowest and 1 highest. The individual desirability scores for the predicted values for each dependent variable were then combined into overall desirability function D. D was

evaluated by computing the weighted individual desirability where ABE concentration and yield were given 0.45 weight and productivity was given 0.1. The weights were obtained from performing analysis in statistica.

$$D = (0.45 \times d_1 + 0.45 \times d_2 + 0.1 \times d_3)$$

Equation 3-1

Where $d_{1,2,3}$ arethe individual desirability of the response variables. The individual desirabilities were used to evaluate overall desirability and their equations are shown. Therefore, according to Meyers and Montgomery (2002)the following one-sided equation has to be used:

$$d_i = 0, \qquad if \ X_i \leq X_i^{min}$$

$$d_i = \frac{X_i - X_i^{min}}{X_i^{max} - X_i^{min}}, \qquad if \ X_i^{min} < X_i < X_i^{max}$$

$$d_i = 1, \qquad if \ X_i \geq X_i^{max}$$

Equation 3-2

Where X_i is the response variable, X_i^{min} and X_i^{max} are the minimum and maximum values of the response variables mentioned in the first paragraph. The weighted overall desirability equation was executed using excel. The results were then rearranged with the decreasing order of ABE Weighted Overall Desirability (see Table 3-2 and Table 3-3). When performing this task, it should be noted that data was separated into fermentation processes in which glucose was supplemented to LCB hydrolysates to increase initial sugar concentration and the processes, where LCB hydrolysate is the only source of sugar. This grouping was done in order to avoid selecting processes having sugar supplementation but still obtain the desirable process without supplementation.

From Table 3:2,it was observed that the maximum weighted overall desirability was obtained from a fed-batch SSF process integrated with *in situ* gas stripping for continuous product removal. On the other hand, where pure LCB hydrolysate was used without sugar supplementation during fermentation; Table 3:3 showed maximum ABE weighted overall desirability from SSF batch process. This process

was integrated with *in situ* gas stripping for continuous product removal. What was also noticeable from Table 3:2 and Table 3:3were that processes with *in situ* product recovery techniques exhibited higher desirability. Therefore,Table 3:3 was used for the choice of processes to model in ASPEN Plus (2013)because only LCB was used as pure glucose supplementation may not industrially be economical. However, it can be possible that glucose supplementation can increase productivity which in return can outweigh the cost of buying glucose in industry.

Table 3:2: Weighted Overall Desirability on the ABE fermentation processes in which sugar was supplemented to LCB Hydrolysates (SSF: Simultaneous Saccharification and Fermentation, SHF: Separate Hydrolysis and Fermentation, GS: Gas Stripping, ButOH Conc: Butanol Concentration, ButOH Prod: Butanol Productivity)

Feedstock	Fermentation Method	Weighted Overall Desirability of ButOH Conc,Yield,Prod	Weighted Overall Desirability of ABE Conc,Yield,Prod	Reference
Wheat Straw	SSF in Fed-batch + GS	0.6470	0.9358	Qureshi et al. 2008b
Corn Stover	SHF in Batch + GS	0.6548	0.6026	Qureshi et al. 2013
Barley Straw	SHF in Batch + GS	0.5408	0.5388	Qureshi et al. 2013
Corn Stover	SHF in Batch	0.1424	0.5060	Qureshi et al. 2010b
Barley Straw	SHF in Batch	0.2989	0.4845	Qureshi et al. 2010a
Cassava Bagasse	SHF in Fed-Batch + GS	0.4063	0.2835	Lu et al. 2012
Switchgrass	SHF in Batch	0.1367	0.2625	Qureshi et al. 2010b
Sweet Sorghum Bagasse	SHF in Batch	0.0234	0.0761	Cai D. et al. 2013

Table 3:3: Weighted Overall Desirability on the ABE fermentation processes in which no 1G sugar was added to supplement LCB Hydrolysates during fermentation (SSF: Simultaneous Saccharification and Fermentation, SHF: Separate Hydrolysis and Fermentation, GS: Gas Stripping, LLE: Liquid-Liquid Extraction, ButOH Conc: Butanol Concentration, ButOH Prod: Butanol Productivity)

Feedstock	Fermentation Method	Weighted Overall Desirability of ButOH Conc,Yield,Prod	Weighted Overall Desirability of ABE Conc,Yield,Prod	References
Wheat Straw	SSF in Batch + GS	0.6191	0.6864	Qureshi et al. 2008c
Corn Stover	SSF in Batch + Vacuum	0.5408	0.6590	Qureshi et al. 2014
Corn Stover	SHF in continuous Bioreactor	0.5728	0.5487	Ni Ye et al. 2013
Cassava Bagasse	SHF in a Batch	0.4764	0.4997	Lu et al. 2012
Rice Straw	Sequential SHF-SSF in Batch	0.5078	0.4960	Cheng C-L et al. 2012
De-oiled Rice Bran	SHF in a Batch	0.4338	0.4768	Al-Shorgani et al. 2012
Corn Fibre	SHF in a Batch	0.4263	0.4742	Lu 2011
Aspen Wood	SSF in Fed-batch + LLE	0.4517	0.4515	Shah and Lee 1992
Corn Stover	SSF in a Batch	0.4061	0.4304	Qureshi et al. 2014
DDGS	SHF in a Batch	0.4297	0.4080	Ezeji and Blaschek 2008
Corn Stover	SHF in a Batch	0.3864	0.3758	Wang and Chen 2011
DDGS	SHF in a Batch	0.2075	0.2128	Wang X. et al. 2013
Sugarcane Bagasse	Sequential SHF-SSF in Batch	0.1756	0.1812	Cheng C-L et al. 2012
Rice Straw	SHF in a Batch	0.1454	0.1347	Moradi F. et al. 2013
Rice Straw	SHF in a Batch	0.1126	0.1245	Moradi F. et al. 2013

3.3.   Process Choice and Flow sheets development

The selection of processes to model in ASPEN Plus (2013)was made from results of overall weighted desirability. Since data collected was from different 2G feedstocks, different methods of fermentation and technology improvements; the processes with the highest weighted overall desirability wereselected for modelling. The other processes were also selected based on desirability, but ensuring that fermentation methods such as batch versus continuous were taken into consideration. Availability of required data for modelling was also a determining factor for the process selection. For instance, some processes had no data for inhibitors concentration, yet pretreatment was done on LCB. In this situation, such a process was overlooked for the next one in terms of weighted desirability and availability of required data. The flow sheets of three main processes chosen are shown in block flow diagrams in Figure 3-1, Figure 3-2 and Figure 3-3.
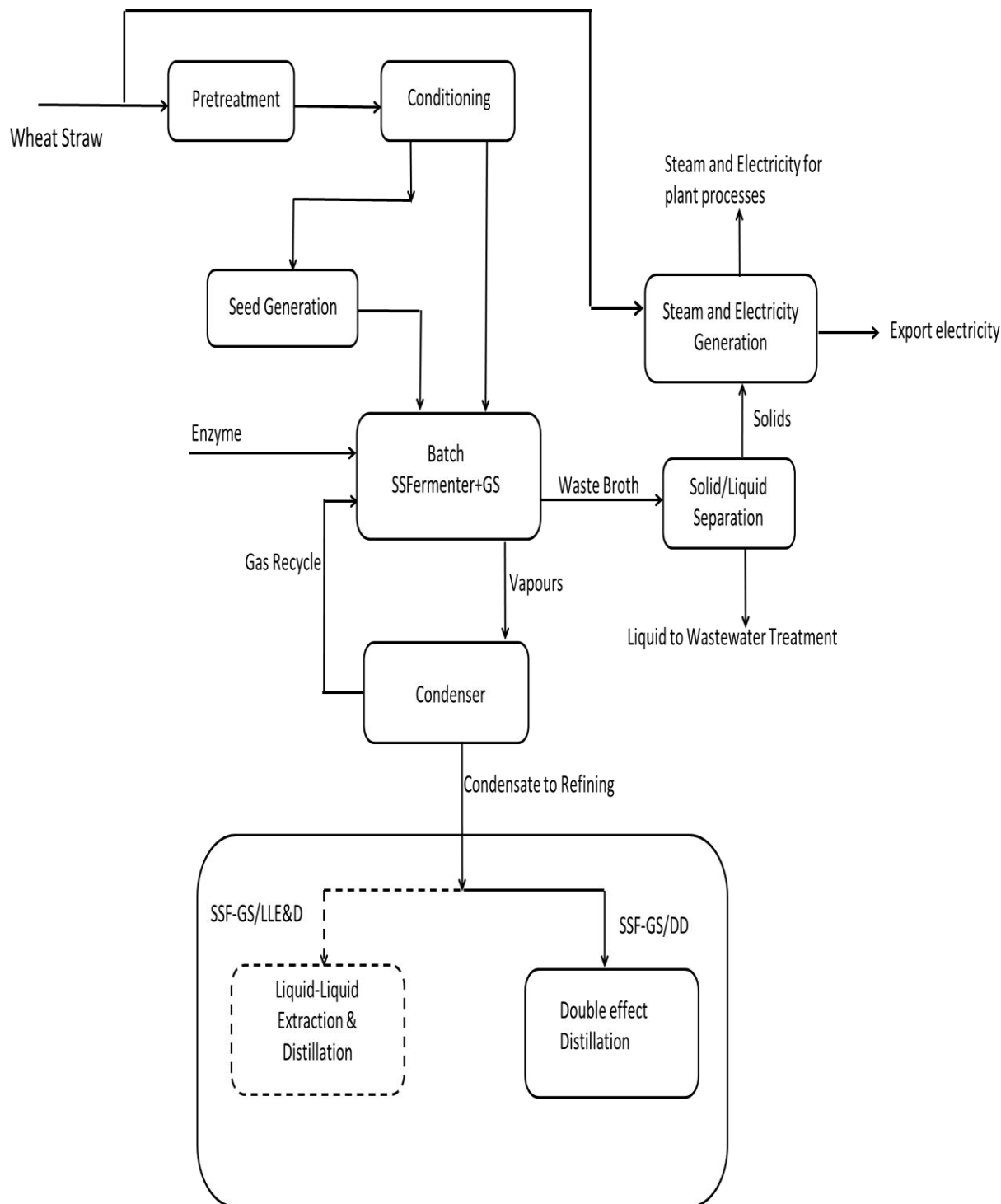
Figure 3-1: Block flow diagram for butanol production from wheat straw: SSF-GS/LLE&D: Batch Simultaneous Saccharification and fermentation-Gas Stripping and Liquid-Liquid Extraction and Distillation used as recovery and purification Method; SSF-GS/DD: Simultaneous Saccharification and fermentation-Gas Stripping and Double effect distillationused as recovery and purification Method
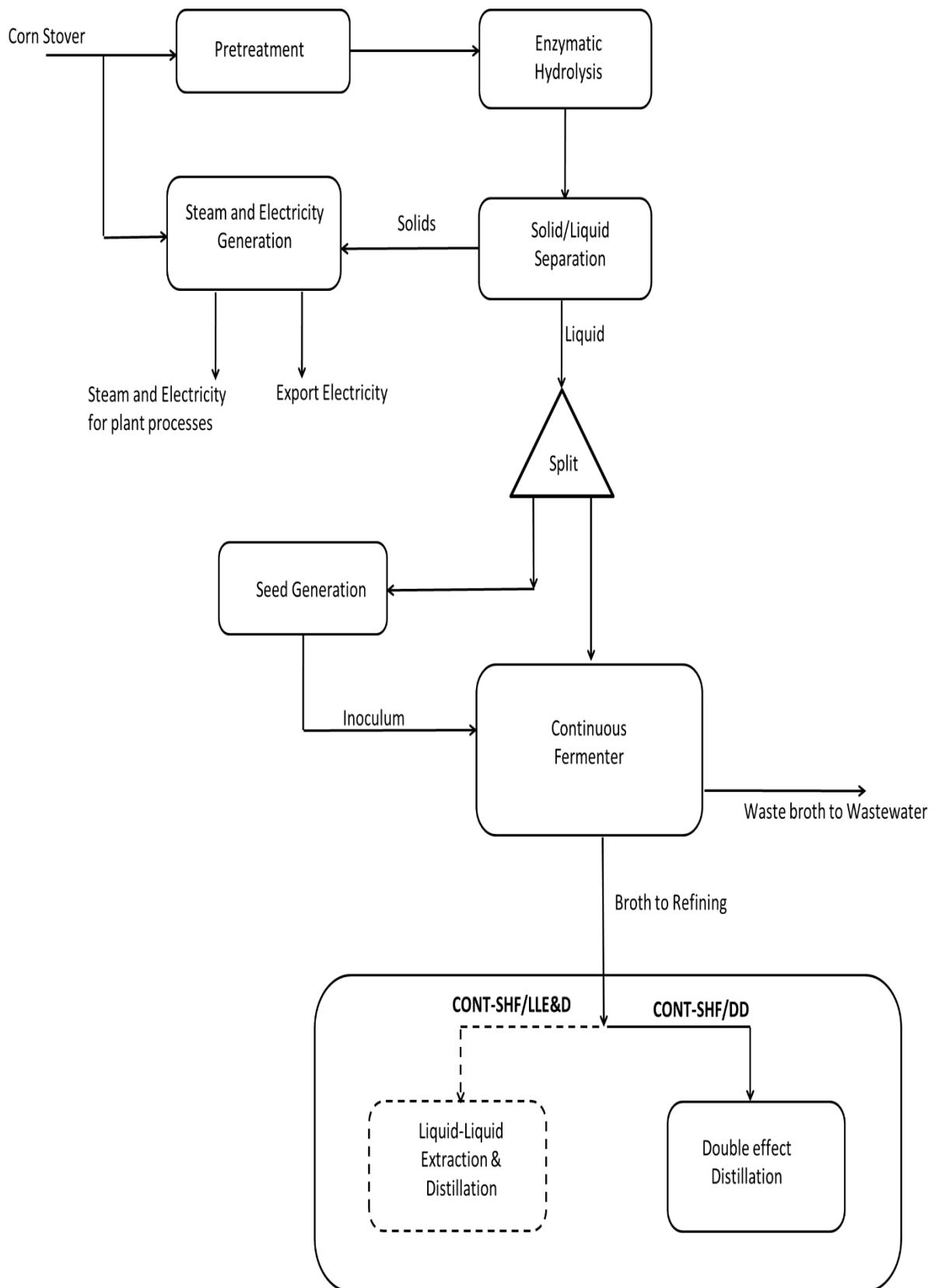
Figure 3-2:Block flow diagram for butanol production from corn stover: CONT-SHF/LLE&D: Continuous Separate Hydrolysis and fermentation and Liquid-Liquid Extraction and Distillation used as recovery and purification Method; CONT-SHF/DD: Continuous Separate Hydrolysis and fermentation andDouble effect distillationas recovery and purification Method
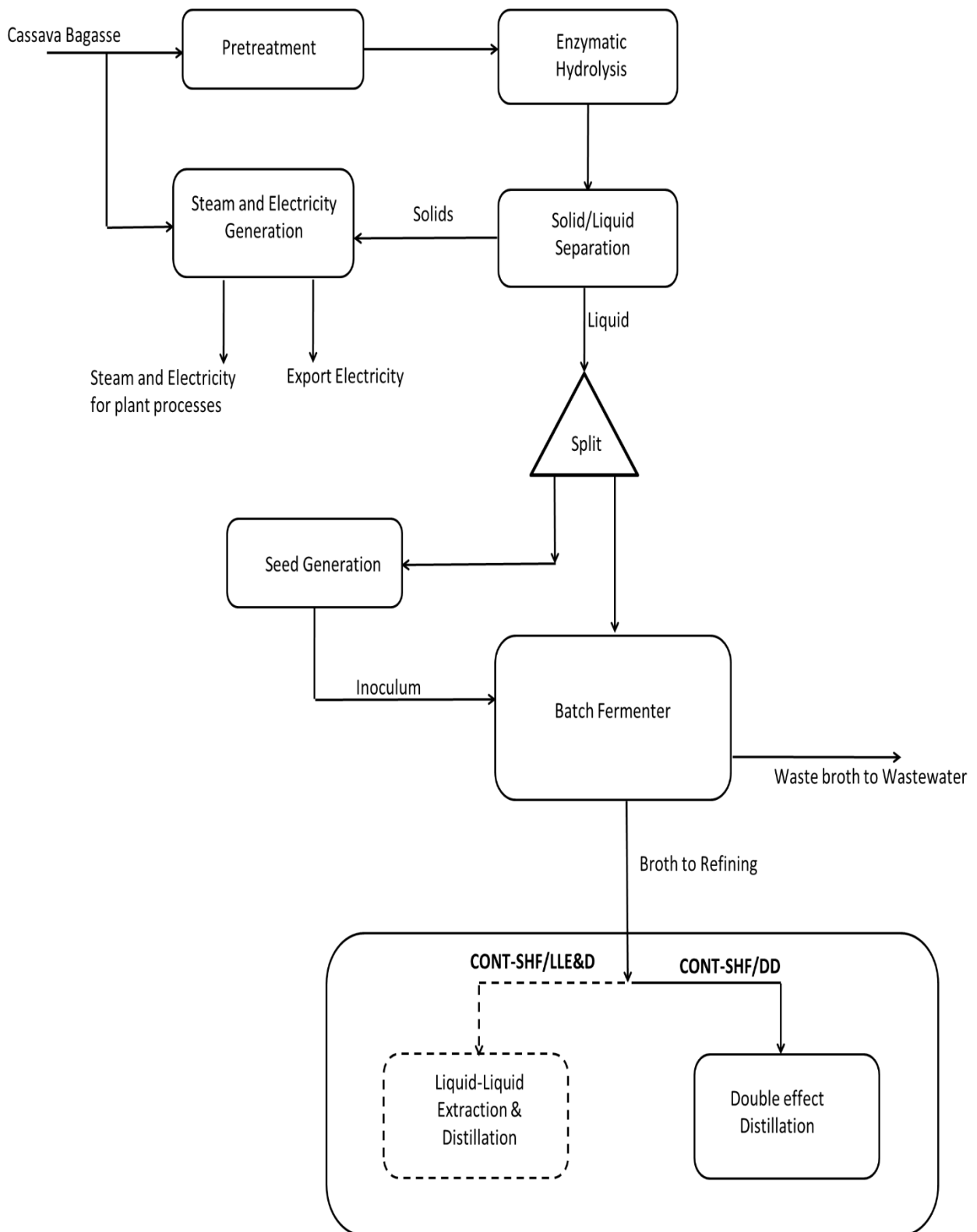
Figure 3-3: Block flow diagram for butanol production from cassava bagasse: B-SHF/LLE&D: Batch Separate Hydrolysis and fermentation and Liquid-Liquid Extraction and Distillation used as recovery and purification Method; B-SHF/DD: Batch Separate Hydrolysis and fermentation andDouble effect distillationas recovery and purification Method

Each selected process was further split into two scenarios, in order to evaluate double effect distillationand liquid-liquid extraction and distillation as refining methods which are described in Section 2.10. The scenarios modelled when the three main processes were further split are shown in Table 3:4.

Table 3:4: Modelled process scenarios for ABE fermentation and recovery and purification methods used to obtain final products. SSF-GS: Batch Simultaneous Saccharification and fermentation integrated with Gas Stripping. CONT-SHF: Continuous Separate Hydrolysis and fermentation. B-SHF: Batch Separate Hydrolysis and fermentation.(DD)Double effect distillation and (LLE&D) Liquid-Liquid Extraction and Distillation are recovery and purification methods used to obtain final products

Process	Double effect Distillation	Liquid-Liquid Extraction & Distillation
1	SSF-GS/DD	SSF-GS/LLE&D
2	CONT-SHF/DD	CONT-SHF/LLE&D
3	B-SHF/DD	B-SHF/LLE&D

The three processes were chosen based on highest overall weighted desirability. SSF-GS process scored the highest weighted overall desirability of 0.686. SSF could play a major role in the economics of the process because of reduced number of equipment, as saccharification and fermentation takes place in one vessel (see section 2.7). In addition, sugar inhibition to microorganism is reduced because the sugar is utilised by microorganism as it is formed. This leads to increased hydrolysis efficiency, ABE yields, fermenter productivity and higher concentration of solvents. The advantages of gas stripping discussed in section 2.8.1 combined with SSF were investigated for their contribution to the energy efficiency and economics of the process.

Second on the list of overall weighted desirability were SSF+Vacuum stripping, but this process was omitted from modelling. The reason for leaving vacuum fermentation was that it has similar objective to gas stripping fermentation. In addition, the same fermentation technique of SSF as that of first chosen process was employed. The second and third processes, continuous SHF and batch SHF respectively, were chosen for the weighted overall desirability of 0.549 and 0.500

respectively. These last two processes would assist when the energy efficiency and economics of processes are evaluated. Their advantages which were discussed earlier in section 2.7 would be assessed if they could bring the needed efficiencies.

3.4. Process Simulation Software

Advanced Simulator Process Engineering(ASPEN) Plus$^{®}$ Version8.2 simulation software was used in modelling different scenarios. Table 3:5 shows the major components in the models used and their state when entered in the component list.

Table 3:5: Chemical components from biomass as entered in ASPEN Plus (2013) component list(Wooley and Putsche 1996)

Compound name	Formula	Normal state
Cellulose	$C_6H_{10}O_5$	Solid
Xylan	$C_5H_8O_4$	Solid
Lignin	$C_{7.3}H_{13.9}O_{1.3}$	Solid
Ash	CaO	Solid
Glucose	$C_6H_{12}O_6$	Liquid
Xylose	$C_5H_{10}O_5$	Liquid
Cellulase	$CH_{1.59}O_{0.42}N_{0.24}S_{0.01}$	Solid
Zymo	$CH_{1.8}O_{0.5}N_{0.2}$	Solid
Protein	$CH_{1.57}O_{0.31}N_{0.29}S_{0.007}$	Solid

ASPEN Plus (2013)requires the fundamental properties of components for the simulation to proceed. The properties will indicate whether liquids, solids or such a

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mixture will be involved in simulation. From Table 3:5, the solids would remain in the solid state throughout the process and would not be in the solution while the liquids were found in aqueous solution. According to Wooley and Putsche (1996), the vapour pressures are lower than boiling point for the sugars in aqueous solution. This meant during flash evaporation, minimal sugars would go into the vapour stream. The production of biobutanol via fermentation involves distillation as a separation process to obtain the final product. Production of gases such as CO_2 and H_2 meant that NRTL activity coefficient model was used and Henry's Law for dissolved gases was used in the simulation. Furthermore, the solution would contain carboxylic acids such as acetic acid and butyric acid. The more robust thermodynamic model that handled the acids was Non-Random Two Liquid activity coefficient with Hayden-O'Connell (NRTL-HOC) (Wooley and Putsche 1996).

In order to simulate a process in ASPEN Plus (2013)interface, the following major steps were done:

- Firstly, a process flow sheet for a particular process was developed by joining blocks which represent certain units in the process plant. The blocks were connected by material, energy and work streams until a complete process was available.

- The next step involved the addition of chemical components in the systems which were used in the process simulation. Prior knowledge of the process being simulated was required because entering of components needs the user to know thermodynamic state of the components, i.e. conventional, solids or non-conventional.

- Lastly, definition of streams and blocks to allow the execution of simulation for calculating mass and energy balances was done. For defining streams, one has to enter material flows, temperature and pressure at which feed streams are and the conditions at which the blocks are operating.

Once all this information had been entered, ASPEN Plus (2013) notified the user that all required input had been provided and the simulation was ready to be run. The simulation ran in an iterative way until the mass and energy balances converged. Once convergence has been achieved, the results became available to the user with information explaining the nature of results. ASPEN Plus (2013) further allowed user

to perform sensitivity analysis to obtain certain design specifications. This was done by specifying the target parameters of the simulation process such as product purity, concentrations and yields. By manipulating the feed stream flows or make-up, the process did iterations to achieve the set specification. This was important when the model robustness was validated by experimental data sourced from scientific literature.

3.5. Models Validation

In this study, three models for fermentative production of biobutanol from LCB were developed and validated by experimental data from published scientific literature. The major processes in the models were pretreatment and enzymatic hydrolysis for sugars generation, fermentation for production of solventsand solvents recovery and purification. The first model was validated by the work of (Qureshi et al. 2008). Wheat straw was used as feedstock for biobutanol production via SSF in a batch process integrated with *in situ* gas stripping. The second model was validated by experimental data from (Ni et al. 2013). Corn stover was used as a feedstock material. In this process SHF was performed in a continuous bioreactor. The third model was validated using experimental data from (Lu et al. 2012). Cassava bagasse was used as feedstock. The process was SHF in a batch bioreactor.

Table 3:6: Chemical Composition Analysis by mass percent on dry basis for the different feedstocks used

Feedstock:	Wheat Straw	Corn Stover	Cassava Bagasse
Cellulose(glucan)	35.50	36.10	27.17
Xylan	20.10	21.10	6.21
Arabinan	3.30	3.60	0.62
Lignin	26.50	20.80	10.00
Ash	4.60	6.90	1.80
Extractive	3.30	6.10	0.00
Protein	3.30	3.50	1.40
Acetate	2.00	3.20	0.00

The importance of the feedstock chemical analysis was that it provided an estimate of the carbohydrate content available in each feedstock. From this information, it could be predicted how much sugar can be produced from the major components of the biomass. Sugars used as carbon source during fermentation were produced by hydrolysis reactions during biomass pretreatment and enzymatic hydrolysis. The sugars were utilised during fermentation for microorganisms' growth and production of solvents. For fermentation reactions, C5 sugars were assumed to react similarly to produce products and the same assumption was made for C6 sugars. In Table 3:7,Table 3:8 andTable 3:9, the reactions shown occur simultaneously to produce the products given. For the microbial growth, it was assumed that the equations used by Mariano et al. (2011) during fermentation would be applicable since there were no equations for clostridia bacteria.

Table 3:7: Hydrolysis reactions which occur during biomass pretreatment (Humbird et al. 2011)

Pretreatment Hydrolysis Reactions				
Cellulose	+	nH_2O	→	nGlucose
Cellulose			→	nHMF + Glucose + $2nH_2O$
Cellulose	+	nH_2O	→	nCellobiose
Xylan	+	nH_2O	→	nXylose
Xylan			→	nFurfural + $2nH_2O$
Arabinan	+	nH_2O	→	nArabinose
Mannan	+	nH_2O	→	nMannose
Galactan	+	nH_2O	→	nGalactose
Acetate			→	Acetic Acid
Lignin			→	nSoluble Lignin

Table 3:8: Hydrolysis reactions which occur during enzymatic digestion of pretreated solids (Humbird et al. 2011)

Enzymatic Hydrolysis Reactions				
Cellulose	+	nH_2O	→	nGlucose
Cellobiose	+	H_2O	→	2Glucose
Xylan	+	nH_2O	→	nXylose
Arabinan	+	nH_2O	→	nArabinose
Mannan	+	nH_2O	→	nMannose
Galactan	+	nH_2O	→	nGalactose

Table 3:9: Hydrolysate sugars are utilised for solvents production and cell growth (Mariano et al. 2011; Tao et al. 2013; 2014; van der Merwe 2010)

Fermentation Reactions for Solvents production and Cell growth

Glucose→ Butanol + $2CO_2$ + H_2O

Glucose + H_2O→ Acetone + $3CO_2$ + $4H_2$

Glucose → 2Ethanol + $2CO_2$

Glucose → 3Acetic Acid

Glucose → Butyric Acid + $2CO_2$ + $2H_2$

Galactose → Butanol + $2CO_2$ + H_2O

Galactose + H_2O→ Acetone + $3CO_2$ + $4H_2$

Galactose → 2Ethanol + $2CO_2$

Galactose → 3Acetic Acid

Galactose → Butyric Acid + $2CO_2$ + $2H_2$

Mannose → Butanol + $2CO_2$ + H_2O

Mannose + H_2O→ Acetone + $3CO_2$ + $4H_2$

Mannose → 2Ethanol + $2CO_2$

Mannose → 3Acetic Acid

Mannose → Butyric Acid + $2CO_2$ + $2H_2$

6Xylose → 5Butanol + $10CO_2$ + $5H_2O$

Xylose → Acetone + $2CO_2$ + $2H_2$

3Xylose→ 5Ethanol + $5CO_2$

2Xylose→ 5Acetic Acid

6Xylose → 5Butyric Acid + $10CO_2$ + $5H_2O$

6Arabinose→ 5Butanol + $10CO_2$ + $5H_2O$

Arabinose→ Acetone + $2CO_2$ + $2H_2$

3Arabinose→ 5Ethanol + $5CO_2$

2Arabinose→ 5Acetic Acid

6Arabinose→ 5Butyric Acid + $10CO_2$ + $5H_2O$

Glucose + $1.1429NH_3$ → 5.7143Microbe + $2.5714H_2O$ + $0.2831CO_2$

Galactose + $1.1429NH_3$ → 5.7143Microbe + $2.5714H_2O$ + $0.2831CO_2$

Mannose + $1.1429NH_3$ → 5.7143Microbe + $2.5714H_2O$ + $0.2831CO_2$

Xylose + $0.9524NH_3$ → 4.7619Microbe + $2.1429H_2O$ + $0.2381CO_2$

Arabinose + $0.9524NH_3$ → 4.7619Microbe + $2.1429H_2O$ + $0.2381CO_2$

3.6. Determination of Pretreatment Yields, Hydrolysis Yields and Fractional Sugar Conversions to Solvents during fermentation

For pretreatment and enzymatic hydrolysis yields evaluation, the equations used by Kim and Holtzapple (2005) and Varga et al.(2002) were used. The following equations were used to evaluate pretreatment yields.

$$Cellulose\ Yield = \frac{g_{cellulose}\ in\ pretreated\ biomass}{g_{cellulose}\ in\ raw\ biomass}$$

<div align="right">**Equation 3-3**</div>

$$Xylan\ Yield = \frac{g_{xylan}\ in\ pretreated\ biomass}{g_{xylan}\ in\ raw\ biomass}$$

<div align="right">**Equation 3-4**</div>

$g_{cellulose}$ and g_{xylan} represent the mass of cellulose and xylan in grams. The cellulose yield was applicable for all hexoses being glucose, galactose and mannose, while the xylan yield was for pentose sugars in the form of xylose and arabinose.

For enzymatic hydrolysis yields evaluation, the following equations were used:

$$Cellulose\ Yield = \frac{g_{glucose} \times 162.2}{g_{cellulose} \times 180.2}$$

<div align="right">**Equation 3-5**</div>

Where $g_{glucose}$ was the mass of glucose in the hydrolysate after enzymatic hydrolysis and 180.2 was glucose molar mass. $g_{cellulose}$ was the mass of cellulose in pretreated biomass and 162.2 was cellulose molar mass. The same equation was also used for yield evaluation for other hexose sugars.

$$Xylan\ Yield = \frac{g_{xylose} \times 132.1}{g_{xylan} \times 150.1}$$

<div align="right">**Equation 3-6**</div>

Where g_{xylose} was the mass of xylose in the hydrolysate after enzymatic hydrolysis and 150.1 was xylose molar mass. g_{xylan} was the mass of xylan in pretreated biomass and 132.1 was xylan molar mass. The equation was also used for yield evaluation for other pentose sugars.

Fractional sugar conversion to solvents during fermentation was approached in a predictive way using excel modelling. This was done because during fermentation, all reactions occur simultaneously (Table 3:9). As a result, it was not clear what fraction of glucose, for instance would be converted to butanol, acetone, ethanol, acetic acid, butyric acid or for cell growth. In addition to this, considering the fact that *Clostridia* are capable of utilising pentose sugars, fractional conversions of sugars to solvents was predicted. To ensure that the predicted fractional conversions were sensible, the Minimised Sum of Squared Error was evaluated. It was evaluated from the solvents concentration predicted by Microsoft excel model and the literature concentration of solvents taken from the scientific papers used for models validation. In addition, fractional sugar conversions used in other studies for ABE fermentations were also compared to the Microsoft excel model (Table 3:10). The values were then used in ASPEN Plus (2013)simulation for production of solvents during fermentation for all three processes.

An overall observation from Microsoft excel predictive model was that highest fractional glucose conversion goes for formation of butanol. In fact, at least 50% of it went to butanol (Table 3:10). Acetone formation came second for around 20% glucose fractional conversion and the rest was split for ethanol, acetic and butyric acid and cell growth with no distinct preference. From literature, Ting et al. (2013) used glucose fractional conversions of 54% and 27% for butanol and acetone respectively. In another work, Van der Merwe (2010)used glucose fractional conversions of 62.88% and 41.08% for butanol and acetone formation respectively. These were the highest used amongst all the scenarios investigated by Van der Merwe (2010) . In this present study, using scientific data from Qureshi et al. (2008c), Ni et al. (2013), and Lu et al. (2012), glucose fractional conversions to butanol and acetone were 57.81% and 27.36%, 61.74% and 28.61% and 49.98% and 27.28% respectively. These are summarised in Table 3:10.

Table 3:10: Fractional conversion data used in this study and other literature studies based on glucose sugar

Solvent	Van der Merwe 2010	Ting et al. (2013)	This study		
			SSF-GS	CONT-SHF	B-SHF
Butanol	62.88%	54.00%	57.81%	61.74%	49.98%
Acetone	41.08%	27.00%	27.36%	28.61%	27.28%
Ethanol	1.13%	4.50%	7.35%	0.001%	5.30%
Butyric acid	1.49%	2.50%	4.27%	1.96%	9.52%
Acetic acid	0.72%	2.50%	3.21%	0.001%	7.92%
Cell mass	0.001%	1.90%	0.001%	7.69%	0.001%

3.7. Equipment Design, Sizing and Simulation

3.7.1. Major Equipment

Mass and energy balance resulted from ASPEN Plus (2013)simulations were used in the design and sizing of the major process equipment. Mass flow rates in conjunction with the residence time and average density of the streams were used to evaluate volume of major equipment like pretreatment reactors, conditioning reactors, hydrolysis reactors, fermentation bioreactors, boiler and biogas digester according toEquation 3-7.

$$V = \frac{\dot{v} * \tau}{\rho}$$

Equation 3-7

Where V = volume in m^3, $\dot{v}$=flow rate in kg/hr, τ = mean residence time in hr and ρ = average density of vessel contents in kg/m^3

Hence, the equipment was described from practical perspective as well as modelling approach. It should be noted for modelling purposes; several units were used to depict just one major unit in practice.

Pretreatment reactor configuration in real plant was determined by method of pretreatment used and largely to solids loading during pretreatment. For instance, in case of this study in which low solids loading less than 10% were used from literature, the type of pretreatment reactor used was a continuous stirred tank reactor (Yang and Wayman 2009). This allowed for easy mixing within the reactor, therefore minimising mass transfer limitations. However, steam explosion pretreatment used high solids loading of more than 20% and reactor type used was a tubular reactor with screw inside for mixing (Humbird et al. 2011). However, when it came to modelling, all pretreatment reactors were modelled as RStoic in ASPEN Plus (2013). The RStoic reactor required equations as well as fractional conversion or yields as input for the reacting components. See Section 3.5 and 3.6for the reactions taking place during pretreatment and how the yields were evaluated.

For SSF-GS process, sulphuric acid (H_2SO_4) at 1% (w/w) used for pretreatment was pumped into the reactor. It was added to the reactor to achieve solids to liquid loading of 8.6% (w/w). The reactor was steam heated to around 121°C and reactants residence time was 1 hour at 2 atm. The high pressure steam used for heating the reactor came from steam and power generation area. After an hour of pretreatment, the slurry was passed through a counter current heat exchanger where the slurry pre-heated the feedstock into the reactor before it went into solid-liquid separator. CONT-SHF process followed similar pretreatment process. The only difference was that solids loading in the process is 7% (w/w) and 1% (w/w) NaOH was used for alkali pretreatment (Ni et al. 2013). B-SHF process used liquid hot water for biomass pretreatment at 10% (w/w) solids loading (Lu et al. 2012). However, the pretreatment time was 30 minutes.

Conditioning and holding tanks for all the processes were the same. Because dilute acid pretreatment generated inhibitors, conditioning of the hemicellulose stream was done in a closed tank. Previously lime was used as the agent, but presently

ammonia is preferred because it does not produce solids residues that would require separation and disposal (Humbird et al. 2011). As a result, ammonia was used to condition SSF-GS hemicellulose liquid stream. For CONT-SHF process, where alkali pretreatment was used, sulphuric acid was used for conditioning and pH adjustment of the hemicellulose and lignin stream. B-SHF process did not have a conditioning tank because the process used liquid hot water pretretament and no inhibitors were reported in the slurry (Lu et al. 2012). In ASPEN Plus (2013), the conditioning tank was modelled as RStoic reactor. The reactions were provided and stoichiometric amount of neutralising agent was added into the reactor. The buffer tank, which was a slurry holding tank, was represented as a mixer. Normally buffer tanks have holding time of 30 minutes (Humbird et al. 2011).

Enzymatic hydrolysis reactors in commercial plants are big tanks with jacketed heating by steam to provide required temperature. These tanks are agitated to provide close contact between enzymes and cellulosic biomass and to aid in reducing mass transfer limitation. The reactor was loaded with slurry from pretreatment and enzymes to meet particular solids loading and the hydrolysis reactions continued for certain period of time. After that period, the reactor contents were sent for solids-liquid separation. Solids were mainly lignin and undigested cellulose and hemicellulose. In ASPEN Plus (2013), the enzymatic hydrolysis reactor was modelled as RStoic and the equations for conversion of cellulose and hemicellulose to glucose and xylose were provided. Only CONT-SHF and B-SHF process had hydrolysis reactors.

B-SHF process had a sequential enzymatic hydrolysis process. In the first reactor, slurry was first hydrolysed by glucoamylase at 65°C for 24 hours to hydrolyse starch that was present in cassava bagasse into glucose (Lu et al. 2012). The hydrolysed slurry was pumped to the next reactor for further hydrolysis where cellulase was added to hydrolyse cellulose content in cassava bagasse. This was done at 50°C for 24 hours(Lu et al. 2012). After 24 hours the slurry was sent to solids-liquid separation modelled as a cyclone. The calculator block was used to achieve required moisture content in the solids stream. The solids were then sent to dryer for further moisture reduction before they were burnt in the combustor. 5% split of liquid hydrolysate stream was sent for seed generation while the rest was pumped into a fermenter (Humbird et al. 2011). In a CONT-SHF process, a single reactor modelled

similar to those of B-SHF process was used. Enzymatic hydrolysis of corn stover happened for 40 hours at 50°C with agitation(Ni et al. 2013).

Fermentation reactors in commercial plants are big tanks with jacketed heating by steam to provide required operating temperature. The fermenters are fitted with temperature probes for temperature monitoring and they also have valves to vent off fermentation gases. Venting is done when *in situ* gas stripping is not applied. In all processes, fermenter was fed with the hydrolysate, inoculum usually 10% (v/v) size of the fermenter, the nutrients and minerals for bacteria. For B-SHF process, the fermenter reactions were allowed to proceed for 40 hours after which the process was stopped. The solvents were drained from the reactor and got pumped to product refining downstream process. The waste broth was sent to separator and dryer before it got burnt in the boiler. For a CONT-SHF process, the hydrolysate was continuously fed into the fermenter at 0.1 h^{-1} dilution rate (Ni et al. 2013). The process was run continuously for many hours until the solvents production rate dropped due to microorganism losing their peak metabolism and started dying. When fermentation was stopped, the downstream processing was similar to that of B-SHF process.

SSF-GS fermentation was done in one reactor which was loaded with pretreatment slurry, inoculum 10% (v/v) and the nutrients and minerals. In addition, enzymes were also added into the fermenter to hydrolyse the LCB. Gas stripping was started after 23 h of fermentation and was run continuously for 49 hours after which the process was stopped, with total hours of fermentation being 72 h (Qureshi et al. 2008). Gas stripping allowed the fermentation gas and vapourised solvents that have accumulated in the head space to flow out of the fermenter. The vapourised solvents were condensed in an external unit to recover solvents and the non-condensable gases were re-compressed and sent back into the fermenter (Qureshi et al. 2014). The condensed solvents were collected in a condensate tank before they were pumped to product purification downstream process. Circulating recompressed fermentation gases through the fermentation broth allowed the continuous removal of solvents.

Batch SSF fermenter integrated with *in situ* gas stripping in ASPEN Plus (2013) was modelled as two sequential RStoic reactors. In the first RStoic reactor, enzymes and

pretreated slurry were fed into a reactor for cellulosic and hemicellulosic hydrolysis to take place at 35°C and 1atm. The hydrolysate was then sent for fermentation into the subsequent RStoic reactor. The second RStoic reactor was connected to a mixer and a flash tank all of them operating at 35°C and 1atm. A stripping agent, which was CO_2 gas make-up stream, was mixed with the outlet stream from the fermenter by a mixer and the combined stream was sent into a flash tank(van der Merwe 2010). The mixer represented the stream of re-circulated non-condensables into the fermenter, while the flash tank represented the vent at which the stripped gases went through into the condenser. The flash tank had two streams leaving it, the gaseous stream as the tops and the liquid and solids as the bottoms.

The stripped gaseous stream from the flash tank was sent to the condenser. According to Qureshi et al. (2008c), gas stripping recovers of butanol, acetone, ethanol, water, acetic acid and butyric acid into the gaseous phase. These fermentation solvents were passed through a condenser, where the latent heat of vapourisation was removed, leading to condensation into liquid stream. The non-condensable gases and traces of solvents were sent for recompression and re-circulated back into the fermenter, to strip more solvents. The condenser was modelled as a heat exchanger operating at -10°C and 1atm and followed by a flash tank at same conditions (van der Merwe 2010). The flash tank represents vent from which the non-condensable gases left the condenser in their way to recompression unit. Lu(2011) and van der Merwe (2010) have operated the condenser below 0°C. They have found that as temperature is lowered more solvents were condensed. That was similar to what others studies found (Groot et al. 1992; Vane 2008).

The boiler for combustion of biomass and steam generation was the same for all processes. It was assumed to be stoker boiler, because a stoker boiler was most efficient for biomass combustion. According to International Renewable Energy Agency(Gielen 2012), a stoker boiler is more efficient for biomass and can handle between 10–60% moisture content of biomass. As a result, this type of a boiler was chosen for purpose of combusting both biomass and biogas. The boiler was modelled as RStoic reactor for combustion of biomass and a pair of heat exchanger (HE) trains in close contact depicting boiler tubes. Each train had a series of three heat exchangers. Heat was extracted from the combustor flue gas stream train to the boiler water stream train generating steam in the process.

Thus, saturated steam was generated, superheated and then got delivered to turbines that generate electricity.Heat for steam generation was produced from combustion reactions. The combustor was modelled with an adiabatic RStoic reactor specified with reactions and fractional conversions of components. Feed was made of the 10% of initial feed of biomass before pretreatment, solids from fermenter, and supplementation of biogas from anaerobic digestion and air fed at more than 20% excess. Complete combustion was assumed in the combustor due to the fact that air was fed in excess (Nsaful et al. 2013). Air was fed in excess to maintain 6% oxygen in the off gas in accordance to Department of Environmental Affairs and Tourism Air Quality Act (2008). Air for combustion was pre-heated by HE_{XD} to raise its temperature to above 200 °C. The flue gas stream then entered the cyclone which resembled an airbag. Particulates were captured by airbag and fall to the bottoms of the cyclone with ash. The particulate free gases were vented into atmosphere.

