Modelling and sustainability analysis of biorefineries using sugarcane lignocellulose to produce polyethylene, sorbitol, glucaric acid and levulinic acid at existing South African sugar mills

by
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Stellenbosch, South Africa.
March 2021

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Abstract

The sugar industry in South Africa and the region has been plagued by factors including the low international sugar prices, reduced cane yields due to climate change and competition from new market entrants producing sweeteners. Therefore, to remain relevant and sustainable, this industry seeks to generate extra revenue by producing bio-based chemicals and bio-energy from part of the bagasse and brown leaves in biorefinery complexes, alongside sugar products.

Using a rapid screening approach, bio-based chemicals polyethylene, sorbitol, glucaric acid and levulinic acid were shortlisted for possible production in such biorefineries **(objective one)**. Conceptual biorefinery process flow diagrams were designed in Aspen Plus® v 8.6 producing the aforementioned chemicals with electricity cogeneration in combined heat and power plants, annexed to a conventional sugar mill **(objective two)**, including a base case scenario that only produced electricity.

This was followed by determining the techno-economic viability of the bio-energy self-sufficient biorefineries using developing countries' economic parameters and a discounted cash flow rate of return methodology on real terms using a 9.7% hurdle rate that reflects South Africa's and developing countries' economic conditions **(objective three)**. The internal rate of return (IRR), net present value (NPV) and minimum product selling price (MPSP) were indicators used to determine profitability.

The most economically viable scenario coproduced levulinic acid, gamma valerolactone, furfural and electricity (LA-GVL-F-E) and attained a 23% IRR and US$ 253 million NPV at a 9.7% hurdle rate, due to economies of scale benefits and increased profit margins from its multiple chemical products followed by LA-F-E with a 17% IRR and US$ 139 million. At present, most second generation bio-based chemicals cannot compete with first generation or fossil–based counterparts due to the large capital investment costs associated with processing lignocelluloses. A substantial premium is required on second-generation bio-based products if they are to compete with fossil-based or first generation products.

In addition to economic viability, the overall sustainability of profitable biorefineries was assessed based on their environmental and social impacts (i.e. job creation) in **objective four**. For the environmental impact, a "cradle to factory gate" life cycle assessment in SimaPro® was used and the AWARE methodology applied for the water footprint. The most sustainable scenario produced glucaric acid via dilute acid pretreatment (Glucaric.$_{DA}$) followed by LA-F-E.

Objective five was a multi criteria decision assessment (MDCA) on profitable scenarios that ranked and scored the biorefineries based on equal and varied national sustainable (economic, environmental and social) representative weightings. When equal representative weightings of 33.33% were applied to the sustainability indicators, scenario LA-F-E attained the highest aggregate score followed by Glucaric.$_{\text{DA}}$ and Sorbitol.$_{\text{DA}}$ (chemicals produced via dilute acid pretreatment) and lastly, LA-GVL-F-E. The generated results can inform key sugar industry stakeholders of the most sustainable biorefineries for future feasibility studies.

Therefore, potential exists at typical sugar mills for the sustainable valorisation of lignocelluloses for revenue generation and the advancement of a green economy. Future studies should investigate the sustainability of biorefineries utilising first and second generation feedstocks and also valorising part of the lignin to produce high-value chemicals.

Opsomming

Die suikerindustrie in Suid-Afrika en die streek word deur faktore geteister soos die lae internasionale suikerpryse, verlaagde rietopbrengs as gevolg van klimaatsverandering en kompetisie van nuwe markdeelnemers wat versoeters vervaardig. Daarom, om relevant en volhoubaar te bly, poog die industrie om ekstra inkomste te genereer deur bio-gebaseerde chemikalieë en bio-energie uit ’n gedeelte van die bagasse en bruin blare in bioraffinaderykompleks, saam met suikerprodukte, te produseer.

Deur ’n vinnige siftingsbenadering, is bio-gebaseerde chemikalieë poliëtileen, sorbitol, suikersuur en levuliniensuur gekortlys vir moontlike produksie in sulke bioraffinaderye (doelwit 1). Konsepsuele bioraffinaderyprosesvloeidiagramme is ontwerp in Aspen Plus® v 8.6 wat die voorafgenoemde chemikalieë met elektrisiteitkogenerasie produseer in aanlegte wat hitte en krag kombineer, geannekseer aan ’n konvensionele suikermeul (doelwit 2), insluitend ’n basis scenario wat slegs elektrisiteit produseer.

Dit is gevolg deur die bepaling van die tegno-ekonomiese uitvoerbaarheid van die bio-energie selfonderhoudende bioraffinaderye deur ontwikkelende lande se ekonomiese parameters te gebruik, en ’n korting op kontantvloeiopbrengsmetodologie op reële terme deur ’n 9.7% versperringskoers te gebruik wat Suid-Afrika en ontwikkelende lande se ekonomiese kondisies reflekteer (doelwit 3). Die interne opbrengskoers (IRR), netto huidige waarde (NPV) en minimum produkverkoopsprys (MPSP) was indikators wat gebruik is om winsgewendheid te bepaal.

Die mees ekonomies uitvoerbare scenario het levuliniensuur, gamma valerolaktoon, furfuraal en elektrisiteit (LA-GVL-F-E) koproduseer en het ’n 23% IRR en US$253 miljoen NPV gehad by ’n 9.7% versperringskoers, as gevolg van skaalbesparingsvoordele en verhoogde winsmarge van sy veelvoudige chemiese produkte, gevolg deur LA-F-E met ’n 17% IRR en US$139 miljoen. Tans kan meeste tweede-generasie bio-gebaseerde chemikalieë nie met eerste generasie of fossiel-gebaseerde teenbeelde kompeteer nie as gevolg van die groot kapitaalbeleggingkostes geassosieer met prosessering van lignosellulose. ’n Aansienlike premie word vereis op tweede-generasie bio-gebaseerde produkte as hulle met fossiel-gebaseerde of eerste-generasie produkte wil kompeteer.

Saam met ekonomiese uitvoerbaarheid, is die algehele volhoubaarheid van winsgewende bioraffinaderye geassesseer gebaseer op hul omgewings- en sosiale impak (i.e. werkskepping) in doelwit 4. Vir die omgewingsimpak is ’n lewenssiklusanalise van die “begin tot fabriekshek” in SimaPro® gebruik en die AWARE-metodologie toegepas vir die watervoetspoor. Die mees volhoubare scenario het suikersuur via verdunde suur voorbehandeling (Glucaric.$_{\text{DA}}$) produseer, gevolg deur LA-F-E.