The heat exchangers representing boiler tubes were at 85 bars, so that steam at that condition was available for electricity generation by turbines (Leibbrandt et al. 2011; Nsaful et al. 2013; Petersen et al. 2014). According to Dias et al. (2011) and Mbohwa (2003), efficient boilers that can generate steam at 90 bars and generate electricity in turbines, are in commercial use. It was assumed combustor flue gas stream houses Train X with heat exchangers HE-$_{X1}$: HE-$_{X2}$: HE-$_{X3}$. Boiler feed water stream has Train Y with heat exchangers HE-$_{Y1}$: HE-$_{Y2}$: HE-$_{Y3}$. This was how pairing of Heat Exchangers for heat recovery to generate steam was arranged: (HE_{X1}+ HE_{Y3}) + (HE_{X2} + HE_{Y2}) + (HE_{X3}+ HE_{Y1}). Pairing in Figure 3-4ensures that HE_{X1}which was at highest temperature in the train was paired with $HE_{Y3}$of which already had saturated steam and thus superheated it. (HE_{X3}+ HE_{Y1}) pairing helped to increase feed water temperature close to boiling point. The arrangement ensured progressive heating, boiling and further temperature increase in steam generated. The design specification was used in ASPEN Plus (2013) to set steam temperature from HE_{Y3} at 525°Cby varying boiler water feed rate.
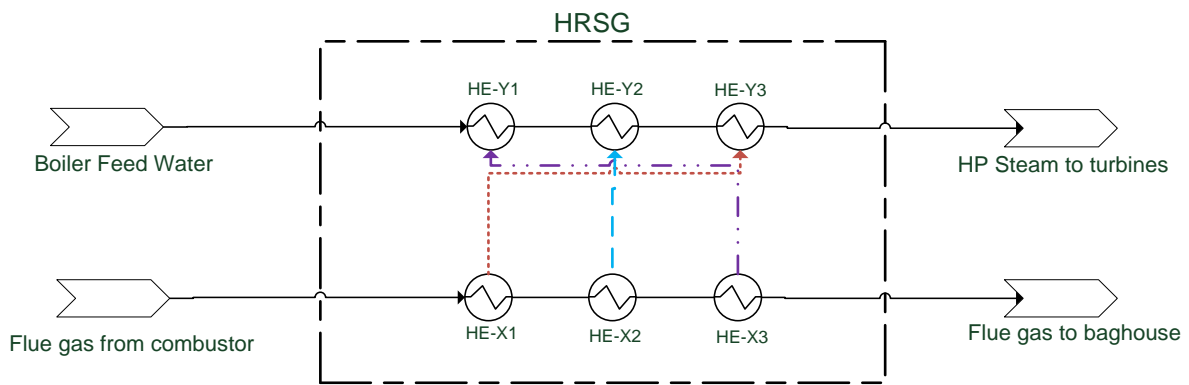
Figure 3-4: A pictorial set up for Heat recovery from boiler to pipes carrying water for steam generation

An industrial biogas digester comes in several types depending on what type of feedstock will be used. Furthermore, the design is influenced by whether biogas production is to be maximised or just to treat the waste. Studies have shown that an Upflow Anaerobic Sludge Blanket (UASB) is the most efficient reactor configuration (Berni et al. 2014). It has short retention time, can accommodate high organic loading and produces maximum biogas yield. In addition, it is able to withstand shock loads when a different influent is pumped into it. This configuration was chosen as a result and it operated at 35°C and 1.5atm, which are mesophilic conditions. The mode of operation was that influent was pumped through the bottom and moved up through the sludge blanket. As it went up, the microorganisms broke down the COD present in the influent. The top of the reactor has a dome vent from which biogas gas produced was collected through. The biogas did not need cleaning and it was sent to the boiler. Near the top, the digestate overflowed and was assumed to go to municipal sewer.

In ASPEN Plus (2013), a biogas digester was modelled as RStoic reactor operating at 35°C and 1.5atm and by a flash tank at the same conditions. The flash tank represented a vent from which the produced biogas was collected through. The biogas stream was sent to boiler for generation of steam. The digestate was assumed to go to municipal sewer since it has reduced at least 90% of COD present in the influent stream.

For downstream separation process, design and sizing of distillation and extraction columns were done based on flow rates of streams from ASPEN Plus (2013) results and the parameters available from literature (Section 9.2). Shortcut methods in

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ASPEN Plus (2013)were used when sizing columns in downstream separation area. The distillation column dimensions were evaluated following a procedure described in (Sinnott 2009). The plate spacing l of 0.5m was assumed. This gave enough space to get in through the column during clean-up purposes. The column diameter was calculated according to the following equations:

$$u_v = (-0.17l^2 + 0.27l - 0.047)\left[\frac{\rho_L - \rho_v}{\rho_v}\right]^{0.5}$$

<div align="right">**Equation 3-8**</div>

Where $u_v$was the maximum allowable vapor velocity, based on the gross (total) column cross sectional area, m/s, and l was the plate spacing in meters.

$$D_c = \sqrt{\frac{4V_w}{\pi \rho_v u_v}}$$

<div align="right">**Equation 3-9**</div>

Where $D_c$was the column diameter m, V_w was the maximum vapor rate in kg/s.

Then the next step was to manually change intensive parameters such as reflux ratio or boil-up ratio in order to meet the desired purities. The column extensive parameters such as distillate rate or bottoms rate were optimised using design specifications in ASPEN Plus (2013). Further optimisation of the columns to reduce energy usage in reboilers and capital cost in terms of column stages was done manually by optimising the number of column stages and reflux ratio (van der Merwe 2010; Mariano et al. 2011). In addition to this, the column parameters used by Roffler etal.(1987) were considered and it was ensured that the current study parameters did not pass those. Still, the product specifications were not violated in the expense of column optimisation.

The liquid-liquid extraction column was designed as a separator block in ASPEN Plus (2013) and the distribution coefficients of solvents in the extractant selected were that used by van der Merwe (2010) sourced from (Dadgar and Foutch 1988; Liu et al. 2004). This was because there was not sufficient information from ASPEN Plus (2013) that could accurately represent a LLE column.

3.7.2. Minor Equipment

The minor equipment includes items such as heat exchangers, turbines for electricity generation, pumps and compressors used within the plant. Energy balances from ASPEN Plus (2013) were used to size the heat exchangers for cooling and heating purposes (see Section 9.2). The important parameter here was the heat transfer area, which was evaluated from the heat duty taken from ASPEN Plus (2013) results. Since the heat exchangers size does not linearly increase with the flow rate, it had to be resized from the changing heat duty whenever flow rate of material was changed.

The pumps in the processes were used to transfer streams from one area to another and also between units in one area. The compressors were used in all processes for provision of air into the combustor. They were also used in process scenarios where gas stripping was integrated with fermentation for recycle of gases from condenser to the fermenter. Pumps were modelled as centrifugal pumps in ASPEN Plus (2013)with isentropic efficiency of 72% (Mariano et al. 2011; van der Merwe 2010). Compressors were sized from the feed streams and they are simulated as "polytropic with ASME method" in ASPEN Plus (2013). Their efficiencies were set at 72% (Mariano et al. 2011; van der Merwe 2010).

3.7.3. Auxiliary Equipment

This section describes the cooling tower system and refrigeration system, which are integral part of ABE fermentation. It should be noted that both cooling tower and refrigeration plants were not modelled in this study. However, their capital costs were taken into account using available literature during evaluation of capital expenditure and energy usage was accounted for in the overall energy demand (Humbird et al. 2011).

Cooling was major requirement in process plants, where streams above 35 °C have to be cooled down for fermentation. Cooling water was assumed to come from evaporative cooling tower and was delivered at 20°C and returned to the tower at 49°C (Turton et al. 2010). In cases where cooling water could not achieve the cooling purpose, especially at cryogenic conditions, refrigeration was applied. More pertinent to this study, refrigeration was applied after gas stripping for condensing

solvents at very low temperatures. Ammonia was chosen as the refrigerant and for maintaining -10°C at which condensation of solvents occurs (van der Merwe 2010).

For cooling tower plant, the electrical energy ($Q_{electrical}$) usage by fans and pumps was estimated by dividing the total heat duty of cooling ($Q_{removed\ from\ low\ temperature}$) taken from ASPEN Plus (2013)by the Coefficient of Performance (COP), which was reported as 7 by Petersen (2012) and Bergsten (2009) for cooling tower plants. The performance of the cooling tower system was determined by evaluation of COP, which is given in the equation below:

$$COP_{sys} = \frac{Q_{removed\ from\ low\ temp}}{Q_{electrical}}$$

Equation 3-10

Rearranging Equation 3-10 in terms of $Q_{electrical}$ allows for evaluation of the net Work input for removal of heat from low temperature state in the system. This was used for both cooling tower plant and the refrigeration cycle plant.

3.8. Farm Design of Seed Production and Fermentation Schedule

   i)   Batch Simultaneous Saccharification and Fermentation integrated with Gas Stripping (SSF-GS)

Seed production for inoculation into main fermenter is produced according to the size of main fermenter used for fermentation. Studies have shown that the size of seed used for inoculation into main fermenter is 10% (v/v) (Qureshi et al. 2008c; Ni et al. 2013; Qureshi et al. 2014). For commercial purposes, where fermenters are large (above 3000 m^3) (Humbird et al. 2011), a single fermenter for seed generation is not enough. As a result, a train of fermenters was used in order to achieve volume of seed that was 10% of the main fermenter volume. The number of fermenters in a seed train was determined by size of inoculum that can be produced from the laboratory. The size increment between the fermenters in a seed train was 10 times from the laboratory prepared inoculum. Normally, seed train fermenters are fed with glucose as carbon source and corn steep liquor as nitrogen source for microorganism growth and maintenance. In addition, vitamins, minerals and buffer

are also added (Humbird et al. 2011). However, in this study sugar split from enzymatic hydrolysis hydrolysate was used as carbon source and ammonia used instead of corn steep liquor.

The schedule for seed generation in a train consisted of fermenters sequentially inoculating after 18 hours of seed growth. The turnaround time of 12 hours was also included after 18 hours of batch fermentation for production of seed in each fermenter (Humbird et al. 2011). A seed train consisted of 5 fermenters and the first seed fermenter of $0.04m^3$ is inoculated by a laboratory prepared inoculum of $0.004m^3$. The deciding factor on how many fermenters were required in a train was the volume of main fermenter. From equipment sizing in this study, main fermenters were of 4000 m^3 capacity. The overall capacity of ABE fermentation was 40000 m^3 from equipment sizing. The volume was divided into 10 smaller fermenters of 4000 m^3 capacity. This capacity was in the range with other literature studies where main fermenters were of size 3600 m^3(Humbird et al. 2011). The fermenters in a seed train were of the order seen in Table 3:11:

Table 3:11: Seed train fermenters from the 1st that gets inoculated by laboratory shake flask to the 5th that inoculates the solvent fermentation tank for SSF-GS process

Fermenter number	1	2	3	4	5
Size (m^3)	0.04	0.4	4	40	400

It was reported that fermentation lasted 72 hours from the time inoculum was added into fermentation medium (Qureshi et al. 2008c). The turnaround time was normally 12 hours (Aden et al. 2002; Humbird et al. 2011), although some literature considered 20 hours (van der Merwe et al. 2013). This time allowed for emptying, steaming for sterilisation and refilling of the reactors with the medium and inoculum. In order to render the process continuous, an optimisation was done on the ten available main fermenters to find how many seed trains will be required.

This was done in EXCEL by setting up days of the week as a column and 24 hours in a day as a row (see Figure 9-1 Appendix 9.3). The first fermenter in the seed train

is inoculated by laboratory prepared inoculum on Sunday at 1:00 hours and allowed to grow for 18hours as mentioned earlier. After 18hours, the seed is inoculated into the second seed fermenter and also grow for 18 hours. The first seed fermenter is emptied and cleaned for 12 hours as a turnaround and next inoculation is made. This process goes on until the inoculum from the fith fermenter is ready to be inoculated into the main fermenter on Wednesday at 18 hours (see Figure 9-1 Appendix 9.3). The next inoculum from the fith fermenter in the same train becomes available at Thursday at 24 hours and it inoculates the second main fermentor. The third inoculum becomes available on Saturday at 6:00 hours and goes into third main fermenter. The fourth inoculum is ready by Sunday at 12:00 hours and looking at the schudule,main fermenter number which would be done by fermentation of 72 hours at 18:00 hours and turnaround time of 18 hours makes it available on Sunday at 12:00 hours. It coincides with the fourth batch inoculum being available to be inoculated. It should be noted that this method of optimisation was followed for the other processes.

This optimisation showed that one seed train could handle three main fermenters. As a result, three seed trains were required for nine main fermenters and the forth train could be used to operate one remaining fermenter. It could also be used as a backup in case of contamination or breakdown of other seed trains. Seed in the train was ready for inoculation in the main fermenter after 90 hours (3.75 days). Fermentation then took place for next 72 hours and was followed by 18 hours of turnaround time, which made a batch cycle of 90 hours. At the end of 90 hours of main fermentation, the seed was ready to be inoculated in the main fermenter for another batch. One seed train alternating between three main fermenters can be seen inAppendix 9.3 Figure 9-1.

ii)   Continuous Separate Hydrolysis and Fermentation (CONT-SHF)

For this process, a different procedure was followed in designing fermentation schedule. It was because of the complexity in maintaining constant feed of fermentation medium in the main fermenter. It should be noted that only final stage of four-stage continuous fermentation was considered, because fermentation parameters and product yields and concentrations were only reported for the final stage. As a result, the volume of one main fermenter is a representation of four-

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staged reactors which was 2482m^3. Here it was found that for all available main fermenters only one seed train will be required since the main fermenters in the stage are not inoculated at the same time. For instance, Ni et al.(2013) first inoculated stages 3 and 4 and allowed incubation for 20 hours before they could inoculate stages 1 and 2. This was done in order to achieve better sugar utilisation in the latter stages once continuous fermentation was started. Another point is that with continuous fermentation, inoculation is done once and fermentation can last for more than nine days (Ni et al. 2013). Inoculum size used was 8% (v/v) but in the models 10% (v/v) was used to keep the inoculum size similar to other processes.

iii)   Batch Separate Hydrolysis and Fermentation (B-SHF)

This process covers B-SHF/DD and B-SHF/LLE&D process scenarios in the models. The procedure for designing fermentation schedule and seed generation is similar to that of process (*i*) above. From equipment design and size, it was found that main fermenters are of 4821m^3 size. As a result, the 5th seed fermenter is of 10% (v/v) of main fermenter hence 482.1m^3. According to Lu et al. (2012), inoculum incubation time was 12-15 hours. However, during schedule design, it was found that 15 hours incubation time was ideal in each seed fermenter from the optimisation work done. From the train, the seed becomes ready for inoculation in the main fermenter every 75 hours (3.125 days).

For 10 main fermenters of 4821m^3 each, it was found that 5 trains of five seed fermenters will be required to render the process continuous. Each seed train can accommodate two main fermenters for provision of seed for inoculation (see Figure 9-2). Fermentation time for production of solvents was reported as 40 hours. To those 40 hours of fermentation, 14 hours turnaround time was added for emptying, cleaning, refilling and sterilising for next batch process, making total fermentation time 54 hours (2.25 days) for each batch. The turnaround time for this process was chosen as 14 hours instead of 12 hours inoculum from final seed fermenter was getting ready for inoculation before fermentation reached completion in the main fermenters.

Table 3:12: Seed train fermenters from 1st that gets inoculated by laboratory shake flask to the 5th that inoculates the solvent fermentation tank for B-SHF/DD and B-SHF/LLE&D process scenarios

Fermenter number	1	2	3	4	5
Size (m^3)	0.0482	0.482	4.82	48.21	482.1

3.9.   Feedstock availability and Plant Size

The economic evaluation of the project was based on South African (SA) context. Therefore, the feed stock availability was evaluated for a plant processing 1million tonnes of LCB per year. According to Lynd et al. (2003), SA has different sources of LCB in the form of agricultural residues, forestry residues and invasive plants. Of these LCB types, agricultural residues are the most studied and for which data is available. The processes used for the current study used wheat straw, corn stover and cassava bagasse as feedstock (Section 3.2 and 3.3). Amongst the three feedstocks, cassava bagasse data was not available, because it is not grown in large quantities in SA (Okudoh et al. 2014). Therefore, a cassava bagasse biobutanol production plant will be a possible plant to be built in SA.Marx and Nguma (2013) investigated potential of producing bioethanol from cassava biomass in SA and found that there is potential of producing cassava biomass in large quantities suitable for bioethanol plant.

Maize production in SA is rain fed in most area planted. As a result yields per hectare (4tonne/ha) are not as high as those in the United States (12 tonne/ha) and Europe (16tonne/ha)(Amigun et al. 2010). According to a report by Crop Estimate Committee within the Department of Agriculture, Forestry and Fisheries South Africa DAFF(2014), maize production for 2014 harvest was 14.250 million tonnes. Taking into account that for every dry tonne of maize produced, a dry tonne of corn stover is produced (Amigun et al. 2010; Lynd et al. 2003), there was roughly 4.750 million tonnes of corn stover available in 2014. This has taken into account that one third of residues must remain in the fields to maintain soil structure and nutrients (Amigun et

al. 2010). Sorghum residues could have added to a value of 0.085 million tonnes in 2014. Almost half of the reported yields for both maize and sorghum came from Free State Province of South Africa. For the same year, wheat production was 1.76 million tonnes and that of malting barley and canola added to 0.180 million tonnes residues nationally. The Western Cape was the largest contributor to wheat in terms of area planted and yields obtained and it was followed by Northern Cape Province.

Forest residues, saw mill residues and invasive plants were categorised together because they are woody LCB. According to Lynd et al. (2003), the invasive alien trees could provide the largest share of woody biomass. The trees are largely concentrated in the Eastern and Western Cape provinces of SA and have been studied (Richardson and Van Wilgen 2004). The Working for Water programme under the Department of Water Affairs has been working to control the wide spread of these invasive trees. The following table summarises the LCB available in SA.

Table 3:13: Summary of data for LCB availability in South Africa

Lignocellulose Biomass Type	Million tonne/year	Reference
Corn stover	4.75	DAFF, 2014
Wheat straw	1.76	DAFF, 2014
Sorghum residue	0.09	DAFF, 2014
Sugarcane Bagasse	5.00	SA Canegrowers (2014)
Forest residue	4.00	Lynd et al. (2003)
Saw mill residue	0.90	Lynd et al. (2003)
Invasive alien trees	8.70	Lynd et al. (2003)

3.10. Plant Location, Delivery Distance and Cost

Although it was evident that LCB is location specific, there must be measures to consider for location of such a biorefinery in order to accommodate delivery costs. If the biorefinery was located at a centralised place, then LCB could be delivered at a reasonable cost to such a facility. Also water availability should be another factor to consider in deciding plant location. From section 3.9, it was evident that most of agricultural residue was concentrated in Free State and KwaZulu-Natal provinces. As a result, a biorefinery would be located to the Eastern part of Free State Province instead of KwaZulu-Natal. The choice was based from the fact that most of the

bagasse from sugarcane mills in KwaZulu-Natal is already used for steam generation(Leibbrandt 2010; Mbohwa 2003; Nsaful et al. 2013). However, there is possibility for mills to diversify their products where they could opt for 2G biobutanol production plant annexed to a mill and use sugarcane bagasse as feedstock(Dias et al. 2014). Then the optimised process can use fermentation residues for steam and electricity generation to meet plant energy demand.Pereira et al. (2014)however warns that rigorous economic studies have to be undertaken to weigh the risks and strategic benefits of including 2G butanol plant in sugarcane biorefineries because the final use of butanol and its target market affect economics. Since in KwaZulu-Natal most of the mills use sugarcane bagasse for steam generation, it leaves corn stover, sorghum stalks and wheat straw as the viable feedstock for a proposed biorefinery in Free State Province.

Leibbrandt (2010)showed that LCB being a high volume but low density material is challenging to transport to a processing facility. It was noted that the cost of delivering LCB to the facility increases with the distance it has to be collected. For instance, at 300km round trip from and to the facility, the cost of bagasse is approximately US$80/tonne whereas if the bagasse is available at facility the cost is US$62/tonne (Figure 3-5).
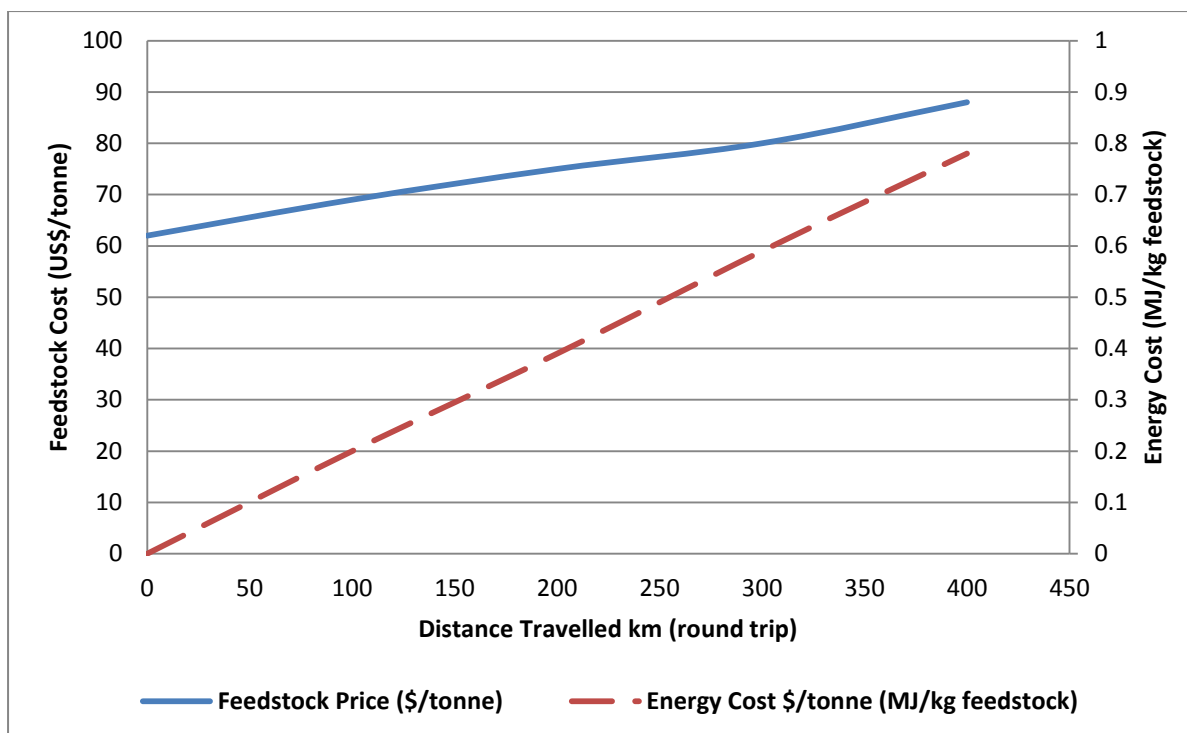
Figure 3-5: Relationship between feedstock delivery distance to processing facility, price and energy cost. Reproduced from (Leibbrandt 2010)

3.11. Process Energy Demand and Efficiency

In ABE fermentation using LCB, certain processes have been identified as major consumers of energy, primarily pretreatment and product recovery (section 2.4). As a result, butanol and ethanol fermentation processes have been studied that generate their own power and heat to meet their energy demand (Mariano and Ezeji 2012; Mariano et al. 2011; 2013). However, energy efficiency at some plants is low when considering amount of steam and electricity generated per tonne of biomass burnt (Mbohwa 2003). Therefore, there has been interest in finding ways in which energy efficiency of processes can be improved. Energy efficiency of processes in this study was evaluated in two ways namely: liquid fuel energy efficiency and overall process energy efficiency.

For evaluation of process energy efficiencies (EE), LCB heating values have to be known because they contain amount of thermal energy that is released when LCB is burned. The energy content is reported in higher heating value at dry basis (HHV_{dry}), which is experimentally determined (Friedl et al. 2005). The HHV_{dry} is defined as enthalpy for complete combustion of LCB and enthalpy for condensation of formed

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water vapour (Friedl et al. 2005; Richardson et al. 2002). There are equations that relate HHV_{dry} to LHV_{dry}(equation 3-11). LHV_{dry} is the enthalpy of complete combustion of LCB but does not take into account the enthalpy for condensation of vaporised water.   Furthermore, it is understood that LCB is not available at biorefinery and CHP plants as dry feedstock due to storage practices and time of storage (Humbird et al. 2011). As a result, the heating value of wet LCB as received at biorefinery (LHV_{ar}) was used in evaluation of EE. The equations which relate $LHV_{dry}$and LHV_{ar} to $HHV_{dry}$are given below:

$$LHV_{dry} = HHV_{dry} - 2.45 \times 0.09 \times H$$

Equation 3-11

$$LHV_{ar} = LHV_{dry} - \frac{2.45MC}{100 - MC}$$

Equation 3-12

Where: HHV_{dry} is the Higher Heating Value (MJ/kg) of LCB as obtained from literature

LHV_{dry} is the Lower Heating Value (MJ/kg) of LCB evaluated

LHV_{ar} is the Lower Heating Value (MJ/kg) of wet LCB as received

2.45 MJ/kg is the energy required to vapourise water at 20°C.

Table 3:14: Composition of energy content of the LCB feedstock used in the study

LCB Type	HHV_{dry} (MJ/kg)	LHV_{dry} (MJ/kg)	LHV_{ar} (MJ/kg)	H% (w/w)	Reference
Wheat straw	17.60	17.86	13.74	6.1	White and Plaskett 1981
Corn stover	17.93	16.73	15.75	5.2	White and Plaskett 1981
Cassava Bagasse	17.60	18.00	17.55	6.9	Adisak Pattiya 2011

3.11.1.   Process Energy Demand

Every process utilises energy and it was important to perform process energy demand analysis.This allowed for identification of process scenarios which were responsible for major energy consumption. In addition, this analysis aided in understanding the sections or areas within the plant that hadhighest impact on energy demand. Energy demand (Q_{ED}) in MJ/kg of butanol produced was evaluated for six process scenarios modelled in ASPEN Plus (2013). Energy demand was evaluated as the ratio of sum of power consumed ($Q_{power\ consumed}$) and steam required ($Q_{steam\ consumed}$) in the selected butanol process to the butanol produced per year ($M_{butanol}$). The equation for evaluation of process energy demand is shown in the equation below.

$$Q_{ED} = \frac{Q_{steam\ consumption} + Q_{power\ consumption}}{M_{butanol}}$$

<div align="right">Equation 3-13</div>

Where M is butanol mass flow rates in kg/year.

In addition, the processes gross energy value was evaluated. This was done for comparison purposes with the study of molasses based butanol production which reported the gross energy value (GEV) of its processes investigated.GEV for process scenario was evaluated by first converting LCB flowrate into input energy content by multiplying it with LCB higher heating value of 18MJ/kg and then dividing it by the butanol output. The energy input was subtracted from butanol higher heating value of 34.34MJ/kg to obtain GEV (van der Merwe 2010). The equation for GEV is shown in the equation below:

$$GEV = HHV_{butanol} - \frac{(M \times HHV)_{feedstock}}{M_{butanol}}$$

<div align="right">Equation 3-14</div>

Where M is mass flow rates in kg/year.

3.11.2.   Liquid Fuel Energy Efficiency

Liquid fuel energy efficiency ($\eta_{liq\ fuel}$) was evaluated to measure the degree at which a process converted thermal energy in LCB feedstock into liquid fuel products

(Leibbrandt 2010; Petersen et al. 2015). According to Hamelinck et al. (2005), this form of efficiency allows for adjustment in the energy input by subtracting the thermal energy of by-products from thermal energy in the LCB feedstock. Furthermore, the electrical energy (kW) that can be produced by LCB was hypothetically converted to thermal energy of LCB feedstock. The assumed electrical efficiency (η_{elec}) was 45%(Hamelinck et al. 2005).

$$\eta_{liquid\ fuel} = \frac{M \times LHV_{fuel\ product}}{M \times LHV_{feedstock} - M \times LHV_{co-product} - \frac{Elect.Export}{\eta_{45\%}}}$$

Equation**3-15**

Where *M* is mass flow rates in kg/s and *LHV* is Lower Heating Value in MJ/kg of feedstock, products and co-products. The co-products here referred to ethanol and acetone, which were not considered main product of the process.

3.11.3.   Overall Energy Efficiency

The significance of overall energy efficiency ($\eta_{overall}$)was, it allowed for analysis of the amount of energy input to the process that was converted into saleable products. Thus it can be deduced what percentage of the incoming energy was used for internal process demands and the rest expended to the environment. From this analysis, decisions can be made, whether a process needs modifications or optimisations to improve the overall efficiency or it is at acceptable state. Overall energy efficiency was evaluated as the ratio of the energy output in products and co-products and net energy available after meeting the power requirements of the plant to the energy available in the feedstock. It also takes into account the extra energy input that may come from fossil fuel source like coal (Laser et al. 2009; Leibbrandt 2010; Petersen et al. 2015). In this study, no fossil fuel was used; hence the fossil energy term is zero.

$$\eta_{overall} = \frac{M \times LHV_{fuel\ product} + M \times LHV_{co\ product} + Elect.Export}{M \times LHV_{feedstock} + Fossil\ Energy}$$

Equation 3-16

Where *M* is mass flow rates in kg/s and *LHV* is Lower Heating Value in MJ/kg of feedstock, products and by-products.

3.12. Process Economic Analysis

The economics of biobutanol production was done on the chosen conceptual process scenarios. Table 3:15 gives the economic parameters used for discounted cash flow analysis with the assumptions used in the evaluation of profitability of the scenarios. The references for the economic parameters can be found in the sub-sections of 3.12.

Table 3:15: Economic parameters used in scenarios economicfeasibility evaluation

Tax Rate[a]	28%
Salvage Value	30%
Working Capital (% of FCI)	5%
Equity	40%
Loan Interest	5.7%
Loan payment term (years)	10
Discount Rate[b]	9.3%
Inflation Rate	6%
Depreciation: straight line (years)	10
Construction Period (years)	3
Start-Up Period (years)	0.25
Economic Project Life	25
Operating hours per year	8000
Butanol Selling Price (US$/kg)[c,d]	0.78
Acetone Selling Price (US$/kg)[d]	1.10
Ethanol Selling Price (US$/kg)[c,d]	0.67
Electricity Selling Price (US$/kWh)[e]	0.093

[a] Sourced: Corporate Income Tax, South African Revenue Services (2015)

[b] Sourced: South African Reserve Bank (2015)

[c] Sourced: BFP (2015); Basic Fuel Price, South Africa. GGE (2015); Gasoline Gallon Equivalence

[d] Sourced: Norceline Chemicals & Lubricants (2015)

[e] Sourced: Based on in-house information (Green electricity) (2015)

3.12.1.   Total Capital Investment (TCI)

TCI is the one-time expense for design, construction and start-up of a new plant (grass-roots plant) or an addition to an existing plant. It is the sum of fixed capital investment (FCI), land and working capital. To estimate TCI, total equipment cost has to be estimated, which is also referred as inside battery limit (ISBL). This covers the purchase and installation of process equipment as well as its piping,

instrumentation and control. The purchase cost of process equipment is sourced from literature using charts, equations and quotes from venders. Due to inflation, costs keep on changing with time and this means costs can apply for only a period of time. Therefore, costs estimation of process equipment at a later date was obtained by Equation 3-17:

$$C_{CEE} = RC * \left(\frac{SP_S}{SP_R}\right)^{SF} * IF * \left(\frac{CEPCI_{FY}}{CEPCI_{RY}}\right)$$

Equation 3-17

Where:

C_{CEE} = Cost estimation of process equipment in 2015

RC = Reference quoted cost

SP_S = Simulated scaling parameter

SP_R = Referenced scaling parameter

SF = Scaling factor

IF = Installation factor

$CEPCI_{FY}$ = Chemical Engineering Plant Cost Index of the first year of analysis

$CEPCI_{RY}$ = Chemical Engineering Plant Cost Index of the reference year

From the total equipment cost which is the summation of all C_{CEE}, total direct capital investment was obtained by the following equation

$$TDCI = BOP + SD + W$$

Equation 3-18

Where:

BOP= balance of plant and it estimates additional costs to piping and instrumentation. It is estimated as 4.5% of ISBL

SD = Site development estimated at 9% of ISBL

W = Warehouse estimated at 4% of ISBL

The total indirect capital investment (TICI)was evaluated from TDCI by Equation 3-19:

$$TICI = TDCI + PC + FE + \ OC + C + O$$

Equation 3-19

Where:

PC = Prorateable expenses which are 10% of $TDCI$.

FE = Field expenses which are 10% of $TDCI$.

OC = Office and construction fees which are 20% of $TDCI$.

C= Contingency which is 10% of $TDCI$. This is an anticipated cost incurred during construction of the plant due to uncertainty when estimating all the costs involved.

O = other costs that can be incurred as well and they are 10% of $TDCI$.

Once these costs have been obtained, total fixed capital investment (TFCI) was evaluated from the sum of TICI costs and cost of land. The cost of land was considered non-depreciable as land does not decrease in value. It was estimated at 2% of total depreciable capital which is the sum of ISBL, TDCI and TICI costs(Seider, Seader, and Lewin 2004). Finally, the total capital investment (TCI) was evaluated from the sum of TFCI and working capital (WC). WC is the cash required to cover overall daily expenses of the plant until payments are received from sales. It was estimated at 5% of TFCI.Therefore, the total capital investment (TCI) is given by:

$$TCI = TFCI + WC$$

Equation 3-20

3.12.2.   Saleable Products

The saleable products from the processes in this study were butanol, ethanol and acetone. Surplus electricity after meeting the process demands can also be sold. Among the main products, butanol was the most important and it was produced in largest quantities from the processes. Butanol and ethanol produced in the

processes were targeted as fuel grade for the transportation industry, while acetone was considered to be sold in the chemical market. In order to estimate the selling price of butanol and ethanol at fuel grade, the basic fuel price (BFP) from South Africa was used. BFP is described as the price that would cost a South African importer of a refined petroleum product to buy the product from an international refinery, transport the product from that refinery, insure the product against losses at sea and land the product on South African shores BFP (2015). The average BFP from January until May 2015 was multiplied by densities of butanol and ethanol respectively to get their basic fuel selling price which was US$0.56/kg butanol and US$0.58/kg ethanol.

Gasoline Gallon Equivalent (GGE) was also used in order to take into account the energy content of biofuels, which are lower than that of gasoline. GGE used for ethanol and butanol were 1.39 and 1.095 respectively Pure Energy Systems Wiki (2015) and GGE (2015). Since the biofuel producers in South Africa will be exempted from fuel taxDME (2007), fuel tax was averaged from January to May 2015 and it was found to be R2.55/L. Densities of ethanol and butanol were applied to fuel tax price and tax amount was used in calculating selling price of ethanol and butanol. Therefore, ethanol and butanol selling prices used in all scenarios were US$0.686/kg ethanol and US$0.778/kg butanol respectively.

$$Biofuel\ Selling\ Price = \frac{BFP}{GGE} + Tax_{exm}$$

<div align="right">Equation 3-21</div>

Acetone selling price was kept at chemical market selling price of US$1.10/kg Norceline Chemicals & Lubricants(2015). It should be noted that when acetone is produced as a by-product of fuel production process, it may end up being being oversupplied. This could lead to its selling price to be depriciated. As it was described in section 2.3, research in metabolic engineering of *Clostridia* toeliminateacetone production pathway in order to produce more alcohols would address challenge of excess acetone being produced. According to NERSA (2011),co-generators operating as Type III Independent Power Producers (IPP) were permitted to sell power directly to buyers. As a result, the selling price of surplus electricity from the processes was set at maximum of US$0.093/kWh which was

comparable to US$0.098/kWh found in South Africa's renewable energy policy roadmaps by Edkins et al. (2010). This was the assumed price at which the export green electricity from solid biomass is sold to Eskom.Therefore, acetone and surplus electricity also contribute to sales revenue.

3.12.3.   Minimum Biobutanol Selling Price

The Minimum Biotutanol Selling Price (MBSP) was evaluated to see if the commercial plant will be economically feasible. MBSP is defined as the minimum selling price of butanol so that the Net Present Value (NPV) is equal to zero at the given Discount Rate (Tao et al. 2013; 2014). In this study 9.3% interest rate was used in all the economic analysis based on the fact that Prime Interest Rate (PIR) from the South African Reserve Bank has been below 10% up until September 2015 when the analysis was done (Figure 3-6). PIR is a base rate used by all South African commercial banks when lending the public and other institutions loans. There is direct link between IRR and discount interest rate and PIR, because when IRR is equal to the discount interest rate, the money can be borrowed and get invested into a venture. At the end life time of the venture, a profitable cash balance will be present only when an IRR equal to or greater than discount rate result in a positive NPV. The negative NPV means the project is not feasible at a given discount rate and that means the IRR is less than the discount rate.
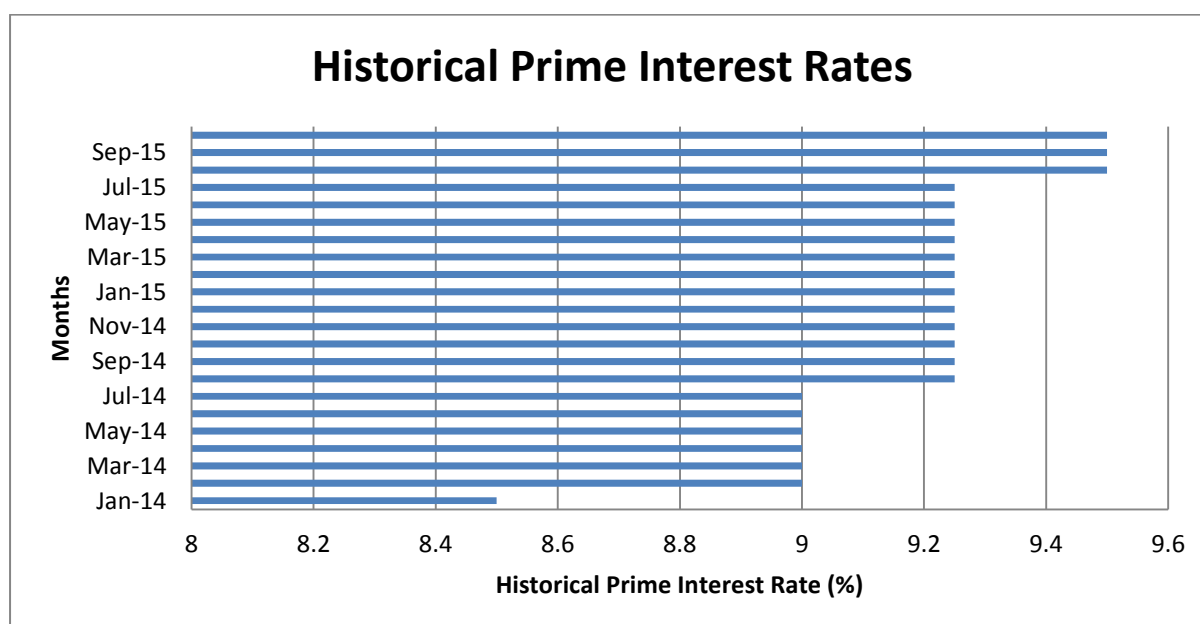
Figure 3-6: Historical South African Prime Interest Rate: reproduced fromSouth African Reserve Bank (2015)

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The Discounted Cash Flow (DCF) analysis was performed in order for MBSP to be evaluated. In order to perform the DCF parameters such as variable costs, fixed costs, capital depreciation, discount rate and income tax has to be gathered. For the processes investigated here, the variable costs include raw materials and utility costs, while fixed costs include labour and overheads.

3.12.4.   Sensitivity Analysis

In order to evaluate the economics feasibility, a sensitivity analysis was done to investigate parameters that had the most significant effect on the MBSP. According to Tao et al. (2013), product yield and product molar ratio had significant effect on the MBSP. Mesfun et al. (2014)found that fermentation time and the reactor size had significant impact on the cost per tonne of butanol produced. Furthermore, parameters such as feedstock price, product price, utility costs and interest rate were investigated by van der Merwe (2013) for their effects on NPV and IRR. Qureshi et al. (2013)investigated effects of a number of parameters on MBSP such as wheat straw price, change in inflation as well as plant size.

In the sensitivity analysis of this study, the effect of IRR on the MBSP was investigated. The IRR was considered a crucial indicator, because investors could either choose to put their money in the bank if the returns are bigger than what the project can give if the money was invested in it. Another factor which was assessed is feedstock cost as a variable operating cost to the project. It can have economic impact on the project depending on whether it is available at no cost, low cost or high cost to the plant. It was one of the major raw materials in the economics and its effects on MBSP were assessed. Lastly, the enzyme cost per tonne of dry feedstock was also assessed. This was because enzyme cost to the biorefineries has been fluctuating and is believed to decrease in future. The low cost of it will contribute to lower operating expenses and directly improve the net profit of the project economics.

In this study, sensitivity analysis was done by varying feedstock price between R20.00/GJ and R100.00/GJ. This was converted into US$/dry tonne by assuming general feedstock Higher Heating Value of 18MJ/kg. Rand to US Dollar exchange rate of R12: US$1 was used (South African Reserve Bank 2015). The conversion gave the feedstock price at US$30/tonne to US$150/tonne and the price was divided

into 30, 60, 80 and 150 US$/tonne to investigate the effect on the MBSP. The base case feedstock price chosen was US$60/tonne. This cost was close to feedstock cost used in other studies such as US$58/tonne corn stover (Humbird et al. 2011) and US$56/tonne cane bagasse (Nsaful et al. 2013). For enzyme cost, it was found that enzyme cost per dry tonne of feedstock vary from different literature sources. But overall it was in the range US$40/tonne to US$120/tonne (Aden and Foust 2009; Kazi et al. 2010; Klein- Marcuschamer et al. 2012; Seabra et al. 2010). The range was divided into 40, 60, 80 and 120 in all scenarios to evaluate the effect on MBSP. The base case cost was chosen to be US$60/tonne feedstock. The IRR used for evaluation of MBSP was 7.2%, 9.3%, 10% and 15%. The base case was chosen to be 9.3%.

4.   Process Descriptions

This chapter provides detailed process descriptions for all the three processes modelled in the current study. It further gives details on the modifications done to the processes information, as described in literature, so that the modelledversions would reflectthe likely industrial operations. Most of the changes were to avoid major energy costs, costs of equipment and raw materials under industrial operations,although the resulting changes are still in line with most of literature(Humbird et al. 2011).

In all the processes, biomass was assumed to be present at the plant in a state that is ready to be pretreated. Biomass preparation such as size reduction, washing and drying were not considered in the process modelling, but were considered in the economics studies. The processes shared the same process utilities in the form of steam, cooling water and electricity. Steam demand was mainly in the distillation reboilers and hydrolysis reactors during pretreatment and saccharification, while cooling water was used in distillation condensers and the scrubber. Electricity was used to power compressors and pumps of the process.

4.1.   Batch Simultaneous Saccharification and Fermentation integrated with Gas Stripping

4.1.1. AREA-100: Biomass Pretreatment and Detoxification

Wheat straw (moisture content 20% by weight) as per normal assumption (Huang et al. 2009)was assumed to be available in required particle size. In the model, 10% of the feedstock is split off and sent to Boiler Area-600 to be burntfor steam generation (see Figure 4-1). The remaining 90% got fed directly to the pretreatment reactor for subsequent conversion to ABE. It should be noted that all the reactors in the models were modelled as RStoic in ASPEN Plus (2013). Sulphuric acid (H_2SO_4) at 1%(w/w) used for pretreatmentwas pumped into the reactor and solids loading was maintained at 8.6% (w/w). The reactor was steam heated to around 121°C and reactants residence time was 1 hour at 2 atm. After an hour of pretreatment, the

slurry was passed througha counter current heat exchanger, where the slurry pre-heated the fresh pretreatment feedstock to 100°C. The pretreated slurry went to solid-liquid separator, which was modelled as a cyclone, althoughin real plant this wouldprobably be a centrifuge or Pneumapress filterCostelloe (2001). The separated liquid stream was sent to a conditioning reactor, where stoichiometric amount of ammonia was added to neutralise the acid. After conditioning, a 5% split stream was channelled to Area-200 for seed generation. The remaining liquid streamwas mixed with water and solids in a slurry holding tank to get required solids loading, whichwas then pumped to AREA-300 for simultaneous saccharification and fermentation (SSF).
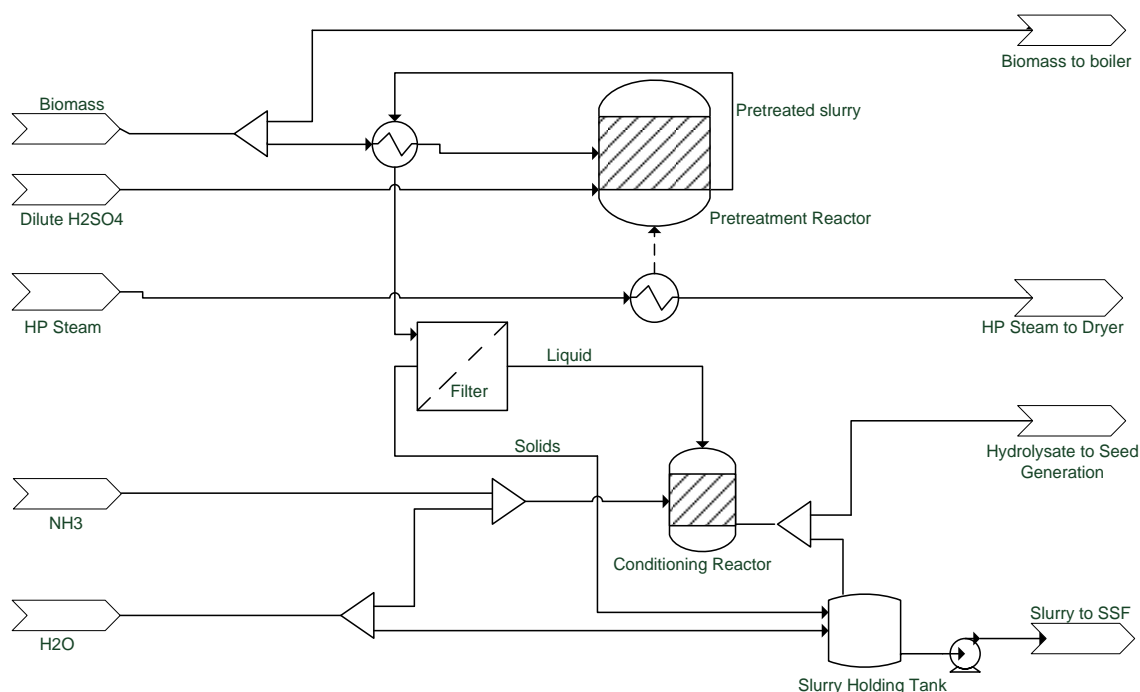
Figure 4-1: Process Flow Diagram for Pretreatment Area-100

4.1.2. AREA-200: Seed Generation

Seed production for inoculation in the fermenter is a crucial part of ABE fermentation. The seed fermenter was modelled as RStoic in ASPEN Plus (2013) operating at 35°C and 1atm. The reactions taking place for microorganism growth can be viewed in Section 3.5 For seed production, the main requirements were carbon source in the

form of glucose (LCB hydrolysate) and nutrients in the form of nitrogen, protein and phosphate (corn steep liquor and diammonium phosphate)(Humbird et al. 2011).

For carbon source, 5% split of hydrolysate was directed to the seed generation fermenter to supplement glucose and thereby reduce costs for glucose purchase. Here the assumption was that *Clostridia* can utilise both C6 and C5 sugars as has been shown by Liu et al (2010); Qureshi et al. (2008a). Another importance of using hydrolysate split as carbon source for seed production was to adapt microorganisms for conditions in the fermenter. With all these fed to the seed fermenter, the inoculum prepared in the laboratory was used to inoculate the seed fermenter. The biomass was allowed to grow for 18 hours before it was ready to be inoculated into the next seed fermenter or the main fermenter.

According to Humbird et al. (2011)a train of batch reactors may be used to allow cycling and growth of cell mass. However, in the present model the inoculum generation in the seed trainwas modelled as a single continuousreactor as can be seen in Figure 4-2. It was further assumed that seed into fermenters were gravity fed in order to minimise the pumping costs.
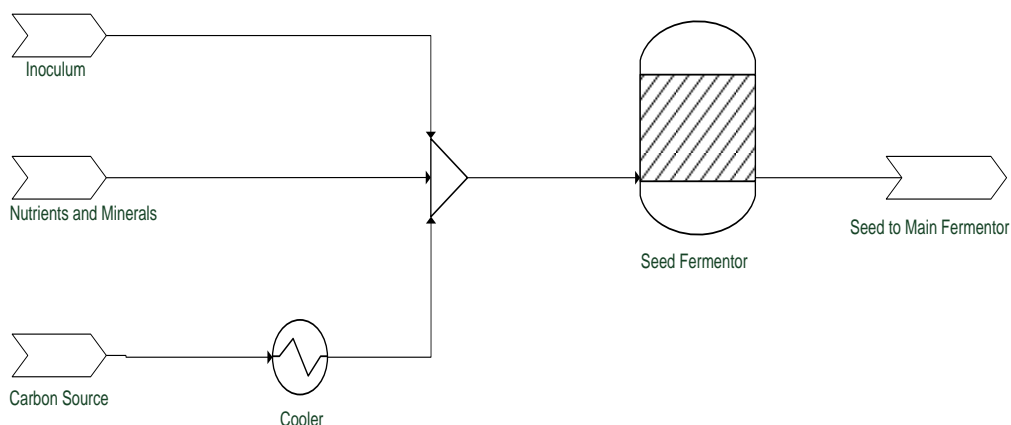
Figure 4-2: Process Flow Diagram for Seed Generation Area

4.1.3. AREA-300: Simultaneous Saccharification and Fermentation

This area was the main process area, where SSFand gas stripping take place. The description given here was that of SSF fermenter integrated with *in situ* gas stripping.SSF reactorwas modelled as two sequential RStoic reactors in ASPEN Plus

(2013) for ease of reactions input (see Figure 4-3), though SSF happens in single reactor. Both of these reactors operate at 35°C and 1atm, which are the operating conditions from literature(Qureshi et al. 2008c). It should be noted that the net heating duty of SSF fermenter was the sum of the two reactors. Enzymes and the pretreated slurry were fed intosaccharification fermenterfor cellulosic and hemicellulosic hydrolysis to take place. The hydrolysate was then sent for fermentation into the subsequent RStoic reactor, wherethe nutrients and inoculum were fed to the reactor for fermentation to occur.In reality these two process steps will occur simultaneously in one reactor. After 23 hours of fermentation, gas stripping was started by circulating fermentation gases (CO_2 and H_2) stream through the fermenter broth and then pumping the stripped off solvents to external condenser. Fermentation lasted for 72 hours and another 12 hours downtime was added for draining, cleaning, refilling and sterilising the fermenters.

In reality, gas stripping is done by pumping the fermentation gases through the reactor and the vapourised solvents.The stripped off solvents are then sent for condensation to recover them, while the gas is recompressed and recycled back into reactor to strip the remaining solvents. The following description is how gas stripping was modelled in ASPEN Plus (2013). *In situ* gas stripping fermenter was modelled as the combination of a second RStoic reactor mentioned in above paragraph, followed by a mixer and a flash tank all of them operating at 35°C and 1atm. A make-up stream of the gaseous CO_2stripping agent was mixed with the outlet stream from the fermenter by a mixer and the combined stream was sent into a flash tank(van der Merwe 2010). The flash tank had two streams leaving it, the gaseous stream with the solvents making the tops and the liquid and solids making the bottoms. The liquid and solids making up the bottoms of the flash tank were sent for solid-liquid separation, solids drying and combustion in a boiler in AREA-600. The liquid was mainly water, residual sugars and unvapourised solvents. The solids part was made of lignin, unhydrolysed cellulose and hemicellulose, enzymes and cells. It should be noted that in reality, the liquid and solids would remain in the fermenter until fermentation stopped. However, for modelling purposes, the stream was assumed to continuously go for solid-liquid separation.

The gaseous stream of the flash tank consisting of the stripped solvents was sent to the condenser where they lose their latent heat of vapourisation and condense into

liquid stream. The condenser was modelled as a heat exchanger operating at -10°C and 1atmand followed by a flash tank at same conditions.Lu(2011) and van der Merwe (2010)both assumed that the condenser would be operated below 0°C.They have found that as temperature was lowered more solvents were condensed. That was similar to what others studies reported(Groot et al. 1992; Vane 2008).In addition, Abdehagh et al. (2014) found from their simulation studies that the quantity of butanol recovered in the cold trap decreased by 20% as the temperature was increased from -40°C to 10°C.

Operating conditions of -10°C and 1atm were thus selected for the condensation unit, to ensure maximum butanol condensation.Although lowering temperature below 0°C was found to recover more solvents, it had disadvantage of water getting condensed with solvents, which required more energy input during subsequent separation in distillation. The condensate from the holding tank was then sent to AREA-400 for purification either by double effect distillationor liquid-liquid extraction with distillation.
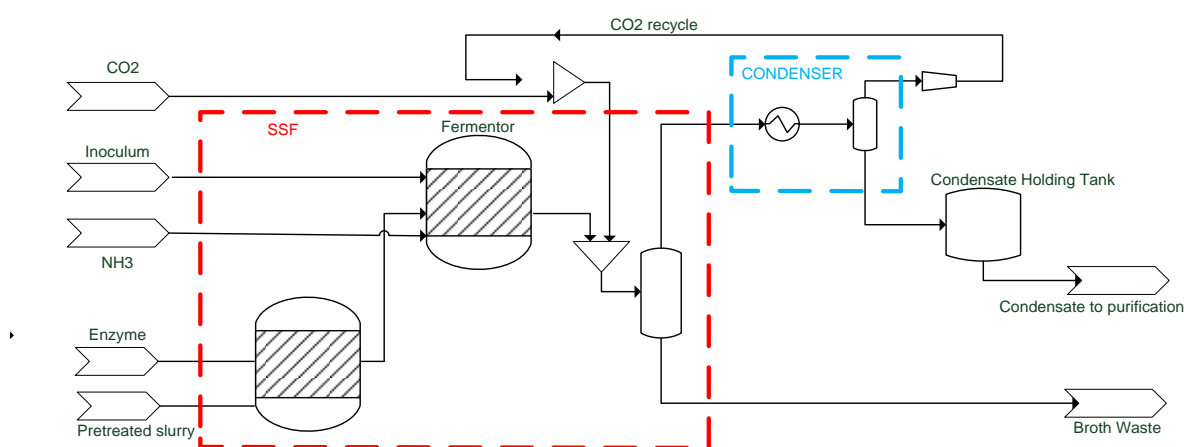
Figure 4-3: Process Flow Diagram for Simultaneous Saccharification and Fermentation integrated with Gas Stripping Area-300

4.1.4. AREA-400: Solvents Separation and Purification

The downstream separation process is the most energy intensive part in the production of biobutanol, as explained in section 2.8. In this study, two separation processes in the form of Double effect distillation(DD) (Figure 4-4) and Liquid-Liquid

Extraction (LLE)withDistillation (Figure 4-5) were used to separate solvents into their respective products.

4.1.4.1.   *Double effect Distillation*

Double effect distillation(DD)shown in Figure 4-4consisted of series of distillation columns to concentrate the beer stream that came from AREA-300, to separate acetone, ethanol and heterogeneous azeotrope of water-butanol mixture. The columns were operated in a decreasing order of pressure from the beer column to the ethanol column(Junqueira et al. 2009). This operation allowedsteam from power and heat generation to be used in the columns reboilers.

The beer column consisted of 45 theoretical stages and the feed was fed on stage 1 of the column(Mariano et al. 2011). This column increased water content to the bottoms stream and butanol in the tops increased to 19% (w/w) compared to 12% (w/w) in the stream fed to the column.It has been found that CO_2 is difficult to totally remove from the solvents stream after fermentation and is normally present during purification(Mariano and Ezeji 2012; van der Merwe et al. 2013). Asa result, flash tanks were used to remove CO_2 from the solvent stream. Flashing of this CO_2resulted in some entrainment of some solvents and these were removed in a scrubber, to meet environmental regulations. The wash water used in a scrubber was process water available from the water plant. Because the scrubber bottoms was 98% (w/w) water, the stream was sent to a waste water treatment plant rather than being pumped back into the acetone column to recover the solvents.

The beer column distillate stream was flashed at atmospheric conditions and 25°C to remove CO_2, and the residual liquid stream was sent into acetone columnthat has 30 theoretical stages. This column operated at 0.7atm in order to make use of heat integration in its reboiler (Mariano et al. 2011). The acetone column distillatewas sent to a compressor to increase its pressure from 0.7atmto atmospheric conditions. The distillate from the compressorwas flashed at atmospheric conditions in a knockout drum, which was modelled as a flash tank to giveliquid product stream of acetone.The gas stream was sent to scrubber to lower solvents release to the environment and vent off CO_2.Acetone purity from the acetone column was 86% and after the knockout drum it was increased to 98% as a final product. The bottoms of acetone column were pumped into ethanol column for recovery of ethanol. Ethanol

column had 30 theoretical stages and it operated at 0.3atm. The distillate was sent to a total condenser and the ethanol product came out at 84% (w/w). If ethanol of higher purity is required, molecular sieves can be used to further dehydrate the stream.

Heterogeneous azeotrope of water-butanol mixture was sent to a decanter operating at66°C and 0.7atmto facilitate phase separation. The butanol rich phase separated on top at 75% (w/w) butanol(Seader et al.1997). Itwas sent to butanol column that produce at96.7wt% butanol. The distillate of the butanol columnwas passed through a condenser and then mixed with another condensed stream from water column distillate.The mixed stream was recycled to the decanter for phase separation again.The aqueous phase containing 5% (w/w) butanol from the decanterwas sent to water column, which produced bottoms at>98% (w/w) water. This water was sent to AREA-500 for anaerobic waste water treatment. The distillate of this column had 7% (w/w) butanol was passed through a condenser and mixed with condensed butanol column distillate.
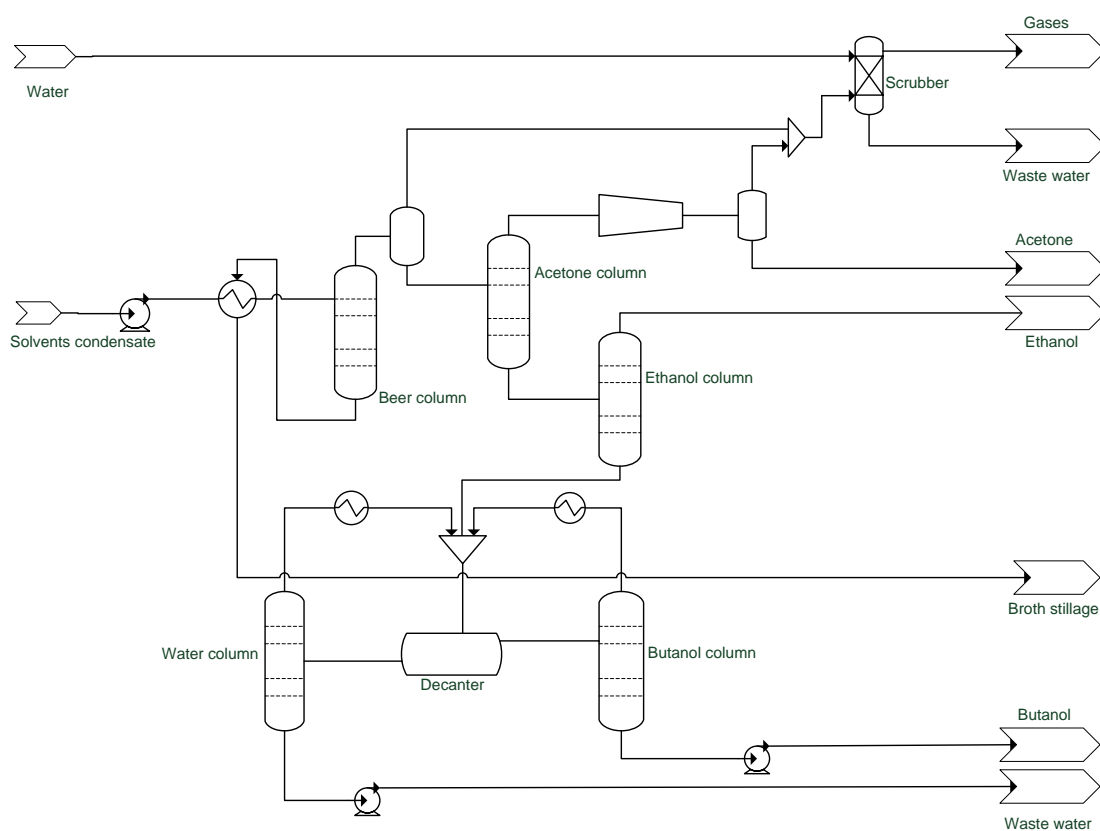
Figure 4-4: Process Flow Diagram for Double effect distillationto obtain ABE as final products. The main equipment's are five columns, Scrubber and a Decanter

4.1.4.2.   Liquid-Liquid Extraction and distillation

The Process Flow Diagram (PFD) for a separation train based on LLE and distillation is shown in Figure 4-5. It should be noted that only when gas stripping was used, the condensate was sent to LLE and distillation. For processes without gas stripping, fermentation broth was sent to LLE and distillation. The solvent stream from condensate holding tank was pumped into an extraction column, where it was contacted with the oleyl alcohol used as an extractant. The mass ratio of solvents stream to the extractantwas 0.983(Liu et al. 2004). After sufficient contact time to allowmaximum extraction of solvents (assumed to be 1hr), the extractant rich in butanol, acetone and little ethanolwas sent to extractant recovery column. It should be noted that this contact time was chosen based on extraction being done outside fermenter where no cell toxicity would be an issue(Qureshi et al.1992). Several studies have shown that oleyl alcohol is less selective towards ethanol than the other two solvents(Dadgar and Foutch 1988; Ishii et al.1985; Liu et al. 2004). The raffinate from the extraction column was sent for anaerobic digestion in water plant for biogas production.The extractant recovery column separated the solvents to the distillate and the extractant to the bottoms. The column achieved 99.99% recovery of extractant and this stream was used to pre-heat feed to the column before being recycled to the extraction column.

The isolated solvents were subsequently pumped into a butanol recovery column that separated butanol from acetone. Due to butanol being less volatile than acetone, it was recovered in the bottoms of the column, while acetone was collected as a product from the distillate stream. There was no need of an extra column to separate acetone from traces of ethanol present in the stream. This was because acetone of high mass purity was still obtained and separating ethanol would have added significant capital and operational costs.

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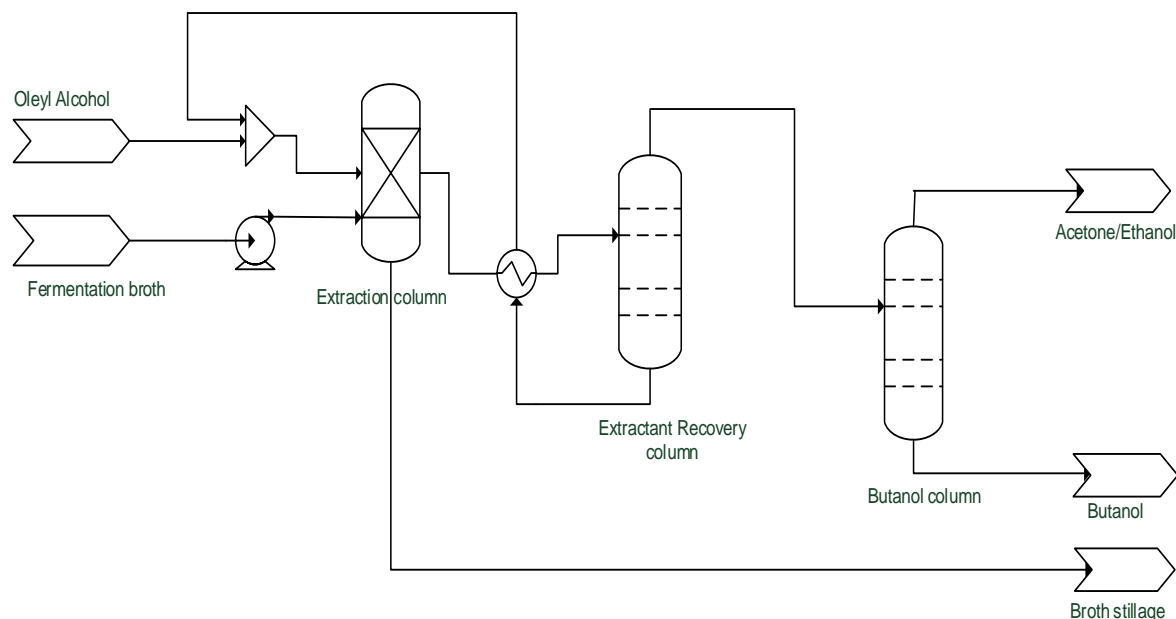
Figure 4-5: Process Flow Diagram for Liquid-Liquid Extraction and Distillation to obtain butanol and mixture of acetone/ethanol as final products. The main equipment's are Extraction column, Extractant Recovery column and a butanol and acetone/ethanol column

4.1.5. AREA-500: Water plant for provision of Boiler Water and Wastewater Treatment

This section of the plant houses two units in the form of anaerobic digestion for biogas production and boiler water cleaner. Anaerobic digestion of waste streams to reduce chemical Oxygen Demand (COD) have been applied in a number of studies(Briggs et al. 2004; Parawira et al. 2005; Simate et al. 2011). High COD is believed to contribute to eutrophication, if the waste streams are discharged to the environment.During anaerobic digestion, biogas is produced and it can be used as fuel for heat or power generation depending on the quantity generated. According to Biogas Handbook (2008), if biogas has to be used in gas turbines for electricity generation, it has to be cleaned of CO_2 and H_2S through water scrubbing. This is due to high solubility of CO_2 and H_2S in water compared to CH_4. The resulting biogas is around 90% (w/w) CH_4 after scrubbing. However, if is used in boilers in CHP plants,it can be sent straight into the combustor without need for extra-cleaning and this was according to Biomass Combined Heat and Power Catalogue Technologies (2007)and International Renewable Energy Agency(Gielen 2012)report.

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Biogas was generated in the reactor modelled as RStoic in ASPEN Plus (2013) with stoichiometric reactions and fractional conversions sourced from literature(Humbird et al. 2011). The reactor mostly studied is the Upflow Anaerobic Sludge Blanket (UASB)and it operates at 35°C and 1.5atm.In this study, the feed to the biodigester consisted of scrubber bottoms and water column bottoms. It further includedthe liquid stream after fermenter broth solid-liquid separation from evaporator section. These feed streams to biodigester contained carbohydrates in the form of residual sugars,residual solvents of ethanol, butanol, acetone, acids and other products that were generated during the process.

The gas mixture produced through anaerobic digestion was collectedin the reactor head space. From the reactor it was passed through a compressor and sent to combustion in Area-600. The liquid stream with reduced COD was assumed to be released to municipal waste water treatment works, because around 60% COD and up to 80% BOD was reduced (Briggs et al. 2004). According to Biogas Handbook (2008) when substrate to the biodigester is carbohydrate, gas yield ratio is around 50% CH_4 and 50% CO_2.At a Hydraulic Retention Time (HRT) of 5 days 45% CH_4 was generated at 50% COD reduction from a brewery wastewater (Cronin and Lo 1998). CH_4 content is similar to the one found in the model of this study at 43% and therefore HRT of 5 days was assumed for the model.

Feed water for the boiler was prepared and pumped from the same water processing area. The holding tank at 1atmreceived water from make-up stream and condensate from power generation plant. The condensate was formed from Low Pressure Steam from third turbine that goes through a heat exchanger and comes out as liquid at 54°C and 1atm, and gets pumped to boiler water feed holding tank. From the holding tank, water gets pumped to de-aerator at 1.1atm to get rid of oxygen,carbon dioxide and other elements that may be present in water. It has been found that unclean boiler water causes problems in the boiler such as corrosion and deposits (Hamer 1960). The de-aeratorwas modelled as a flash tank operating at 55°C and 1.1atm. According toStraub(1939), theaddition of chemicals such as sodium hydroxide or bisulphite to water can also be used to react with oxygenand further reduce its content in boiler water. However, that was not considered in this study becausede-aerator was assumed to remove oxygen totally. The liquid stream of the de-

aeratorwas pumped to boiler as feed water to Area-600. The de-aerator has a vent that released oxygen to the atmosphere (see Figure 4-6).
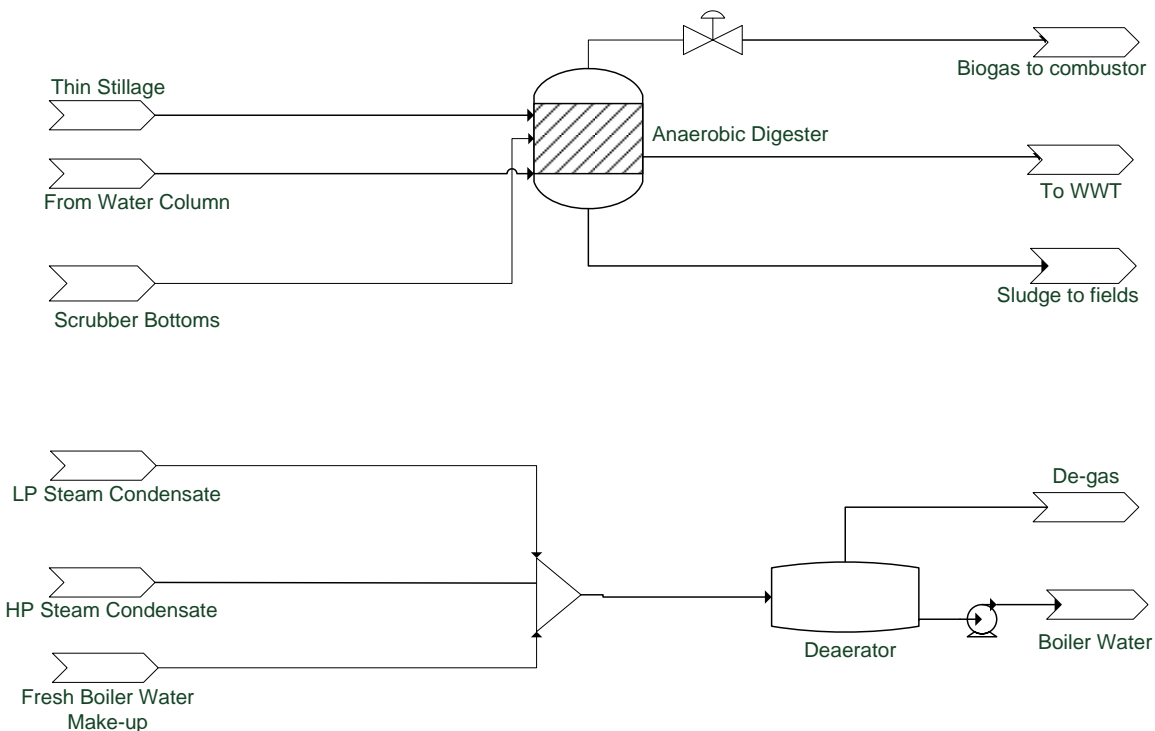
Figure 4-6: Process Flow Diagram for Water Plant showing anaerobic digester and boiler water purification

4.1.6. AREA-600: Boiler

This area was important for overall operation of the process, because it consisted of a boiler for generation of steam which was used in subsequent stages for electricity generation as well as heating purposes. The description of the boilerand how it was modelled in ASPEN Plus (2013)can be found in section 3.7.1.

Within this area, there is dryer/evaporation unit where the solids parts of the fermenter broth are dried to less than 50% moisture content. Feed to boiler having high moisture content has to be dried before it gets combusted. This was because, high moisture content feed utilises energy, which otherwise would go for steam generation (Biomass Combined Heat and Power Catalogue Technologies (2007). Reduction in moisture content of feed also reduces volume of flue gas generated by

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water vapour presence (Khan et al. 2009). In this model, the fermenter broth was sent into a filter for solids-liquid separation, which was modelled as a cyclone. The liquid stream from cyclone was sent to water treatment area for biogas production because it had high water content and henceconcentrating it to generate boiler fuel would be energy intensive. Only solids from cyclone were considered for boiler feed. The solids were sent into evaporator modelled as Flash block in ASPEN Plus (2013). The HP steam stream from pretreatment in AREA-100 was used to provide energy for evaporation. Moisture content of the solids was 48% prior to evaporation and after that has reduced to less than 10%.Although boiler chosen for this study (stoker boiler) could handle higher moisture content, the efficiency of steam generation is improved with decreasing moisture content of biomass(Nsaful et al. 2013). As a result, the secondary heat present in steam stream after heating pretreatment reactor was used in a dryer to reduce moisture content of solids residues prior to sending them to the boiler. It should be noted that the aim was not to reduce the moisture content to less than 10% but heat content of the steam stream managed that.
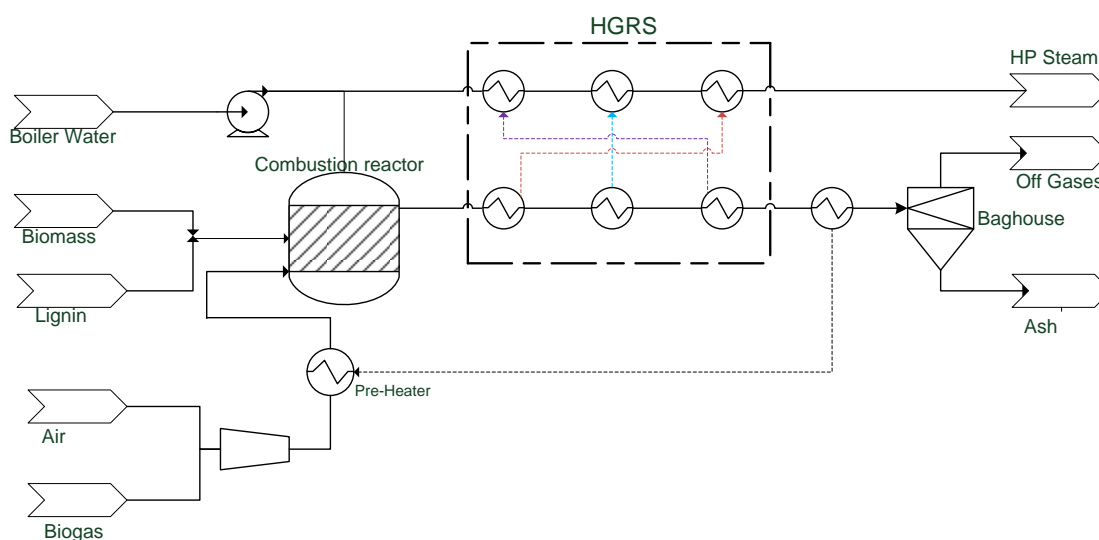
Figure 4-7:Process Flow Diagram for boiler area including combustor, heat generation recovery system representing pipes and a baghouse

4.1.7. AREA-700: Steam and Power Generation

Combined Heat and Power (CHP) generation is usedextensively to produce electricity and useful heat in the form of steamBiomass Combined Heat and Power Catalogue Technologies (2007). For this study, Condensation-Extraction Steam Turbine (CEST) was selected to generate powerand heat energy. Power is used within the plant, while surplus electricity productionis sold to the national grid to boost process revenues. In addition, there is a significant steam demand within the process for heating purposes.The extracted steam is used within the plant to provide heating in the reboilers of distillation columns and in pretreatment reactor. According toGrković (1990), it is crucial to evaluate the locations at which steam is extracted from the turbine for purposes of heating. The importance of this is to minimise the exergy loss and ensure the steam is at required pressure.

Steam was extracted from the turbine in two qualities,one in the form of high pressure steam (HPS) and one of low pressure steam (LPS). The turbine was modelled as three turbines in series connected by splitters in between for steam extraction. The super-heated steam (85bar; 525°C) from AREA-600 was expanded in the first turbinespecified atanisentropic efficiencyof 85% to 13bar as HPS.Steam was extracted for the thermal energy demand of the plant and the restwent to second turbine to generate more electricity. The second turbine expanded toLPS at 7.6bar,whichwent through a splitter and required amount of steam was drawn depending if there was need within the plant. The rest was sent to the last turbine which generated electricity and expanded to exhaust steam at 0.15bar(Petersen et al. 2014).This steam was sent to AREA-500, where it was condensed through a heat exchanger and pumped into holding tank for boiler feed water.
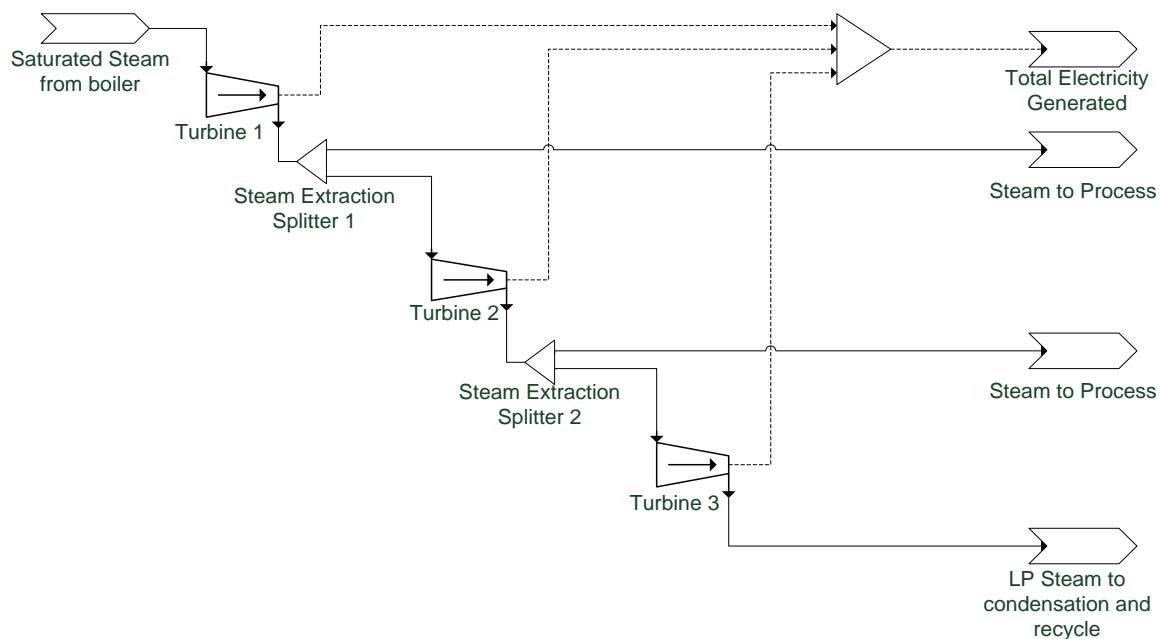
Figure 4-8: Process Flow Diagram for power generation and steam extraction

4.2. Continuous Separate Hydrolysis and Fermentation

4.2.1. AREA-100: Biomass Pretreatment and Detoxification

Pretreatment of biomass mass took place in this area. Dilute NaOH was prepared in the holding tank by adding stoichiometric amounts of water and NaOH to obtain 1% (w/w) NaOH. This base was then pumped to the pretreatment reactor, where it reacted with biomass at solids loading of 7% (w/w)(Ni et al. 2013). Pretreatment was done at 120°C and 2 bars for 2 hours and the heat provided by high pressure steam generated within the plant to attain the temperature (Ni et al. 2013).

From the pretreatment reactor, the slurry went through a counter-current heat exchanger for pre-heating the biomass feedstock before feeding it into the reactor. This was done as heat integration means to save on the energy demand of pretreatment. Due to the fact that NaOH pretreatment solubilised high percentage of lignin from the biomass (Chen et al. 2009; Varga et al. 2002), a separator modelled as cyclone was put in place, to filter off the solids from the liquid stream. Ni et al. (2013) used a centrifuge in order to obtain the hydrolysate from the solids. A calculator block was also used in order to account for the moisture content of 50% in

the cake. The liquid stream was sent for neutralisation in a reactor with H_2SO_4 before being sent to fermenter. The neutralisation process was done in R-Stoic reactor where stoichiometric amount of H_2SO_4 was added to neutralise NaOH.That was also achieved by use of calculator block. The liquid stream after neutralisation was mixed with the solids which were re-slurried with water to get required solids loading that should be sent to AREA-200 for enzymatic hydrolysis

4.2.2. AREA-200: Enzymatic Hydrolysis

Enzymatic hydrolysis was performed in a bioreactor modelled as RStoic in ASPEN Plus (2013) operating at 50°C and 1atm for 40 hours(Ni et al. 2013). Pretreated slurry was sent to the enzymatic hydrolysis reactor at the total solids' loading was 9% (w/w) using design specification in ASPEN Plus (2013)and the enzyme loading was set at 51.70FPIU/ml.When hydrolysis was complete, the reactor contents were sent to separation unit modelled as a cyclone.In their study Ni et al. (2013) used a centrifuge to separate the solids from the hydrolysate. Humbird et al. (2011) have shown that pneumatic pressure filter could be used but they affirmed that centrifuge would be the best solid-liquid separator. In ASPEN Plus (2013), a centrifuge was modelled as cyclone and with use of a calculator block, 100% of solids were retained the calculator block was used where moisture content of cake was set to 50% and the liquid split that will ensure that 50% moisture content in cake was worked out using Fortran equations.The remaining liquid stream was sent for a splitter. In a splitter, 5% goes to seed generation Area-300 and the remaining stream goes to AREA-400 for solvents production.

4.2.3. AREA-300: Seed Generation

For seed generation, same procedure and conditions as seed generation for batch SSF (Area 200 in Section 4.1) were followed.

4.2.4. AREA-400: Fermentation

Under this area, fermentation process took place at continuous mode at temperature of 35°C and 1atm for 40 hours(Ni et al. 2013). At the end of fermentation, 100% of glucose fed and 50% of xylose, arabinose and cellobiose fed were utilised to produce solvents, gaseous products and for cell growth. In real plant there will be

storage or reservoir tank for the provision of continuous pumping of hydrolysate to the main fermenter at the dilution rate of 0.15/hr (Ni et al. 2013).

4.2.5.   AREA-500 Solvent recovery and purification

For solvent separation and purification, the same procedure as outlined in Section 4.1.4for batch SSF was followed. The respective process flow diagrams are shown in that section as well. The only difference was with double effect distillation, because in this processmore CO_2 gas camein with the solvents in the separation columns. This was because no recycling of fermentation gases to the fermenter was done as compared to SSF integrated with gas stripping.A flash tank was included after beer column to reduce CO_2 and H_2 gases present in the stream just for modelling purpose. During flash cooling at atmospheric conditions, a fraction of solvents was also lost with the gas stream. This stream was sent to the scrubber to remove those lost solvents,before releasing the gas to atmosphere. However, the solvents were not returned into acetone column as was done byvan der Merwe (2013). The reason was that the stream was very dilute and will just contribute to an increase in column sizes in the subsequent separation columns. The scrubber bottoms were rather sent for anaerobic digestion.

4.2.6. AREA-600: Boiler

The boiler area was as described in Section 4.1.6. The same equipment was present and the difference was only in the stream flow rates. Clearly amounts of solids generated, biogas produced in anaerobic digestion and amounts of unconverted sugars differ in all the scenarios.

4.2.7. AREA-700: Steam and Power Generation

CHP area was the same for all scenarios and is described in Section 4.1.6. Under that area a detailed description was given on how the plant meets its steam and power demand.

4.2.8. AREA-800: Water plant for provision of Boiler Water and Wastewater Treatment

Water plant housed anaerobic digestion of all waste water streams and it also supplied the boiler with boiler water for steam generation.Section 4.1.5 described

preparation of boiler water and treatement, as well as anaerobic digestion of waste water streams.

4.3.   Batch Separate Hydrolysis and Fermentation

4.3.1. AREA-100: Biomass Pretreatment

Cassava bagasse was pretreated by liquid hot water at121°C (Lu et al. 2012)with the heat being provided by steam generated within the plant to maintain the temperature for 30 minutes.From the pretreatment reactor, the slurry went through a counter current heat exchanger to pre-heat the feedstock into the reactor before it was sent to slurry holding tank. In the slurry holding tank, it was further mixed with a stream of water to achieverequired solids loadings for enzymatic hydrolysis. The slurry holding time in the tank is normally 30 to 60 minutes(Humbird et al. 2011) and then it was pumped to Area-200 for enzymatic hydrolysis.The holding tank ensuredthat there was available buffer for pretreated slurry.

4.3.2. AREA-200:Enzymatic Hydrolysis

Enzymatic hydrolysis was done sequentially in two parts in process model. The pretreated slurry was first hydrolysed by glucoamylase at 65°C for 24 hours in a reactor modelled as RStoic. This was done in order to hydrolyse starch that was present in cassava bagasseinto glucose(Lu et al. 2012). The hydrolysed slurry was pumped to the next reactor for further hydrolysis, where cellulase was added to hydrolyse cellulose content in cassava bagasse. This was done at 50°C for 24 hours(Lu et al. 2012). After these hours the slurry was sent for solids-liquid separation in a centrifuge, which in this study is modelled as a cyclone. A centrifuge was modelled as cyclone and with use of a calculator block, 100% of solids were retained the calculator block was used where moisture content of cake was set to 50% and the liquid split that will ensure that 50% moisture content in cake was worked out using Fortran equations. The solids were then sent to dryer for further moisture reduction before they were burnt in the combustor. From the hydrolysate stream, 5% split of it was sent for seed generation in Area-300 and the remaining portion was sent for fermentation in Area 400.

4.3.3. AREA-300: Seed Generation

Since general procedure is the same for seed generation in all scenarios, refer to section 4.1.2for detailed description.

4.3.4. AREA-400: Fermentation

Fermentation in this main process occurred at 37°C for 40 h in a batch reactor(Lu et al. 2012).*C.acetobutylicum* JB200 was used in the study from which the data was taken and the fermentation was stopped after 40 h when the glucose was depleted(Lu et al. 2012). Thisstrain wasreported to prefer utilisation of glucose over xylose and arabinose and hence fermentation was stopped, when all the glucose in the hydrolysate was depleted (Lu et al. 2012). Even in the models, there was residual xylose and arabinose that was present in fermentation broth at the end of fermentation. After 40 h of fermentation, the broth was sent for separation in a cyclone, where cell biomass was separated from the solvents and residual sugars. The liquid stream was then sent for downstream separation either double effect distillationor LLE and distillation depending on the scenario. Cell biomass was sent to dryer in boiler area before it can be burnt in the combustor.

4.3.5. AREA-500: Solvents Separation and Purification

The solvent stream from fermentation area was separated and purified into final products in this area as described earlier. Refer to section 4.1.4 for detailed description of purification methods.

4.3.6. AREA-600: Boiler

This area is the same for all the scenarios and the reader is referred to section 4.1.6 for detailed description

4.3.7. AREA-700: Steam and Power Generation

This area of the plant consists of steam turbines for generation of electricity and extraction of steam that is required in other areas within the plant. See section 4.1.7 for detailed description on steam extraction and factors to be considered for modelling it.

4.3.8. AREA-800: Water plant for provision of Boiler Water and Wastewater Treatment

Water plant area is also the same for all the scenarios investigated. Detailed description of the area was given in section 4.1.5.

5.   Results and Discussion: Process Energy Demand and Efficiency

5.1.   Process energy demand and energy efficiencies for butanol production from lignocellulose

The differences between the three processes with regards to energy demand and energy efficiency were considered to be due to the selection of process units and conditions, and not due to chemical composition properties of different types of LCB used. Based on available literature, it was only possible to compare process scenarios by assuming that different LCB and their chemical properties will not influence processing conditions and performance significantly. This was because there was no experimental data available for all process scenarios considered using the same feedstock. However, in practice different LCB chemical properties will have differing impacts on the processing(Huang et al. 2009).For instance, it was shown that corn stover required higher pretreatment temperature than wheat straw and switchgrass to release sugars due to their different chemical properties(Qureshi et al. 2010). Nontheless, those impacts are likely to be smaller than those seen in the process scenariosin this study where different processes were compared.

5.1.1. Pretreatment methods and Heat Integration around Pretreatment area on process energy demand and efficiency

As it was discussed in section 2.4, pretreatment is a common feature in ABE fermentation when using LCB as feedstock. It is also important to note that different methods of pretreatment can use different solids loading and have different implications on energy requirements. For instance, low solids loading<20% in pretreatment would require excessive energy to operate at suitable temperatures (Elander et al. 2009, Moiser et al. 2005). With low solids loading, a low amount of biomass is pretreated, although a disproportionally large amount of process energy is required, both to heat the matter present to pretreatment temperatures, and for downstream removal of the water to concentrate sugars and/or fermentation products. Such excessive energy requirement will subsequently lead to lower overall

energy efficiency of the process, which has a negative impact on the energy self-sufficiency of the process. In order to reduce excessive energy demand during pretreatment, higher solids loadings are recommendedwith steam explosion (STEX) method of pretreatment being used.

The pretreatment methods used in the study had low solids loading of 10% (w/w)or below as described under process descriptions. Theselow solids loading have directly contributed to high energy demand as well as low liquid and overall energy efficiencies of the processes. Pretreatment area in particular was found to be the major consumer of energy. Dilute acid pretreatment of wheat straw for SSF-GS processes required the largest amount of steam for pretreatment reactor to reach 121°C. 111 MW of steam was used, and this meant that a 60% split of high pressure steam was extracted from the turbines to meet that demand. This high steam requirement also had impact on the electricity generated by the process. As it could be seen from Table 5:1, SSF-GS processes had lowest amount of electricity generated (58MW) compared to other processes. Another point that is worth noting is that during dilute acid pretreatment, there is high solubilisation of hemicellulose(Tao et al. 2011). This leads to high digestibility of cellulose during enzymatic hydrolysis. According to Qureshi et al. (2008c) the SSF intergrated with gas stripping achieved 90% of cellulose digestion. It translates to low solids residues which go to boiler for generation of steam and electricity. Therefore, low electricity generation was also affected by amount of solid residues left after fermentation.For CONT-SHF and B-SHF processes, with solids loadings of 7% (w/w) and 10% (w/w) respectively, steam consumptionon pretreatment dropped below 100MW (see Table 5:1). This contributed to electricity generation for these processes being greater than that of SSF-GS process scenarios

Since it was noted that pretreatment area was contributing significantly than all other plant areas to high steam usage, hence high energy demand, it was investigated if heat integration around that area could bring down the usage. It should be emphasised that without any heat integration around pretreatment reactor, ASPEN Plus(2013)results showed on average steam demand of 163MW. However, after energy integration the energy demand dropped to an average of 70MW. In all the process scenarios, more than 50% of high pressure steam was extracted from the turbines to provide heating for the pretreatment reactor. Indirect steam injection

aroundpretreatment reactor was used to provide heating in order to attain pretreatment reaction temperatures. The secondary energy present in the stream after heating pretreatment reactor was used as drying medium of fermentation residues before sending them to the boiler. In addition, feedstockwas pre-heated with the pretreatment product stream to increase its temperature and that was found to have decreased pretreatment reactor energy demand.This pretreatment heat integration was done in all processes and it was found that it has impacted in lowering pretreatment energy demand. With the outcome shown by the heat integration around pretreatment reactor, it could be inferred that an overall process heat integration can even lower the energy demand further. This would lead to less steam being extracted from the turbines and leave more for electricity generation.