Doelwit vyf was ’n multikriteriabesluitassessering (MDCA) op winsgewende scenario’s wat bioraffinaderye rangskik en punte gee gebaseer op gelyke en gevarieerde nasionale volhoubaarheid (ekonomies, omgewing, en sosiaal) verteenwoordigende gewigstoekennings. Toe gelyke verteenwoordigende gewigstoekennings van 33.33% toegepas is op die volhoubaarheidsindikators, het scenario LA-F-E die hoogste aggregaattelling behaal, gevolg deur Glucaric.$_{\text{DA}}$ en Sorbitol.$_{\text{DA}}$ (chemikalieë geproduseer via verdunde suur voorbehandeling), en laaste, LA-GVL-F-E. Die gegenereerde resultate kan sleutel suikerindustriebelanghebbers van die mees volhoubare bioraffinaderye inlig vir toekomstige uitvoerbaarheidstudies.

Potensiaal bestaan daarom by tipiese suikermeule vir die volhoubare valorisasie van lignosellulose vir inkomstegenerasie en die bevordering van ’n groen ekonomie. Toekomstige studies moet die volhoubaarheid van bioraffinaderye wat eerste- en tweede-generasie toevoermateriale gebruik, ondersoek, en ook die valorisering van ’n gedeelte van die lignien om hoë waarde chemikalieë te produseer.

Declaration of contributions to the work

Declaration by candidate

The nature and scope of my contributions, with regard to the chapters as detailed below were as follows:

Chapter	Pages	Nature of Contribution	Contribution (%)
4	111-142	Details on page 112	80
5	143-169	Details on page 144	80
6	171-199	Details on page 172	80

The contributions by the co-authors to the chapters are as follows:

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		5	143-169	Details provided on page 144	10
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Declaration by co-authors

The undersigned hereby confirm that:

1. The declaration above accurately reflects the nature and extent of the contributions of the candidate and co-authors to the chapters as specified above.
2. no other authors contributed to these chapters besides those specified above, and
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Acknowledgements

Romans 11: 33-36

[33] "Oh, the depth of the riches both of the wisdom and knowledge of God! How unsearchable are His judgements and His ways past finding out!"

[34] "For who has known the mind of the Lord? Or who has become His counselor?"

[35] "Or who has first given to Him and it shall be repaid to him?"

[36] "For of Him and through Him and to Him are all things, to whom be glory forever. Amen."

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Dedication

To my husband, Josephat Kapalu Kakoma,

and

our children, Likoji David and Musole

Naomi,

this thesis is affectionately dedicated.

List of acronyms and abbreviations

ADP	Abiotic depletion potential
AP	Acidification potential
ASL	Acid soluble lignin
BETE	Bio-ethanol to ethylene
BIG/GTCC	Biomass integrated gasifier/gas turbine combined cycle
BRTEM	Biorefinery Techno-Economic Modelling
CAGR	Compounded annual growth rate
CEPCI	Chemical Engineering Plant Cost Index
CEST	Condensing Extraction Steam Turbine
CHP	Combined Heat and Power
COD	Chemical oxygen demand
CS factor	Combined severity factor
CSTR	Continuous stirred tank reactor
DA	Dilute acid
DCFROR	Discounted Cash Flow Rate of Return
DM	Dry mass
DoE	Department of Energy
DST	Department of Science and Technology
DTI	Department of Trade and Industry
ELECT-NRTL	Electrolyte non-random two-liquid
EP	Eutrophication potential
ETE	Ethanol to Ethylene
ETOH	Ethanol
EU	European Union
FC	Fixed carbon

FCI	Fixed capital investment
GHG	Greenhouse gases
GVL	Gamma valerolactone
GWP	Global warming potential
1G, 2G, 3G	First, second, third generation
HDPE	High Density Polyethylene
HHPS	High High Pressure Steam
HPS	High Pressure Steam
HV, LV	High volume, low value
IEA	International Energy Agency
IRR	Internal rate of return
ISBL	Inside battery limit
LA	Levulinic acid
LCA	Life cycle assessment
LCIA	Life cycle inventory assessment
LDPE	Low Density Polyethylene
LLDPE	Linear Low Density Polyethylene
LPS	Low Pressure Steam
LV, HV	Low volume, high value
MCDA	Multi criteria decision assessment
MPSP	Minimum product selling price
MSW	Municipal solid waste
MW	Mega Watt
MWh	Mega Watt hour
NISIR	National Institute for Scientific and Industrial Research
NREL	National Renewable Energy Laboratory
NPV	Net Present Value

NRF	National Research Foundation
ODP	Ozone layer depletion potential
OSBL	Outside battery limits
PE	Polyethylene
PFR	Plug Flow Reactor
POCP	Photochemical oxidation potential
POLYNRTL	Polymer non-random two-liquid
RW	Representative weighting
SADC	Southern African Development Community
SASA	South African Sugar Association
SB	Sugarcane bagasse
SMRI	Sugar Milling Research Institute
STEP-Bio	Sugar Technology enabling programme for bio-energy
STEX	Steam explosion
SUN	Stellenbosch University
TCI	Total capital investment
TCOP	Total cost of production
TDC	Total direct costs
TEA	Techno-Economic Assessment
TIC	Total indirect costs
TRL	Technology Readiness Level
USA	United States of America
UK	United Kingdom
VM	Volatile matter
WM	Wet mass
VOC	Variable operating costs

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Chapter 1

1.0. Introduction

In chapter 1, the background to the research problem is detailed. This is in order to clarify the motivation for the research. The project goal and key research questions are presented, followed by the project scope and limitations. Lastly, the novelty and significance of this study is highlighted, and an overview of the whole thesis structure given.