It should be noted that direct comparison was not possible between pretreatment at low solids loading in this study with those of high solids loading using STEX. However, when low solids loading of 10% (w/w)were investigated in this study, low overall energy efficiencies were found in the range of 23% – 34% (Table 5:1). This was as a result of high steam requirement during pretreatment to maintain temperatures at 121°C. On the other hand, pretreatment at high solids loading of 50% (w/w) using STEX resulted in higher overall energy efficiency(Leibbrandt 2010)for production of bioethanol. Leibbrandt (2010) reported liquid energy efficiency of 40.9% and overall energy efficiency of 55.8%. Energy demand was low due to high solids loading of 50% in pretreatment and subsequently led to higher energy efficiency.Peterson et al.(2014; 2015) found Net energy efficiency of 32.91% as the highest in the cogeneration of second generation ethanol and electricity from sugarcane bagasse and pretreatment residues. It was reported that for pretreatment, higher solids loading of 50% (w/w) were used because the model was modified from that of Leibbrandt(2010).

5.1.2. Fermentation technologies and Refining methods on process energy demand and efficiency

In this section of results, the discussion on process energy demand and efficiency is centredon the product recovery and purification methods coupled with fermentation technologies for a plant processing 1million dry tonnes of feedstock per year. The

reasons for this approach were because different fermentation methods and technologies were used and therefore direct comparison between all the scenarios was not possible. In addition, the upstream processes were the same for each fermentation method hence energy demand was roughly the same for the upstream processes. However, the two product recovery and purificationmethods were used in each process and the implications of each were evaluated and discussed. It should be noted that each process was split into two scenarios because of the product recovery and purification methods applied (see section 3.3 for scenarios definition)

5.1.2.1.   SSF-GS

SSF-GS process provideda pre-concentrated stream of solvents to the downstream purification section, which required lower energy demand when compared to process without integrated product recovery technique(Qureshi and Ezeji 2008). Between the two scenarios under this process, SSF-GS/DDhad the highest amount of butanol produced at 84259 tonnes/yearcompared to 78032 tonnes/year forSSF-GS/LLE&D.It was found that more butanol was lost to the raffinate in extraction column and got sent to anaerobic water treatment in SSF-GS/LLE&D as compared to butanol lost to bottoms of beer column in SSF-GS/DD. This was caused by butanol distribution coefficient that was obtained from literature(van der Merwe 2010) which could not be changed while for beer column under SSF-GS/DD, column parameters such as reboiler ratio were optimised to recover more butanol to the tops.Furthermore, the raffinate was not recycled back into the extraction column in this study which in essence could make positive contribution by recovering lost solvents.

The energy demand in this study showed that energy requirement in (MJ/kg butanol) for SSF-GS/DD was greater than that of SSF-GS/LLE&D by 6% (Table 5:1).This was because more steam was used in DD even though the columns were in order of decreasing pressures,allowing previous column reboiler stream to provide heating on the subsequent column reboiler. This configuration which was found to requireless steam forthe reboilers of the columns has also been used before(Mariano et al. 2011). The decreasing order of steam usage in the DD columns was beer column > acetone column > ethanol column. Although the benefits of operating distillation as DD was taken, the overall steam consumption was higher. It was due to presence of impurities in solvents which contributed to high steam usage even when DD has

been applied. Steam demand in LLE and distillation was found to be lower because only two columns used it, the extractant and butanol column reboilers. In order to provide heat for vapourisation in the extractant recovery column reboiler, steam was required because the extractant (oleyl alcohol) has higher boiling point of 360°C than butanol at 117°C.In addition, the ratio of extractant to solvents used was 0.983 (w/w) and this meant in extractant recovery column there was more oleyl alcohol to vapourise in the reboiler. In total, the SSF-GS/LLE&D scenario still had the overall steam consumption lower than that of SSF-GS/DD scenario.The lower energy demand in LLE and distillation meant that moresteam was available for electricity generation as could be seen from Table 5:1.van der Merwe (2013) also found that LLE and distillation had the lowest energy demand among all the processes investigated.

In terms of liquid fuel efficiency and overall energy efficiency, Table 5:1 shows that SSF-GS/DD has both efficiencies greater than that of SSF-GS/LLE&D.Since SSF-GS/DD process had the higher butanol production, this contributed to liquid fuel energy efficiency of 26% as compared to 23% of SSF-GS/LLE&D. The liquid efficiency is greater because out of the energy input of feedstock, more butanol was produced. When assessing all the saleable products which are butanol, ethanol, acetone and electricity, SSF-GS/DD process efficiency was better in converting energy input from LCB feedstock into these products than SSF-GS/LLE&D hence the reason it has higher overall energy efficiency.

5.1.2.2.   Continuous SHF

Continuous SHF process has an advantage of operating for long periods of time and that leads to improved reactor productivity (Ni et al. 2013). In addition, concentrated feed stream of sugars can be used in continuous fermentation because dilution reduces sugar inhibition(Gapes 2000). However, high dilution rates during continuous fermentation have been found to result in dilute product concentration (Vane 2008). This has detrimental effect on the subsequent process of product purification, especially when double effect distillationis used to evaporate large volume of water from the purification feed (Mariano and Filho 2012).The energy demand (MJ/kg butanol) for CONT-SHF/LLE&D was 17% greater than that of CONT-SHF/DD. This was caused mainly by CONT-SHF/LLE&D having lower

butanol yield as final purified product than CONT-SHF/DD. Steam consumption for CONT-SHF/LLE&D was found to be lower than that of CONT-SHF/DD by 6%, leading to more electricity generation for the process. It was found that the same reasoning as that discussed for SSF-GS process contributed to this similar result. The overall energy efficiency of CONT-SHF/DD was found to be 15% higher, because of the higher butanol yield obtained as a final product and ethanol as a saleable product that was obtained too. With CONT-SHF/LLE&D, ethanol got lost in the raffinate stream due to low selectivity of oleyl alcohol towards it. As a result, when it comes to how efficient the process is in converting input energy in feedstock to saleable products, the process loses out to that of CONT-SHF/DD.

5.1.2.3.   Batch SHF

Batch SHF process is the most practised method of ABE fermentation because of its simplicity. However, it has many challenges such as sugar feed being limited to around 60g/l, in order to avoid sugar inhibition (Qureshi et al. 2013). The most serious challenge is that of product inhibition by butanol at concentrations of 20g/l in the fermenter (Ezeji et al. 2007). Firstly, B-SHF/LLE&D scenario had larger amount of butanol 62174 tonnes/year as a final product compared to 44701 tonnes/year of B-SHF/DD scenario (Table 5:1).The opposite result to what was obtained by the SSF-GS and Continuous SHF was found to be caused by butanol loss in the beer column which was carried with water in the bottoms. When design specifications in ASPEN Plus (2013)were used to recover most butanol in the top, the column intrinsic parameter such as boil-up ratio did not meet specifications and the reboiler net duty escalated to 80 MW. As a result, lower butanol was recovered to the gaseous stream in the beer column. It should be noted steam consumption for B-SHF/LLE&D was still lower than that of B-SHF/DD by 14%. It was also found that energy requirement for water cooling tower system for B-SHF/DD was higher due to cooling water recirculation pumping needs. The energy demand (MJ/kg butanol) for B-SHF/LLE&D was 38% lower than that of B-SHF/DD. This result was found to be in agreement with literature where energy demand of extractive-distillation has been found to be lower than that of double effect distillation(Kraemer et al. 2011).When energy demand is lower, it translates to higher overall energy efficiency of the process. This was found to be true because B-SHF/LLE&D has overall energy efficiency that is 7% greater than that of B-SHF/DD.

Table 5:1:Performance Parameters for the LCB Butanol Plant Energy Demand and Efficiency

Parameter	Process Model Scenarios					
	SSF-GS/DD	SSF-GS/LLE&D	CONT-SHF/DD	CONT-SHF/LLE&D	B-SHF/DD	B-SHF/LLE&D
Butanol (tonne/year)	84344.00	78032.00	66428.00	51425.00	44701.00	62174.00
Ethanol (tonne/year)	15143.00	-	3909.60	-	10774.00	-
Acetone (tonne/year)	31012.00	29520.00	24998.00	1737.00	22399.00	19425.00
Power Generated (MWe)	58.87	54.61	69.83	72.98	76.92	77.22
Power Consumed (MWe)	33.81	31.70	26.11	23.16	23.12	20.70
Power Exported to the grid (MWe)	25.06	22.91	43.72	49.82	53.81	56.53
Pretreatment Steam Consumption (MW)	111.41	112.11	72.59	71.85	93.96	91.94
Total Steam Consumption (MW)	172.66	147.80	113.31	106.73	120.83	103.43
Energy Demand (power + steam consumption) (MJ/kg butanol)	70.50	66.25	60.45	72.74	92.74	57.50
Liquid Fuel Energy Efficiency (%)	26.82	23.53	18.85	14.66	11.68	16.00
Overall Process Energy Efficiency (%)	36.00	30.68	27.84	23.59	23.01	24.73

5.2. Comparison of butanol production from lignocellulose to butanol production from molasses (2G vs. 1G)

The results of best performing SSF-GS/DD process scenario from this study were compared with those from previous study at Stellenbosch University(van der Merwe 2010). That study used molasses as feedstock for production of biobutanol andinvestigateddifferent process scenarios in terms of energy efficiency and economics. The study was different from the present one because molasses is regarded as 1G feedstock, while LCB is 2G feedstock and therefore direct comparison is not applicable.Therefore, in order to compare the processes, the annual butanol production of SSF-GS/DD process was scaled up to match that of best performing molasses based butanol (Table 5:2). This meant that the processes were compared on the basis of equal annual butanol production.

For the purposes of the comparison,the Process Design 3(van der Merwe 2010)was selected as a preferred 1G-process option, due to reported performance in terms of energy efficiency and economics.Process Design 3 implemented both Gas Stripping (GS) and Liquid-liquid Extraction (LLE) for recovery and separation of the solvents. According to van der Merwe (2013), this process resulted in the lowest energy requirement mainly due to LLE than contribution of GS. It was explained that increase in product purity requirement drove up the energy requirement while the composition of the solvents in the broth also had effect on the energy requirement. The process had 23.15MJ/kg butanol (an equivalence of 18.75MJ/L butanol)as grossenergy value (GEV) (Table 5:2).GEV was found by subtracting the total energy input of molasses and utilities from total energy output present in butanol as a product. The GEV was converted to energy/kg butanol, in order to compare it with the best selected scenario investigated in the current study(Table 5:2).

Table 5:2: Comparison of energy demand and gross energy value between molasses based butanol production model and scaled-up LCB butanol production model.

Process Scenario	Feedstock Type	Butanol Flowrate (tonnes/year)	Energy Demand (MJ/kg butanol)	Gross Energy Value (MJ/kg butanol)
SSF-GS/DD	LCB	118800.00	58.75	-117.12
Process Design 3	Molasses	118800.00	8.23	23.15

From Table 5:2, the notable difference was that butanol production from LCB had an energy demand per kg of butanol that was six times larger than the process utilising molassesas feedstock. Energy demand for SSF-GS/DD was 58MJ/kgof butanolafter the process butanol production rate has been scaled up to 118800 tonnes per year (Table 5:2).Thisenergy demand was the combinationof upstream and downstream processes. Mariano et al. (2012)reported energy demand of 32.4MJ/kg of butanol. That energy demand was the sum of energy from *in situ* continuous vacuum fermentation and distillative recovery. If energy demand for upstream processes was taken into consideration, then energydemand reported byMariano et al. (2012) would have increased and possibly beclose to 50MJ/kg, as reported in the present study. In the study by van der Merwe (2013), energy demand was low 8.23MJ/kg when compared to the scenario reported in this study and to that of Mariano et al. (2012). There reason for that could be attributed to the absence of lignocellulose pretreatment and concentration of butanol present as the final product, which was achievable due to the absence of fermentation inhibitors from pretreatment.

The study in which closer energy demand per kg of butanol produced by van der Merwe (2013)is that ofQureshi et al. (2005). In that study, energy demand of 8.4MJ/kg butanol was reported for extraction as an*in situ* product recovery technology and adsorption required 8.2MJ/kg butanol as the least energy demanding recovery and purification method. Groot et al. (1992)emphasised that different recovery systems and downstream separations for ABE fermentation have different energy demands which are depended on final butanol concentration. As a result,

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care should be taken when energy demand is compared between different techniques.Furthermore, distinction has to be made on whether the energy demand investigation included both upstream and downstream. This was because the comparison in this study showed that energy demand for whole process was higher than that of downstream process.

GEVfor SSF-GS/DDscenariowas-117MJ/kg butanol as seen from Table 5:2, indicating that more energy was required to produce butanolthan energy content present in butanol as a product (34.34MJ/kg). With molasses based butanol, a different result was observed where a positive GEV was obtained. The reason for thedifference still points to the fact that LCB butanol production requires more energy irrespective of same butanol capacity.From molasses based butanol point of view, it was evident feedstock type contributed in obtaining positive GEV because after the comparison was based on same butanol production volume, the molasses based process still outperforms the LCB based butanol. Therefore, factors such as feedstock and feedstock preparation to get sugars for fermentation have been identified ascontributing to GEV.

From these comparisons, it was evident that production of butanol using LCB as feedstock was more energy intensive than when using molasses as feedstock. Nonetheless, this study has shown that LCB butanol production can be self-sustaining in terms of energy. It was found that full process energy demand couldbe met by splitting off some of the LCB feedstock as direct feed for production of heat and power, rather than using this as feedstock for butanol production.On the other hand, molasses based butanol can score very low when it comes to GHG emissions. The reason is because all the energy demand for 1G butanol production was met through the use of fossil fuels, since LCB may not be readily available for process energy. Fossil fuels are believed to be main contributors to GHG emissions (García et al. 2011; Raganati et al. 2012), and 1G butanol processes will need to consider replacing these with LCB to achieve the desired environmental benefits of butanol production and use as biofuel.

6.   Results and Discussion: Economic Evaluation

With regards to current economics, the analysis of butanol production was based on feedstock of different LCB namely wheat straw, corn stover and cassava bagasse. The feedstock flow rate was assumed to be 1million dry tonnes per year. From this throughput, different yields of ABE were used as per literaturedata from which the processes being modelled were taken. This was done in order to maintain the concentration of solvents in the fermentation broth similar to thatreported in the literature.Similar to section 5, it was assumed that the impacts of the properties of specific LCB feedstocks on processing and economics of butanol production would be negligible compared to differences between process configurations. In essence this assumes that the different types of lignocellulose would all respond in an identical manner to a particular type of processing, thus allowing comparisons between different process scenarios, even when experimental data for each is collected with different types of LCB.

The major considerations in the economic analysis were Operation and maintenance Expenditure (OPEX) and Capital Expenditure (CAPEX). Of the OPEX, the raw materials were feedstock cost, chemical costs for H_2SO_4, NaOHand NH_3. Enzymes cost, refrigerant, glucose, nutrients and disposal costs of ash and waste water to the municipal sewers were other costs. Material and energy balances together with flow rates from ASPEN Plus (2013) were used to size equipment and carry out CAPEX. Most of the capital costs were sourced from the detailed NREL Report (Humbird et al. 2011). From the OPEX and CAPEX, a Discounted Cash Flow (DCF) analysis was done in Microsoft Excel to evaluate the profitability of each plant processing 1million dry tonnes LCB per year. Profitability assessment was done in all the process scenarios and the assumptions on economic parameters can be seen from Table 3:15 in Section 3.9.

6.1.   Economics of butanol production from lignocelluloses

Under this section, results are presented for all six scenarios for butanol production from LCB in terms of Total Capital Investment, Profitability Indicators such as Net

Present Value and Internal Rate of Return for year 2015 and are shown in Figure 6-1.
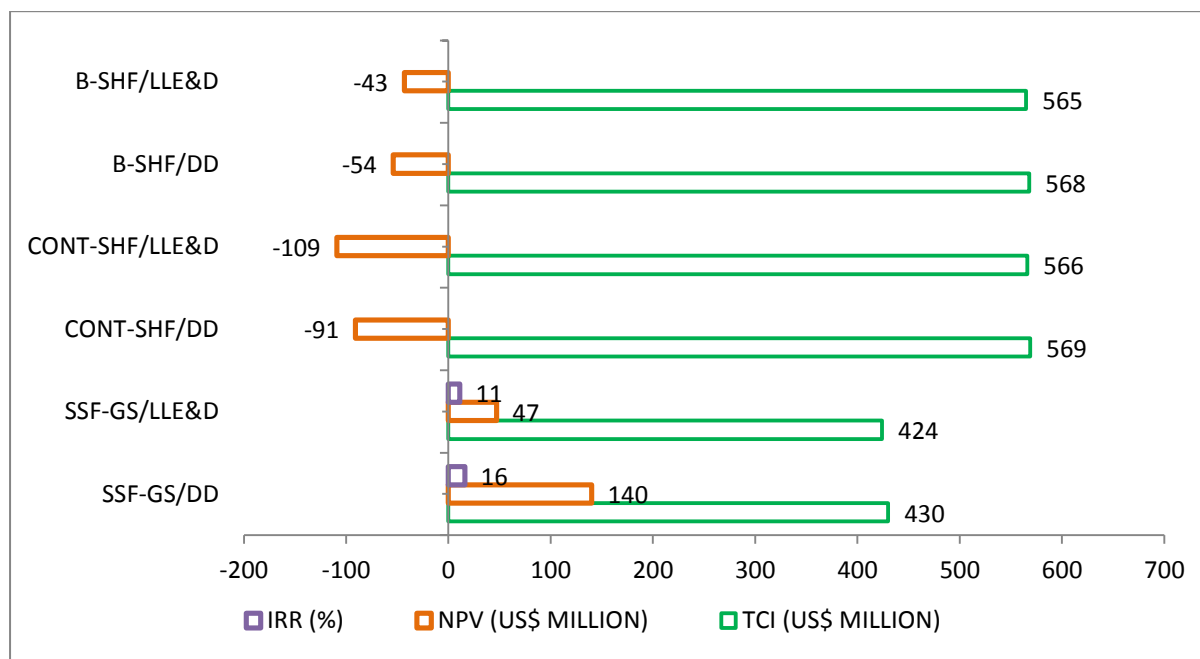
Figure 6-1: Comparison of main economic results for different process scenarions for year 2015

From Figure 6-1, it can be seen that DCF analysis from SSF-GS/DD scenario gave a NPV of US$140million and IRR of 16%. The discount rate used was 9.3% and since the IRR found was greater than the discount rate, meant the scenario was feasible in the present market. The TCI of the SSF-GS/DD scenario was US$430million (Figure 6-1). The major contributors to the revenue in this scenario were butanol which was sold at basic fuel price (BFP) of US$0.78/kg, ethanol at BFP of US$0.69/kg and acetone which was sold at chemical market price of US$1.10/kg respectively. In addition, there was surplus green electricity of 25MW which was left after all the plant processes usage had been met (Table 5:1). This was assumed to be sold to the South African national grid as explained in section 3.12.2.

For SSF-GS/LLE&D process scenario, the NPV of US$47million and the IRR of 11% were obtained. It can be seen that economic viability of the scenario was also feasible in the current market though not as attractive as that of SSF-GS/DD process scenario. The reason for this was the sales revenue of the scenario came from butanol as a fuel, acetone and surplus electricity only. Ethanol as a co-product was not present because of low selectivity during liquid-liquid extraction by oleyl alcohol.

In addition, the butanol produced from this scenario was7.39% lower (78032tonnes/year vs 84259tonnes/year) than that ofSSF-GS/DD process scenario. Therefore, selling butanol, acetone and electricity provided sale revenues that were not as high as those when ethanol was present like in SSF-GS/DD process scenario. Unlike SSF-GS/DD process scenario, this process scenario would be strained of cash but in the long run would have returns for its investors. The TCI of the project was US$424million and it was less than that of SSF-GS/DD process scenario by 1.4% which was US$430million.

The CONT-SHF/DD process scenario showed negative cash flow for all years of operation. The profitability analysis gave a NPV of US$-91million (see Figure 6-1). This was an indication that the project was also not profitable. Although the saleable products were present, their contributions to the revenues were not enough to yield a positive NPV. The biorefinery investment is considered medium to high risk investment. The TCI for this scenario was US$569million. It was observed that the TCI increased to above US$500million in this process as compared to SSF-GS process scenarios. This was due to enzymatic hydrolysis and fermentation occurring separately causing an increase in number of process units. It was evident that sales revenue from the products was not enough to cover the operating expenses of the plant. Even from literature byNi et al. (2013), the process produced low concentration of butanol and co-solvents. This translated to low volumes of butanol, acetone and ethanol at the end of process. In addition, separation processes were not 100% efficient and lead to products loss to waste streams. Other possibility could be that the process was in a continuous fermenter. Continuous fermentation in ABE fermentation is known for low product concentration due to high dilution rates (Gapes 2000). However, the fact that it was continuous fermentation could take advantage of higher productivities due to prolonged period of operations.

CONT-SHF/LLE&D process scenario with NPV of US$-109million, meant that the project was not feasible and would not attract investors too. In order to improve the economics for this scenario, one could consider selling butanol in the chemical market as opposed to biofuel. It is a possibility, because butanol of highest purity of 99.99% was obtained from this scenario. This could bring a positive change as it was observed in a study by Pereira et al. (2014)in which it was shown that selling butanol in the chemical market was more profitable than when it was sold as a fuel. Even

though it could be profitable to sell butanol in the chemical market, the size of market from South African point of view is small. So not so many plant could be built. The total capital investment of this scenario was US$566million. TCI of this process scenario is observed to be slightly lower than that of CONT-SHF/DD because of fewer recovery and purification equipment meaning the purchased equipment cost was lower.

From Figure 6-1, B-SHF/DD process scenario returned NPV of US$-54million. The scenario was not a feasible project because the NPV was negative. Therefore, investors cannot invest in it in the current market. It was found from the sales revenues that butanol, ethanol, acetone and surplus electricity were not enough to cover up the expenses of the project. The TCI of the scenario was US$568million. The TCI of the process scenario increased when compared to previous processes under SSF-GS mainly because of enzymatic hydrolysis area and it was the same for both process scenarios under B-SHF. The contribution of this area due to its two steps sequential enzymatic hydrolysis to TCI was significant. On the other hand, installed purchase cost due to pretreatment area dropped because there was no solid-liquid separator within pretreatment but in enzymatic hydrolysis area. In addition, the process used liquid hot water for pretreatment and there was no conditioning reactor required in pretreatment like in other processes. DCF analysis for B-SHF/LLE&D process scenario showed that the scenario had a negative cash flow for all the years of analysis. The NPV of US$-43million was found, which made it an unattractive investment. TCI of this scenario was found to be US$565million(Figure 6-1).

6.1.1. Process Scenario SSF-GS/DD

Figure 6-2 shows the contribution of each raw material to the overall cost in US$/kg butanol produced. Wheat straw was the main contributor to the cost at US$0.65/kg butanol produced. This accounted for 80% to the overall cost of raw materials of the process.Similar contribution of cellulosic feedstock to overall annual production cost of 65% was reported by Kumar et al. (2012). In some techno-economic studies, it has been found that feedstock cost was the major operating cost to the production of butanol among all the raw materials. For instanceTao et al. (2013)showed that corn

stover contributed highest percentage of 25% to the overall raw materials cost. Furthermore,Qureshi and Blaschek(2000)found that price of corn as feedstock had the greatest effect on the butanol production cost.

The second contributing material was by enzyme cost where cellulase cost atUS$0.07/kg butanol produced contributed 3% to the total operating costs (Figure 6-2).Cost of enzymes contributed significantly to the cost of production in this study. Tao et al. (2013)also found that enzymes contributed 15% to the overall cost of raw materials and it was the highest after corn stover. Kumar et al. (2012)however reported a lower contribution of 6% by enzymes to the annual cost of raw materials. Another notable contributor to raw material cost in this study was ammonia at US$0.03/kg butanol(Figure 6-2). This was used as conditioning agent after pretreatment and also as nutrients for microorganism growth. Humbird et al.(2011)stated that ammonia could be used during detoxification process and subsequently be utilised as nutrients by microorganism during fermentation. In addition ammonia has been used as nutrients source in techno-economic studies by Tao et al. (2013).
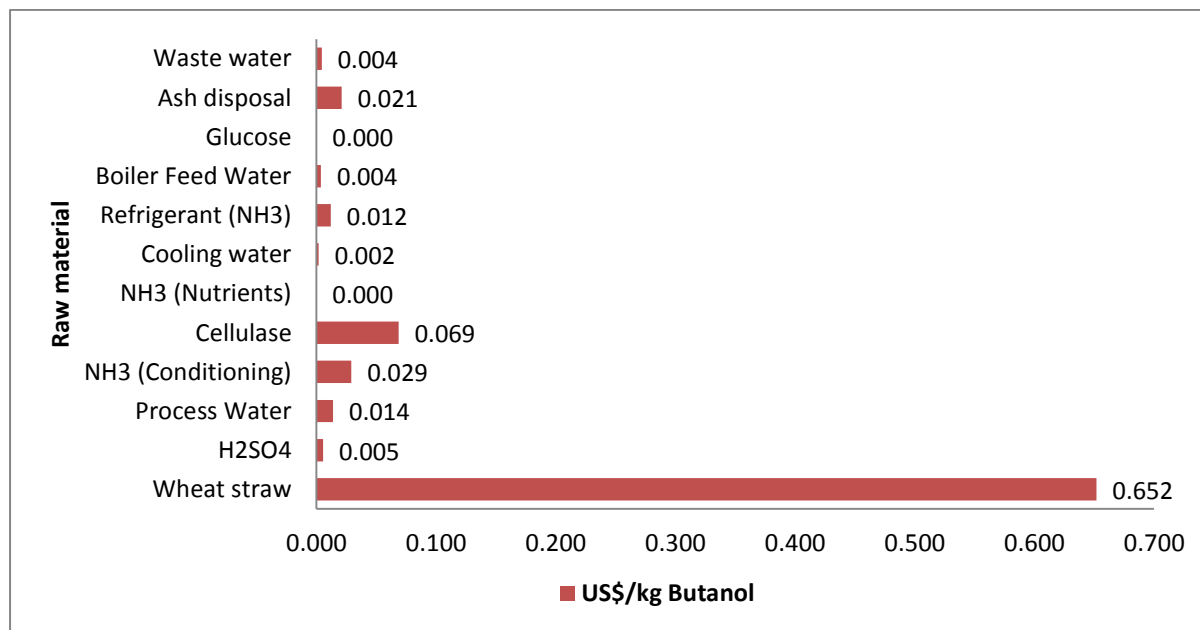
Figure 6-2: Variable operating costs for raw materials in (US$/kg butanol) produced for process scenario SSF-GS/DD

Capital cost of the process scenario was also broken down into cost per plant area as seen in Figure 6-3. Most of the equipment costs were sourced from NREL Report (Humbird et al.(2011). The area that contributed most to the capital cost was feedstock pretreatment atUS$102.87million and it had a share of 31% of all the plant areas. In terms of size, the equipment design showed that the pretreatment reactor was 752m^3 which in reality would be two reactors in series. The size and material of pretreatment reactor were the reasons for the high cost because Incoloy 825-clad steel was used(Tao et al. 2011). This was because of the severe conditions at which pretreatment took place. The conditions include high temperatures and acidic conditions and to avoid corrosion of equipment Incoloy 825-clad steel was used Humbird et al.(2011). SSF area was second after pretreatment and it contributed US$80.42million. In terms of capital cost percentage share, it contributed 24% (Figure 6-3). The cost of SSF area was made up of 10 SSF fermenters each with a volume of 4852m^3. The reactors size are in similar range of size to those used in enzymatic hydrolysis of corn stover byHumbird et al.(2011) which were at 3600m^3. In addition, this area had heat exchanger for condensation of gaseous solvents recovered by gas strippingand also compressor for recycling of non-condensables and these contributed to high cost.
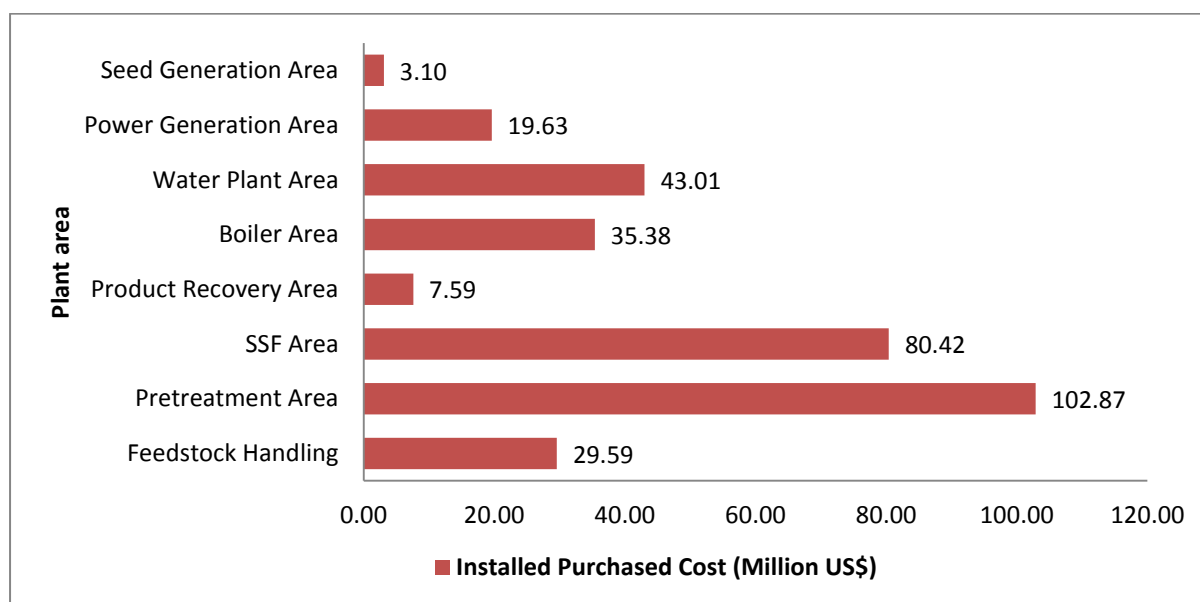
Figure 6-3: Installed purchased cost (Million US$) for different areas within the plant for process scenario SSF-GS/DD

6.1.2. Process Scenario SSF-GS/LLE&D

In SSF-GS/LLE&D process scenario, both raw materials cost per kg of butanol produced (Figure 6-4) and installed purchased cost of equipment per area (Figure 6-5) were found to be similar to that of SSF-GS/DD process scenario. However, there were minor exceptions because SSF-GS/LLE&D process scenario had product purification technology that was different from that of SSF-GS/DD process scenario. As a result, an extra cost in the oleyl alcohol was present per kg butanol produced in the raw materials of SSF-GS/LLE&D(Figure 6-4), which was not present in SSF-GS/DD(Figure 6-2). From Figure 6-4,oleyl alcohol cost did not contribute significantly to the cost of butanol per kg because oleyl alcohol was a once-off cost. This was made possible by recycling 99% of the oleyl alcohol during product recovery process. In order to minimise accumulation in the process, there was a constant bleeding of the oleyl alcohol stream. The make-up stream cost of oleyl alcohol was included in the costs to account for that make-up.
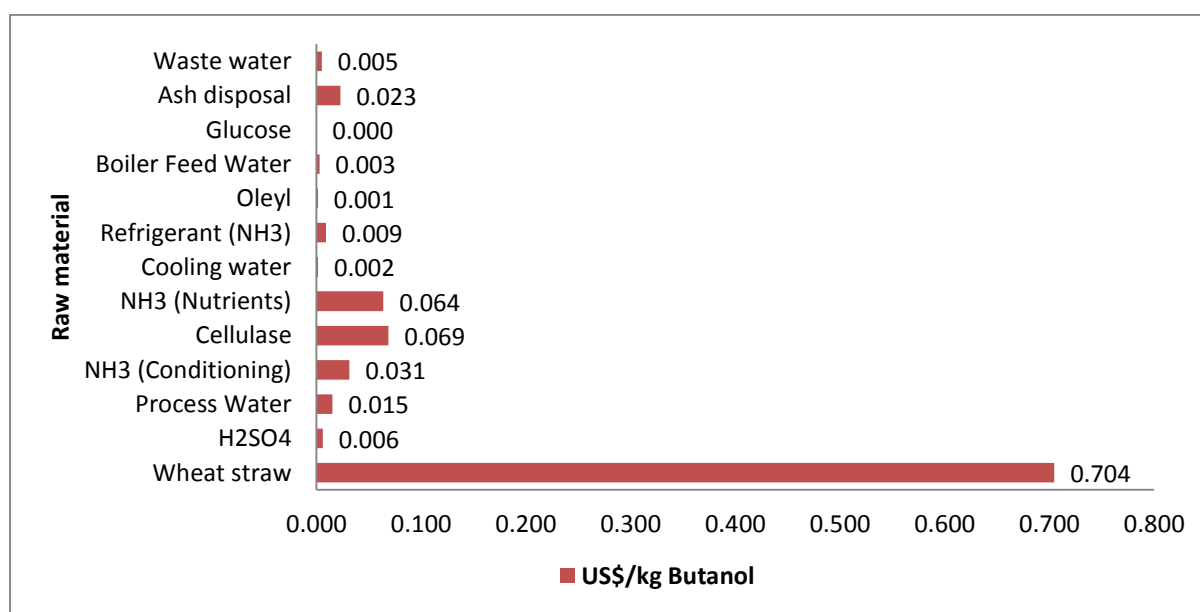
Figure 6-4: Variable operating costs of raw materials in (US$/kg butanol) produced for process scenario SSF-GS/LLE&D

Figure 6-5 showed that installed purchase cost for product recovery area was US$2.73million.This product recovery area cost is less than that of SSF-GS/DD (Figure 6-3) process scenario by 64%. The difference was that SSF-GS/LLE&D process scenario had three main separation equipment namely extraction column,

extractant recovery column and butanol column, whereas SSF-GS/DD process scenario had five main columns for double effect distillation(see Figure 4-4andFigure 4-5) for comparison. The capital cost for other areas remained relatively the same.
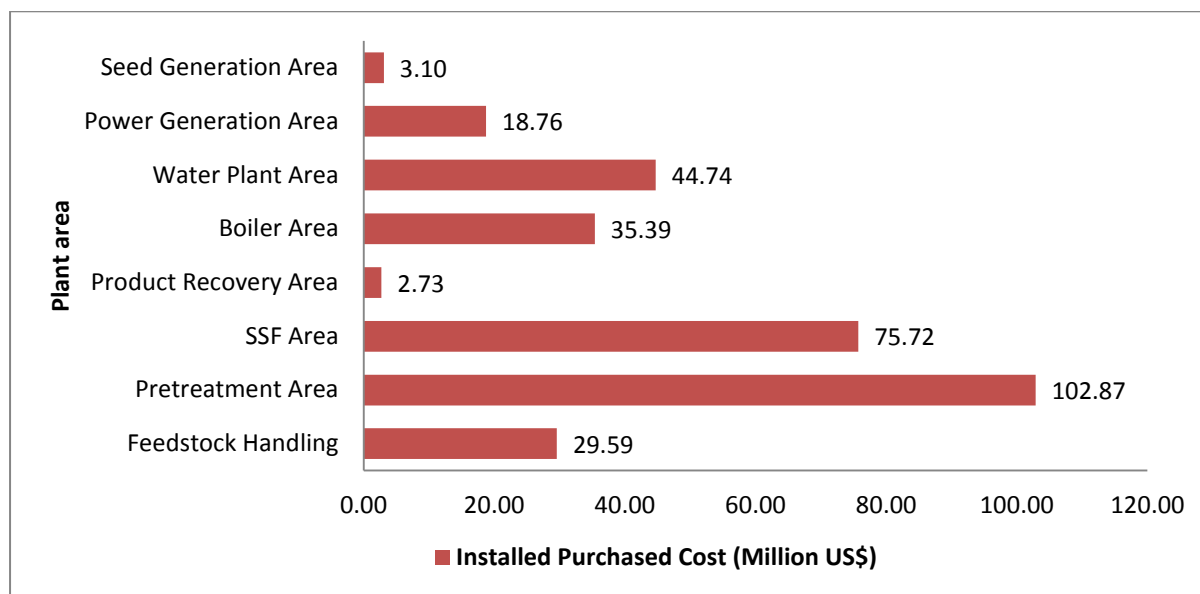
Figure 6-5: Installed purchased cost (Million US$) for different areas within the plant for process scenario SSF-GS/LLE&D

6.1.3. Process Scenario CONT-SHF/DD

The raw materials cost for this CONT-SHF/DD process scenario are shown in Figure 6-6. Feedstock cost was the major raw material accounting for 76% of the total raw material costs when all the raw materials costs were divided by total butanol produced (Table 9:24). When compared to previous scenarios of SSF-GS, the percentage contribution of feedstock cost was higher with CONT-SHF/DD. This was caused by lower butanol amounts produced in CONT-SHF than in SSF-GS (Table 5.1). NaOH and H_2SO_4contributed to equal amount of 7%, because the acid was used to neutralise the base which was used for pretreatment. Cellulase cost contributed to 6% of the raw material cost and waste disposal accounted for 2% (Table 9:24). Currently ash from CHP plants is disposed of at municipal landfills and there are costs associated with that. These percentage contributions confirmed that feedstock have greatest effects on the raw material costs of biorefineries. Therefore,

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ways in which feedstock can be found at lower costs to the biorefineries will improve the economics.
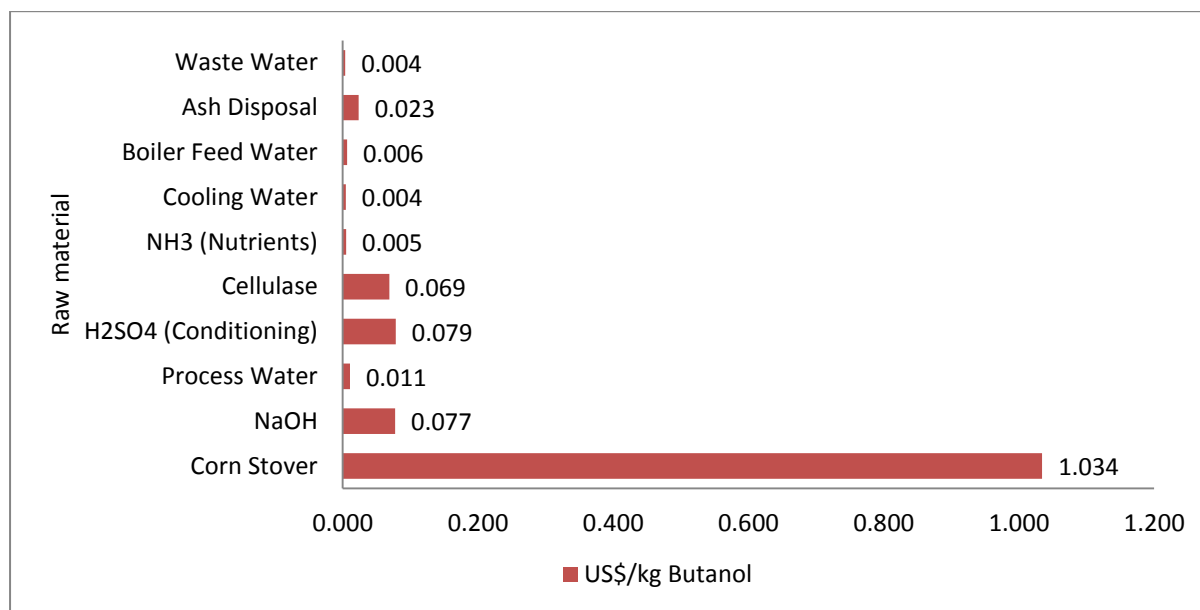
Figure 6-6: Variable operating costs of raw materials in (US$/kg butanol) produced for process scenario CONT-SHF/DD

Figure 6-7showed the breakdown of each plant area contribution to the overall purchased capital cost. In each area, total cost was the sum of all purchased equipment found within that area. Enzymatic hydrolysis area and fermentation area have largest purchased capital cost with contributions of roughly 25% each. Pretreatment area has 18.97% and the other areas have less than 1% contribution to capital cost. From equipment design and sizing, it was found that enzymatic hydrolysis has ten reactors. The cost of this area was slightly greater than that of fermentation because it has hydrolysate holding tanks. These tanks acted as buffer because the process is continuous fermentation and hydrolysate had to be fed continuously into main fermenters. Pretreatment purchased cost dropped from being the highest. It was because some operations were moved to the enzymatic hydrolysis area. For instance, it was in enzymatic hydrolysis where solid-liquid separation took place at the end of saccharification. The hydrolysate split for seed generation stream also occurred in this area not in pretreatment. Furthermore, the reactors were costed individually for saccharification and fermentation unlike SSF process where saccharification and fermentation takes place in one fermenter.
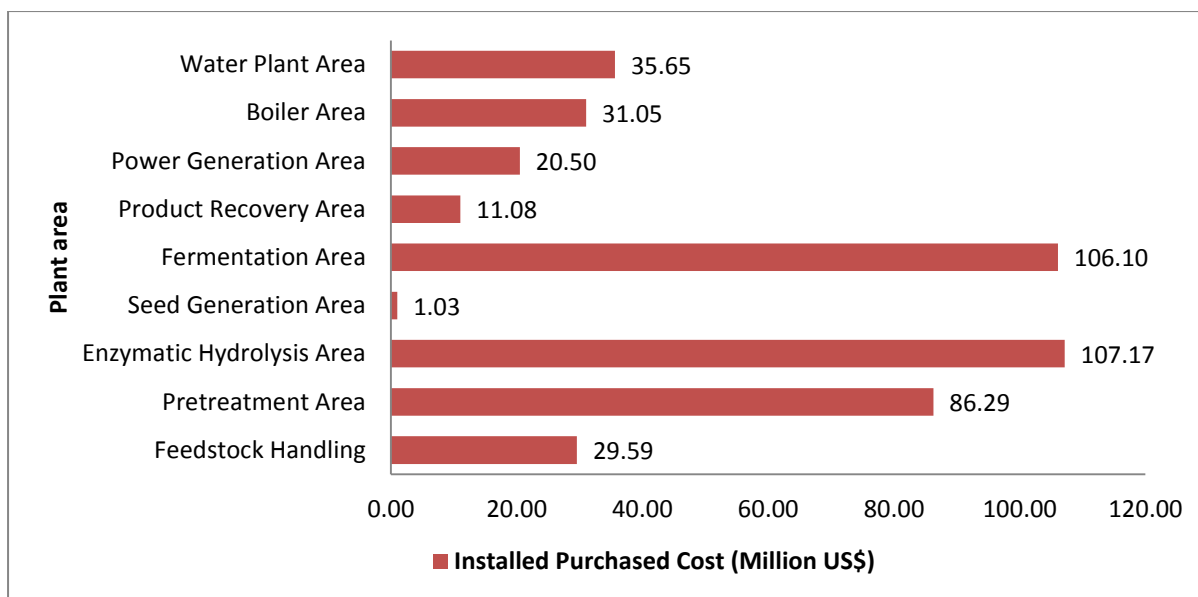
Figure 6-7: Installed purchased cost (Million US$) for different areas within the plant for process scenario CONT-SHF/DD

6.1.4. Process Scenario CONT-SHF/LLE&D

Figure 6-8 showed that CONT-SHF/LLE&D process scenario had feedstock at a cost of US$0.96/kg butanol and it was the main contributor at 73% to the overall raw materials cost. NaOH and H_2SO_4 contributed 7.64% and 7.73% of the raw material costs respectively (Table 9:27). NaOH was used for pretreatment purpose and the H_2SO_4 for neutralisation and pH maintenance. The reason for their equal contribution was that during neutralisation, the stoichiometry equal amount of H_2SO_4 was added. From process scenarios SSF-GS/DD and SSF-GS/LLE&D, it was found that enzyme cost was highest operating expense after feedstock. However, in CONT-SHF/DD and CONT-SHF/LLE&D process scenarios, enzyme cost came after the cost of chemicals used in pretreatment in the overall raw materials cost (Figure 6-6 and 6-8). The reason for the low enzyme cost in this process could be that SHF method was used. Unlike in SSF process, SHF process allowed for maximum digestion of cellulose by the enzymes because hydrolysis took place at optimum temperature of 50 °C (Ni et al. 2013).

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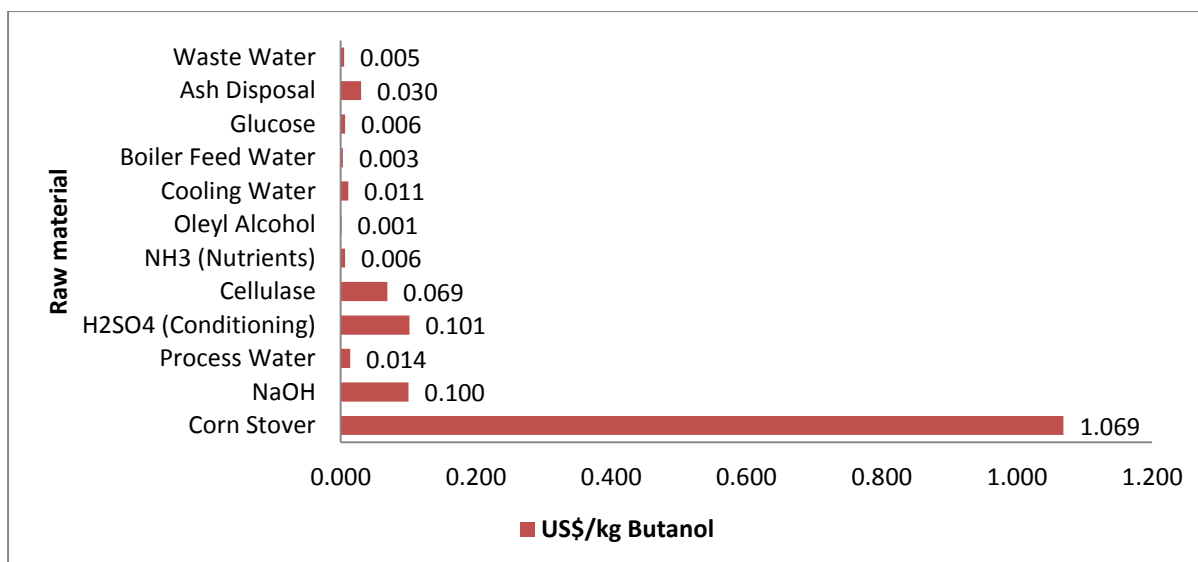
Figure 6-8: Variable operating costs of raw materials in (US$/kg butanol) produced for process scenario CONT-SHF/ LLE&D

The total installed purchased cost for each area in the scenario can be seen from Figure 6-9. It could be seen that fermentation area and enzymatic area had the largest contributions at US$106million and US$107.17million. Their percentage allocation was each 25.83% and 25.68% respectively. These areas were foundto have almost equal installed purchased cost because of similar number of equipment. Although enzymatic hydrolysis reactors were of smaller size relative to fermentation fermenters, their hydrolysis cost was increased by buffer tanks to continuously supply hydrolysate to fermentation. Also solid-liquid separation and the hydrolysate split for seed generation equipment were under enzymatic hydrolysis area. The costs of these units added to the cost of hydrolysis reactors in the area moving it close to that of fermentation. Pretreatment area was not to be the biggest contributor to the overall plant total capital cost but still accounted for 20%. The reason for a decrease in pretreatment capital cost in the current scenario was the areas of solid-liquid separation and the hydrolysate split for seed generation were moved from pretreatment area to enzymatic hydrolysis area, while in SSF-GS/DD and SSF-GS/LLE&D process scenarios solid-liquid separation and hydrolysate split should happen in the pretreatment area before SSF (hydrolysis and fermentation area), as hydrolysis and fermentation occur simultaneously in one reactor.

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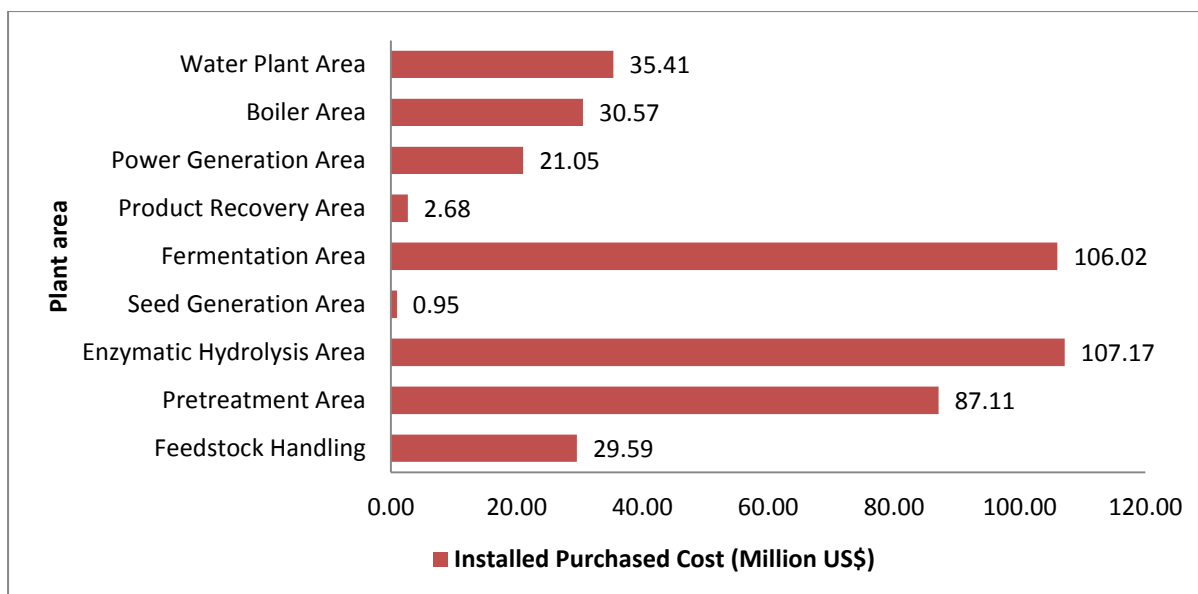
Figure 6-9: Installed purchased cost (Million US$) for different areas within the plant for process scenario CONT-SHF/ LLE&D

6.1.5. Process Scenario B-SHF/DD

For B-SHF/DDprocess scenario, Figure 6-10showed that cassava bagasse feedstock was the major raw material cost at US$1.35/kg butanol accounting for 91%. It was followed by an enzyme cost at US$0.069/kg butanol with a contribution of 7%. The percentage contributions could be seen in Table 9:30. This scenario did not have huge raw materials cost in terms of chemicals used for pretreatment because only liquid hot water was used(Lu et al. 2012). Minimal quantity of H_2SO_4 was used for pH regulation.
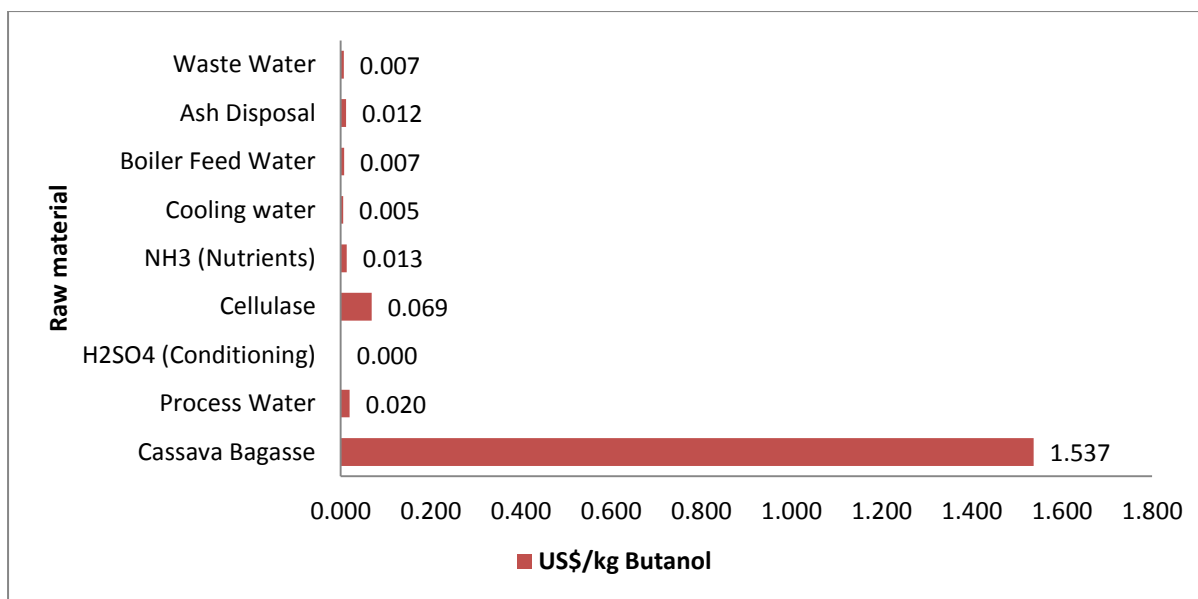
Figure 6-10: Variable operating costs of raw materials in (US$/kg butanol) produced for process scenario B-SHF/DD

When the capital cost for each plant area was studied, it was found that enzymatic hydrolysis area had the largest installed capital cost of all the areas at US$126million. It can be seen from Figure 6-11that enzymatic hydrolysis was followed by fermentation area at US$124million. The reason for enzymatic hydrolysis for having the largest installed purchased cost was that it had two sequential hydrolysis stages. First one was for hydrolysing of starch present in cassava bagasse and the second one was for hydrolysis of cellulose to glucose. The conditions for these two stages were different at 65°C and 50°C respectively each for 24 hours(Lu et al. 2012). The enzymes used in each stage were different and they could not operate at the same conditions. As a result, equipment design and sizing showed that ten saccharification reactors would be required in each stage. Therefore, the capital cost of the area was escalated. The major exception from the previous scenarios was reduced capital cost from pretreatment area in this scenario. It contributed US$39million to the overall capital cost. The reason for decreased capital cost in pretreatment area was that solid-liquid separation unit after pretreatment and conditioning tank was not required. Solid-liquid separation unit was not required under pretreatment because whole slurry was sent for enzymatic hydrolysis. Conditioning tank was also not required because only hot water was used to pretreat cassava bagasse instead of chemicals (Lu et al. 2012).
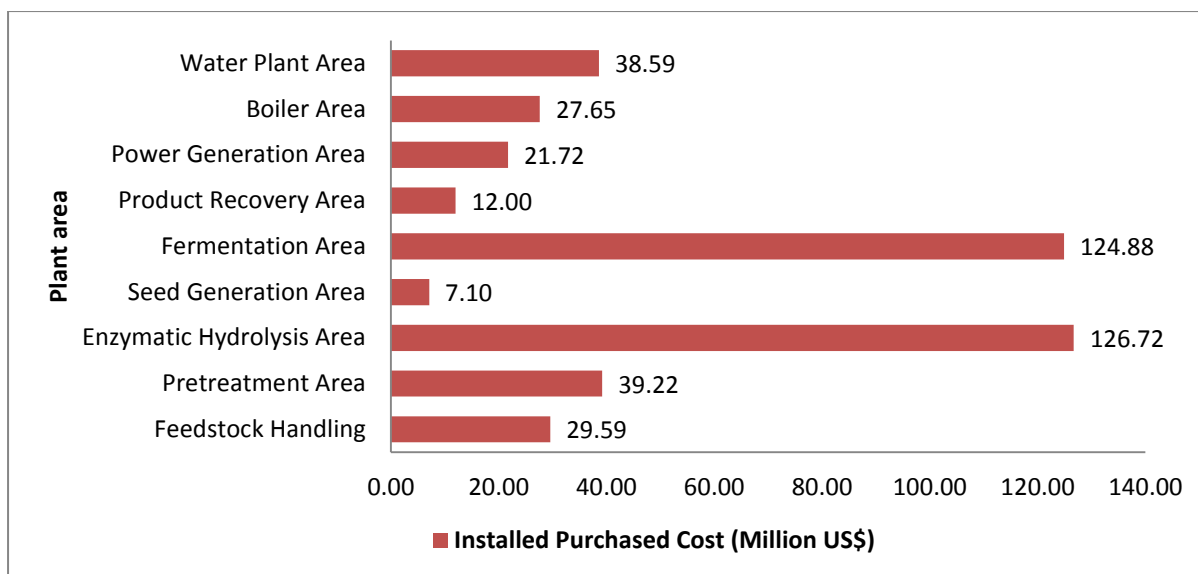
Figure 6-11: Installed purchased cost (Million US$) for different areas within the plant for process scenario B-SHF/DD

6.1.6. Process Scenario B-SHF/LLE&D

B-SHF/LLE&D process scenario operating costs per kg butanol produced can be seen from Figure 6-12. Like the other scenarios, feedstock price accounts for the largest operating cost. In this scenario feedstock price was US$0.96/kg butanol produced, making it to have 86% to the raw material costs (Table 9:33). Comparing this with US$1.35/kg butanol in B-SHF/DD process scenario, the cost was less by US$0.39/kg butanol making them to differ by 28.9%. The difference was caused by the amount of butanol obtained as final product at the end of separation process. This was because both scenarios had same feed rate of feedstock into the process. It was found that more butanol was recovered in B-SHF/LLE&D process scenario than in B-SHF/DD process scenario. As a result, the ratio of feedstock cost to butanol produced was low for B-SHF/LLE&D as compared to that of B-SHF/DD.B-SHF/LLE&D process scenario also had extra raw material cost of oleyl alcohol that was used in LLE as an extractant. All other raw materials cost for these two process scenarios were same with less than 2% difference in the cost per kg butanol produced.

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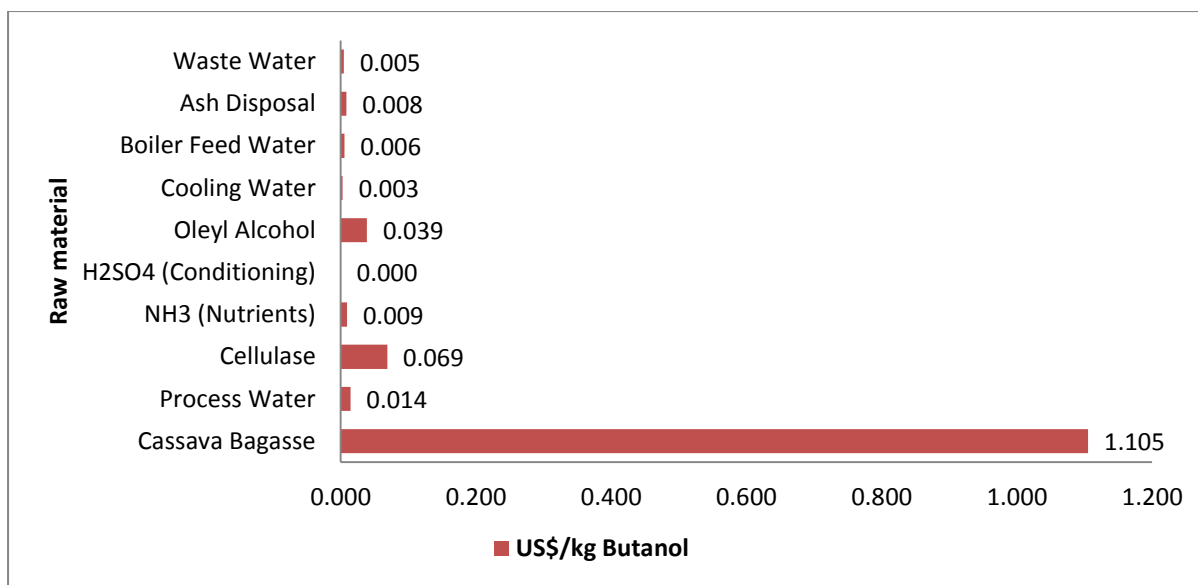
Figure 6-12: Variable operating costs of raw materials in (US$/kg butanol) produced for process scenario B-SHF/ LLE&D

The capital cost for each area within the plant was shown in Figure 6-13. It is similar to that of B-SHF/DD process scenario except for product recovery area. In B-SHF/LLE&D process scenario, product recovery area cost US$4.23million while that of B-SHF/DD process scenario was US$12million. This difference was caused by a different downstream purification process which involved few separation units in B-SHF/LLE&D process scenario as compared to B-SHF/DD process scenario. Refer to Figure 4-4 and Figure 4-5.
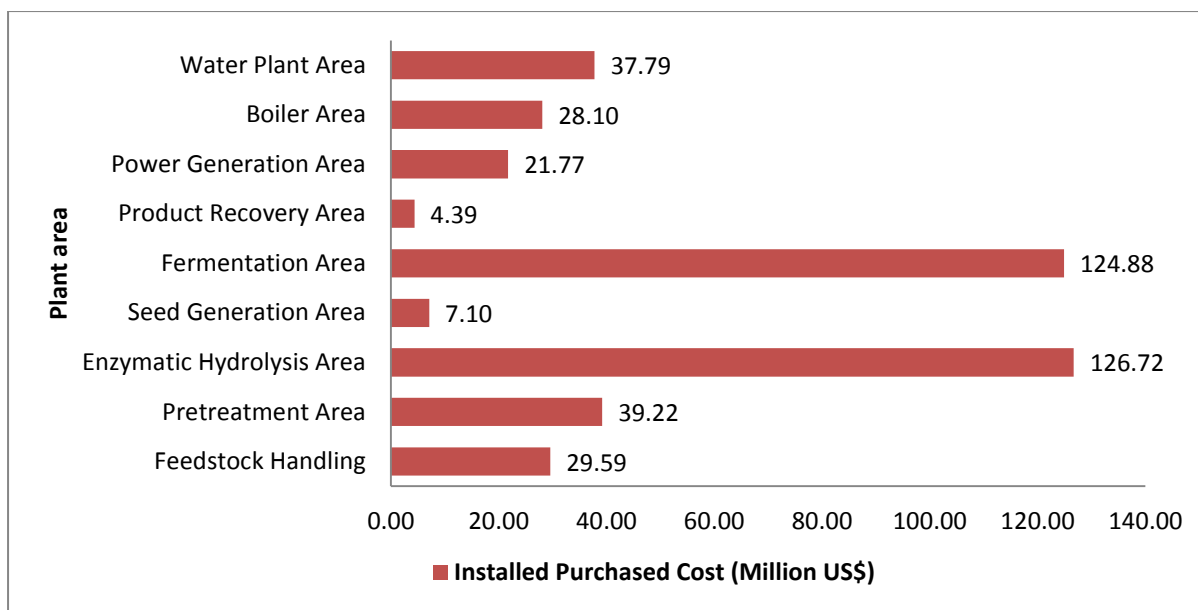
Figure 6-13: Installed purchased cost (Million US$) for different areas within the plant for process scenario B-SHF/ LLE&D

6.1.7. Comparison of Scenarios through Sensitivity Analysis

As described in Section 3.12.4, a sensitivity analysis was done on feedstock price, enzyme cost per tonne of lignocellulose and discount rate in order to investigate their effect on the MBSP of the scenarios. It should be noted that the main aim of the study was production of fuel grade biobutanol which can be used to replace gasoline. It was therefore necessary to investigate the impact of changes in mentioned parameters on the MBSP. This was done for all six scenarios and the effects were compared and discussed in the subsequent sections. When performing sensitivity analysis, the selling price of ethanol was kept at basic fuel selling price. Acetone was kept constant at chemical market price. To get to MBSP, solver in Microsoft excel®was used to vary selling price of butanol such that the NPV of each scenario was zero at a given discount rate using solver.

6.1.7.1. IRR effect on MBSP

Figure 6-14showed the comparison among six scenarios with regards to MBSP when IRR was varied from 7.2% to 15%. In general, it was observed that when IRR was increased, the MBSP also increased in all the scenarios. Noting that the current

butanol selling price evaluated from Equation 3-21 was US$0.78/kg, it could be seen from the figure that only SSF-GS/DD and B-SHF/LLE&D process scenarios had their MBSP less than US$0.78/kg at IRR of 7.2%. For SSF-GS/DD process scenario, at IRR of 7.2% when the NPV was zero, MBSP was US$0.67/kg, while that for B-SHF/LLE&D process scenario was US$0.73/kg. When the IRR was increased to 15%, MBSP increased to US$0.87/kg and US$1.10/kg for SSF-GS/DD and SSF-GS/LLE&D process scenarios respectively. This was because with increase in IRR, the cash outflow of the project also increases and in order to balance that the MBSP increases. In a study by Tao et al. (2013), the MBSP from corn stover at IRR of 10% was US$3.33/gal which was equivalent to US$1.08/kg in 2007. Furthermore, Qureshi et al. (2013)found MBSP in the range of US$1.20 – 1.41/kg at IRR of 10%. From this study, at IRR of 10%, SSF-GS/DD and SSF-GS/LLE&D process scenarios gave MBSP of US$0.74/kg and US$0.93/kg. Both of these were lower than MBSP found in studies mentioned. Several reasons could have contributed to this. One of the reasons could be the price of feedstock used in those studies. In this study US$60/tonne was used, while Tao et al. (2013)used US$58.50/tonne. Qureshi et al. (2013)used wheat straw price in the range of US$18-60/tonne and argued that feedstock price at US$60/tonne was considered expensive especially for agricultural residues. Also enzyme cost was found to vary a lot in literature and choice of enzyme cost per tonne of feedstock could have led to the difference as well.

The MBSP from scenarios SSF-GS/LLE&D, CONT-SHF/DD, CONT-SHF/LLE&D, B-SHF/DD and B-SHF/LLE&D were found to be higher than the wholesalefuel selling price of US$0.78/kg as given by South African BFP (Figure 6.14). All these process scenarios except for SSF-GS/LLE&D were found unprofitable in the current market since their NPVs were negative. It did not surprise that in the range of IRR investigated, the MBSP was above calculated wholesale fuel selling price of US$0.78/kg. When choosing the IRR at 10% which was similar to that used byTao et al. (2013; 2014), it was found that scenarios CONT-SHF/DD and CONT-SHF/LLE&D had MBSP of US$1.13/kg and US$1.43/kg. B-SHF/DD and B-SHF/LLE&D process scenarios had MBSP of US$1.10/kg and US$0.88/kg respectively. Assessing these values, it was found that scenarios would only be feasible at IRR of 10% and above. The findings from the impact of change in IRR on the MBSP were clear that an increase in IRR led to increase in MBSP. However, in a study by Qureshi et al.

(2013)they found no change in butanol price per kg when they changed IRR from 7% to 5%. They believed that in that current economic situation, IRR of 5% could be used, because banks prime rates are quite low. Therefore, it was found that an increase in IRR resulted in an increase in MBSP, the exception being at low discount rate.

Effect of IRR on MBSP
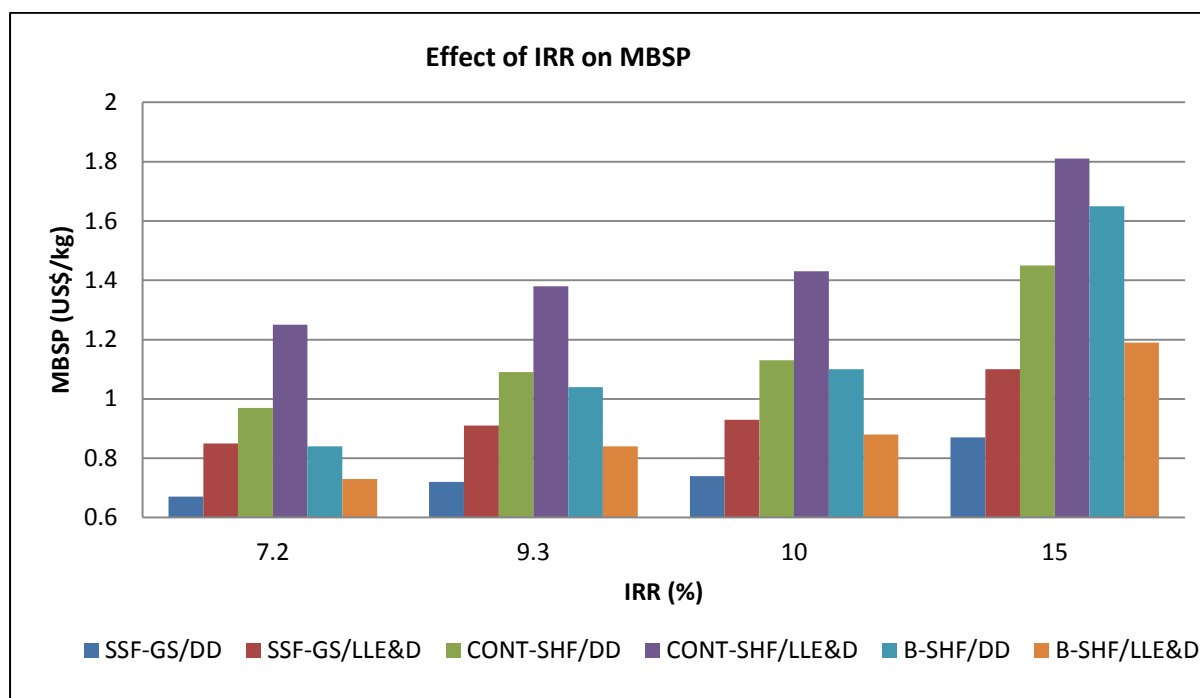
Figure 6-14: Impact of changes in IRR on the MBSP

6.1.7.2.   Feedstock Price effect on MBSP

Feedstock price for production of biofuels is one of the parameters which are investigated extensively for its impact on the techno-economic viability of biorefineries (Sassner et al. 2008; Qureshi et al. 2013; Tao et al. 2013). Figure 6-15showed the impact of change in feedstock price on the MBSP in all six scenarios. In general, a linear relationship between feedstock price and MBSPwas observed because as feedstock price was increased, MBSP also increased. The feedstock influence was also seen in the variable operating costs, where feedstock cost contributed to roughly 70% per kg butanol produced in all scenarios. Other economic studies have shown that cost of cellulosic feedstock was most sensitive and vital to economic feasibility of butanol production process since an increment in feedstock

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cost by 50% resulted in 22% increase in the production cost of butanol (Kumar et al. 2012).

At a feedstock cost of US$30/tonne, all the scenarios have MBSP less than US$1.00/kg butanol produced. As the feedstock price increased to US$60/tonne, MBSP for all scenarios increased to above US$1.00/kg butanol except for SSF-GS/DD process scenario, which was US$0.83/kg (Figure 6-15). The difference can be traced back to the fact that only SSF-GS/DD and SSF-GS/LLE&D process scenarios were found economically feasible at the base conditions of analysis. As a result, the rest of scenarios resulted in sharp increase in MBSP as the feedstock price increased. Qureshi et al. (2013)used wheat straw price in the range of US$18 - 60/tonne and argued that feedstock price at US$60/tonne was considered expensive especially for agricultural residues. In the range of feedstock prices, they found butanol selling price at US$1.20/kg and US$1.41/kg at discount rate of 5%. In a study by Tao et al. (2013), the MBSP from corn stover at discount rate of 10% was US$3.33/gal, which was equal to US$1.08/kg at corn stover price of US$58.50/tonne. In the current study, at discount rate of 9.3% and feedstock price of US$60/tonne, scenarios CONT-SHF/DD, CONT-SHF/LLE&D and B-SHF/DD gave MBSP that were close to one another at US$1.23/kg, US$1.56/kg and US$1.25/kg. These values were close to that of Qureshi et al. (2013)at US$1.41/kg. The difference could be due to different discount rate value of 9.3% used in this study as compared to their 5%. It can be concluded that feedstock price has significant impact on the MBSP at any given discount rate. This can be further compounded by other factors such as $H_2SO_4$and NaOH, which were used during feedstock pretreatment.
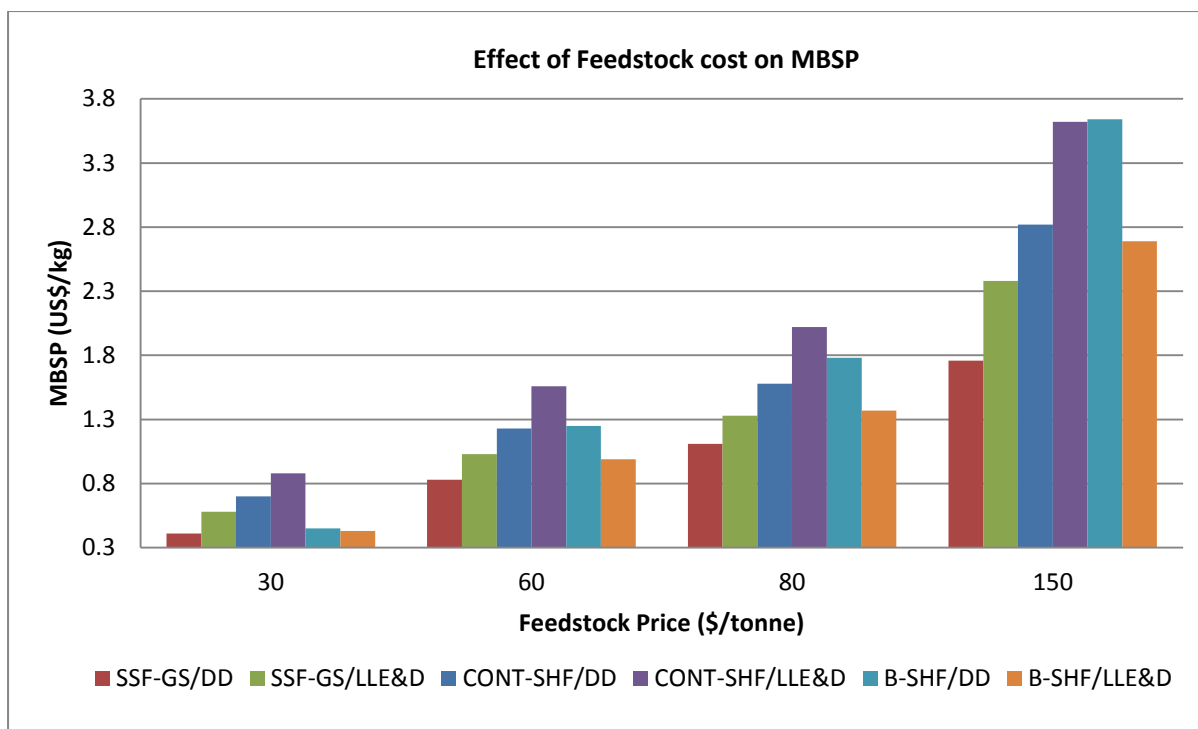
Figure 6-15: Impact of changes in feedstock cost on the MBSP

6.1.7.3. Enzyme Cost effect on MBSP

Enzyme cost in biochemical conversion of biomass into value chemicals or biofuel plays important role in the biorefinery concept. Literature shows differing opinions with regards to enzyme cost(Aden and Foust 2009; Kazi et al. 2010; Klein-Marcuschamer et al. 2012; Seabra et al. 2010). Regardless of their cost as an operating variable, the sensitivity results for its impact on MBSP, when the cost was changed were shown in Figure 6-16.It is observed that an increase in enzyme cost resulted in an increase in MBSP. At enzyme cost in the range of US$40 – US$120/tonne feedstock investigated, only SSF-GS/DD process scenario showed MBSP lower than the basic selling price of US$0.78/kg butanol. At that range, values of MBSP obtained were US$0.70/kg and US$0.79/kg respectively. The reason for thatwas SSF-GS/DD process scenario produced the highest amount of butanol per year when compared to other scenarios (see Table 5:1). Furthermore, this scenario was also deemed economically viable from profitability assessment. The remaining scenarios had the MBSP above US$0.80/kg which was just above US$0.78/kg that was evaluated from BFP in South Africa. When enzyme cost was increased, MBSP also increased accordingly. Special attention has to be taken when dealing with

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enzyme cost because of variation in their cost price, as it was outlined in section 3.12.4.
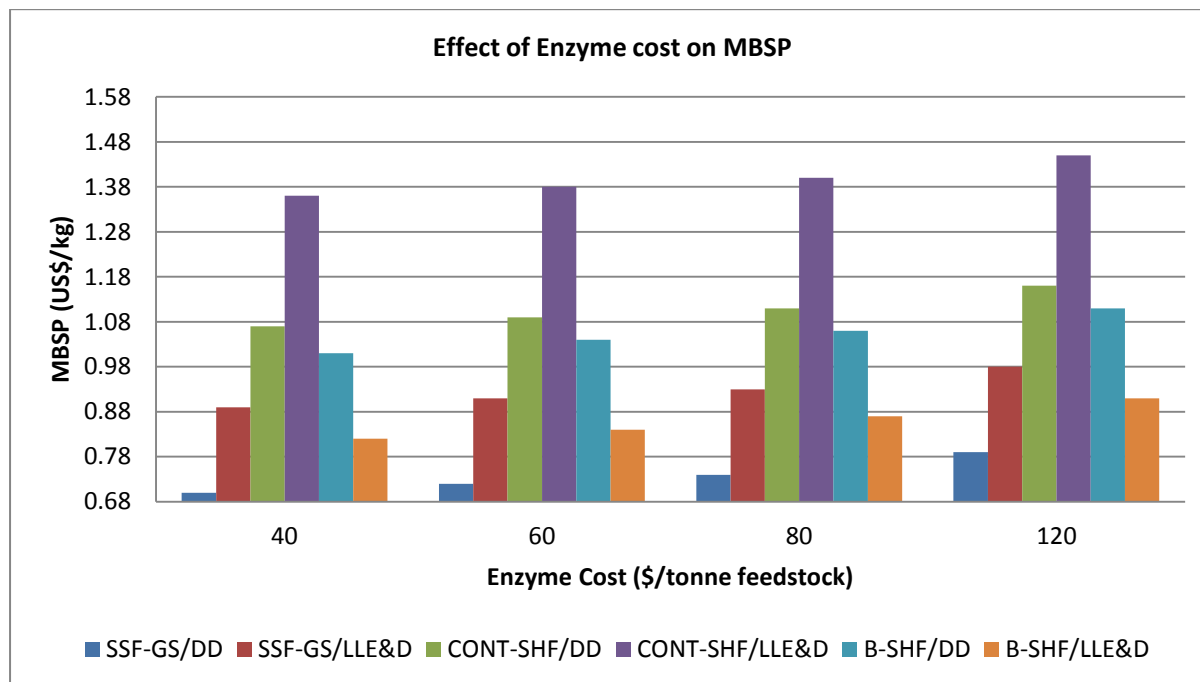
Figure 6-16: Impact of changes in enzyme cost on the MBSP

6.2.   Comparison of Economics of butanol production from lignocellulose and butanol production from molasses(2G vs 1G)

The economics of butanol production from lignocellulose were compared to those of butanol production from molasses using a basis of equal annual butanol production as explained in Section 5.2 with economics being done on 2G butanol production only. It should also be made clear that economics for molasses (1G) butanol process were not done; they were only used for comparison purposes taken from van der Merwe et al.(2013)as they have been reported. Since 2G butanol plant was now of a different size, in base year of 2015 after increasing butanol throughput, its plant cost was adjusted to that of new capacity and year 2007 which was the analysis year for molasses based plant using the following equation:

$$New\ Cost = Original\ Cost\ \times \left(\frac{New\ Capacity}{Old\ Capacity}\right)^n \times \left(\frac{New\ Year\ CEPI}{Base\ Year\ CEPI}\right)$$

Equation 6-1

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Where *n* is the exponential factor in the range of 0.6 – 0.8 and *CEPI* is Chemical Engineering Plant Cost Index (Sinnott and Towler2009).
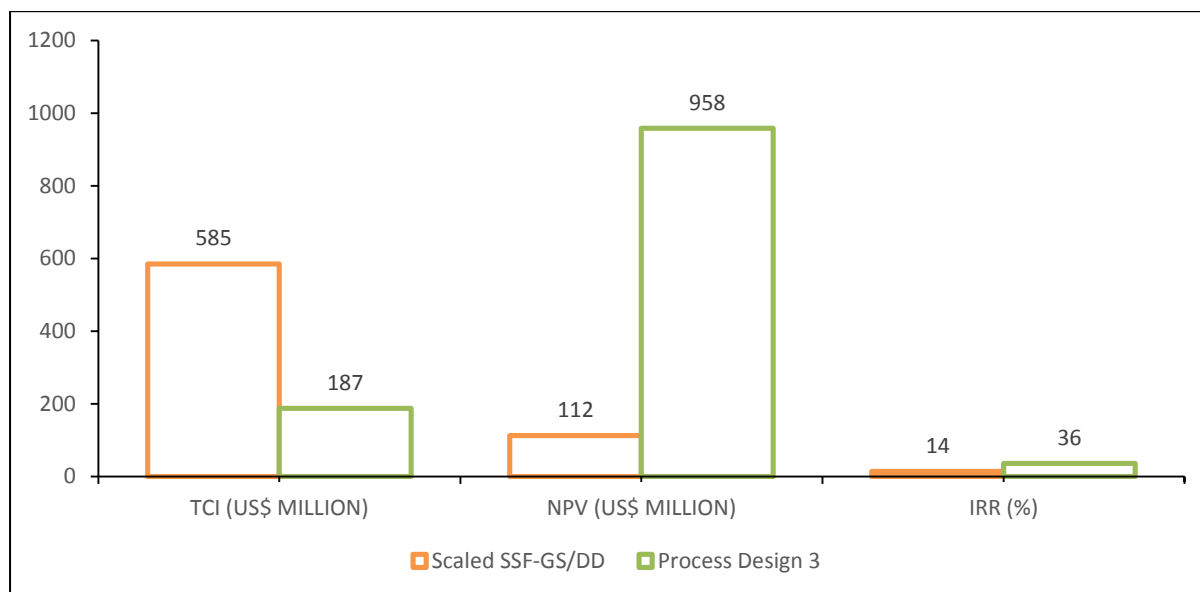
Figure 6-17: Comparison of economics of butanol production from lignocellulose and butanol production from molasses

With the new costs and revenues, the DCF analysis was done to evaluate the economic feasibility of the new plant capacity as explained and discussed in the first paragraph of this sectiom. It should be noted that SSF-GS/DDprocess scenario which was found to be the best from all the six scenarios in this study was compared to Process Design 3 that involved fed-batch fermentation with *in situ* product recovery by gas stripping, followed by LLE and steam stripping distillation that was best scenario in butanol production from molasses study.The techno-economic study by van der Merwe et al.(2013)showed that TCI, NPVand IRR of the Process Design 3 were attractiveUS$187.34million, US$958million and 36% compared to US$585million, US$112million and 14% ofSSF-GS/DD process scenario (Figure 6-17).

The major difference between 2G and 1G butanol in terms of TCI was because 1G process did not require feedstock handling and preparation, pretreatment, detoxification, boiler plant and steam and electricity generation plant as compared to 2G process. These plant areas which did not form part of TCI for 1G process, contributed significantly to the TCI for 2G process. With molasses, only sterilisation was required before feedstock could be sent into fermentation vessel (van der

Merwe 2010).Kumar et al. (2012) also showed that TCI for a plant producing butanol from glucose was 37% lower than that of cellulosic butanol plant. It was also shown by Tao et al. (2013) that TCI for butanol production from corn grain was 30% lower than that of corn stover at US$311million and US$443million respectively. In this study, a molasses butanol production plant was found to be 68% lower than a LCB butanol plant in terms of TCI with the same butanol throughput per year.

In terms of profitability and ability to attract investors, molasses butanol production is well positioned with IRR of 36% compared to 14% for LCB butanol. It was shown by Dias et al. (2014) that different values of revenues lead to different IRRs when butanol was sold in chemical and fuel market. Similarly in this comparison, the revenues from the studies would be different because 2G butanol process have by-product credit from surplus green electricity while 1G did not have that. However, the cost for chemicals used for pretreatment and detoxification would also increase the expenses and so will be ash disposal cost for 2G process. Ultimately, the revenues were low relative to the expenses and led to low IRR since cash flows out of the project were high. For these reasons, the IRR of the 2G process was found to be low compared to that of 1G process.

7.   Conclusions and Recommendations

7.1.   Conclusions

Thisstudy investigated six process scenarios in terms of energy efficiency and economics. The effects of three differentfermentation methods and each with two different recovery and purification methods were analysed for their contribution in energy demand and energy efficiency. Also, sensitivity analysis was also done on the economic parameters to investigate their impact on MBSP. Furthermore, a comparison was made between molasses based butanol production and LCB butanol production of same capacity in terms of energy demand, grossenergy value and economics. From the results and discussions, the following conclusions were reached:

- SSF-GS/DD and SSF-GS/LLE&D process scenarios were the only profitable scenarios with positive NPV for the current market and MBSP below or similar to anticipated butanol market prices. These were the scenarios on which process technology improvement of *in situ* gas stripping was applied during fermentation. This indicates the importance of *in situ* solvent recovery in improving product concentration and process economics

- SSF-GS/DD process scenario gave NPVof US$140million and IRR of 16% while SSF-GS/LLE&D process scenario had NPV of US$47million and IRR of 11%. The MBSP for SSF-GS/DD and SSF-GS/LLE&D were US$0.72/kg and US$0.91/kg respectively compared to US$0.78/kg which was the market price at IRR of 9.3%. These were the only feasible process scenarios for a plant capacity of 1million dry tonnes feedstock per year.

- In all the scenarios, feedstock cost was the major raw material cost per kg butanol produced and it accounted for more than 70%.

- MBSP was impacted by changes in IRR, feedstock cost and enzyme cost but it was more sensitive towards changes in feedstock cost.

- B-SHF and CONT-SHF process scenarioswere the most expensive projectsand SSF-GS the lowestTCI.

- SSF-GS/DD and SSF-GS/LLE&D process scenariosresulted in the highest liquid fuel efficiencies of 26% and 23% as well as highest overall energy efficiencies of 36% and 30%.Process scenarios with highest energy efficiencies were having lowest TCI.

- Heat integration around pretreatment reactor reduced pretreatment energy demand. By pre-heating the pretreatment reactor feed with its hot outlet stream prior sending it to subsequent processes and also steam heating it, pretreatment energy demand was reduced from 163MW to 70MW.

- Molasses based biobutanol production presented lower overall energy demand of 23MJ/kg butanol compared 58MJ/kg butanol of best selected SSF-GS/DD process scenario with both processes at the same butanol production of 118800 tonnes per year

- Molasses based butanol production has lower TCI US$187.34million when compared to that of scaled SSF-GS/DD US$585million which was best selected LCB process scenario. In addition, molasses based butanol production IRR of 36% was more attractive to investors than 14% of scaled up SSF-GS/DD process scenario with both plants at 118800 tonnes per year of butanol.

- Molasses based butanol was not necessarily bio-energy self-sufficient in terms of energy demand,in particular when fossil fuel is used to provide process energy, as compared to LCB based butanol. LCB based butanol sourced its energy from burning of some LCB and solids residues from fermentation; a similar practise is required to achieve GHG emission benefits from 1G butanol production, which is likely to increase operating costs.

7.2. Recommendations

- For all process scenarios, it would be ideal to change the focus from selling biobutanol as biofuel and consider chemical market which is more lucrative. However, this would mean high purity butanol will be required and tax exemptions from the state government will be forfeited. This investigation would point to which direction can capital be invested.

- Further sensitivity analysis should be done for parameters such as plant capacity, product molar ratio and sugar yields. This will allow the study to be compared with the ones available in literature. For instance, Qureshi and Blaschek(2000) investigated the effect of solvents yield on the selling price of butanol per kg.

- During economics evaluation, there are other areas of the processes which were not modelled but values taken from literature. They include refrigeration and cooling tower plants. For an in-depth understanding of the real economics contributed by these plants, they will need to be modelled.

- Experimental work will need to be undertaken where one type of feedstock can be used. This will assist when that work is used in process simulation in order to have same base line.

- Heat integration around pretreatment reactor has shown that energy demand could be reduced. Therefore, it is recommended that in future the whole process heat integration be investigated. This would include both upstream and downstream processes.

- The solids loading in all the scenarios investigated were equal or less 10%. It has been proven that low solids loading during pretreatment leads to high steam demand and in general affect energy efficiency and economics. As a result, it is recommended that in future, a deterministic study be done in which solids loadings in pretreatment and enzymatic hydrolysis are varied.

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9.   Appendices

9.1.   Mass Balances for process scenarios taken from ASPEN Plus (2013)

The tables which follow under this section give overall stream mass balances on the Plant AREAS for SSF-GS/DDProcess Scenario. It should be noted that streams which had zero flowrates were not included for purpose of the tables to fit in pages which are already on landscape orientation. However, full Microsoft Excel® sheets will accompany the thesis in a Compact Disc with mass and energy balances for all scenarios.