1.1. Project Motivation and Background

The sugar industry, producing only raw and refined sugar products, was once an attractive global and local trade with high profit margins. However, in the recent decade or so, this agro-industry has been negatively affected by fluctuating and low global sugar prices, threats of global warming and unfavourable weather patterns, which have led to a reduction of sugarcane yields and production capacities (SASA, 2017; Posada et al., 2013; Charlton et al., 2009; McConnell et al., 2009). In addition, new market entrants such as sweetener producers, have also brought in a competitive edge to conventional sugar mills that house aging and inefficient plant infrastructure, especially in developing countries like South Africa and the surrounding region (Southern African Development Community-SADC) (SASA, 2017; Pop et al., 2013; Maher, 2013). With approximately 1 million people directly or indirectly relying on the sugar industry in South Africa, the running of conventional South African sugar mills and producing primarily one or similar products (brown and white refined sugar, syrups and molasses), is therefore, no longer sustainable (Botha and von Blottnitz, 2006).

As a remedial measure to improve the mills' sustainability, the sugar industry is aiming to add value to the entire sugarcane plant by processing those agricultural residues in biorefinery complexes which are bioenergy self-sufficient and meet their energy demands, using part of the biomass feedstock, with the exclusion of coal. The biorefinery approach processes bio-based feedstock into a range of products, minimises waste generation (Cherubini, 2010) and is economically attractive, with added socio-economic and environmental benefits (Mohlala et al., 2016; Biofuels Industrial Strategy of the Republic of South Africa, 2007), capable of benefiting the whole sugarcane value chain. Therefore, research into and development of the biorefinery approach is essential in order to determine the economic, environmental and social impact on typical sugar mills for future feasibility studies.

Furthermore, global communities have in recent years moved towards green economies, with biorefineries also gaining ground and so an opportunity exists at local sugar mills to use lignocellulose agricultural residues as feedstock to produce bio-based chemicals and bio-energy, even as the political landscape is in support of such economies. Some examples of green economy initiatives include supportive policies and strategies to projects such as the carbon capturing plants in Zurich, which remove CO_2 from air to greenhouse plants (Farrell, 2019), where compressed CO_2 is used to manufacture fertilisers, carbonated drinks and carbon-neutral fuels. In America, DuPont cellulosic ethanol plant commissioned in 2015 was the world's largest producer of ethanol from corn stover, with the ethanol product used as a fuel blend and in laundry detergents (EERE, 2015). However, due to high production costs, a still-maturing technology and uncertainty in regulatory policies, the plant has had to minimise its operative capacity. In Southern Africa, Malawi currently blends 10-25% (E10-E25) of its national energy system with biofuels produced from sugarcane ethanol (Hermann et al., 2018). Therefore, varied initiatives are being implemented as countries thrive towards green economies and it is key that sustainability studies are also conducted on lignocellulose biorefineries in a developing country context.

At local traditional sugar mills, bio-based products supporting green economy initiatives can be realised if the inefficient burning of biomass in boilers, usually done as a way of disposing off the bagasse (Renouf et al., 2013) to produce low pressure steam for the sugar mill process energy, is replaced with efficient means (Leibbrandt et al., 2011). In order to attain a bioenergy self-sufficient biorefinery annexed to a sugar mill, old boilers should be replaced with efficient ones in combined heat and power (CHP) plants. In that way, part of the available biomass that is currently burnt or used as fodder (Pandey et al., 2000), is used to generate steam and electricity to sustain the combined energy demands of the sugar mill and the biorefinery, while the remainder is liberated for conversion to valuable bio-based chemicals. The sugar mill is provided only with high-pressure steam (HPS) as the existing mill's back extraction turbines are still used to produce electricity. Hence, the use of efficient boilers reduces the amount of agricultural residues combusted for the combined energy demand of these processes, leading to increased volumes of feedstock for the biorefinery.

Lignocellulose agricultural residues constitute sugarcane bagasse, the fibrous waste produced after sugar juice (sucrose) extraction, and part of the leaves (brown leaves or trash) left in the fields at mills practicing non-burn harvesting (Sindhu et al., 2016). The remaining green leaves are left in the fields for nutrient and soil moisture retention (Galdos et al., 2013; Leal et al., 2013; Alonso Pippo et al., 2011).

Sugarcane bagasse is the world's most abundant agricultural residue (followed by maize), with approximately 2.6 million t/y of bagasse generated in South Africa alone (Mandegari et al., 2017a). It is also cheap (although costly to process), making it suitable for the production of a variety of value-added chemicals to broaden the revenue base of this industry (Isikgor and Becer, 2015). Even if this feedstock is not a first line option due to extensive processing requirements, it avoids the use of food components, namely sucrose or molasses substrates, to produce bio-based chemicals. Also, sugarcane bagasse and leaves do not pose any threat to arable land because they are extracted from existing sugarcane fields and therefore no competition for arable land exists and food security is not compromised (Radford and van Rijswijk, 2016).

With this backdrop, the current research will contribute to the techno-economic and sustainability assessments of biorefineries producing polyethylene (PE), sorbitol, glucaric acid and levulinic acid, using 2nd generation (2G) feedstocks. Additionally it will contribute to the Sugar Technology Enabling Programme Bioenergy (STEP-Bio) for bio-based products and processes, annexed to conventional South African sugar mills under the Biorefinery Techno-Economic Modelling (BRTEM) cluster. Consequently, it will advance the development of a database of techno-economic studies on biorefinery scenarios producing different chemicals. At present, techno-economic assessments of biorefineries producing chemicals including ethanol, butanol, methanol, furfural, succinic acid, itaconic acid, glutamic acid, citric acid and xylitol, have been conducted but none have assessed the chemicals polyethylene, sorbitol, glucaric acid and levulinic acid produced from sugarcane bagasse and brown leaves via chemical means. In addition, this research will inform potential investors of possible sustainable chemicals for future feasibility studies. It also has the potential to sensitise policy makers to relevant issues faced in the sector and will generate inventories of the environmental impact of such approaches. This study forms part of the Department of Science and Technology (DST)'s advancement of science and innovation in South Africa under a programme titled "Sugarcane Technology Enabling Programme for Bioenergy (STEP-Bio)–A Bridge to a Fully Integrated Sugarcane Biorefinery".

1.2. Research goals

The overall aim of this study is to determine the economic, environmental and social impacts (sustainability) of using brown leaves and sugarcane bagasse to produce polyethylene, sorbitol, glucaric acid or levulinic acid alongside sugar products, in bioenergy self-sufficient biorefinery complexes. Connected to the biorefinery is a combined heat and power (CHP) plant and the whole setup is annexed to a typical sugar mill. The developed scenarios are also compared to a base case scenario, only producing electricity as a potential new investment for conventional sugar mills. The study also scores and ranks the profitable or close to profitable biorefineries based on identified economic, environmental and social (sustainability) indicators for sugar industry stakeholders.