SSF-GS/DDProcess Scenario

Table 9:1: Area-100 Pretreatment

	Units	L101	L102	L103	L104	L105	L106	L107	L108	L109
TOT Mass Flow	KG/HR	986451.00	986451.00	125000.00	112500.00	12500.00	170941.00	170941.00	1098950.00	1011190.00
Mass Enthalpy	CAL/SEC	-1.04E+09	-1.04E+09	-6.49E+07	-5.84E+07	-6.49E+06	-1.47E+08	-1.76E+08	-1.07E+09	-1.01E+09
Mass flow rate										
GLUCOSE	KG/HR	0.00	0.00	0.00	0.00	0.00	0.00	0.00	3339.42	3244.86
CELLULOS	KG/HR	0.00	0.00	48608.89	43748.00	4860.89	0.00	0.00	40611.27	406.11
XYLOSE	KG/HR	0.00	0.00	0.00	0.00	0.00	0.00	0.00	18638.69	18110.89
XYLAN	KG/HR	0.00	0.00	20851.90	18766.71	2085.19	0.00	0.00	1426.27	14.26
LIGNIN	KG/HR	0.00	0.00	8176.54	7358.89	817.65	0.00	0.00	6990.94	69.91
ARABINOS	KG/HR	0.00	0.00	0.00	0.00	0.00	0.00	0.00	3339.88	3245.30
GALACTOS	KG/HR	0.00	0.00	0.00	0.00	0.00	0.00	0.00	969.79	942.33
MANNOSE	KG/HR	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1831.83	1779.96
ARABINAN	KG/HR	0.00	0.00	3736.47	3362.82	373.65	0.00	0.00	423.72	4.24

MANNAN	KG/HR	0.00	0.00	2049.03	1844.13	204.90	0.00	0.00	195.48	1.95
GALACTAN	KG/HR	0.00	0.00	1084.78	976.30	108.48	0.00	0.00	103.49	1.03
H2O	KG/HR	984885.00	984885.00	25020.02	22518.01	2502.00	170941.00	170941.00	1004440.00	975994.00
ACETATE	KG/HR	0.00	0.00	2001.60	1801.44	200.16	0.00	0.00	0.00	0.00
AACID	KG/HR	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1801.44	1750.43
H2SO4	KG/HR	1566.17	1566.17	0.00	0.00	0.00	0.00	0.00	1566.17	1521.82
ASH	KG/HR	0.00	0.00	6685.35	6016.81	668.53	0.00	0.00	6016.81	60.17
EXTACTIV	KG/HR	0.00	0.00	3302.64	2972.38	330.26	0.00	0.00	2972.38	2888.21
FURFURAL	KG/HR	0.00	0.00	0.00	0.00	0.00	0.00	0.00	682.43	663.11
HMF	KG/HR	0.00	0.00	0.00	0.00	0.00	0.00	0.00	102.08	99.19
PROTEIN	KG/HR	0.00	0.00	3482.79	3134.51	348.28	0.00	0.00	3134.51	31.35
SOLBLIGN	KG/HR	0.00	0.00	0.00	0.00	0.00	0.00	0.00	367.94	357.53
Mass vapor fraction		0.00	0.00	0.00	0.00	0.00	1.00	0.00	0.01	0.01
Mass solid fraction		0.00	0.00	0.77	0.77	0.77	0.00	0.00	0.05	0.00
Mass flow rate	KG/HR	986451.00	986451.00	125000.00	112500.00	12500.00	170941.00	170941.00	1098950.00	1011190.00
Volume flow rate	L/MIN	16550.84	16550.89	1137.53	1023.78	113.75	570717.00	2971.70	176286.00	170992.00
Temperature	C	25.00	25.00	25.00	25.00	25.00	291.11	100.00	120.84	120.84
Pressure	ATM	1.00	1.10	1.00	1.00	1.00	12.83	13.00	2.00	2.00
Molecular weight		18.04	18.04	55.04	55.04	55.04	18.02	18.02	19.43	18.58

Table 9:1 Continued

	Units	L110	L111	L112	L113	L114	L115	L116	L117	L118	L119	L120
Mass Flow	KG/HR	87764.46	1024.91	10.00	4.00	6.00	1028.91	1012220.00	50610.76	961604.00	1049380.00	1049380.00
Mass Entha	CAL/SC	-5.14E+7	-1.83E+5	-1.05E+4	-4.21E+3	-6.32E+3	-1.87E+5	-1.04E+9	-5.18E+7	-9.85E+08	-1.04E+09	-1.04E+09
Mass FR												
GLUCOSE	KG/HR	94.56	0.00	0.00	0.00	0.00	0.00	3244.86	162.24	3082.62	3177.18	3177.18
CELLULOS	KG/HR	40205.15	0.00	0.00	0.00	0.00	0.00	406.11	20.31	385.81	40590.96	40590.96

XYLOSE	KG/HR	527.79	0.00	0.00	0.00	0.00	0.00	18110.89	905.54	17205.35	17733.14	17733.14
XYLAN	KG/HR	1412.01	0.00	0.00	0.00	0.00	0.00	14.26	0.71	13.55	1425.56	1425.56
LIGNIN	KG/HR	6921.03	0.00	0.00	0.00	0.00	0.00	69.91	3.50	66.41	6987.45	6987.45
ARABINOS	KG/HR	94.58	0.00	0.00	0.00	0.00	0.00	3245.30	162.27	3083.04	3177.61	3177.61
GALACTOS	KG/HR	27.46	0.00	0.00	0.00	0.00	0.00	942.33	47.12	895.21	922.67	922.67
MANNOSE	KG/HR	51.87	0.00	0.00	0.00	0.00	0.00	1779.96	89.00	1690.96	1742.83	1742.83
ARABINAN	KG/HR	419.48	0.00	0.00	0.00	0.00	0.00	4.24	0.21	4.03	423.50	423.50
MANNAN	KG/HR	193.52	0.00	0.00	0.00	0.00	0.00	1.95	0.10	1.86	195.38	195.38
GALACTAN	KG/HR	102.45	0.00	0.00	0.00	0.00	0.00	1.03	0.05	0.98	103.44	103.44
H2O	KG/HR	28442.58	0.00	10.00	4.00	6.00	4.00	975998.00	48799.88	927198.00	955646.00	955646.00
AACID	KG/HR	51.01	0.00	0.00	0.00	0.00	0.00	1.75	0.09	1.66	52.67	52.67
H2SO4	KG/HR	44.35	0.00	0.00	0.00	0.00	0.00	1.52	0.08	1.45	45.79	45.79
LIME	KG/HR	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
ASH	KG/HR	5956.65	0.00	0.00	0.00	0.00	0.00	60.17	3.01	57.16	6013.81	6013.81
EXTACTIV	KG/HR	84.17	0.00	0.00	0.00	0.00	0.00	2888.21	144.41	2743.80	2827.97	2827.97
FURFURAL	KG/HR	19.32	0.00	0.00	0.00	0.00	0.00	663.11	33.16	629.95	649.28	649.28
HMF	KG/HR	2.89	0.00	0.00	0.00	0.00	0.00	99.19	4.96	94.23	97.12	97.12
NH3	KG/HR	0.00	1024.91	0.00	0.00	0.00	1024.91	1.02	0.05	0.97	0.97	0.97
NH4ACETA	KG/HR	0.00	0.00	0.00	0.00	0.00	0.00	2244.59	112.23	2132.37	2132.37	2132.37
PROTEIN	KG/HR	3103.16	0.00	0.00	0.00	0.00	0.00	31.35	1.57	29.78	3132.94	3132.94
SOLBLIGN	KG/HR	10.42	0.00	0.00	0.00	0.00	0.00	357.53	17.88	339.65	350.07	350.07
NH4SO4	KG/HR	0.00	0.00	0.00	0.00	0.00	0.00	2048.27	102.41	1945.86	1945.86	1945.86
Mass VaFr		0.00	1.00	0.00	0.00	0.00	1.00	0.00	0.00	0.00	0.00	0.00
Mass SoFr		0.66	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.06	0.06
Mass FR	KG/HR	87764.46	1024.91	10.00	4.00	6.00	1028.91	1012220.00	50610.76	961604.00	1049380.00	1049380.00
Volume FR	L/MIN	5293.56	4907.74	0.17	0.07	0.10	24254.62	17349.75	867.49	16482.26	17346.20	17346.26
Temperature	C	120.84	25.00	25.00	25.00	25.00	20.46	50.00	50.00	50.00	52.84	52.84
Pressure	ATM	2.00	5.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.10

Molecular weight	41.07	17.03	18.02	18.02	18.02	17.03	18.60	18.60	18.60	19.49	19.49

Table 9:2: Area-200 Seed Generation Plant

	Units	L201	L202	L203	L204	L205	L206	L207
Mass Flow	KG/HR	50610.76	50610.76	0.00	5.00	0.05	6.06	50621.87
Mass Enthalpy	CAL/SEC	-5.18E+07	-5.20E+07	-1.39E+00	-1.76E+03	-2.58E+01	-1.08E+03	-5.20E+07
Components								
GLUCOSE	KG/HR	162.24	162.24	0.00	0.00	0.00	0.00	154.94
CELLULOS	KG/HR	20.31	20.31	0.00	0.00	0.00	0.00	20.31
XYLOSE	KG/HR	905.54	905.54	0.00	0.00	0.00	0.00	866.61
XYLAN	KG/HR	0.71	0.71	0.00	0.00	0.00	0.00	0.71
LIGNIN	KG/HR	3.50	3.50	0.00	0.00	0.00	0.00	3.50
ARABINOS	KG/HR	162.27	162.27	0.00	0.00	0.00	0.00	155.45
GALACTOS	KG/HR	47.12	47.12	0.00	0.00	0.00	0.00	45.23
MANNOSE	KG/HR	89.00	89.00	0.00	0.00	0.00	0.00	84.99
ARABINAN	KG/HR	0.21	0.21	0.00	0.00	0.00	0.00	0.21
MANNAN	KG/HR	0.10	0.10	0.00	0.00	0.00	0.00	0.10
GALACTAN	KG/HR	0.05	0.05	0.00	0.00	0.00	0.00	0.05
H2O	KG/HR	48799.88	48799.88	0.00	0.00	0.00	0.00	48814.36
CO2	KG/HR	0.00	0.00	0.00	0.00	0.00	0.00	5.91
H2	KG/HR	0.00	0.00	0.00	0.00	0.00	0.00	0.00
BUTANOL	KG/HR	0.00	0.00	0.00	0.00	0.00	0.00	1.77
AACID	KG/HR	0.09	0.09	0.00	0.00	0.00	0.00	0.09
H2SO4	KG/HR	0.08	0.08	0.00	0.00	0.00	0.00	0.08
LIME	KG/HR	0.00	0.00	0.00	0.00	0.00	0.00	0.00
ASH	KG/HR	3.01	3.01	0.00	0.00	0.00	0.00	3.01
EXTACTIV	KG/HR	144.41	144.41	0.00	0.00	0.00	0.00	144.41
FURFURAL	KG/HR	33.16	33.16	0.00	0.00	0.00	0.00	33.16

HMF	KG/HR	4.96	4.96	0.00	0.00	0.00	0.00	4.96
NH3	KG/HR	0.05	0.05	0.00	0.00	0.00	6.06	0.21
CLOSTRID	KG/HR	0.00	0.00	0.00	5.00	0.00	0.00	47.67
KH2PO4	KG/HR	0.00	0.00	0.00	0.00	0.01	0.00	0.01
NH4ACETA	KG/HR	112.23	112.23	0.00	0.00	0.04	0.00	112.27
PROTEIN	KG/HR	1.57	1.57	0.00	0.00	0.00	0.00	1.57
SOLBLIGN	KG/HR	17.88	17.88	0.00	0.00	0.00	0.00	17.88
NH4SO4	KG/HR	102.41	102.41	0.00	0.00	0.00	0.00	102.41
Mass vapor fraction		0.00	0.00	0.00	0.00	0.00	1.00	0.00
Mass solid fraction		0.00	0.00	0.00	1.00	0.00	0.00	0.00
Mass flow rate, mixture	KG/HR	50610.76	50610.76	0.00	5.00	0.05	6.06	50621.87
Volume flow rate, mixture	L/MIN	867.49	854.46	0.00	0.06	0.00	145.19	854.52
Temperature	C	50.00	35.00	25.00	25.00	25.00	25.00	35.00
Pressure	ATM	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Molecular weight, mixture		18.60	18.60	180.16	24.62	87.78	17.03	18.58

Table 9:3: Area-300 Simultaneous Saccharification and Fermentation

	Units	L301	L302	L303	L304	L305	L306	L307	L308
Mass Flow	KG/HR	1049380.00	854.78	1050230.00	1879.29	50621.87	1102730.00	154000.00	1256730.00
Mass Enthalpy	CAL/SEC	-1.04E+09	-1.74E+05	-1.04E+09	-3.35E+05	-5.20E+07	-1.10E+09	-9.13E+07	-1.19E+09
Components									
GLUCOSE	KG/HR	3177.18	0.00	46023.06	0.00	154.94	0.00	0.00	0.00
CELLULOS	KG/HR	40590.96	0.00	2029.55	0.00	20.31	2049.85	0.00	2049.85
XYLOSE	KG/HR	17733.14	0.00	19272.09	0.00	866.61	0.00	0.00	0.00
XYLAN	KG/HR	1425.56	0.00	71.28	0.00	0.71	71.99	0.00	71.99
LIGNIN	KG/HR	6987.45	0.00	6987.45	0.00	3.50	6990.94	0.00	6990.94
ARABINOS	KG/HR	3177.61	0.00	3658.87	0.00	155.45	0.00	0.00	0.00

GALACTOS	KG/HR	922.67	0.00	1031.86	0.00	45.23	676.41	0.00	676.41
MANNOSE	KG/HR	1742.83	0.00	1959.92	0.00	84.99	0.01	0.00	0.01
ARABINAN	KG/HR	423.50	0.00	0.00	0.00	0.21	0.21	0.00	0.21
MANNAN	KG/HR	195.38	0.00	0.00	0.00	0.10	0.10	0.00	0.10
GALACTAN	KG/HR	103.44	0.00	5.17	0.00	0.05	5.22	0.00	5.22
H2O	KG/HR	955646.00	0.00	951087.00	0.00	48814.36	1005910.00	0.00	1005910.00
CO2	KG/HR	0.00	0.00	0.00	0.00	5.91	31328.05	154000.00	185328.00
H2	KG/HR	0.00	0.00	0.00	0.00	0.00	786.41	0.00	786.41
BUTANOL	KG/HR	0.00	0.00	0.00	0.00	1.77	12251.03	0.00	12251.03
ETHANOL	KG/HR	0.00	0.00	0.00	0.00	0.00	1993.20	0.00	1993.20
ACETONE	KG/HR	0.00	0.00	0.00	0.00	0.00	6071.54	0.00	6071.54
AACID	KG/HR	52.67	0.00	52.67	0.00	0.09	1552.84	0.00	1552.84
BACID	KG/HR	0.00	0.00	0.00	0.00	0.00	949.98	0.00	949.98
H2SO4	KG/HR	45.79	0.00	45.79	0.00	0.08	45.87	0.00	45.87
ASH	KG/HR	6013.81	0.00	6013.81	0.00	3.01	6016.81	0.00	6016.81
EXTACTIV	KG/HR	2827.97	0.00	2827.97	0.00	144.41	2972.38	0.00	2972.38
FURFURAL	KG/HR	649.28	0.00	649.28	0.00	33.16	682.43	0.00	682.43
HMF	KG/HR	97.12	0.00	97.12	0.00	4.96	102.08	0.00	102.08
NH3	KG/HR	0.97	0.00	0.97	1879.29	0.21	3.19	0.00	3.19
CLOSTRID	KG/HR	0.00	0.00	0.00	0.00	47.67	13616.70	0.00	13616.70
CELLULAS	KG/HR	0.00	854.78	854.78	0.00	0.00	854.78	0.00	854.78
KH2PO4	KG/HR	0.00	0.00	0.00	0.00	0.01	0.01	0.00	0.01
NH4ACETA	KG/HR	2132.37	0.00	2132.37	0.00	112.27	2244.63	0.00	2244.63
PROTEIN	KG/HR	3132.94	0.00	3132.94	0.00	1.57	3134.51	0.00	3134.51
SOLBLIGN	KG/HR	350.07	0.00	350.07	0.00	17.88	367.94	0.00	367.94
NH4SO4	KG/HR	1945.86	0.00	1945.86	0.00	102.41	2048.27	0.00	2048.27
Mass vapor fraction		0.00	0.00	0.00	1.00	0.00	0.03	1.00	0.15
Mass solid fraction		0.06	1.00	0.02	0.00	0.00	0.03	0.00	0.03
Mass flow rate, mixture	KG/HR	1049380.00	854.78	1050230.00	1879.29	50621.87	1102730.00	154000.00	1256730.00

Volume flow rate, mixture	L/MIN	17368.28	9.02	17187.17	44994.46	854.52	506248.00	1474660.00	2054960.00
Temperature	C	54.09	25.00	35.00	25.00	35.00	35.00	35.00	33.04
Pressure	ATM	1.10	1.00	0.99	1.00	1.00	1.00	1.00	1.00
Molecular weight, mixture		19.49	24.02	19.58	17.03	18.58	18.93	44.01	20.35

Table 9.3Continued

	Units	L309	L310	L311	L312	L313	L314	L315	L316
Mass Flow	KG/HR	1040530.00	216193.00	216193.00	186578.00	186578.00	1049380.00	29615.03	29615.03
Mass Enthalpy	CAL/SEC	-1.07E+09	-1.22E+08	-1.23E+08	-1.10E+08	-1.10E+08	-1.04E+09	-1.41E+07	-1.41E+07
Components									
GLUCOSE	KG/HR	0.00	0.00	0.00	0.00	0.00	3177.18	0.00	0.00
CELLULOS	KG/HR	2049.85	0.00	0.00	0.00	0.00	40590.96	0.00	0.00
XYLOSE	KG/HR	0.00	0.00	0.00	0.00	0.00	17733.14	0.00	0.00
XYLAN	KG/HR	71.99	0.00	0.00	0.00	0.00	1425.56	0.00	0.00
LIGNIN	KG/HR	6990.94	0.00	0.00	0.00	0.00	6987.45	0.00	0.00
ARABINOS	KG/HR	0.00	0.00	0.00	0.00	0.00	3177.61	0.00	0.00
GALACTOS	KG/HR	676.32	0.09	0.09	0.00	0.00	922.67	0.09	0.09
MANNOSE	KG/HR	0.01	0.00	0.00	0.00	0.00	1742.83	0.00	0.00
ARABINAN	KG/HR	0.21	0.00	0.00	0.00	0.00	423.50	0.00	0.00
MANNAN	KG/HR	0.10	0.00	0.00	0.00	0.00	195.38	0.00	0.00
GALACTAN	KG/HR	5.22	0.00	0.00	0.00	0.00	103.44	0.00	0.00
H2O	KG/HR	1001530.00	4380.70	4380.70	145.31	145.31	955646.00	4235.40	4235.40
CO2	KG/HR	147.62	185180.00	185180.00	183306.00	183306.00	0.00	1874.86	1874.86
H2	KG/HR	0.00	786.40	786.40	761.09	761.09	0.00	25.32	25.32
BUTANOL	KG/HR	32.64	12218.39	12218.39	37.88	37.88	0.00	12180.51	12180.51
ETHANOL	KG/HR	448.11	1545.09	1545.09	87.85	87.85	0.00	1457.24	1457.24
ACETONE	KG/HR	0.83	6070.71	6070.71	2224.62	2224.62	0.00	3846.10	3846.10

AACID	KG/HR	245.95	1306.88	1306.88	13.28	13.28	52.67	1293.60	1293.60
BACID	KG/HR	648.11	301.87	301.87	0.03	0.03	0.00	301.84	301.84
H2SO4	KG/HR	45.87	0.00	0.00	0.00	0.00	45.79	0.00	0.00
ASH	KG/HR	6016.81	0.00	0.00	0.00	0.00	6013.81	0.00	0.00
EXTACTIV	KG/HR	2972.38	0.00	0.00	0.00	0.00	2827.97	0.00	0.00
FURFURAL	KG/HR	221.66	460.78	460.78	2.69	2.69	649.28	458.08	458.08
HMF	KG/HR	102.08	0.00	0.00	0.00	0.00	97.12	0.00	0.00
NH3	KG/HR	0.24	2.95	2.95	0.00	0.00	0.97	2.95	2.95
CLOSTRID	KG/HR	13616.70	0.00	0.00	0.00	0.00	0.00	0.00	0.00
CELLULAS	KG/HR	854.78	0.00	0.00	0.00	0.00	0.00	0.00	0.00
KH2PO4	KG/HR	0.00	0.01	0.01	0.00	0.00	0.00	0.01	0.01
NH4ACETA	KG/HR	0.00	2244.63	2244.63	0.00	0.00	2132.37	2244.63	2244.63
PROTEIN	KG/HR	3134.51	0.00	0.00	0.00	0.00	3132.94	0.00	0.00
SOLBLIGN	KG/HR	336.03	31.92	31.92	0.00	0.00	350.07	31.92	31.92
NH4SO4	KG/HR	385.79	1662.48	1662.48	0.00	0.00	1945.86	1662.48	1662.48
Mass vapor fraction		0.00	1.00	0.82	1.00	1.00	0.00	0.00	0.00
Mass solid fraction		0.03	0.00	0.00	0.00	0.00	0.06	0.00	0.00
Mass flow rate, mixture	KG/HR	1040530.00	216193.00	216193.00	186578.00	186578.00	1049380.00	29615.03	29615.03
Volume flow rate, mixture	L/MIN	17958.76	2185360.00	1583130.00	1652480.00	1251690.00	17041.40	587.14	587.16
Temperature	C	35.00	35.00	-10.00	-10.00	25.84	35.00	-10.00	-10.00
Pressure	ATM	1.00	1.00	1.00	1.00	1.50	1.00	1.00	1.00
Molecular weight, mixture		18.40	41.45	41.45	40.63	40.63	19.49	47.44	47.44

Table 9:4: Area-400 Solvents Separation and Purification

	Units	L401	L402	L403	L404	L405	L406	L407	L408	L409
Mass Flow	KG/HR	142473.00	142473.00	142473.00	31491.23	110982.00	110982.00	7177.51	24313.72	24313.72
Mass Enthalpy	CAL/SEC	-1.37E+08	-1.37E+08	-1.35E+08	-1.62E+07	-1.14E+08	-1.16E+08	-2.46E+06	-1.62E+07	-1.64E+07

Components										
H2O	KG/HR	122855.00	122855.00	122855.00	12285.51	110570.00	110570.00	38.52	12246.99	12246.99
CO2	KG/HR	1951.17	1951.17	1951.17	1951.17	0.00	0.00	1951.17	0.00	0.00
H2	KG/HR	60.17	60.17	60.17	60.17	0.00	0.00	60.14	0.03	0.03
BUTANOL	KG/HR	10402.44	10402.44	10402.44	10402.44	0.00	0.00	0.04	10402.39	10402.39
ETHANOL	KG/HR	1381.00	1381.00	1381.00	1381.00	0.00	0.00	9.53	1371.47	1371.47
ACETONE	KG/HR	5169.81	5169.81	5169.81	5169.81	0.00	0.00	5118.11	51.70	51.70
ACETATE	KG/HR	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
AACID	KG/HR	279.04	279.04	279.04	37.28	241.77	241.77	0.00	37.28	37.28
BACID	KG/HR	201.11	201.11	201.11	30.28	170.84	170.84	0.00	30.28	30.28
EXTACTIV	KG/HR	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
FURFURAL	KG/HR	171.21	171.21	171.21	171.21	0.00	0.00	0.00	171.21	171.21
NH3	KG/HR	2.37	2.37	2.37	2.37	0.00	0.00	0.00	2.37	2.37
Mass vapor fraction		0.00	0.00	0.01	1.00	0.00	0.00	1.00	0.00	0.00
Mass solid fraction		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Mass flow rate, mixture	KG/HR	142473.00	142473.00	142473.00	31491.23	110982.00	110982.00	7177.51	24313.72	24313.72
Volume flow rate, mix	L/MIN	2401.85	2401.89	18062.07	505265.00	2016.48	1890.57	97898.61	480.08	459.88
Temperature	C	0.00	0.02	44.50	89.65	100.03	40.00	31.22	82.09	50.00
Pressure	ATM	1.00	1.50	1.50	1.00	1.00	1.00	0.70	0.70	1.00
Molecular weight, mix		19.89	19.89	19.89	30.92	18.06	18.06	43.60	28.48	28.48

Table 9.4Continued

	Units	L410	L411	L412	L413	L414	L415	L416	L417
Mass Flow	KG/HR	7177.51	3285.32	110982.00	2001.41	112266.00	3892.19	1416.00	22897.72
Mass Enthalpy	CAL/SEC	-2.45E+06	-1.46E+06	-1.16E+08	-1.18E+06	-1.16E+08	-1.15E+06	-5.10E+05	-1.57E+07
Components									
H2O	KG/HR	38.52	4.74	110570.00	102.46	110472.00	33.78	69.78	12177.22

CO_2	KG/HR	1951.17	1906.87	0.00	1837.62	69.26	44.30	0.00	0.00
H_2	KG/HR	60.14	59.97	0.00	59.89	0.08	0.17	0.00	0.03
BUTANOL	KG/HR	0.04	0.00	0.00	0.00	0.00	0.04	0.00	10402.39
ETHANOL	KG/HR	9.53	1.15	0.00	0.00	1.15	8.38	1294.51	76.96
ACETONE	KG/HR	5118.11	1312.58	0.00	0.77	1311.81	3805.53	51.70	0.00
AACID	KG/HR	0.00	0.00	241.77	0.35	241.41	0.00	0.00	37.28
BACID	KG/HR	0.00	0.00	170.84	0.31	170.52	0.00	0.00	30.28
FURFURAL	KG/HR	0.00	0.00	0.00	0.00	0.00	0.00	0.00	171.21
NH_3	KG/HR	0.00	0.00	0.00	0.00	0.00	0.00	0.01	2.36
Mass vapor fraction		1.00	1.00	0.00	1.00	0.00	0.00	1.00	0.00
Mass solid fraction		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Mass flow rate, mixture	KG/HR	7177.51	3285.32	110982.00	2001.41	112266.00	3892.19	1416.00	22897.72
Volume flow rate, mixture	L/MIN	73608.91	38473.49	1890.60	33062.04	1919.59	81.98	48473.84	440.14
Temperature	C	53.78	20.00	40.02	40.10	40.59	20.00	50.39	63.64
Pressure	ATM	1.00	1.00	1.50	1.00	1.00	1.00	0.30	0.30
Molecular weight, mixture		43.60	34.23	18.06	25.93	18.22	56.68	43.08	27.90

Table 9.4Continued

	Units	L418	L419	L420	L421	L422	L423	L424	L425	L426	L427	L428
Mass Flow	KG/HR	22897.72	13763.76	36661.48	22922.32	12389.84	10532.48	13739.15	1373.91	13763.76	12365.24	12365.24
Mass Entha Components	CAL/SEC	-1.57E+7	-8.70E+6	-2.44E+7	-1.09E+7	-6.72E+06	-2.95E+6	-1.36E+7	-7.23E+5	-7.44E+06	-1.27E+7	-1.27E+7
H_2O	KG/HR	12177.22	6324.81	18502.03	5730.63	5724.90	5.73	12771.40	599.94	6324.83	12171.46	12171.46
H_2	KG/HR	0.03	0.00	0.03	0.03	0.00	0.03	0.00	0.00	0.00	0.00	0.00
BUTANOL	KG/HR	10402.39	6827.81	17230.20	16454.23	6131.53	10322.70	775.96	696.24	6827.76	79.72	79.72

ETHANOL	KG/HR	76.96	520.99	597.94	451.67	451.48	0.19	146.28	69.51	520.98	76.77	76.77
AACID	KG/HR	37.28	10.57	47.85	31.65	9.62	22.03	16.20	0.96	10.57	15.25	15.25
BACID	KG/HR	30.28	0.58	30.86	29.65	0.52	29.13	1.21	0.06	0.58	1.15	1.15
FURFURAL	KG/HR	171.21	78.99	250.20	222.11	71.78	150.32	28.10	7.21	78.99	20.89	20.89
Mass VFra		0.00	0.00	0.00	0.00	1.00	0.00	0.00	1.00	0.98	0.00	0.00
Mass SFra		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Mass FR mix	KG/HR	22897.72	13763.76	36661.48	22922.32	12389.84	10532.48	13739.15	1373.91	13763.72	12365.24	12365.24
Vol FR mix	L/MIN	437.86	273.16	710.68	465.62	631610.00	234.62	244.99	42189.76	219740.00	220.23	220.24
Temperature	C	64.47	80.00	70.25	70.00	63.78	86.33	70.00	75.08	93.05	79.91	79.93
Pressure	ATM	1.10	1.00	1.00	0.70	0.30	0.30	0.70	0.50	1.00	0.50	1.00
Molecular weight		27.90	30.22	28.72	41.43	30.13	74.17	19.00	31.02	30.22	18.22	18.22

Table 9:5: Area-500 Water Plant

	Units	L501	L502	L503	L504	L505	L506	L507	L508
Mass Flow	KG/HR	19715.40	19715.40	19715.40	199345.00	219060.00	219060.00	0.00	219060.00
Mass Enthalpy	CAL/SEC	-1.78E+07	-2.06E+07	-2.06E+07	-2.10E+08	-2.30E+08	-2.30E+08	0.00E+00	-2.29E+08
Components									
H2O	KG/HR	19715.40	19715.40	19715.40	199345.00	219060.00	219060.00		219060.00
Mass vapor fraction		0.91	0.00	0.00	0.00	0.00	0.00		0.00
Mass solid fraction		0.00	0.00	0.00	0.00	0.00	0.00		0.00
Mass flow rate, mixture	KG/HR	19715.40	19715.40	19715.40	199345.00	219060.00	219060.00		219060.00
Volume flow rate, mixture	L/MIN	2999390.00	333.19	339.95	3345.73	3685.33	3685.59		3788.75
Temperature	C	53.91	53.91	52.05	25.00	27.43	27.50		55.00
Pressure	ATM	0.15	0.15	4.20	1.00	1.00	3.00		3.30
Molecular weight, mixture		18.02	18.02	18.02	18.02	18.02	18.02		18.02

Table 9.5 Continued

	Units	L509	L510	L511	L512	L513	L514	L515	L516
Mass Flow	KG/HR	835896.00	835896.00	112266.00	12365.24	211742.00	1172270.00	9399.38	1162870.00
Mass Enthalpy	CAL/SEC	-8.76E+08	-8.76E+08	-1.16E+08	-1.27E+07	-2.20E+08	-1.23E+09	-4.60E+06	-1.22E+09
Components									
GALACTOS	KG/HR	642.59	642.59	0.00	0.00	0.00	0.00	0.00	0.00
MANNOSE	KG/HR	0.01	0.01	0.00	0.00	0.00	0.00	0.00	0.00
H2O	KG/HR	830388.00	830388.00	110472.00	12171.46	210905.00	1162360.00	215.85	1162150.00
CO2	KG/HR	6.19	6.19	69.26	0.00	0.00	6090.28	5510.70	579.57
H2	KG/HR	0.01	0.01	0.08	0.00	0.00	20.29	20.24	0.05
BUTANOL	KG/HR	1739.30	1739.30	0.00	79.72	0.00	0.00	0.00	0.00
ETHANOL	KG/HR	568.68	568.68	1.15	76.77	0.00	0.00	0.00	0.00
ACETONE	KG/HR	379.54	379.54	1311.81	0.00	0.00	0.00	0.00	0.00
AACID	KG/HR	1198.00	1198.00	241.41	15.25	437.56	0.00	0.00	0.00
BACID	KG/HR	711.40	711.40	170.52	1.15	0.00	0.00	0.00	0.00
H2SO4	KG/HR	43.97	43.97	0.00	0.00	0.07	44.04	0.00	44.04
EXTACTIV	KG/HR	14.86	14.86	0.00	0.00	0.00	0.00	0.00	0.00
FURFURAL	KG/HR	105.90	105.90	0.00	20.89	399.11	0.00	0.00	0.00
HMF	KG/HR	96.94	96.94	0.00	0.00	0.03	0.00	0.00	0.00
NH3	KG/HR	0.67	0.67	0.00	0.00	0.00	0.67	0.00	0.67
CH4	KG/HR	0.00	0.00	0.00	0.00	0.00	3752.71	3652.59	100.12
Mass vapor fraction		0.00	0.00	0.00	0.00	0.00	0.01	1.00	0.00
Mass solid fraction		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Mass flow rate, mixture	KG/HR	835896.00	835896.00	112266.00	12365.24	211742.00	1172270.00	9399.38	1162870.00
Volume flow rate, mixture	L/MIN	14036.45	14036.92	1919.59	220.24	3719.88	109380.00	152872.00	19517.65
Temperature	C	25.00	25.03	40.59	79.93	70.00	35.00	25.00	25.00
Pressure	ATM	0.50	1.50	1.00	1.00	1.00	1.50	1.00	1.00
Molecular weight, mixture		18.10	18.10	18.22	18.22	18.07	18.06	25.07	18.02

Table 9:6: Area- 600 Boiler

	Units	L601	L602	L603	L604	L605	L606	L607	L608	L609
Mass Flow	KG/HR	219060.00	12500.00	919698.00	1442520.00	9399.38	835896.00	45938.98	1451920.00	1451920.00
Mass Enthalpy	CAL/SEC	-2.29E+08	-6.49E+6	-9.35E+08	6.18E-09	-4.60E+06	-8.76E+08	-2.07E+7	-4.60E+06	-3.45E+06
Components										
CELLULOS	KG/HR	0.00	4860.89	2049.85	0.00	0.00	0.00	2049.85	0.00	0.00
XYLAN	KG/HR	0.00	2085.19	71.99	0.00	0.00	0.00	71.99	0.00	0.00
LIGNIN	KG/HR	0.00	817.65	6990.94	0.00	0.00	0.00	6990.94	0.00	0.00
GALACTOS	KG/HR	0.00	0.00	676.41	0.00	0.00	642.59	33.82	0.00	0.00
MANNOSE	KG/HR	0.00	0.00	0.01	0.00	0.00	0.01	0.00	0.00	0.00
ARABINAN	KG/HR	0.00	373.65	0.21	0.00	0.00	0.00	0.21	0.00	0.00
MANNAN	KG/HR	0.00	204.90	0.10	0.00	0.00	0.00	0.10	0.00	0.00
GALACTAN	KG/HR	0.00	108.48	5.22	0.00	0.00	0.00	5.22	0.00	0.00
H2O	KG/HR	219060.00	2502.00	874092.00	0.00	215.85	830388.00	6071.16	215.85	215.85
CO2	KG/HR	0.00	0.00	6.52	0.00	5510.70	6.19	0.00	5510.70	5510.70
H2	KG/HR	0.00	0.00	0.01	0.00	20.24	0.01	0.00	20.24	20.24
BUTANOL	KG/HR	0.00	0.00	1830.84	0.00	0.00	1739.30	2.55	0.00	0.00
ETHANOL	KG/HR	0.00	0.00	598.61	0.00	0.00	568.68	0.61	0.00	0.00
ACETONE	KG/HR	0.00	0.00	399.52	0.00	0.00	379.54	0.14	0.00	0.00
ACETATE	KG/HR	0.00	200.16	0.00	0.00	0.00	0.00	0.00	0.00	0.00
AACID	KG/HR	0.00	0.00	1261.05	0.00	0.00	1198.00	6.89	0.00	0.00
BACID	KG/HR	0.00	0.00	748.84	0.00	0.00	711.40	8.45	0.00	0.00
H2SO4	KG/HR	0.00	0.00	46.29	0.00	0.00	43.97	2.31	0.00	0.00
ASH	KG/HR	0.00	668.53	6016.81	0.00	0.00	0.00	6016.81	0.00	0.00
EXTACTIV	KG/HR	0.00	330.26	2972.38	0.00	0.00	14.86	2957.52	0.00	0.00
FURFURAL	KG/HR	0.00	0.00	111.47	0.00	0.00	105.90	0.53	0.00	0.00
HMF	KG/HR	0.00	0.00	102.05	0.00	0.00	96.94	5.07	0.00	0.00
NH3	KG/HR	0.00	0.00	0.71	0.00	0.00	0.67	0.00	0.00	0.00
CLOSTRID	KG/HR	0.00	0.00	13611.61	0.00	0.00	0.00	13611.61	0.00	0.00

O2	KG/HR	0.00	0.00	0.00	335987.00	0.00	0.00	0.00	335987.00	335987.00
CELLULAS	KG/HR	0.00	0.00	854.78	0.00	0.00	0.00	854.78	0.00	0.00
NH4ACETA	KG/HR	0.00	0.00	1698.93	0.00	0.00	0.00	1698.93	0.00	0.00
NAOH	KG/HR	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
N2	KG/HR	0.00	0.00	0.00	1106530.00	0.00	0.00	0.00	1106530.00	1106530.00
PROTEIN	KG/HR	0.00	348.28	3134.51	0.00	0.00	0.00	3134.51	0.00	0.00
CH4	KG/HR	0.00	0.00	0.00	0.00	3652.59	0.00	0.00	3652.59	3652.59
SOLBLIGN	KG/HR	0.00	0.00	367.91	0.00	0.00	0.00	367.34	0.00	0.00
NH4SO4	KG/HR	0.00	0.00	2047.62	0.00	0.00	0.00	2047.62	0.00	0.00
Mass vapor fraction		0.00	0.00	0.00	1.00	1.00	0.00	0.00	1.00	1.00
Mass solid fraction		0.00	0.77	0.04	0.00	0.00	0.00	0.71	0.00	0.00
Mass flow rate, mixture	KG/HR	219060.00	12500.00	919698.00	1442520.00	9399.38	835896.00	45938.98	1451920.00	1451920.00
Volume flow rate, mixture	L/MIN	3788.75	113.75	15392.66	20387500.00	152872.00	14036.45	575.57	20540400.00	19405000.00
Temperature	C	55.00	25.00	35.00	25.00	25.00	25.00	85.66	25.00	36.69
Pressure	ATM	3.30	1.00	0.07	1.00	1.00	0.50	0.50	1.00	1.10
Molecular weight, mixture		18.02	55.04	18.56	28.85	25.07	18.10	35.72	28.82	28.82

Table 9.6 Continued

	Units	L610	L611	L612	L613	L614	L615	L616	L617
Mass Flow	KG/HR	1451920.00	1510360.00	1510360.00	1510360.00	1510360.00	1510360.00	6685.55	1503670.00
Mass Enthalpy	CAL/SEC	1.27E+07	-1.45E+07	-3.41E+07	-5.12E+07	-6.23E+07	-7.85E+07	-4.96E+6	-7.36E+07
Components									
H2O	KG/HR	215.85	42528.78	42528.78	42528.78	42528.78	42528.78	0.00	42528.78
CO2	KG/HR	5510.70	90196.30	90196.30	90196.30	90196.30	90196.30	0.00	90196.30
H2	KG/HR	20.24	20.24	20.24	20.24	20.24	20.24	0.00	20.24
ACETATE	KG/HR	0.00	0.20	0.20	0.20	0.20	0.20	0.20	0.00
ASH	KG/HR	0.00	6685.35	6685.35	6685.35	6685.35	6685.35	6685.35	0.00

NH3	KG/HR	0.00	0.01	0.01	0.01	0.01	0.01	0.00	0.01
O2	KG/HR	335987.00	260276.00	260276.00	260276.00	260276.00	260276.00	0.00	260276.00
N2	KG/HR	1106530.00	1109560.00	1109560.00	1109560.00	1109560.00	1109560.00	0.00	1109560.00
SO2	KG/HR	0.00	1085.43	1085.43	1085.43	1085.43	1085.43	0.00	1085.43
NO2	KG/HR	0.00	0.05	0.05	0.05	0.05	0.05	0.00	0.05
CH4	KG/HR	3652.59	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Mass vapor fraction		1.00	1.00	1.00	1.00	1.00	1.00	0.00	1.00
Mass solid fraction		0.00	0.00	0.00	0.00	0.00	0.00	1.00	0.00
Mass flow rate, mixture	KG/HR	1451920.00	1510360.00	1510360.00	1510360.00	1510360.00	1510360.00	6685.55	1503670.00
Volume flow rate, mixture	L/MIN	29664700.00	74130100.00	62308400.00	51604300.00	44468300.00	33764200.00	33.31	33764200.00
Temperature	C	200.50	765.66	600.00	450.00	350.00	200.00	200.00	200.00
Pressure	ATM	1.10	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Molecular weight, mixture		28.82	28.88	28.88	28.88	28.88	28.88	56.08	28.82

Table 9.6 Continued

	Units	L618	L619	L620	L621	L622	L623	L624
Mass Flow	KG/HR	211742.00	211742.00	211742.00	219060.00	219060.00	219060.00	219060.00
Mass Enthalpy	CAL/SEC	-1.86E+08	-2.20E+08	-2.20E+08	-2.29E+08	-2.18E+08	-2.00E+08	-1.81E+08
Components								
XYLOSE	KG/HR	0.10	0.10	0.10	0.00	0.00	0.00	0.00
ARABINOS	KG/HR	0.05	0.05	0.05	0.00	0.00	0.00	0.00
H2O	KG/HR	210905.00	210905.00	210905.00	219060.00	219060.00	219060.00	219060.00
AACID	KG/HR	437.56	437.56	437.56	0.00	0.00	0.00	0.00
H2SO4	KG/HR	0.07	0.07	0.07	0.00	0.00	0.00	0.00
FURFURAL	KG/HR	399.11	399.11	399.11	0.00	0.00	0.00	0.00
HMF	KG/HR	0.03	0.03	0.03	0.00	0.00	0.00	0.00
SOLBLIGN	KG/HR	0.03	0.03	0.03	0.00	0.00	0.00	0.00

Mass vapor frac		1.00	0.00	0.00	0.00	0.00	0.49	1.00
Mass solid frac		0.00	0.00	0.00	0.00	0.00	0.00	0.00
Mass flow rate,	KG/HR	211742.00	211742.00	211742.00	219060.00	219060.00	219060.00	219060.00
Volume flow rate,	L/MIN	5982500.00	3719.88	3719.90	3800.31	4825.38	57686.33	156152.00
Temperature	C	100.15	70.00	70.00	57.94	233.88	300.97	525.00
Pressure	ATM	1.00	1.00	1.10	85.00	85.00	85.00	85.00
Molecular weight		18.07	18.07	18.07	18.02	18.02	18.02	18.02

Table 9:7: Area-600A Evaporator

	Units	EL101	EL102	EL103	EL104	EL105	EL106	EL107
Mass Flow	KG/HR	940999.00	896483.00	44516.01	3510.18	41005.83	170941.00	170941.00
Mass Enthalpy	CAL/SEC	-9.56E+08	-9.34E+08	-2.19E+07	-2.99E+06	-1.80E+07	-1.76E+08	-1.77E+08
Components								
CELLULOS	KG/HR	2049.85	0.00	2049.85	0.00	2049.85	0.00	0.00
XYLAN	KG/HR	71.99	0.00	71.99	0.00	71.99	0.00	0.00
LIGNIN	KG/HR	6990.94	0.00	6990.94	0.00	6990.94	0.00	0.00
GALACTOS	KG/HR	676.41	642.59	33.82	0.00	33.82	0.00	0.00
MANNOSE	KG/HR	0.01	0.01	0.00	0.00	0.00	0.00	0.00
ARABINAN	KG/HR	0.21	0.00	0.21	0.00	0.21	0.00	0.00
MANNAN	KG/HR	0.10	0.00	0.10	0.00	0.10	0.00	0.00
GALACTAN	KG/HR	5.22	0.00	5.22	0.00	5.22	0.00	0.00
H2O	KG/HR	894260.00	885317.00	8942.60	3324.78	5617.82	170941.00	170941.00
CO2	KG/HR	43.77	41.58	2.19	2.19	0.00	0.00	0.00
H2	KG/HR	0.01	0.01	0.00	0.00	0.00	0.00	0.00
BUTANOL	KG/HR	2040.93	1938.89	102.05	85.16	16.89	0.00	0.00
ETHANOL	KG/HR	651.10	618.55	32.56	27.19	5.36	0.00	0.00
ACETONE	KG/HR	447.81	425.42	22.39	20.70	1.70	0.00	0.00

AACID	KG/HR	1298.35	1233.43	64.92	28.06	36.86	0.00	0.00
BACID	KG/HR	768.35	729.93	38.42	13.64	24.77	0.00	0.00
H2SO4	KG/HR	45.87	43.58	2.29	0.00	2.29	0.00	0.00
ASH	KG/HR	6016.81	0.00	6016.81	0.00	6016.81	0.00	0.00
EXTACTIV	KG/HR	2972.38	2823.76	148.62	0.00	148.62	0.00	0.00
FURFURAL	KG/HR	289.39	274.92	14.47	8.42	6.05	0.00	0.00
HMF	KG/HR	102.08	96.97	5.10	0.00	5.10	0.00	0.00
NH3	KG/HR	0.81	0.77	0.04	0.03	0.01	0.00	0.00
CLOSTRID	KG/HR	13616.70	0.03	13616.67	0.00	13616.67	0.00	0.00
CELLULAS	KG/HR	854.78	0.00	854.78	0.00	854.78	0.00	0.00
KH2PO4	KG/HR	0.01	0.00	0.01	0.00	0.01	0.00	0.00
NH4ACETA	KG/HR	2244.63	0.00	2244.63	0.00	2244.63	0.00	0.00
PROTEIN	KG/HR	3134.51	0.00	3134.51	0.00	3134.51	0.00	0.00
SOLBLIGN	KG/HR	367.94	349.55	18.40	0.00	18.39	0.00	0.00
NH4SO4	KG/HR	2048.27	1945.86	102.41	0.00	102.41	0.00	0.00
Mass vapor fraction		0.00	0.00	0.00	1.00	0.00	0.00	0.00
Mass solid fraction		0.03	0.00	0.74	0.00	0.80	0.00	0.00
Mass flow rate, mixture	KG/HR	940999.00	896483.00	44516.01	3510.18	41005.83	170941.00	170941.00
Volume flow rate, mixture	L/MIN	15759.86	15195.05	564.69	96246.66	520.48	2971.70	3036.25
Temperature	C	35.00	35.00	35.00	102.37	102.37	100.00	80.00
Pressure	ATM	0.10	1.00	1.00	1.00	1.00	13.00	1.00
Molecular weight, mixture		18.57	18.20	31.26	18.73	33.16	18.02	18.02

Table 9:8: Area-700 Steam and Power generation

	Units	L701	L702	L703	L704	L705	L706	L707	L708
Mass Flow	KG/HR	244201.00	244201.00	170941.00	73260.41	73260.41	65934.37	7326.04	7326.04
Mass Enthalpy	CAL/SEC	-2.02E+08	-2.09E+08	-1.47E+08	-6.28E+07	-6.33E+07	-5.70E+07	-6.33E+06	-6.61E+06
Components									
H2O	KG/HR	244201.00	244201.00	170941.00	73260.41	73260.41	65934.37	7326.04	7326.04
Mass vapor fraction		1.00	1.00	1.00	1.00	1.00	1.00	1.00	0.91
Mass solid fraction		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Mass flow rate, mixture	KG/HR	244201.00	244201.00	170941.00	73260.41	73260.41	65934.37	7326.04	7326.04
Volume flow rate, mixt	L/MIN	174073.00	815309.00	570717.00	244593.00	376468.00	338821.00	37646.81	1115650.00
Temperature	C	525.00	291.11	291.11	291.11	234.59	234.59	234.59	53.91
Pressure	ATM	85.00	12.83	12.83	12.83	7.50	7.50	7.50	0.15
Molecular weight, mix		18.02	18.02	18.02	18.02	18.02	18.02	18.02	18.02

9.2.   Equipment Design and Sizing

Under this section the main equipment sizes are presented with their incoming flowrates. For equipment such as fermenters and buffer tanks, the flowrates, density and residence time were used to size them using the following equation:

$$V = \frac{\dot{v} * \tau}{\rho}$$

Where V = volume in m^3, $\dot{v}$= flow rate in kg/hr, τ = mean residence time in hr and ρ = average density of vessel contents in kg/m^3

Shortcut methods in ASPEN Plus (2013)were used when sizing columns in downstream separation area. The columns dimensions were evaluated following a procedure described in (Sinnott 2009). The plate spacing$l$ of 0.5m was assumed. This gives enough space to get in through the column during clean-up purposes.The column diameter was calculated according to the following equations:

$$u_v = (-0.17l^2 + 0.27l - 0.047)\left[\frac{\rho_L - \rho_v}{\rho_v}\right]^{0.5}$$

Where u_v is the maximum allowable vapor velocity, based on the gross (total) column cross sectional area, m/s, and l is the plate spacing in meters.

$$D_c = \sqrt{\frac{4V_w}{\pi \rho_v u_v}}$$

Where $D_c$is the column diameter m, V_w is the maximum vapor rate in kg/s.

SSF-GS/DDProcess Scenario

Table 9:9: Major Equipment Sizes in upstream processes for SSF-GS/DD process scenario (the working volume represents 10 units)

	Equipment Name							
	Pretreatment Reactor	Conditioning Reactor	Conditioned Slurry Tank	SSF Fermenter	Condensate Tank	Decanter	Biogas Digester	De-aerator
Mass (kg/hr)	1098951	1012218.91	1049374.46	1050234.78	132389	55021.21	944186.35	249843
Residence Time (hr)	1	0.5	1	72	4	2	72	0.5
Mass Desnsity (kg/m^3)	1459.791067	981.2589	1670.33	1807.250355	1005.008	920.4701	953.8428	957.962
Volume (m^3):working	752.8138958	618.93079	628.24	46024.94287	526.9171987	131.5052624	71271.09114	130.4034

Table 9:10: Column Sizing in downstream separation and purification process for SSF-GS/DD process scenario

Name	Beer Column	Acetone Column	Ethanol Column	Butanol Column	Water Column	Scrubber Column
Stream	L404	L409	L418	L426	L428	L416
V max vapour rate (kg/s)	18.18	17.39	15.75	2.84	0.29	1.37
N theor from Aspen/Lit	45.00	30.00	40.00	15.00	15.00	2.00
ε tray efficiency	0.70	0.70	0.70	0.70	0.70	0.70
l plate spacing (m)	0.50	0.50	0.50	0.50	0.50	0.50
H:D	28.12	16.55	31.54	25.22	73.61	5.39
N actual=N/ε	64.29	42.86	57.14	21.43	21.43	2.86
ρv gas mixture	0.76	1.33	0.39	0.74	0.76	1.51
MG gas Mr	23.09	22.61	21.19	30.95	31.86	38.89
ρM gas molar desnsity	3.30E-05	4.15E-02	1.12E-05	2.39E-05	2.39E-05	3.89E-05
ρl liq mixture	904.73	937.98	920.47	730.52	924.39	232.99
V vap velocity	1.57	1.21	2.20	1.43	1.58	0.56
*H tower height=2.3*N actual*	147.86	98.57	131.43	49.29	49.29	6.57
D_T tower diameter	5.26	5.96	4.17	1.95	0.67	1.22

SSF-GS/LLE&D Process Scenario

Table 9:11: Major Equipment Sizes in upstream processes for SSF-GS/LLE&D process scenario (the working volume represents 10 units)

	Equipment Name						
	Pretreatment Reactor	Conditioning Reactor	Conditioned Slurry Tank	SSF Fermenter	Condensate Tank	Biogas Digester	De-aerator
Mass (kg/hr)	1098951	1012214.91	1049374	1050234.78	29615.02	1012086.25	152894
Residence Time (hr)	1	0.5	1	72	4	72	0.5
Mass Desnsity (kg/m^3)	1459.791067	981.3109	1669.322	1807.27635	840.6529	515.85575	954.3046
Volume (m^3):working	752.8138958	515.74629	628.623	46024.2807	140.9143774	141260.8273	80.10754637

Table 9:12: Column Sizing in downstream separation process for SSF-GS/LLE&D process scenario

Name	LLE Column	Extraction Recovery	Butanol Recovery
Stream	EX-401	ER-402	BU-403
V max vapour rate (kg/s)	n/a	3.734	1.025
N theor from Aspen/Lit	6.00	15.000	15.000
ε tray efficiency	0.70	0.700	0.700
*l*plate spacing (m)	0.50	0.500	0.500
H:D	20.00	7.838	16.560
N actual=N/ε	8.57	21.429	21.429
ρv gas mixture	n/a	744.173	709.562
MG gas Mr	n/a	67.635	54.949
ρM gas molar density	n/a	11.003	13.484
ρl liq mixture	n/a	789.049	740.919
V vap velocity	n/a	0.011	0.010
*H tower height=2.3*N actual*	19.7143	49.286	49.286
D_T tower diameter	n/a	6.288	2.976

Sizing of heat exchangers, reboilers and condensers was done by getting the heat duty Q of equipment from ASPEN Plus®. Then Log Mean Temperature Difference (LMTD) for heat exchanger was calculated. The heat transfer coefficients (*U*) were sourced from literature. Heat transfer area (*A*) was then calculated from equation shown. It was assumed that all heat exchangers are counter-current with the process stream being the stream that needs to either cool down or be heated. The service stream was either of cooling water, refrigerant or steam. For heat integration purposes, the service stream is that of high temperature used to heat up the low temperature stream. ΔT_1 is the temperature difference between hot inlet stream and cold outlet stream while ΔT_2 is the temperature difference between hot outlet stream and cold inlet stream.

$$LMTD = \frac{\Delta T_1 - \Delta T_2}{ln(\frac{\Delta T_1}{\Delta T_2})}$$

$$A = \frac{Q}{\cup * LMTD}$$

SSF-GS/DDProcess scenario

Table 9:13: A summary for Heat exchangers, condensers and reboilers sizing for SSF-GS/DD process scenario (the Area represents 10 units)

HEAT EXCHANGERS		HE-301	HE-302	HE-401
Stream		L301	L310	L402
Type		Floating-head S&T	Floating-head S&T	Floating-head S&T
Area	m^2	1331.33	3155.35	210.51
Q (Duty)	MW (MJ/s)	-10.38	-98.26	7.74
U	W/m^2K	850.00	950.00	850.00
LMTD	^{o}C	9.17	32.78	43.26
Process Stream Temps				
T_{in}	^{o}C	54.09	35.00	0.02
T_{out}	^{o}C	35.00	-10.00	44.50
Service Stream Temps				
T_{in}	^{o}C	20.00	-33.00	89.65
T_{out}	^{o}C	49.00	-10.00	100.03
Cp (specific heat capacity)	kJ/kg.^{o}C	0.00	0.04	0.00
m.Cp (heat capacity rate)	MW/^{o}C	0.54	2.18	0.17
Stream Flowrate (m)	Kg/hr	1049380.00	216193.00	142473.00

Table 9:13 Continued

HEAT EXCHANGERS		HE-402	HE-403	BE-401 Reboiler	AC-402 Condenser
Stream		L409	L427	L405	L408
Type		Floating-head S&T	Floating-head S&T	Kettle	Partial Vapour
Area	m^2	99.73	154.53	81.43	1023.57
Q (Duty)	MW (MJ/s)	-0.79	-5.23	17.88	-19.89
U	W/m^2K	850.00	850.00	850.00	850.00
LMTD	^{o}C	9.31	39.80	258.33	22.86
Process Stream Temps					
T_{in}	^{o}C	50.00	79.91	44.50	89.65
T_{out}	^{o}C	53.78	70.25	100.03	31.22
Service Stream Temps					
T_{in}	^{o}C	20.00	20.00	331.59	20.00
T_{out}	^{o}C	49.00	49.00	331.59	49.00
Cp (specific heat capacity)	kJ/kg.^{o}C	0.03	0.16	0.01	0.05
m.Cp (heat capacity rate)	MW/^{o}C	0.21	0.54	0.32	0.34
Stream Flowrate (m)	Kg/hr	24313.72	12365.24	110982.00	24313.72

Table 9:13 Continued

HEAT EXCHANGERS		AC-402 Reboiler	ET-403 Condenser	ET-403 Reboiler	WA-404 Reboiler
Stream		L409	L417	L418	L427
Type		Kettle	Partial Vapour	Kettle	Kettle
Area	m^2	46.57	1820.71	60.09	2.98
Q (Duty)	MW (MJ/s)	9.73	-13.32	14.03	0.65
U	W/m^2K	850.00	850.00	850.00	850.00
LMTD	^{o}C	245.70	8.61	274.71	256.60
Process Stream Temps					
T_{in}	^{o}C	89.65	50.00	50.00	70.00
T_{out}	^{o}C	82.09	50.39	63.64	79.91
Service Stream Temps					
T_{in}	^{o}C	331.59	20.00	331.59	331.59
T_{out}	^{o}C	331.59	49.00	331.59	331.59
Cp (specific heat capacity)	$kJ/kg.^{o}C$	0.19	5.35	0.16	0.02
m.Cp (heat capacity rate)	$MW/^{o}C$	1.29	34.00	1.03	0.07
Stream Flowrate (m)	Kg/hr	24313.72	22897.72	22897.72	12365.24

Table 9:13Continued

HEAT EXCHANGERS		BU-405 Reboiler	HE-501	HE-201
Stream		L423	L501	L202
Type		Kettle	Floating-head S&T	Floating-head S&T
Area	m^2	23.31	925.87	967.79
Q (Duty)	MW (MJ/s)	5.02	-11.81	-5.38
U	W/m^{2}K	850.00	850.00	850.00
LMTD	^{o}C	253.33	15.01	6.54
Process Stream Temps				
T_{in}	^{o}C	70.00	53.91	50.00
T_{out}	^{o}C	86.33	53.91	35.00
Service Stream Temps				
T_{in}	^{o}C	331.59	20.00	20.00
T_{out}	^{o}C	331.59	49.00	49.00
Cp (specific heat capacity)	kJ/kg.^{o}C	0.08	-	0.03
m.Cp (heat capacity rate)	MW/^{o}C	0.31	0.00	0.36
Stream Flowrate (m)	Kg/hr	13739.15	19715.40	50610.76

Table 9:14: A summary for Heat exchangers, condensers and reboilers sizing for SSF-GS/LLE&D scenario (the Area represents 10 units)

HEAT EXCHANGERS		HE-301	HE-302	HE-401
Stream		L301	L310	L402
Type		Floating-head S&T	Floating-head S&T	Floating-head S&T
Area	m^2	1331.33	3155.34	125.43
Q (Duty)	MW (MJ/s)	-10.38	-98.26	7.74
U	W/m^2K	850	950	850
LMTD	^oC	9.17	32.78	72.59
Process Stream Temps				
T_{in}	^oC	54.09	35	-10.70
T_{out}	^oC	35	-10	10
Service Stream Temps				
T_{in}	^oC	20	-33	185.90
T_{out}	^oC	49	-10	-0.30
Cp (specific heat capacity)	$kJ/kg.^oC$	0.0018	0.0364	0.033
m.Cp (heat capacity rate)	$MW/^oC$	0.544	2.183	0.374
Stream Flowrate (m)	Kg/hr	1049380	216193	40061.65

Table 9:14 Continued

HEAT EXCHANGERS		ER-402 Reboiler	ER-402 Condenser	BU-403 Reboiler	BU-403 Condenser
Stream		L409	L412	L415	L414
Type		Kettle	Total	Kettle	Total
Area	m^2	114.50	1256.12	402.74	77.02
Q (Duty)	MW (MJ/s)	17.88	-33.80	23.62	-13.32
U	W/m^2K	850	850	850	850
LMTD	^{o}C	183.71	31.65	69.01	203.54
Process Stream Temps					
T_{in}	^{o}C	10	10	80.06	80.05
T_{out}	^{o}C	185.82	10	117.70	58.92
Service Stream Temps					
T_{in}	^{o}C	191.92	20	191.9158	20
T_{out}	^{o}C	191.92	49	191.9158	49
Cp (specific heat capacity)	kJ/kg.^{o}C	0.0081	0.312	0.232	0.615
m.Cp (heat capacity rate)	MW/^{o}C	0.1017	1.165	0.627	0.630
Stream Flowrate (m)	Kg/hr	45152.16	13444	9754	3690

Table 9:14 Continued

HEAT EXCHANGERS		HE-601	HE-501	HE-201
Stream		L609	L501	L201
Type		Floating-head S&T	Double-Pipe	Floating-head S&T
Area	m^2	77.11	20.22	967.79
Q (Duty)	MW (MJ/s)	14.02	-0.38	-5.38
U	W/m^{2}K	850	850	850
LMTD	^{o}C	213.84	22.45	6.54
Process Stream Temps				
T$_{in}$	^{o}C	36.68	53.91	50
T$_{out}$	^{o}C	243.06	53.91	35
Service Stream Temps				
T$_{in}$	^{o}C	350	20	20
T$_{out}$	^{o}C	350	49	49
Cp (specific heat capacity)	kJ/kg.^{o}C	0.000168	-	0.0255
m.Cp (heat capacity rate)	MW/^{o}C	0.06791	4.27831E-05	0.3586
Stream Flowrate (m)	Kg/hr	1456850	9020.264	50610.76

9.3. Fermentation Schedule

Fermentation schedule for all processes was designed after equipment sizing. This was because the schedule depends onsize of inoculum needed. The size of inoculum in terms of volume also depends on size of main fermenters.

Fermentation schedule for SSF-GS/DD and SSF-GS/LLE&D Process Scenarios
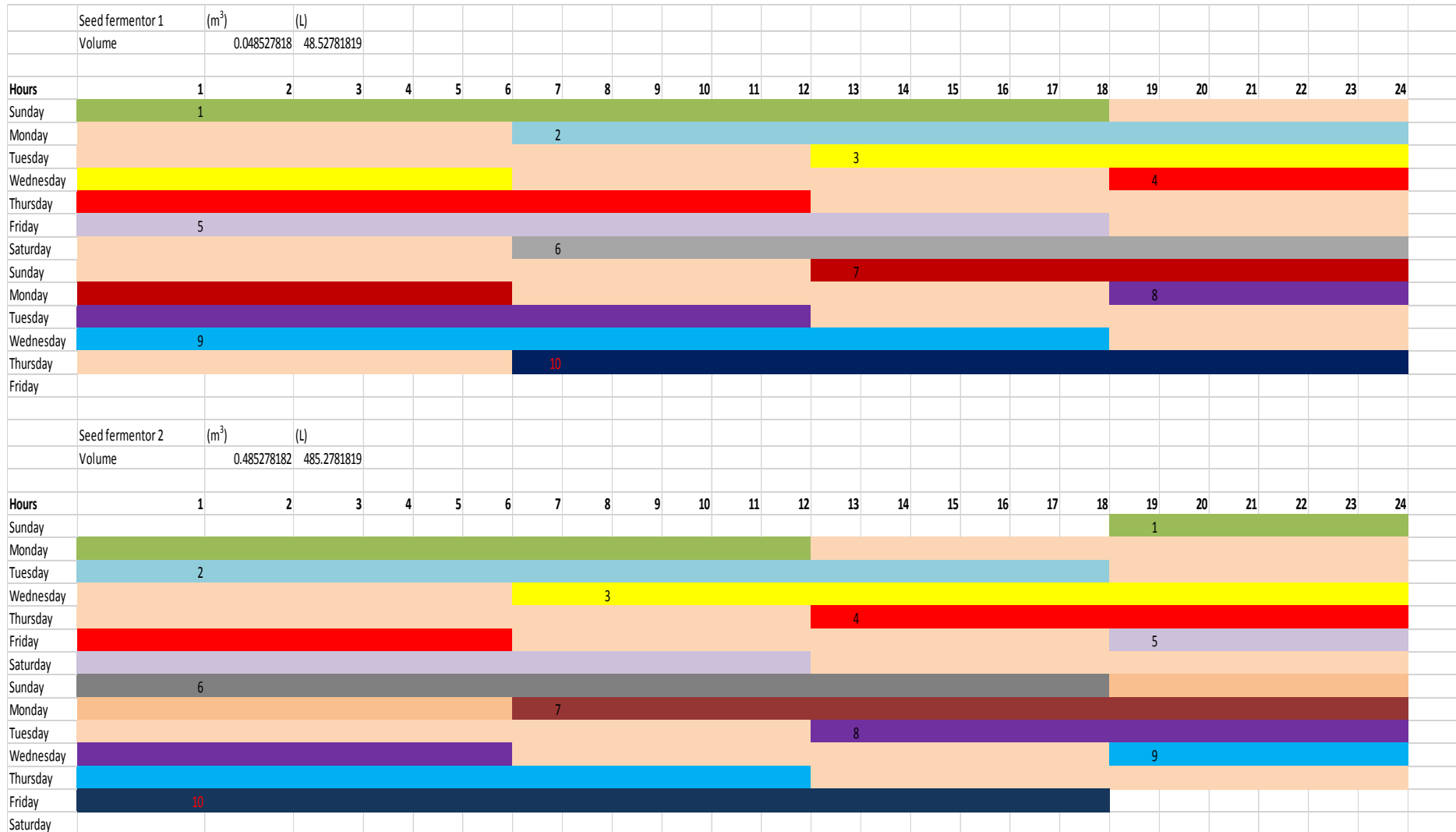
Figure 9-1: A train of 5 seed fermenters that alternate between 3 main fermenters for SSF-GS/DD and SSF-GS/LLE&D Process Scenarios

	Seed fermentor 3	(m³)	(L)
	Volume	4.852781819	4852.781819

Hours	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24
Monday													1											
Tuesday																			2					
Wednesday																								
Thursday	3																							
Friday							4																	
Saturday													5											
Sunday																			6					
Monday																								
Tuesday	7																							
Wednesday							8																	
Thursday													9											
Friday																			10					
Saturday	10																							

	Seed fermentor 4	(m³)	(L)
	Volume	48.52781819	48527.81819

Hours	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24
Tuesday							1																	
Wednesday													2											
Thursday																			3					
Friday	4																							
Saturday	4																							
Sunday								5																
Monday													6											
Tuesday																			7					
Wednesday																								
Thursday	8																							
Friday								9																
Saturday													10											
Sunday																								
Monday																								

Figure 9-1 Continued.

Figure 9-1 Continued.

Figure 9-1 Continued.

Fermentation schedule for CONT-SHF/DD and CONT-SHF/LLE&D process scenarios

The whole schedule is divided into seed fermenters 1,2; 3,4 and seed fermenter 5 and 2 main fermenters which will be maintained by a train of 5 seed fermenters. This breakdown is only because of spacethat cannot accommodate the train and two fermenters. However, the full schedule can be checked in the DD that accompanies the thesis. What can be seen from Figure 9-2 is that seed fermenter 5 is the one that inoculates main fermenter where seed becomes ready after 15 hours. For these scenarios, only one seed train was required because the processes are of continuous fermentation. This schedule is similar to that of B-SHF/DD and B-SHF/LLE&D process scenarios. The difference is that B-SHF/DD and B-SHF/LLE&D process scenarios requires 5 seed trains since it has been shown from the schedule that one train can supply two main fermenters.
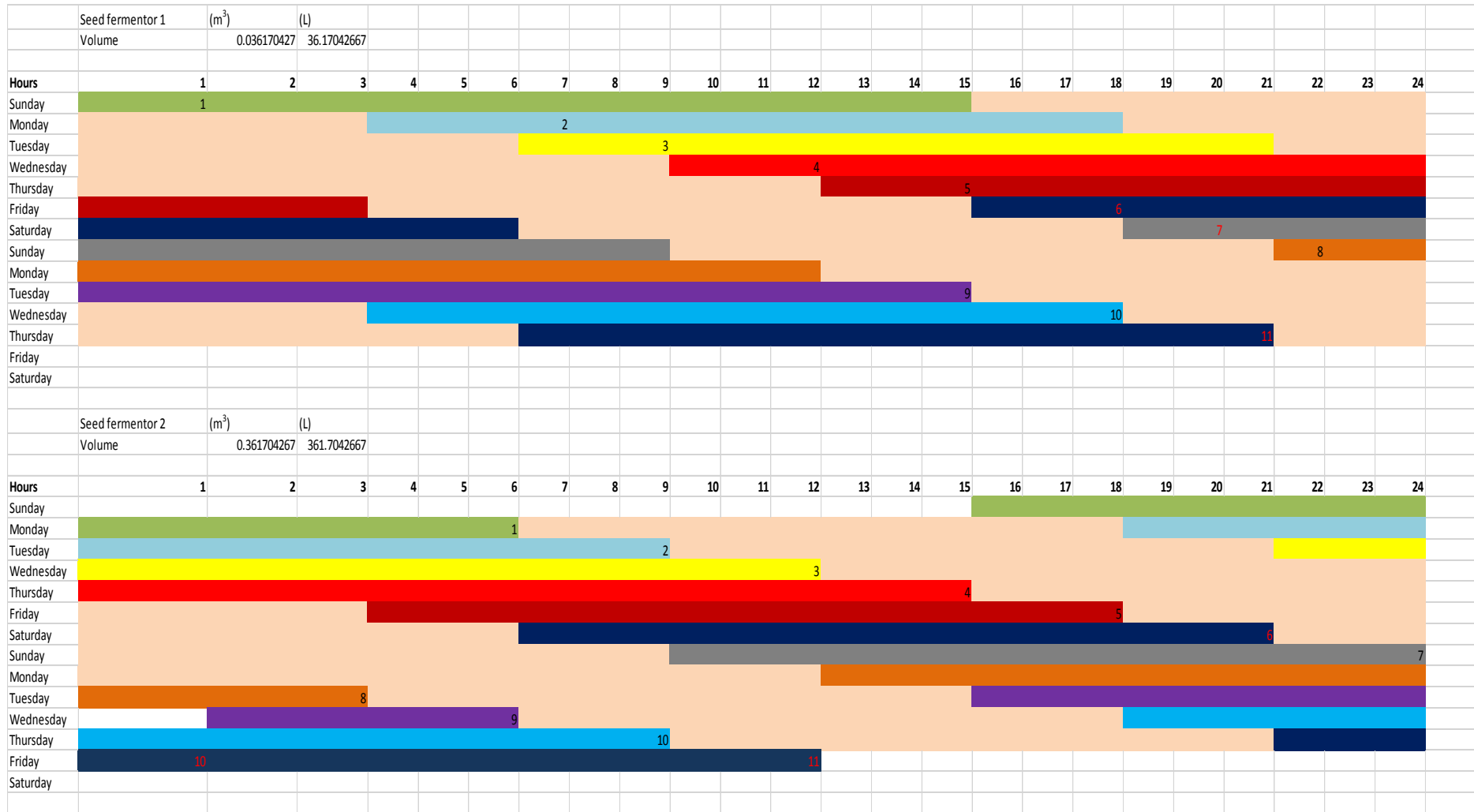
Figure 9-2: A train of 5 seed fermenters that alternate between 2 main fermenters for CONT-SHF/DD and CONT-SHF/LLE&D process scenarios

| | Seed fermentor 3 | (m³) | (L) | | | | | | | | | | | | | | | | | | | | | |
| | Volume | 3.617042667 | 3617.042667 | | | | | | | | | | | | | | | | | | | | | |

Hours	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24
Sunday																								
Monday							1																	
Tuesday										2														
Wednesday												3												
Thursday	4													4										
Friday	5																	5						
Saturday	6																				6			
Sunday																								
Monday	7														7									
Tuesday				8														8						
Wednesday																			9					
Thursday										10														10
Friday												11												
Saturday	10																							

| | Seed fermentor 4 | (m³) | (L) | | | | | | | | | | | | | | | | | | | | | |
| | Volume | 36.17042667 | 36170.42667 | | | | | | | | | | | | | | | | | | | | | |

Hours	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24
Sunday																								
Monday																						1		
Tuesday							1																	
Wednesday										2														
Thursday														3										
Friday																		4						
Saturday																								5
Sunday											6													
Monday														7										
Tuesday																	8							
Wednesday																			9					
Thursday	8																							
Friday										10														
Saturday												11												
Sunday																								

Figure 9-2 Continued

Figure 9-2 Continued.

9.4.   Fermentation Parameters

Table 9:15: Fermentation kinetics for all six process scenarios

	Operating Conditions		
	SSF-GS/DD and SSF-GS/LLE&D process scenarios	CONT-SHF/DD and CONT-SHF /LLE&D process scenario	B-SHF/DD and B-SHF /LLE&D process scenario
Temperature (℃)	35	35	37
Pressure (bar)	1	1	1
Fermentation time (h)	72	40	40
ABE Yield (g/g)	0.41	0.37	0.33
ABE Productivity (g/l/h)	0.31	0.34	0.39
Gas Flowrate (l/min)	4	n/a	n/a
A:B:E	6.4:12.9:2.1	3.85: 9.29: 0.3	4.33: 9.71: 1.33

9.5. Economic Assessment Results

The tables under this section give summary of the economic results such as DCF analysis, Raw materials cost per kg butanol and summary of economic parameters including total capital investment for all scenarios

SSF-GS/DD Process Scenario

Table 9:16: Discounted cash flow analysis for profitability assessment for SSF-GS/DD processscenario

			Discounted Cash Flow								
Year	Loan Payment	Loan Principal	Loan Payment Interest	Revenue	Expenses	Gross Profit	Depreciation	Net Profit	Cash Flow	DCF	Cummulative DCF
-2		19599716.34	1234782.129						-14194631.56	-16957602.40	-16957602.40
-1		166597588.9	10495648.1						-97998581.68	-107112449.77	-124070052.17
0		244996454.2	15434776.61						-72682281.41	-72682281.41	-196752333.59
1	33761893.56	226669337.2	15434776.61	91525929.40	81412712.03	10113217.37	28582919.66	-13298185.65	15284734.01	13984203.12	-182768130.47
2	33761893.56	207187611.93	14280168.25	122034572.53	81412712.03	40621860.50	28582919.66	8668037.41	37250957.06	31181507.76	-151586622.71
3	33761893.56	186478537.92	13052819.55	122034572.53	81412712.03	40621860.50	28582919.66	8668037.41	37250957.06	28528369.40	-123058253.30
4	33761893.56	164464792.25	11748147.89	122034572.53	81412712.03	40621860.50	28582919.66	8668037.41	37250957.06	26100978.41	-96957274.89
5	33761893.56	141064180.60	10361281.91	122034572.53	81412712.03	40621860.50	28582919.66	8668037.41	37250957.06	23880126.64	-73077148.26
6	33761893.56	116189330.42	8887043.378	122034572.53	81412712.03	40621860.50	28582919.66	8668037.41	37250957.06	21848240.29	-51228907.97
7	33761893.56	89747364.67	7319927.816	122034572.53	81412712.03	40621860.50	28582919.66	8668037.41	37250957.06	19989240.89	-31239667.08
8	33761893.56	61639555.08	5654083.974	122034572.53	81412712.03	40621860.50	28582919.66	8668037.41	37250957.06	18288418.01	-12951249.07
9	33761893.56	31760953.49	3883291.97	122034572.53	81412712.03	40621860.50	28582919.66	8668037.41	37250957.06	16732312.91	3781063.84
10	33761893.56	0.00	2000940.07	122034572.53	81412712.03	40621860.50	28582919.66	8668037.41	37250957.06	15308611.99	19089675.83
11	0.00	0.00	0.00	122034572.53	81412712.03	40621860.50	28582919.66	8668037.41	37250957.06	14006049.40	33095725.23
12	0.00	0.00	0.00	122034572.53	81412712.03	40621860.50	28582919.66	8668037.41	37250957.06	12814317.84	45910043.08
13	0.00	0.00	0.00	122034572.53	81412712.03	40621860.50	28582919.66	8668037.41	37250957.06	11723987.05	57634030.12
14	0.00	0.00	0.00	122034572.53	81412712.03	40621860.50	28582919.66	8668037.41	37250957.06	10726429.14	68360459.26
15	0.00	0.00	0.00	122034572.53	81412712.03	40621860.50	28582919.66	8668037.41	37250957.06	9813750.35	78174209.61
16	0.00	0.00	0.00	122034572.53	81412712.03	40621860.50	28582919.66	8668037.41	37250957.06	8978728.59	87152938.21
17	0.00	0.00	0.00	122034572.53	81412712.03	40621860.50	28582919.66	8668037.41	37250957.06	8214756.26	95367694.47
18	0.00	0.00	0.00	122034572.53	81412712.03	40621860.50	28582919.66	8668037.41	37250957.06	7515787.98	102883482.45
19	0.00	0.00	0.00	122034572.53	81412712.03	40621860.50	28582919.66	8668037.41	37250957.06	6876292.75	109759775.20
20	0.00	0.00	0.00	122034572.53	81412712.03	40621860.50	28582919.66	8668037.41	37250957.06	6291210.20	116050985.41
21	0.00	0.00	0.00	122034572.53	81412712.03	40621860.50	28582919.66	8668037.41	37250957.06	5755910.53	121806895.93
22	0.00	0.00	0.00	122034572.53	81412712.03	40621860.50	28582919.66	8668037.41	37250957.06	5266157.85	127073053.78
23	0.00	0.00	0.00	122034572.53	81412712.03	40621860.50	28582919.66	8668037.41	37250957.06	4818076.71	131891130.49
24	0.00	0.00	0.00	122034572.53	81412712.03	40621860.50	28582919.66	8668037.41	37250957.06	4408121.42	136299251.91
25	0.00	0.00	0.00	122034572.53	81412712.03	40621860.50	28582919.66	8668037.41	37250957.06	4033047.96	140332299.87

Figure 9-3: A cumulative discounted cash flow (DCF) for scenario SSF-GS/DD

Table 9:17: Summary of Sales Revenues, Operating Costs and Total Capital Investment for SSF-GS/DD processscenario

Techno-Economic Analysis for SSF-GS/DD Process Scenario	
Butanol Production Rate (kg/yr)	84344016.00
Market Value (US$/kg)	0.78
Acetone Production Rate (kg/yr)	31012264.00
Market Value (US$/kg)	1.10
Ethanol Production Rate (kg/yr)	15143272.00
Market Value (US$/kg)	0.69
Total Operating Costs (US$)	81412712.03
Sales Revenue (US$)	122034572.53
Fixed Capital Investment (US$)	408327423.66
Land (US$)	1128154.00
Working Capital (US$)	20416371.18
Total Capital Investment (US$)	429871948.85
Return On Investment: ROI (%)	1.81
Net Present Value: NPV ($)	140332299.87
Payback Period: PBP (years)	11.23
Internal Rate of Return: IRR (%)	16.19

Table 9:18: Raw materials cost per kg Butanol Produced for SSF-GS/DD processscenario

Raw Material	US$/kg Butanol	(%)
Wheat straw	0.652	80.30
H2SO4	0.005	0.67
Process Water	0.014	1.71
NH3 (Conditioning)	0.029	3.58
Cellulase	0.069	8.47
NH3 (Nutrients)	0.000	0.00
Cooling water	0.002	0.22
Refrigerant (NH3)	0.012	1.48
Boiler Feed Water	0.004	0.45
Glucose	0.000	0.00
Ash disposal	0.021	2.58
Waste water	0.004	0.54
SUM	0.812	100

SSF-GS/LLE&D Process Scenario

Table 9:19: Discounted cash flow analysis for profitability assessment for SSF-GS/LLE&D processscenario

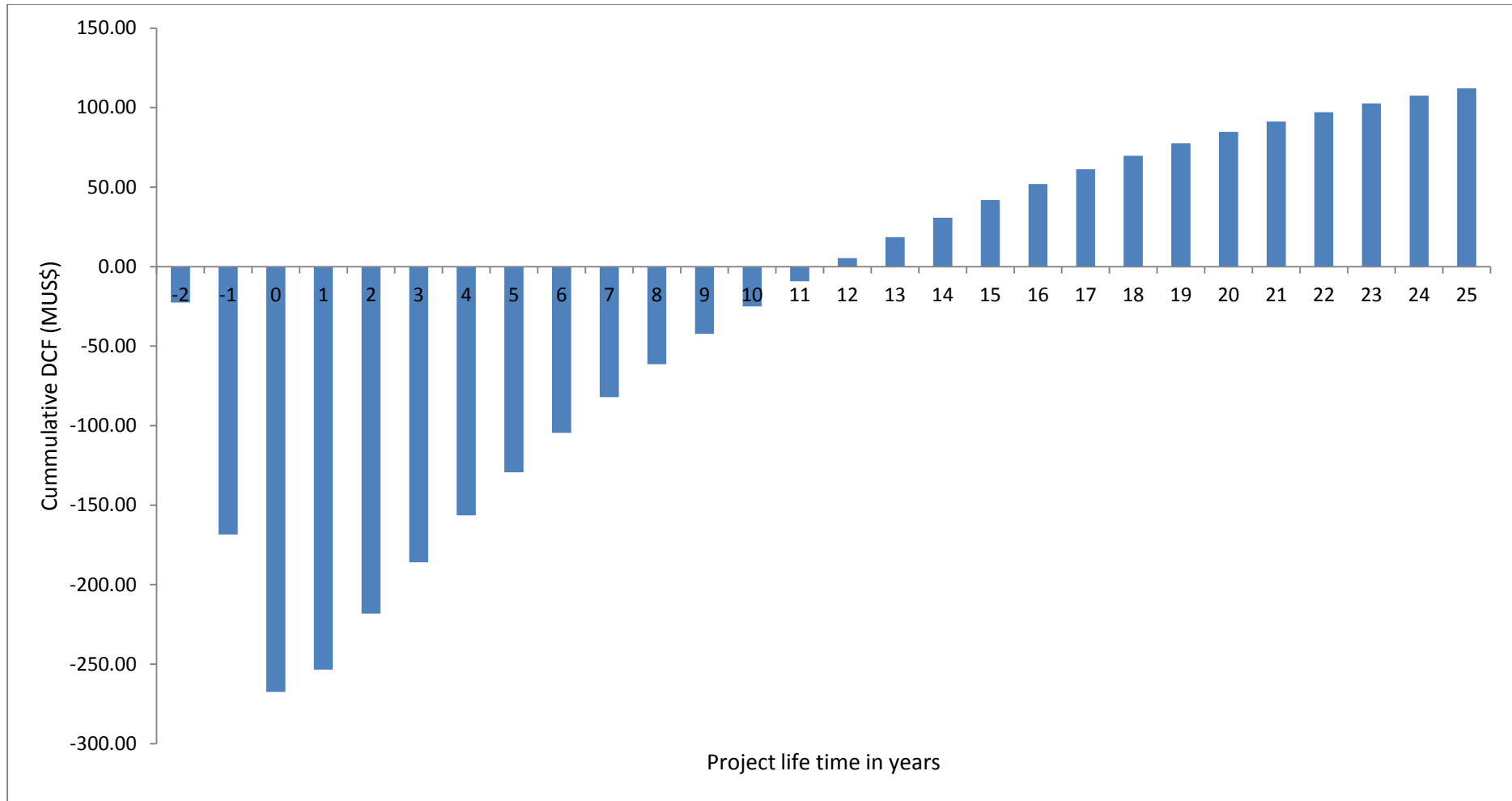|						Discounted Cash Flow					
Year	Loan Payment	Loan Principal	Loan Payment Interest	Revenue	Expenses	Gross Profit	Depreciation	Net Profit	Cash Flow	DCF	Cummulative DCF
-2		19853904.47	1250795.982						-14364090.32	-17160046.13	-17160046.13
-1		168758188	10631765.84						-99269522.35	-108501587.93	-125661634.06
0		248173805.9	15634949.77						-73624895.74	-73624895.74	-199286529.81
1	34199750.55	229609005.1	15634949.77	82831985.52	85690737.15	-2858751.63	33089840.78	-25882986.54	7206854.24	6593645.24	-192692884.57
2	34199750.55	209874621.87	14465367.32	110442647.36	85690737.15	24751910.21	33089840.78	-6003310.01	27086530.77	22673212.61	-170019671.96
3	34199750.55	188896972.50	13222101.18	110442647.36	85690737.15	24751910.21	33089840.78	-6003310.01	27086530.77	20744018.86	-149275653.11
4	34199750.55	166597731.22	11900509.27	110442647.36	85690737.15	24751910.21	33089840.78	-6003310.01	27086530.77	18978974.25	-130296678.86
5	34199750.55	142893637.74	10495657.07	110442647.36	85690737.15	24751910.21	33089840.78	-6003310.01	27086530.77	17364111.85	-112932567.01
6	34199750.55	117696186.37	9002299.178	110442647.36	85690737.15	24751910.21	33089840.78	-6003310.01	27086530.77	15886653.11	-97045913.90
7	34199750.55	90911295.56	7414859.741	110442647.36	85690737.15	24751910.21	33089840.78	-6003310.01	27086530.77	14534906.78	-82511007.12
8	34199750.55	62438956.63	5727411.62	110442647.36	85690737.15	24751910.21	33089840.78	-6003310.01	27086530.77	13298176.38	-69212830.75
9	34199750.55	32172860.35	3933654.268	110442647.36	85690737.15	24751910.21	33089840.78	-6003310.01	27086530.77	12166675.55	-57046155.20
10	34199750.55	0.00	2026890.202	110442647.36	85690737.15	24751910.21	33089840.78	-6003310.01	27086530.77	11131450.64	-45914704.56
11	0.00	0.00	0.00	110442647.36	85690737.15	24751910.21	33089840.78	-6003310.01	27086530.77	10184309.83	-35730394.73
12	0.00	0.00	0.00	110442647.36	85690737.15	24751910.21	33089840.78	-6003310.01	27086530.77	9317758.30	-26412636.43
13	0.00	0.00	0.00	110442647.36	85690737.15	24751910.21	33089840.78	-6003310.01	27086530.77	8524938.98	-17887697.45
14	0.00	0.00	0.00	110442647.36	85690737.15	24751910.21	33089840.78	-6003310.01	27086530.77	7799578.21	-10088119.24
15	0.00	0.00	0.00	110442647.36	85690737.15	24751910.21	33089840.78	-6003310.01	27086530.77	7135936.14	-2952183.10
16	0.00	0.00	0.00	110442647.36	85690737.15	24751910.21	33089840.78	-6003310.01	27086530.77	6528761.34	3576578.24
17	0.00	0.00	0.00	110442647.36	85690737.15	24751910.21	33089840.78	-6003310.01	27086530.77	5973249.17	9549827.41
18	0.00	0.00	0.00	110442647.36	85690737.15	24751910.21	33089840.78	-6003310.01	27086530.77	5465003.81	15014831.22
19	0.00	0.00	0.00	110442647.36	85690737.15	24751910.21	33089840.78	-6003310.01	27086530.77	5000003.49	20014834.71
20	0.00	0.00	0.00	110442647.36	85690737.15	24751910.21	33089840.78	-6003310.01	27086530.77	4574568.61	24589403.32
21	0.00	0.00	0.00	110442647.36	85690737.15	24751910.21	33089840.78	-6003310.01	27086530.77	4185332.67	28774735.99
22	0.00	0.00	0.00	110442647.36	85690737.15	24751910.21	33089840.78	-6003310.01	27086530.77	3829215.62	32603951.61
23	0.00	0.00	0.00	110442647.36	85690737.15	24751910.21	33089840.78	-6003310.01	27086530.77	3503399.47	36107351.07
24	0.00	0.00	0.00	110442647.36	85690737.15	24751910.21	33089840.78	-6003310.01	27086530.77	3205306.01	39312657.08
25	0.00	0.00	0.00	110442647.36	85690737.15	24751910.21	33089840.78	-6003310.01	27086530.77	2932576.40	42245233.48
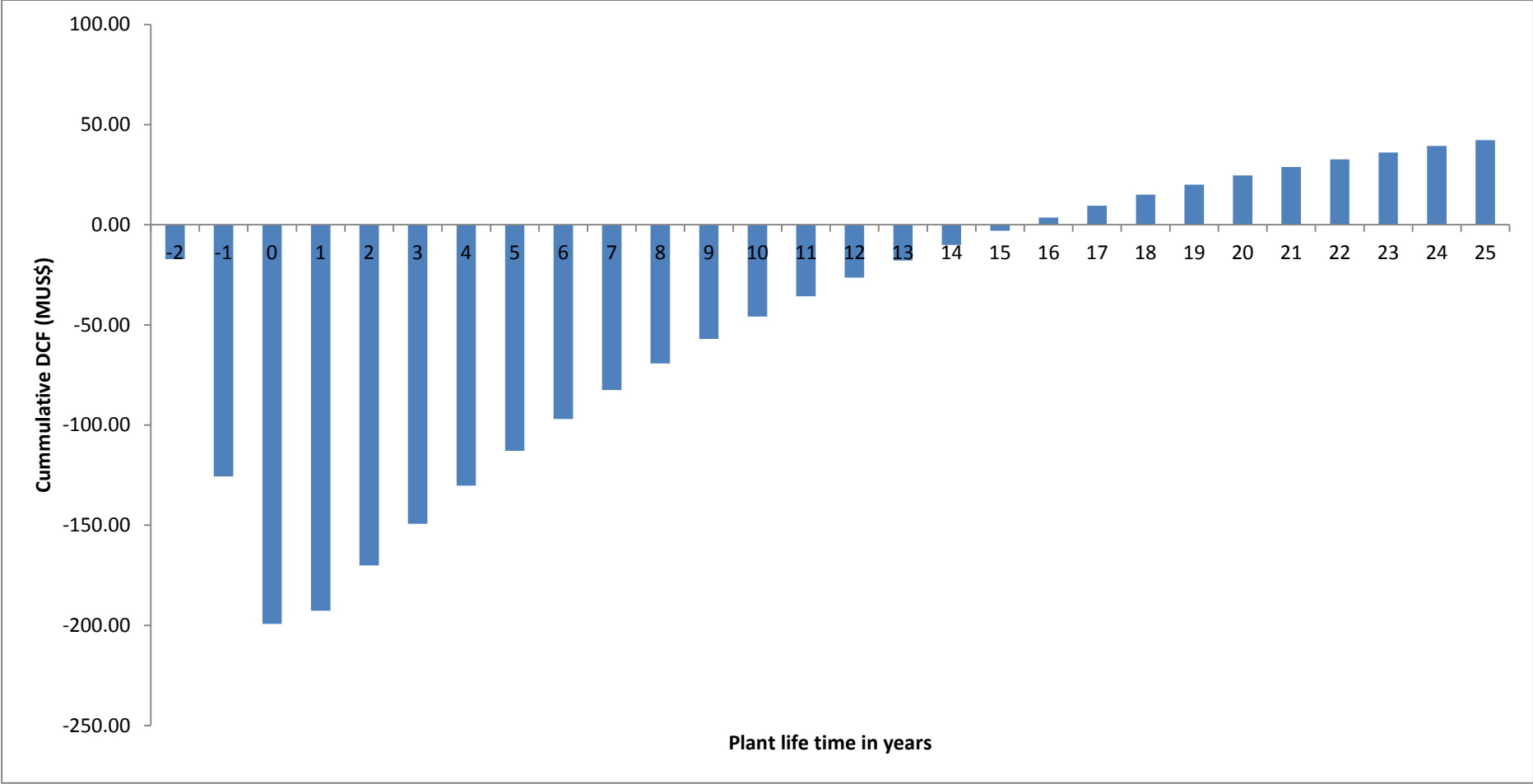
Figure 9-4: A cumulative discounted cash flow for scenario SSF-GS/LLE&D