1.2.1. Research questions

The following research questions were therefore defined:

- Why were the chemicals polyethylene, sorbitol, glucaric acid and levulinic acid selected for the biorefinery studies?
- Would annexing a bioenergy self-sufficient biorefinery and CHP plant to a typical sugar mill to produce a chemical alongside sugar bring about sustainable (economic, environmental and social) gains for the sugar mills or would it be more beneficial to invest in a simpler system that will burn all the biomass and produce surplus electricity?
- How would the biorefineries perform if scored and ranked based on weighted economic, environmental and social indicators that reflect the sugar industry's interests and what are the trade-offs between these indicators?

1.2.2. Research objectives

The project goal and research questions identified in section 1.2 were realised through the following specific objectives:

- **From literature sources identify and shortlist potential bio-based chemicals that can be produced from lignocellulose biomass for the South African sugar industry (objective 1).**

A systematic approach using certain criteria was used in the identification and shortlisting exercise where polyethylene, sorbitol, glucaric acid and levulinic acid were shortlisted as mentioned in chapter 2 with more detail given in Appendix A.

- **Develop discrete conceptual biorefinery scenarios for the production of the four shortlisted chemicals, annexing a biorefinery to an existing sugar mill and model a utility supply system in the form of a combined heat and power (CHP) plant (objective 2).**

The developed Aspen Plus ® biorefineries are covered in chapters 3 (polyethylene), 4 (sorbitol and glucaric acid) and 5 (levulinic acid).

- **Evaluate the techno-economic viability of the developed biorefinery scenarios in accordance with South Africa's/ developing countries' economic parameters (objective 3) (chapters 3, 4 and 5) and conduct environmental and social impact assessments on the profitable scenarios (objective 4) (chapter 6).**

The techno-economic and social assessments for polyethylene, sorbitol, glucaric acid and levulinic acid production were covered in chapters 3, 4 and 5 respectively, whilst chapter 6 considered the environmental impact of profitable or near profitable scenarios only.

- **Score and rank the biorefinery scenarios based on weighted economic, environmental and social (sustainability) indicators (objective 5) (chapter 7).**

This objective, based on multi criteria decision assessments (MCDAs), is covered in chapter 7 of the thesis.

1.3. Scope and limitations

1.3.1. Scope

This research is a desktop modelling project using the computer software ASPEN Plus ® version 8.6, Microsoft Excel and literature data to model the biorefinery scenarios, size of equipment and determine the plant techno-economics. The economic viability of the developed models were based on assumptions that reflect developing countries' economic landscapes. Parameters used to determine profitability include the internal rate of return (IRR), minimum product selling price (MPSP) and net present value (NPV) over a project life of 25 years. Product selling prices required to reach a threshold IRR of 20% needed to attract private investors for such projects, will also be determined. The sensitivity of the biorefineries' IRRs and MPSPs was assessed using economic variables within a ± 30% diversion from the baseline value.

The model for the biorefinery annexed to a typical mill consists of an integrated process and acombined heat and power (CHP) plant for each scenario, apart from the base case that only comprises an investment in a new CHP plant to produce surplus electricity. The CHP plant consists of a combustor, boiler and a condensing extraction steam turbine (CEST) to provide process energy in the form of steam and electricity. No coal or natural gas was directly utilised in the modelled biorefinery or CHP plants. However, scenarios with a hydrogenation stage (glucose to sorbitol and levulinic acid to gamma valerolactone) assumed the hydrogen gas purchased and used in their processes, was produced from natural gas.

The process areas for the biorefinery include biomass pretreatment, hydrolysis, conversion, purification and recovery of saleable chemicals. Material handling and value-addition processes of the chemicals into finished products were excluded from this study. However; the chemicals' possible end-uses are highlighted. In addition, the wastewater treatment and enzyme production plants were not modelled. However, the costs of the wastewater treatment and enzyme production units were adjusted based on process throughputs and accounted for in the economic assessments, using models from previous studies conducted in the same research group (Farzad et al., 2017; Mandegari et al., 2017a). Figure 1-1 shows the scope (shaded region) of this research based on an economic analysis, which comprises a biorefinery with its CHP plant, producing bio-based chemicals and energy from dried leaves and sugarcane bagasse obtained from the sugar mill.

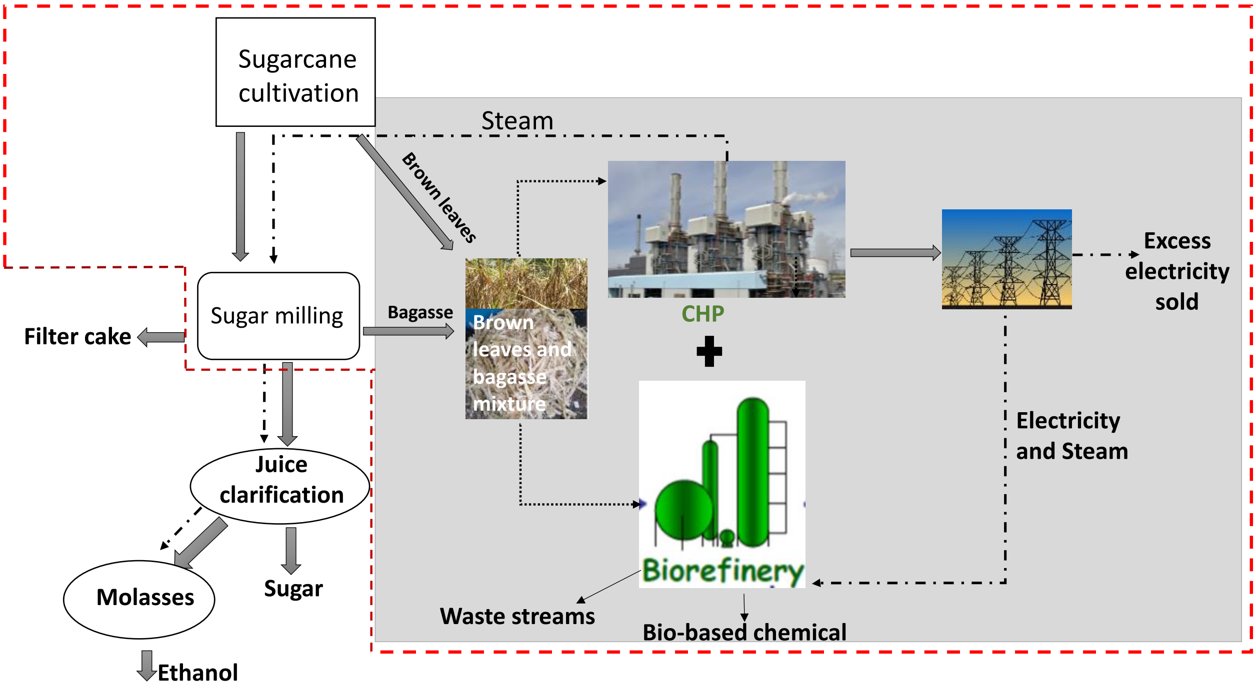

Figure 1-1: A biorefinery and CHP plant configuration annexed to a conventional sugar mill