Table 9:20: Summary of Sales Revenues, Operating Costs and Total Capital Investment for SSF-GS/LLE&D processscenario

Techno-Economic Analysis for SSF-GS/LLE&D Scenario	
Butanol Production Rate (kg/yr)	78032008.00
Market Value (US$/kg)	0.78
Acetone/ethanol Production Rate (kg/yr)	29520000.00
Market Value (US$/kg)	1.10
Total Operating Costs (US$)	85690737.15
Sales Revenue (US$)	110442647.36
Fixed Capital Investment (US$)	413623009.80
Land (US$)	1128154.00
Working Capital (US$)	20681150.49
Total Capital Investment (US$)	435432314.30
Return On Investment: ROI (%)	n/a
Net Present Value (US$)	42245233.48
Payback Period: PBP (years)	15.73
Internal Rate of Return: IRR (%)	11.50

Table 9:21: Raw materials cost per kg Butanol Produced for SSF-GS/LLE&D processscenario

Raw Material	US$/kg Butanol	(%)
Wheat straw	0.704	75.60
H2SO4	0.006	0.63
Process Water	0.015	1.61
NH3 (Conditioning)	0.031	3.36
Cellulase	0.069	7.37
NH3 (Nutrients)	0.064	6.86
Cooling water	0.002	0.16
Refrigerant (NH3)	0.009	0.98
Oleyl	0.001	0.14
Boiler Feed Water	0.003	0.30
Glucose	0.000	0.00
Ash disposal	0.023	2.43
Waste water	0.005	0.54
SUM	0.932	100.00

CONT-SHF/DDProcess Scenario

Table 9:22: Discounted cash flow analysis for profitability assessment for CONT-SHF/DD process scenario

|											
				Discounted Cash Flow							
Year	Loan Payment	Loan Principal	Loan Payment Interest	Revenue	Expenses	Gross Profit	Depreciation	Net Profit	Cash Flow	DCF	Cummulative DCF
-2		25594153.06	2047532.245						-18190922.71	-21731767.62	-21731767.62
-1		217550301	17404024.08						-127970765.3	-139872046.46	-161603814.09
0		319926913.2	25594153.06						-94911650.92	-94911650.92	-256515465.01
1	47678544.30	297842522	25594153.06	77415112.10	96465969.59	-19050857.50	42656921.76	-44429601.07	-1772679.30	-1621847.49	-258137312.50
2	47678544.30	273991379.44	23827401.76	103220149.46	96465969.59	6754179.87	42656921.76	-25849974.16	16806947.60	14068523.56	-244068788.94
3	47678544.30	248232145.50	21919310.36	103220149.46	96465969.59	6754179.87	42656921.76	-25849974.16	16806947.60	12871476.27	-231197312.67
4	47678544.30	220412172.84	19858571.64	103220149.46	96465969.59	6754179.87	42656921.76	-25849974.16	16806947.60	11776282.04	-219421030.64
5	47678544.30	190366602.37	17632973.83	103220149.46	96465969.59	6754179.87	42656921.76	-25849974.16	16806947.60	10774274.51	-208646756.13
6	47678544.30	157917386.26	15229328.19	103220149.46	96465969.59	6754179.87	42656921.76	-25849974.16	16806947.60	9857524.71	-198789231.42
7	47678544.30	122872232.87	12633390.9	103220149.46	96465969.59	6754179.87	42656921.76	-25849974.16	16806947.60	9018778.32	-189770453.10
8	47678544.30	85023467.20	9829778.629	103220149.46	96465969.59	6754179.87	42656921.76	-25849974.16	16806947.60	8251398.28	-181519054.81
9	47678544.30	44146800.28	6801877.376	103220149.46	96465969.59	6754179.87	42656921.76	-25849974.16	16806947.60	7549312.25	-173969742.57
10	47678544.30	0.00	3531744.022	103220149.46	96465969.59	6754179.87	42656921.76	-25849974.16	16806947.60	6906964.54	-167062778.02
11	0.00	0.00	0.00	103220149.46	96465969.59	6754179.87	42656921.76	-25849974.16	16806947.60	6319272.23	-160743505.80
12	0.00	0.00	0.00	103220149.46	96465969.59	6754179.87	42656921.76	-25849974.16	16806947.60	5781584.84	-154961920.96
13	0.00	0.00	0.00	103220149.46	96465969.59	6754179.87	42656921.76	-25849974.16	16806947.60	5289647.61	-149672273.35
14	0.00	0.00	0.00	103220149.46	96465969.59	6754179.87	42656921.76	-25849974.16	16806947.60	4839567.80	-144832705.55
15	0.00	0.00	0.00	103220149.46	96465969.59	6754179.87	42656921.76	-25849974.16	16806947.60	4427783.90	-140404921.65
16	0.00	0.00	0.00	103220149.46	96465969.59	6754179.87	42656921.76	-25849974.16	16806947.60	4051037.42	-136353884.23
17	0.00	0.00	0.00	103220149.46	96465969.59	6754179.87	42656921.76	-25849974.16	16806947.60	3706347.14	-132647537.09
18	0.00	0.00	0.00	103220149.46	96465969.59	6754179.87	42656921.76	-25849974.16	16806947.60	3390985.49	-129256551.61
19	0.00	0.00	0.00	103220149.46	96465969.59	6754179.87	42656921.76	-25849974.16	16806947.60	3102456.99	-126154094.62
20	0.00	0.00	0.00	103220149.46	96465969.59	6754179.87	42656921.76	-25849974.16	16806947.60	2838478.49	-123315616.13
21	0.00	0.00	0.00	103220149.46	96465969.59	6754179.87	42656921.76	-25849974.16	16806947.60	2596961.10	-120718655.03
22	0.00	0.00	0.00	103220149.46	96465969.59	6754179.87	42656921.76	-25849974.16	16806947.60	2375993.69	-118342661.34
23	0.00	0.00	0.00	103220149.46	96465969.59	6754179.87	42656921.76	-25849974.16	16806947.60	2173827.71	-116168833.62
24	0.00	0.00	0.00	103220149.46	96465969.59	6754179.87	42656921.76	-25849974.16	16806947.60	1988863.42	-114179970.21
25	0.00	0.00	0.00	103220149.46	96465969.59	6754179.87	42656921.76	-25849974.16	16806947.60	1819637.16	-112360333.05
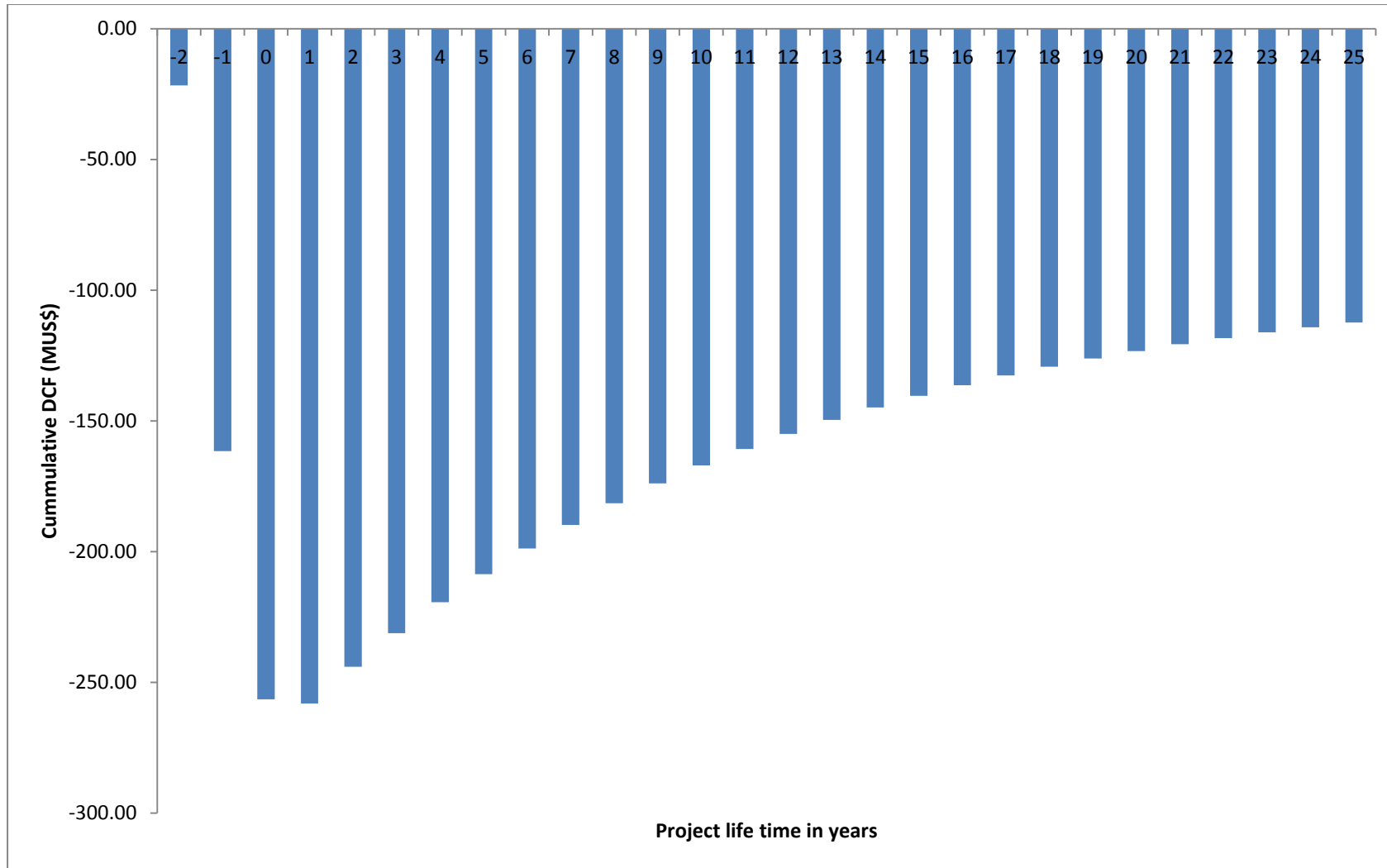
Figure 9-5: A cumulative discounted cash flow for scenario CONT-SHF/DD

Table 9:23: Summary of Sales Revenues, Operating Costs and Total Capital Investment for CONT-SHF/DD process scenario

Techno-Economic Analysis for CONT-SHF/DD Process Scenario	
Butanol Production Rate (kg/yr)	66428600.00
Market Value (US$/kg)	0.78
Acetone Production Rate (kg/yr)	24998384.00
Market Value (US$/kg)	1.10
Ethanol Production Rate (kg/yr)	3909805.60
Market Value (US$/kg)	0.69
Total Operating Costs (US$)	104289631.31
Sales Revenue (US$)	114636045.08
Fixed Capital Investment (US$)	540914135.74
Land (US$)	1128154.00
Working Capital (US$)	27045706.79
Total Capital Investment (US$)	569087996.54
Return On Investment: ROI (%)	-4.31
Net Present Value: NPV ($)	-91472190.61
Payback Period: PBP (years)	28.86
Internal Rate of Return: IRR (%)	n/a

Table 9:24: Raw materials cost per kg Butanol Produced for CONT-SHF/DD process scenario

Raw Material	US$/kg Butanol	(%)
Corn Stover	1.034	78.79
NaOH	0.077	5.90
Process Water	0.011	0.81
H_2SO_4 (Conditioning)	0.079	5.98
Cellulase	0.069	5.23
NH_3 (Nutrients)	0.005	0.38
Cooling Water	0.004	0.34
Boiler Feed Water	0.006	0.49
Ash Disposal	0.023	1.78
Waste Water	0.004	0.29
SUM	1.313	100

CONT-SHF/LLE&D Process Scenario

Table 9:25: Discounted cash flow analysis for profitability assessment for CONT-SHF/LLE&D process scenario

| Year	Loan Payment	Loan Principal	Loan Payment Interest	Revenue	Expenses	Gross Profit	Depreciation	Net Profit	Cash Flow	DCF	Cummulative DCF
-2		25838687.23	1627837.296						-18353945.49	-21926522.63	-21926522.63
-1		219628841.5	13836617.01						-129193436.2	-141208425.72	-163134948.35
0		322983590.4	20347966.2						-95818465.15	-95818465.15	-258953413.50
1	44508960.90	298822595.7	20347966.2	72318538.27	89215528.92	-16896990.65	43064478.72	-43172257.95	-107779.23	-98608.63	-259052022.13
2	44508960.90	273139458.32	18825823.53	96424717.69	89215528.92	7209188.77	43064478.72	-25815808.77	17248669.95	14438274.30	-244613747.83
3	44508960.90	245838283.29	17207785.87	96424717.69	89215528.92	7209188.77	43064478.72	-25815808.77	17248669.95	13209766.06	-231403981.77
4	44508960.90	216817134.23	15487811.85	96424717.69	89215528.92	7209188.77	43064478.72	-25815808.77	17248669.95	12085787.79	-219318193.98
5	44508960.90	185967652.78	13659479.46	96424717.69	89215528.92	7209188.77	43064478.72	-25815808.77	17248669.95	11057445.37	-208260748.61
6	44508960.90	153174654.01	11715962.13	96424717.69	89215528.92	7209188.77	43064478.72	-25815808.77	17248669.95	10116601.44	-198144147.17
7	44508960.90	118315696.30	9650003.202	96424717.69	89215528.92	7209188.77	43064478.72	-25815808.77	17248669.95	9255811.01	-188888336.15
8	44508960.90	81260624.27	7453888.867	96424717.69	89215528.92	7209188.77	43064478.72	-25815808.77	17248669.95	8468262.59	-180420073.56
9	44508960.90	41871082.69	5119419.329	96424717.69	89215528.92	7209188.77	43064478.72	-25815808.77	17248669.95	7747724.24	-172672349.32
10	44508960.90	0.00	2637878.21	96424717.69	89215528.92	7209188.77	43064478.72	-25815808.77	17248669.95	7088494.27	-165583855.05
11	0.00	0.00	0.00	96424717.69	89215528.92	7209188.77	43064478.72	-25815808.77	17248669.95	6485356.15	-159098498.90
12	0.00	0.00	0.00	96424717.69	89215528.92	7209188.77	43064478.72	-25815808.77	17248669.95	5933537.19	-153164961.71
13	0.00	0.00	0.00	96424717.69	89215528.92	7209188.77	43064478.72	-25815808.77	17248669.95	5428670.81	-147736290.90
14	0.00	0.00	0.00	96424717.69	89215528.92	7209188.77	43064478.72	-25815808.77	17248669.95	4966761.95	-142769528.96
15	0.00	0.00	0.00	96424717.69	89215528.92	7209188.77	43064478.72	-25815808.77	17248669.95	4544155.49	-138225373.47
16	0.00	0.00	0.00	96424717.69	89215528.92	7209188.77	43064478.72	-25815808.77	17248669.95	4157507.31	-134067866.16
17	0.00	0.00	0.00	96424717.69	89215528.92	7209188.77	43064478.72	-25815808.77	17248669.95	3803757.83	-130264108.34
18	0.00	0.00	0.00	96424717.69	89215528.92	7209188.77	43064478.72	-25815808.77	17248669.95	3480107.80	-126784000.53
19	0.00	0.00	0.00	96424717.69	89215528.92	7209188.77	43064478.72	-25815808.77	17248669.95	3183996.16	-123600004.37
20	0.00	0.00	0.00	96424717.69	89215528.92	7209188.77	43064478.72	-25815808.77	17248669.95	2913079.74	-120686924.63
21	0.00	0.00	0.00	96424717.69	89215528.92	7209188.77	43064478.72	-25815808.77	17248669.95	2665214.77	-118021709.86
22	0.00	0.00	0.00	96424717.69	89215528.92	7209188.77	43064478.72	-25815808.77	17248669.95	2438439.86	-115583270.00
23	0.00	0.00	0.00	96424717.69	89215528.92	7209188.77	43064478.72	-25815808.77	17248669.95	2230960.53	-113352309.47
24	0.00	0.00	0.00	96424717.69	89215528.92	7209188.77	43064478.72	-25815808.77	17248669.95	2041134.98	-111311174.49
25	0.00	0.00	0.00	96424717.69	89215528.92	7209188.77	43064478.72	-25815808.77	17248669.95	1867461.10	-109443713.39

Figure 9-6: A cumulative discounted cash flow for scenario CONT-SHF/ LLE&D

Table 9:26: Summary of Sales Revenues, Operating Costs and Total Capital Investment for CONT-SHF/LLE&D process scenario

Techno-Economic Analysis for CONT-SHF/LLE&D Process Scenario	
Butanol Production Rate (kg/yr)	51425136.00
Market Value (US$/kg)	0.78
Acetone/ethanol Production Rate (kg/yr)	17374864.00
Market Value (US$/kg)	1.10
Total Operating Costs (US$)	89215528.92
Sales Revenue (US$)	96424717.69
Fixed Capital Investment (US$)	538305984.00
Land (US$)	1128154.00
Working Capital (US$)	26915299.20
Total Capital Investment (US$)	566349437.20
Return On Investment: ROI (%)	-4.68
Net Present Value (US$)	-109443713.39
Payback Period: PBP (years)	32.51737267
Internal Rate of Return: IRR (%)	n/a

Table 9:27: Raw materials cost per kg Butanol Produced for CONT-SHF/LLE&D process scenario

Raw Material	US$/kg Butanol	(%)
Corn Stover	1.069	75.48
NaOH	0.100	7.07
Process Water	0.014	0.97
H2SO4 (Conditioning)	0.101	7.16
Cellulase	0.069	4.85
NH3 (Nutrients)	0.006	0.45
Oleyl Alcohol	0.001	0.08
Cooling Water	0.011	0.77
Boiler Feed Water	0.003	0.23
Glucose	0.006	0.45
Ash Disposal	0.030	2.13
Waste Water	0.005	0.35
SUM	1.416	100

B-SHF/DDProcess Scenario

						Discounted Cash Flow					
Year	Loan Payment	Loan Principal	Loan Payment Interest	Revenue	Expenses	Gross Profit	Depreciation	Net Profit	Cash Flow	DCF	Cummulative DCF
-2		25905432.43	1632042.243						-18398442.29	-21979680.68	-21979680.68
-1		220196175.6	13872359.06						-129527162.1	-141573188.21	-163552868.89
0		323817905.3	20400528.04						-96065978.58	-96065978.58	-259618847.48
1	44623934.21	299594499.2	20400528.04	80305341.47	91626975.32	-11321633.85	43175720.71	-39238095.29	3937625.42	3602585.02	-256016262.46
2	44623934.21	273845018.40	18874453.45	107073788.62	91626975.32	15446813.30	43175720.71	-19964813.34	23210907.38	19429060.23	-236587202.23
3	44623934.21	246473320.35	17252236.16	107073788.62	91626975.32	15446813.30	43175720.71	-19964813.34	23210907.38	17775901.40	-218811300.83
4	44623934.21	217377205.33	15527819.18	107073788.62	91626975.32	15446813.30	43175720.71	-19964813.34	23210907.38	16263404.76	-202547896.07
5	44623934.21	186448035.05	13694763.94	107073788.62	91626975.32	15446813.30	43175720.71	-19964813.34	23210907.38	14879601.79	-187668294.28
6	44623934.21	153570327.05	11746226.21	107073788.62	91626975.32	15446813.30	43175720.71	-19964813.34	23210907.38	13613542.35	-174054751.92
7	44623934.21	118621323.45	9674930.604	107073788.62	91626975.32	15446813.30	43175720.71	-19964813.34	23210907.38	12455208.01	-161599543.92
8	44623934.21	81470532.62	7473143.377	107073788.62	91626975.32	15446813.30	43175720.71	-19964813.34	23210907.38	11395432.76	-150204111.15
9	44623934.21	41979241.96	5132643.555	107073788.62	91626975.32	15446813.30	43175720.71	-19964813.34	23210907.38	10425830.52	-139778280.63
10	44623934.21	0.00	2644692.244	107073788.62	91626975.32	15446813.30	43175720.71	-19964813.34	23210907.38	9538728.75	-130239551.88
11	0.00	0.00	0.00	107073788.62	91626975.32	15446813.30	43175720.71	-19964813.34	23210907.38	8727107.73	-121512444.15
12	0.00	0.00	0.00	107073788.62	91626975.32	15446813.30	43175720.71	-19964813.34	23210907.38	7984545.04	-113527899.11
13	0.00	0.00	0.00	107073788.62	91626975.32	15446813.30	43175720.71	-19964813.34	23210907.38	7305164.72	-106222734.39
14	0.00	0.00	0.00	107073788.62	91626975.32	15446813.30	43175720.71	-19964813.34	23210907.38	6683590.78	-99539143.61
15	0.00	0.00	0.00	107073788.62	91626975.32	15446813.30	43175720.71	-19964813.34	23210907.38	6114904.65	-93424238.96
16	0.00	0.00	0.00	107073788.62	91626975.32	15446813.30	43175720.71	-19964813.34	23210907.38	5594606.26	-87829632.70
17	0.00	0.00	0.00	107073788.62	91626975.32	15446813.30	43175720.71	-19964813.34	23210907.38	5118578.47	-82711054.23
18	0.00	0.00	0.00	107073788.62	91626975.32	15446813.30	43175720.71	-19964813.34	23210907.38	4683054.41	-78027999.82
19	0.00	0.00	0.00	107073788.62	91626975.32	15446813.30	43175720.71	-19964813.34	23210907.38	4284587.75	-73743412.08
20	0.00	0.00	0.00	107073788.62	91626975.32	15446813.30	43175720.71	-19964813.34	23210907.38	3920025.39	-69823386.69
21	0.00	0.00	0.00	107073788.62	91626975.32	15446813.30	43175720.71	-19964813.34	23210907.38	3586482.51	-66236904.18
22	0.00	0.00	0.00	107073788.62	91626975.32	15446813.30	43175720.71	-19964813.34	23210907.38	3281319.77	-62955584.40
23	0.00	0.00	0.00	107073788.62	91626975.32	15446813.30	43175720.71	-19964813.34	23210907.38	3002122.39	-59953462.01
24	0.00	0.00	0.00	107073788.62	91626975.32	15446813.30	43175720.71	-19964813.34	23210907.38	2746681.05	-57206780.96
25	0.00	0.00	0.00	107073788.62	91626975.32	15446813.30	43175720.71	-19964813.34	23210907.38	2512974.43	-54693806.53

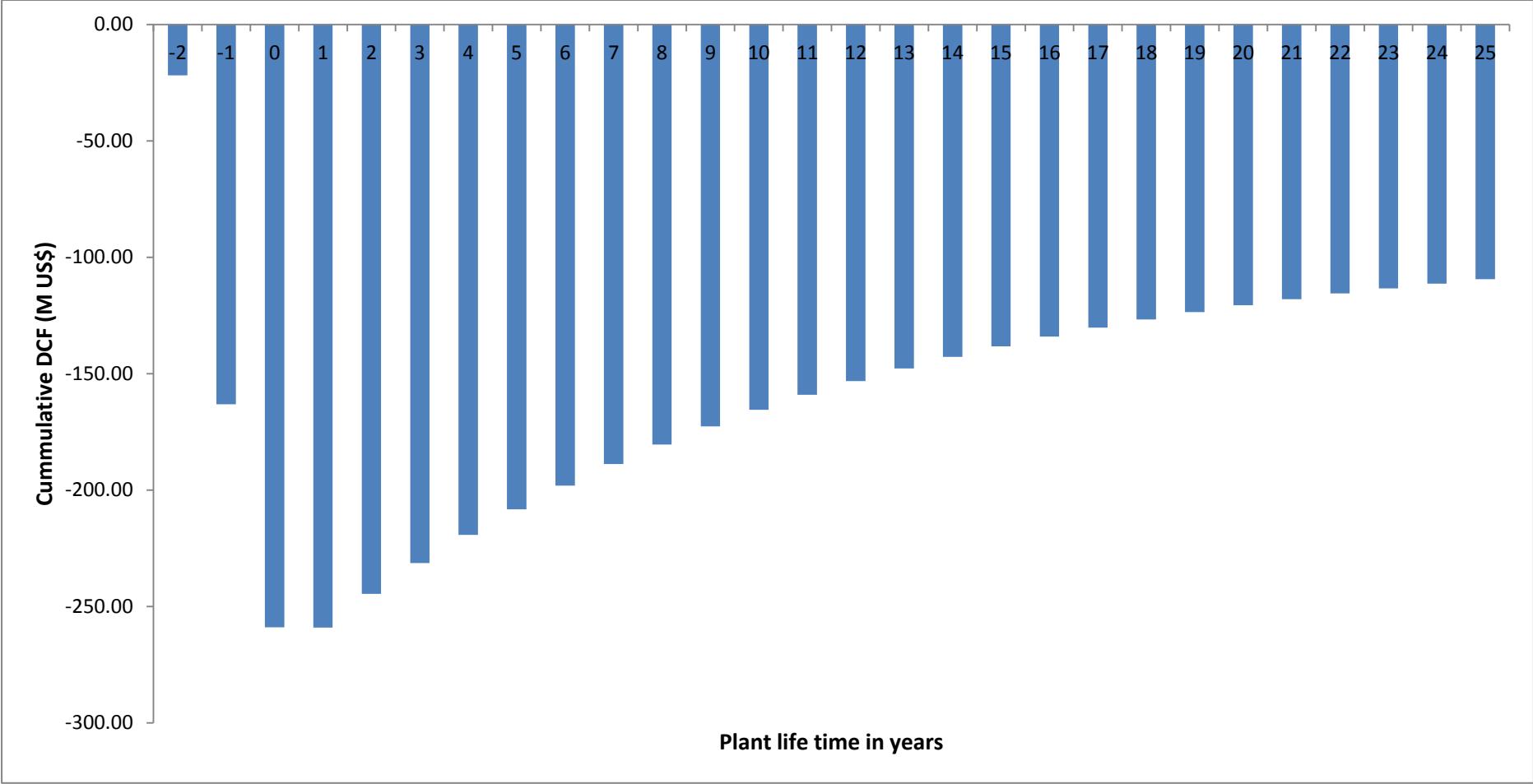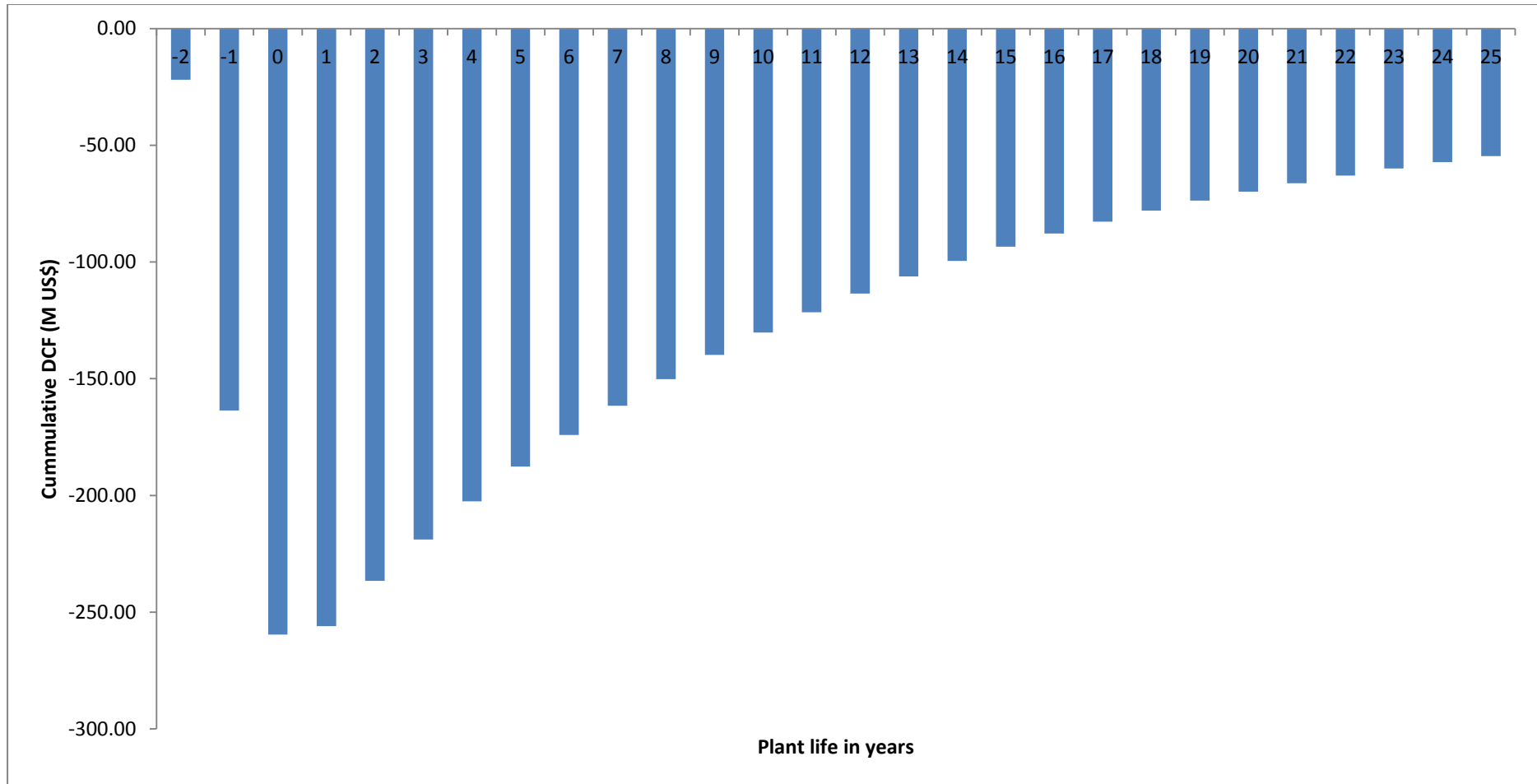Figure 9-7: A cumulative discounted cash flow for scenario B-SHF/DD

Table 9:29: Summary of Sales Revenues, Operating Costs and Total Capital Investment for B-SHF/DD process scenario

Techno-Economic Analysis for B-SHF/DD Process Scenario	
Butanol Production Rate (kg/yr)	44701392.00
Market Value (US$/kg)	0.78
Acetone Production Rate (kg/yr)	22399744.00
Market Value (US$/kg)	1.10
Ethanol Production Rate (kg/yr)	10774968.00
Market Value (US$/kg)	0.69
Total Operating Costs (US$)	91626975.32
Sales Revenue (US$)	107073788.62
Fixed Capital Investment (US$)	539696508.89
Land (US$)	1128154.00
Working Capital (US$)	26984825.44
Total Capital Investment (US$)	567809488.34
Return On Investment: ROI (%)	-3.65
Net Present Value: NPV ($)	-54693806.53
Payback Period: PBP (years)	24.05
Internal Rate of Return: IRR (%)	n/a

Table 9:30: Raw materials cost per kg Butanol Produced for B-SHF/DD process scenario

Raw Material	US$/kg Butanol	(%)
Cassava Bagasse	1.537	92.07
Process Water	0.020	1.19
H2SO4 (Conditioning)	0.000	0.00
Cellulase	0.069	4.12
NH3 (Nutrients)	0.013	0.78
Cooling water	0.005	0.32
Boiler Feed Water	0.007	0.44
Ash Disposal	0.012	0.69
Waste Water	0.007	0.40
SUM	1.6696	100.00

B-SHF/LLE&D Process Scenario

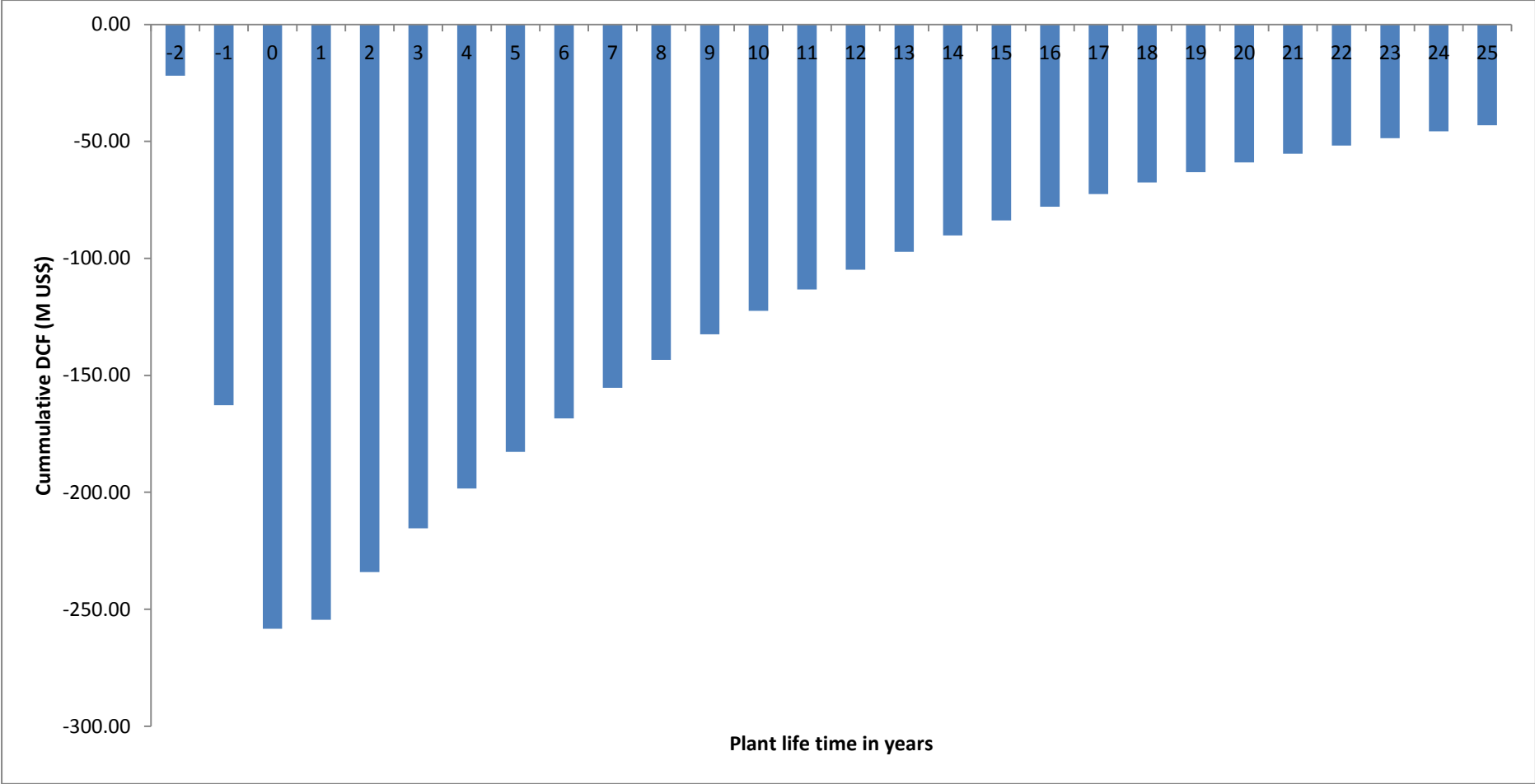|										Discounted Cash Flow	
Year	Loan Payment	Loan Principal	Loan Payment Interest	Revenue	Expenses	Gross Profit	Depreciation	Net Profit	Cash Flow	DCF	Cummulative DCF
-2		25777756.36	1623998.65						-18313324.91	-21877995.29	-21877995.29
-1		219110929	13803988.53						-128888781.8	-140875438.49	-162753433.78
0		322221954.5	20299983.13						-95592513.16	-95592513.16	-258345946.93
1	44404003.17	298117934.4	20299983.13	84054843.23	94928729.23	-10873886.00	42962927.26	-38762505.55	4200421.71	3843020.78	-254502926.15
2	44404003.17	272495361.11	18781429.87	112073124.31	94928729.23	17144395.08	42962927.26	-18589343.17	24373584.09	20402297.32	-234100628.83
3	44404003.17	245258565.68	17167207.75	112073124.31	94928729.23	17144395.08	42962927.26	-18589343.17	24373584.09	18666328.75	-215434300.09
4	44404003.17	216305852.15	15451289.64	112073124.31	94928729.23	17144395.08	42962927.26	-18589343.17	24373584.09	17078068.39	-198356231.70
5	44404003.17	185529117.66	13627268.69	112073124.31	94928729.23	17144395.08	42962927.26	-18589343.17	24373584.09	15624948.20	-182731283.50
6	44404003.17	152813448.90	11688334.41	112073124.31	94928729.23	17144395.08	42962927.26	-18589343.17	24373584.09	14295469.54	-168435813.96
7	44404003.17	118036693.01	9627247.281	112073124.31	94928729.23	17144395.08	42962927.26	-18589343.17	24373584.09	13079112.11	-155356701.85
8	44404003.17	81069001.49	7436311.659	112073124.31	94928729.23	17144395.08	42962927.26	-18589343.17	24373584.09	11966250.79	-143390451.07
9	44404003.17	41772345.41	5107347.094	112073124.31	94928729.23	17144395.08	42962927.26	-18589343.17	24373584.09	10948079.40	-132442371.67
10	44404003.17	0.00	2631657.761	112073124.31	94928729.23	17144395.08	42962927.26	-18589343.17	24373584.09	10016541.08	-122425830.58
11	0.00	0.00	0.00	112073124.31	94928729.23	17144395.08	42962927.26	-18589343.17	24373584.09	9164264.48	-113261566.10
12	0.00	0.00	0.00	112073124.31	94928729.23	17144395.08	42962927.26	-18589343.17	24373584.09	8384505.48	-104877060.62
13	0.00	0.00	0.00	112073124.31	94928729.23	17144395.08	42962927.26	-18589343.17	24373584.09	7671093.76	-97205966.87
14	0.00	0.00	0.00	112073124.31	94928729.23	17144395.08	42962927.26	-18589343.17	24373584.09	7018384.04	-90187582.83
15	0.00	0.00	0.00	112073124.31	94928729.23	17144395.08	42962927.26	-18589343.17	24373584.09	6421211.38	-83766371.45
16	0.00	0.00	0.00	112073124.31	94928729.23	17144395.08	42962927.26	-18589343.17	24373584.09	5874850.30	-77891521.14
17	0.00	0.00	0.00	112073124.31	94928729.23	17144395.08	42962927.26	-18589343.17	24373584.09	5374977.40	-72516543.74
18	0.00	0.00	0.00	112073124.31	94928729.23	17144395.08	42962927.26	-18589343.17	24373584.09	4917637.15	-67598906.59
19	0.00	0.00	0.00	112073124.31	94928729.23	17144395.08	42962927.26	-18589343.17	24373584.09	4499210.57	-63099696.02
20	0.00	0.00	0.00	112073124.31	94928729.23	17144395.08	42962927.26	-18589343.17	24373584.09	4116386.61	-58983309.41
21	0.00	0.00	0.00	112073124.31	94928729.23	17144395.08	42962927.26	-18589343.17	24373584.09	3766135.97	-55217173.44
22	0.00	0.00	0.00	112073124.31	94928729.23	17144395.08	42962927.26	-18589343.17	24373584.09	3445687.07	-51771486.37
23	0.00	0.00	0.00	112073124.31	94928729.23	17144395.08	42962927.26	-18589343.17	24373584.09	3152504.18	-48618982.19
24	0.00	0.00	0.00	112073124.31	94928729.23	17144395.08	42962927.26	-18589343.17	24373584.09	2884267.32	-45734714.87
25	0.00	0.00	0.00	112073124.31	94928729.23	17144395.08	42962927.26	-18589343.17	24373584.09	2638853.91	-43095860.96

Figure 9-8: A cumulative discounted cash flow for scenario B-SHF/ LLE&D

Table 9:32: Summary of Sales Revenues, Operating Costs and Total Capital Investment for B-SHF/LLE&D process scenario

Techno-Economic Analysis for B-SHF/LLE&D Process Scenario	
Butanol Production Rate (kg/yr)	62174136.00
Market Value (US$/kg)	0.78
Acetone/Ethanol Production Rate (kg/yr)	19425864.00
Market Value (US$/kg)	1.10
Total Operating Costs (US$)	112073124.31
Sales Revenue (US$)	537036590.76
Fixed Capital Investment (US$)	1128154.00
Land (US$)	26851829.54
Working Capital (US$)	565016574.30
Total Capital Investment (US$)	565016574.30
Return On Investment: ROI (%)	-3.43
Net Present Value	-43095860.96
Payback Period: PBP (years)	22.79
Internal Rate of Return: IRR (%)	n/a

Table 9:33: Raw materials cost per kg Butanol Produced for B-SHF/LLE&D process scenario

Raw Material	US$/kg Butanol	(%)
Cassava Bagasse	1.105	87.88
Process Water	0.014	1.14
Cellulase	0.069	5.46
NH3 (Nutrients)	0.009	0.74
H2SO4 (Conditioning)	0.000	0.00
Oleyl Alcohol	0.039	3.08
Cooling Water	0.003	0.22
Boiler Feed Water	0.006	0.44
Ash Disposal	0.008	0.66
Waste Water	0.005	0.38
SUM	1.25762	100

9.6.   Evaluation for Butanol and Ethanol Basic Fuel Price

This section gives the method on which the selling price of butanol and ethanol was evaluated from Basic Fuel Price of gasoline in South Africa. The equation below was used once the average BFP and Tax_{exm} starting January to May 2015 was found.

$$Biofuel\ Selling\ Price = \frac{BFP}{GGE} + Tax_{exm}$$

Where GGE and Tax_{exm} are Gasoline Gallon Equivalent (GGE) was also used in order to take into account the energy content of biofuels and fuel tax in South Africa. Ethanol (E85) GGE is 1.39 and Butanol GGE is 1.10. Ethanol and butanol selling prices were found to be were US$0.686/kg and US$0.778/kg using Rand to USUS$ exchange rate of 12:1

Table 9:34: Average basic fuel price in South Africa Jan to May 2015

Basic Fuel Price: Source-http://www.energy.gov.za/files/esources/petroleum/May2015/Basic-Fuel-Price.pdf

Month	Pet 95% Unleaded Cents/litre	R/litre	USUS$/litre	USUS$/kg Ethanol	USUS$/kg Butanol
Jan	533.25	5.33	0.44	0.56	0.55
Feb	440.25	4.40	0.37	0.46	0.45
Mar	536.25	5.36	0.45	0.57	0.55
Apr	615.65	6.16	0.51	0.65	0.63
May	615.65	6.16	0.51	0.65	0.63
Average	548.21	5.48	0.46	0.58	0.56

9.7. Results from simulated processes and economic analysis of molasses based butanol

Table 9:35: Summary of results from the simulated processes and economic analysis reproduced from (van der Merwe et al. 2013)

Process Design	1.1	1.2	1.3	2	3
Molasses					
Mass flow(T/h)	147.21	147.21	147.21	147.21	35.28
Volume flow(L/h)	118178	118178	118178	118178	28322.1
Energy density (MJ/L)	1.02	1.02	1.02	1.02	1.02
Total energy (MJ/h)	121023	121023	121023	121023	29003.7
Energy input (MJ/L of butanol)	5.62	4.51	4.06	4.64	1.39
Butanol					
Mass flow (T/h)	14.86	18.71	20.83	18.6	14.85
Volume flow (L/h)	21547.8	26814.3	29821.8	26108.1	20860.1
Energy density (MJ/L)	26.81	26.81	26.81	26.81	26.81
Total energy (MJ/h)	577717	718919	799553	699984	559280
Utilities					
High pressure steam (MJ/h)	508241	496231	535416	161341	20782.4
Electricity (MJ/h)	67766	87386	126788	89955.6	118396
Total Energy (MJ/h)	576007	583617	662204	251296	139178
Energy input (MJ/L of butanol)	26.73	21.77	22.21	9.63	6.67
Energy performance					
Net energy value (MJ/L)	-5.54	0.53	0.55	12.55	18.75
Energy ratio	0.83	1.02	1.02	1.88	3.33
Energy ratio (only utility inputs)	1	1.23	1.21	2.79	4.02
Total utility energy requirements/Molasses (MJ/T)	3912.78	3964.47	4498.31	1707.04	3944.96
Total utility energy requirements/Butanol (MJ/T)	38749.9	31190.4	31797.5	13513.9	9373.87
Economic indicators					
Total Project Capital Cost (US$ millions)	320.64	377.28	531.7	426.96	187.34
Net present value (after 25 years) (US$ millions)	-1828.7	-1858.9	-1380	-1747.1	958.27
Internal rate of return (%)	n/a	n/a	n/a	n/a	35.96