For uniformity in the scenarios, pinch analysis was only conducted on the biorefineries' process areas in all scenarios. The scenario's CHP plants were heat integrated (but not via pinch analysis) for consistency with the existing cellulosic ethanol's CHP plant (black box) modelled by Mandegari et al., (2017) and to which the polyethylene model was connected. Heat exchangers with a heat duty below 1000 kW (Dias et al., 2009) and hot streams with temperatures below 150 °C (except flue gas streams) were excluded from the study due to their low thermal integration potential, which makes the design and purchase of heat exchanger networks costly (Van der Westhuizen, 2013). A log mean temperature difference ΔTmin, of 10 °C was selected, which is in line with chemical processes (Kemp, 2007).

Life cycle-assessment (LCA) was applied to study the environmental impacts of the biorefinery scenarios. Life cycle analyses were conducted using the software package SimaPro ® whilst the water footprint of the scenarios was based on AWARE software. Literature data, SimaPro ® in-built databases, mass and energy balances from the Aspen Plus ® models and expert advice were used to compile the input data required to perform the environmental impact assessments using 11 environmental impact categories. The system boundary for the LCA was a "cradle to factory gate", which includes the sugarcane cultivation, cane transportation and milling (excluding ethanol production, sugar and molasses processing), biorefinery and CHP plant as shown by the red dotted boundary in Figure 1-1.

The social impact indicator used in this study is the number of additional permanent jobs (skilled and unskilled) created by the construction and operation of a biorefinery and CHP plant due to complexities associated with measuring qualitative social indicators. The approach was taken for comparative purposes with similar studies done on sugarcane biorefineries connected to a typical sugarcane mill (Farzad et al., 2017). "Green cane harvesting techniques at sugar mills, increase the amount of feedstock processed and also create additional jobs in harvesting. Since the amount of brown leaves collected is constant (25 t/h brown leaves dry mass), it is assumed that the total number of harvesting jobs was 89000 man-day/year (Farzad et al., 2017) based on an 8 man hours/day shift for a mill operated for 9 months. The number of jobs at the biorefinery was based on the complexity of each process and determined quantitatively by counting the number of skilled, semi- and unskilled personnel required at each process area. Generally, the number of jobs created at the biorefinery was low because the biorefineries are assumed to be highly automated (Farzad et al., 2017).

Multi criteria decision assessments (MCDAs) were conducted for the developed profitable and marginally unprofitable scenarios, using a rating methodology on chosen impact indicators. The sustainability criteria used are based on weighted scales of the economic, environmental and social categories and their representative indicators that are in line with the South African sugar industry's stakeholders.

1.3.2. Limitations

The inherent limitations of the study methods used in achieving the set objectives are discussed herein. The computer software ASPEN Plus ® only assumes a steady state mode; therefore, the model developer should factor in the operations and quantities of batch units. ASPEN Plus ® is useful for simulating common equipment; however, the contained databank does not capture specific equipment and so in such instances, the equipment is sized and costings are done manually. The software components database does not capture and is unable to define certain chemical components and so equivalent chemicals with similar properties were used especially for the lignocellulose components as defined by Humbird et al., (2011).

In addition, it was challenging to define polyethylene (PE) in Aspen Plus®; therefore, the polymer was defined using proximate and ultimate analyses data from Al Amoodi et al., (2013). The biorefinery producing ethanol, the feedstock for PE production, was not modelled in this study. Instead it was obtained from an existing bio-ethanol biorefinery and CHP plant generated by Mandegari et al., (2017a). Therefore, the PE biorefinery scenario was modelled as an extension of an existing model, considered as a black box in this current study (outside the scope of this study). This additional PE process area led to an increase in energy demand for the overall plant and the amount of feedstock (termed passby ratio), fed to the CHP plant, required an upward adjustment or a cost allocation to the additional utilities.

Literature provided the data to model the scenarios; unfortunately, some key information on process conditions needed to model sugarcane biorefineries producing the identified chemicals is not readily available. Another limitation is that the data obtained is not always based on sugarcane bagasse and so there are differences in material compositions although it was assumed that the small variances do not affect the results significantly. To this end, corn stover and wheat straw were used when data was limited. In addition, most pretreatment and hydrolysis studies in literature have been on ethanol production; hence, most results presented are usually for combined xylose and glucose sugar yields, fermented to produce ethanol. This poses a challenge particularly to this study where only glucose is the precursor to the production of the bio-based chemicals under consideration and independent glucose yields are not readily unavailable. In this study, xylose and other material components not utilised in the biorefinery were sent to the wastewater treatment plant for energy production. In addition, the majority of studies focus on enzymes used in fermentative processes to produce ethanol but this research focused on enzymatic hydrolysis to produce sugars for chemical conversions. It was therefore assumed that the enzyme performance for fermentative routes are comparable to those for chemically catalysed processes as well as that enzyme performances are dependent on the properties of lignocellulose feedstock. Appendix A-3 details overall key assumptions used in this study (and chapters 4 and 5).

A standard life cycle assessment (LCA) methodology used in this study is one of the most used methodologies in environmental impact assessments and it covers a wider range of impact categories. However, according to Arodudu et al's., (2017) study on the strengths and weaknesses of a LCA framework revealed that most of the sub-elements of the LCA such as biodiversity and land use, which cover the majority of the economic and social impact categories, have not been adequately incorporated in the current LCA frameworks because of difficulties that arise in quantifying certain indicators. Despite this limitation, the environmental impact categories quantified in LCAs give a wider range of indicators for environmental impact assessments than just determining GHG emissions that contribute to the global warming potential (GWP_{100a}).

For the social indicators, the major limitation lies in quantifying sustainability aspects such as the quality of life, human health and wellbeing, food, water and energy security (Arodudu et al., 2017; Patel et al., 2016; Hermann et al., 2007). To avoid these complexities, a simplified approach used quantifies the social indicator as the number of additional permanent jobs created by constructing and operating the biorefinery and CHP plant annexed to a conventional South African sugar mill. Another challenge usually lies in the difficulty in obtaining quality data for remuneration packages of different jobs.

Multi criteria decision assessments (MCDAs) are a useful multi-level strategy tool in accounting for multiple and conflicting criteria but are not necessarily comparable especially where different methods for ranking are used. This is because each method treats preference data differently and the criterion weights are interpreted differently (Kangas and Kangas, 2005).

Thus, due to the limitations that lie in the different methodologies chosen, it is necessary that these results be validated. Model outputs can be validated against parameters such as experimental data and pilot plant findings, expert intuitions and real system measurements, although this sometimes is not always achievable. It is therefore, important that collaborations take place between academic institutions and different stakeholders in industry for the enhancement of efficient validation.

1.4. Research novelty and significance

- **Product identification and shortlisting**

The identification and selection of bio-based chemicals for the South African sugar industry mentioned in chapter 2 is not novel in approach nor are the chosen chemicals unique from others already identified in literature. Nonetheless, the shortlisting exercise was important to identify potential bio-based chemicals to produce in a local context, taking into consideration the possible feedstock sources. To this end, agricultural residues at sugar mills provided this opportunity. It was from this final list that biorefineries producing various chemicals for the Sugar Technology Enabling Programme-Bioenergy (STEP-Bio) initiative, originated. The shortlisted chemicals and biorefinery complexes will form part of the database for different bio-based chemicals under the Biorefinery Techno-Economic Modelling (BRTEM) cluster.

Chemicals advanced in different studies vary depending on country specific interests. It is therefore, key that chemicals be identified for the local and developing countries' context. To this end, a quick shortlisting exercise conducted in this study identified 13 key chemicals for future feasibility studies by the Sugarcane Technology Enabling Programme for Bioenergy (STEP-Bio). The four chemicals under consideration in this study, as highlighted in section 2.2.2, are polyethylene (chapter 3), sorbitol (chapter 4), glucaric acid (chapter 4) and levulinic acid (chapter 5).

- **Novel contribution of chapter 3**

No techno-economic assessments (TEAs) are available on the production of polyethylene from lignocelluloses. Additionally, no TEAs on biorefineries producing PE and annexed to sugar mills, are available, to the best of the author's knowledge, although ethanol to ethylene biorefineries and their TEAs, are available. Ethanol is the starting material for polyethylene production, it is first converted to ethylene and finally to polyethylene. This study (as seen in chapter 3), was the first design, simulation and techno-economic assessment (TEA) of an integrated ethylene to polyethylene biorefinery annexed to a sugar mill and using lignocellulose feedstocks (sugarcane bagasse for the local context).

- **Novel contribution of chapter 4**

Studies on sorbitol and glucaric acid bioenergy self-suficient biorefineries from glucose, derived from sugarcane agricultural residues in chapter 4, and annexed to a conventional sugar mill, were the first to design and model a combination of pretreatment, hydrolysis, conversion and purification processes. This study also compared glucose yields after enzymatic hydrolysis for process routes using SO_2-steam explosion and dilute acid pretreatment. Secondly, it offered detailed TEAs and the social impact (based on the additional jobs created), of these biorefineries.

Some economic studies on the stand-alone production of sorbitol from first generation feedstocks via biological means, although not detailed, have been conducted (Silveira and Jonas, 2002). Concerning glucaric acid, its commercial production is conventionally via the oxidation of glucose using nitric acid and more recently, advancements (under proprietary rights) use a one pot single-process to produce glucaric acid from first generation (1G) glucose (Solmi et al., 2017). Additionally, a recent TEA on a biorefinery producing glucaric acid from corn stover has been conducted by Thaore et al., (2019). This biorefinery in addition to burning solid agricultural residues also used natural gas to meet its energy needs. At laboratory scale, glucaric acid production from biological means using *E. coli* have been investigated (Reizman et al., 2015).

- **Novel contribution of chapter 5**

Furthermore, chapter 5, investigating levulinic acid production from lignocellulose feedstocks was the first to conduct a techno-economic and social assessment of levulinic acid biorefineries using the Biofine process and annexed to a conventional sugar mill. This was done so as to generate multiple products including gamma valerolactone derivative (via levulinic acid hydrogenation). This study also took into consideration the impact which overproduction of levulinic acid would have on the market selling price of this chemical, assuming that producing 10% of the total global production capacities would affect selling prices. Levulinic acid is currently serving a niche market and valued at between US$ 5000/t–US$ 8000/t (Grand View Research, 2017).

Some techno-economic studies on levulinic acid production from sugarcane bagasse are available (van Benthem et al., 2002). However, the economic studies have been conducted in isolation, without integration into sugar mills, and no investigations were conducted into the impact which mass levulinic acid production would have on its market-selling price.

- **Novel contribution of chapter 6**

The life cycle assessments (LCA) conducted in chapter 6 are the first detailed studies on biorefineries producing sorbitol, glucaric acid and levulinic acid from lignocellulose feedstocks at sugar mills. The only other LCA studies on sorbitol (from first generation (1G) food feedstocks), glucaric acid (from corn stover) and levulinic acid (from wood) only used up to three impact categories, with global warming potential (GWP_{100a}) being the main environmental indicator. However, in the current study, eleven impact categories were used. Additionally, the environmental impacts per process area were considered including determining which pretreatment technology (SO_2-steam explosion or dilute acid) has more environmental benefits than the other. Overall, the most sustainable scenario was also determined using a combination of the environmental (chapter 6), social and economic impacts (from chapters 4 and 5) and the results were used as confirmation in chapter 7 where sustainability was determined using another approach, a multi criteria decision assessment (MCDA).

- **Novel contribution of the multi-criteria decision assessment**

A multi criteria decision assessment (MCDA) covered in chapter 7 is not novel, but was the first MCDA used for the purpose of scoring and ranking sorbitol, glucaric acid and levulinic acid biorefineries for the sugar industry stakeholders. This will offer initial insight into the sustainability of biorefinery complexes. This study was the first to formulate the sustainability impact indicators used in the MCDA for the chemicals under review.

Overall, this study is significant because it will provide key sugar industry stakeholders with detailed sustainability data required prior to any feasibility studies being undertaken on biorefineries at South African conventional sugar mills. This study also has potential to inform policy makers of major issues surrounding the bio-based chemical industry.

1.5. Thesis Structure

Chapter 1 is an introductory chapter and includes the project motivation and background, goal, research questions, project novelty and scope covered in this study.

In **chapter 2**, a literature review was conducted in order to highlight the shortcomings identified in relation to the research questions on this research topic. Areas covered included the biorefinery concept and its classifications, methodologies used in other studies and this current research for product identification and selection of potential bio-based chemicals for modelling in biorefinery complexes. This led to the shortlisting of polyethylene, sorbitol, glucaric acid and levulinic acid for this current study. **Chapter 2** also covers the chemical composition and characteristics of biomass and discusses the pretreatment and hydrolysis techniques used for the recovery of glucose recovery as the starting material for the short-listed chemicals. Furthermore, the semi commercial/commercial production processes of the shortlisted chemicals and their applications are outlined including the market projections of these chemicals, followed by the techno-economic, environmental and social impact studies.

Chapters 3, 4 and 5 are presented as separate studies, with chapter 3 considering the techno-economic and social impact of a polyethylene biorefinery built as an extension of an existing bio-ethanol biorefinery (black box).

The techno-economic assessment and social impacts of sorbitol and glucaric acid (chapter 5) and levulinic acid (chapter 6) biorefineries prepared in article format are compared to a combined heat and power (CHP) base case scenario that only produced electricity.

Chapter 6, also prepared in article format is on the environmental impacts of the profitable scenarios using life cycle assessments based on eleven (11) impact categories.

Chapter 7 is on a multi-criteria decision assessment where the profitable and marginally unprofitable scenarios (excluding polyethylene), are scored and ranked based on weighted economic, environmental and social indicators.

Chapter 8 provides a summary, conclusions and recommendations for future research.

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Chapter 2

2.0. Literature Review

Chapter 2 identifies the different chemicals as well as the selection of promising bio-based chemicals for production in biorefineries. It then defines the biorefinery concept, biorefinery classifications observed and the advancement of this approach over time. It then goes to cover the global sugar (including sweetener) and sugarcane capacities from which sugarcane bagasse and dried leaves are obtained. Also considered is lignocellulose feedstock availability (after sugar production), its composition and technologies used in industry to extract the four chemicals of interest (mostly from first generation and fossil fuel sources). Furthermore, the industrial applications, market performance and forecasts of the shortlisted chemicals are evaluated.

Techno-economic assessments of biorefineries, in particular for the production of polyethylene, sorbitol, glucaric acid and levulinic acid in a bioenergy self-sufficient way (where the use of fossil fuels is eliminated) is evaluated. In addition, the environmental and social impacts of lignocellulose biorefineries are considered. This is followed by a review of multi criteria decision assessments of biorefineries.

2.1. Identification and prioritisation of bio-based chemicals

2.1.1. Global studies (lists) on building block and derivative bio-based chemicals

Following the advancement of a green circular economy, several studies at an international level have identified promising bio-based building block and derivative chemicals with potential to positively impact global markets in bio-economies. The most notable and detailed studies have been the United States of America (USA), Department of Energy (DoE) reports conducted by the National Renewable Energy Laboratories (NREL) between 2004 and 2016 that identified 10-12 bio-based chemicals of interest. Table 2-1 summarises the building block and derivative chemicals shortlisted from the three NREL studies. Building block (or platform) chemicals are those chemicals that are starting materials for the production of co-products (de Jong et al., 2012b) whilst a derivative chemical is a final product usually with one particular application.

Table 2-1: Promising bio-based building block and derivative chemical targets as assessed in the USA DoE 2004, 2010 and 2016 reports (Biddy et al., 2016; Bozell and Petersen, 2010; Werpy and Petersen, 2004)

Top 12 chemicals-2004	Top 10 chemicals-2010	Top 12 chemicals-2016
1,4-Dicarboxylic acids (succinic, malic)	Succinic acid	Succinic acid
2,5-Furan dicarboxylic aid (FDCA)	Furans, incl. FDCA	Furfural
3-Hydroxypropionic acid (3-HPA)	3-HPA/aldehyde	-
Glycerol	Glycerol and derivatives	Glycerin
Sorbitol	Sorbitol	-
Xylitol/ Arabinitol	Xylitol	-
Levulinic acid	Levulinic acid	-
Aspartic acid	-	-
Glucaric acid	-	-
Glutamic acid	-	-
Itaconic acid	-	-
3-Hydroxybutyrolactone	-	-
-	Biohydrocarbons	-
-	Lactic acid (LA)	Lactic acid
-	Ethanol	-
-	-	Ethyl lactate
-	-	Xylene (para)
-	-	Propylene glycol
-	-	1,3-Propanediol
-	-	1,3-Butadiene
-	-	1,4-Butanediol (BDO)
-	-	Fatty alcohols
-	-	Isoprene

From the 2004 NREL report, 12 chemical building blocks considered as potential chemicals for future bio-economies were identified, which included sorbitol, glucaric acid and levulinic acid. This was followed by a 2010 report, updated with new building block chemicals (biohydrogens, lactic acid and ethanol), whilst other chemicals from the 2004 list were omitted (aspartic acid, glucaric acid, glutamic acid itaconic acid and 3-hydroxybutyrolactone), leaving a total number of 10 chemicals that included sorbitol and levulinic acid (Bozell and Petersen, 2010; Werpy and Petersen, 2004). More recently, a 2016 report with a list of 12 promising bio-based chemicals has been published. From the 2016 report, only the furans (furfural), succinic acid, lactic acid and glycerin from the previous 2004 and 2010 reports made it to this list.

Furthermore, other studies conducted in Germany (Van Ree et al., 2011), the Netherlands (Posada et al., 2013) and European countries (under the European commission) (Patel et al., 2006) have developed lists that have included chemicals not on the USA DoE lists such as acrylic acid, adipic acid, 1,4-Butanediol, farnesene, iso-butene and polyethylene (Taylor et al., 2015), fumaric acid and other carboxylic acids (Patel et al., 2006; Van Ree et al., 2011; Posada et al., 2013).

Generally, there were variations in the chemicals considered by different researchers with some chemicals common to most studies. Similarly, there were variations in the feedstock choices used for the different assessments of potential chemicals. Studies by Taylor et al., (2015) largely considered potential chemicals and biofuels from the sugar platform (C5 and C6 sugars excluding oligosaccharides and polysaccharides that are difficult to digest by various organisms) whilst Posada et al., (2013) focused on bioethanol-based products. Studies by Van Ree et al., (2011) and Patel et al., (2006) together with the 2016 and 2004 NREL reports (Biddy et al., 2016; Werpy and Petersen, 2004), were based on biomass feedstocks. These, according to the NREL reports were broken down to starch, hemicellulose, cellulose, lignin and oil, whilst the 2010 report considered potential products from carbohydrates. Therefore, this gives a useful indication of the different viable feedstock sources available to produce potential bio-based chemicals for bio-economies.

2.1.2. Local studies (lists) on building block and derivative bio-based chemicals

In the case of South Africa, a technical report compiled by the sugar industry (SMRI, 2015) listed 47 bio-based candidates of interest for the sugar industry stakeholders (see Table 2-2). This technical report comprises chemical products that can be produced from different feedstocks, including 1G, 2G and glycerol sources.

Table 2-2: List of bio-based candidates of interest to the South African sugar industry (SMRI, 2015).

1,2 Propanediol	Glutamic acid	Phenolic compounds
Acetate	Glycerol	Potassium chloride
Artificial sugars[a]	Hydroxymethylfurfural esters	Potassium sulphate
Butadiene	Iso-butanol	Propionate
Butyl and ethyl esters of levulinic acid	Isoprene	Propylene glycol
Carboxymethyl cellulose	Itaconic acid	Sacpol[c]
Cellulose acetate	Lactate esters	Sorbitol
Citric acid	Lactic acid	Styrene
Cogeneration[b]	Levulinic acid	Succinic acid
Ethanol	Lysine	Sucrose acetates
Ethyl lactate	Maltulose	Bio-syncrude oil[d]
Ethylene	Methanol	Terephthalic acid
Ethylene glycol	Methionine	Vanillin
Furanics	Nanocellulose	Volatile fatty acids
Furfural	n-Butanol	Wax
Furfural alcohol	Poly (furfural alcohol)	Xylitol

[a] Artificial sugars–produced from sucrose

[b] Cogeneration-steam and electricity generation from biomass

[c] SMRI produced biopolymer

[d] Syn-crude-produced from the catalytic cracking of pyrolysis vapours from lignocelluloses

As indicated in Table 2-2, some of the chemicals on this list are common to the 2004, 2010 and 2016 notable NREL lists, whilst chemicals including carboxymethyl cellulose, cellulose acetate, maltulose, methionine, nanocellulose, lysine, isoprene, sacpol and vanillin are unique to the local context and not listed by other reports highlighted in section 2.1.1.

Additionally, a study conducted by the author of this research specifically for this current study, shortlisted polyethylene, sorbitol, glucaric acid and levulinic acid as four of the 10-15 potential bio-based chemicals selected for production using lignocellulose feedstocks as summarised in Table 2-3 (in fulfilment of objective 1 of this study) (also see Appendix A-1 for the detailed chemicals identified prior to the shortlisting). In a local context, the most viable lignocellulose feedstock identified was agricultural residues from conventional sugar mills, which would be processed in bioenergy self-sufficient biorefinery complexes and annexed to the mill.

Table 2-3: Thirteen shortlisted chemicals for current study grouped according to their most common production routes (author's compilation from shortlisting exercise)

Non-fermentative pathways	Fermentative pathways
Building Blocks	
Sorbitol	PHA's
Levulinic acid	Glutamic acid
Glucaric acid	Itaconic acid
Xylitol	Succinic acid
Derivatives	
Cellulose acetate	Acetic acid
Vanillin	Citric acid
Polyethylene	

Table 2-3 presents the final list of chemicals, grouped as building block or derivative products produced via fermentative or non- fermentative (chemical) routes. The chemicals were shortlisted for the STEP-Bio programme. Therefore, from the groupings shown in Table 2-3, the present study investigated biorefineries producing polyethylene (PE), sorbitol, glucaric acid and levulinic acid, generated from non-fermentative (chemicals) means.

The variations observed in the local and international lists of potential chemicals for bio-economies suggest that the chemicals shortlisted are time dependent and location specific (Harrison et al., 2016). Their selection is influenced by factors including the availability of feedstocks, prevailing market demands of a given locality and the policy support mechanisms which are in place.

2.2. Approaches and criteria for product selection

Two approaches for screening bio-based chemicals come to the forefront. One involves detailed screening of these different chemicals (Biddy et al., 2016; Taylor et al., 2015; Bozell and Petersen, 2010; Werpy and Petersen, 2004), whilst the other adopts a quick way of shortlisting the chemicals at early stage design (Posada et al., 2013). The shortlisting conducted in this current research for the Sugarcane Technology Enabling Programme for Bioenergy (STEP-Bio) of South Africa involved a quick screening approach. Four criteria points were applied; technology maturity, not under consideration by other researching partners and has a low product to raw material ratio. This short study led to the selection of 10-15 chemicals as summarised in Table 2-3 for multiple, simultaneous postgraduate biorefinery projects. Also see Appendix A-1 for the full details on the criteria used to shortlist them.

Generally, with regards to product selection criteria, indicators used in the different studies ranged from as low as three to about ten, with the detailed approaches using more indicators for product screening than studies based on quick screening due to time constraints. One key criterion common to most reports was the economic indicator as it is the primary indicator that drives any business venture and was expressed in terms of product selling price, product market value, market demand, maturity, size and potential (Biddy et al., 2016; Posada et al., 2013; Bozelle and Petersen, 2010; Patel et al., 2006; Werpy and Petersen, 2004). Another indicator used as a criterion in most studies, including this current research was the maturity of a technology, termed "Technology Readiness Level (TRL)" (Biddy et al., 2016; Taylor et al., 2015; Posada et al., 2013; Bozelle and Petersen, 2010; Patel et al., 2006; Werpy and Petersen, 2004), which establishes how far a technology is from commercialisation. As the global awareness towards green economies has been increasing, recent studies have reflected this drive by considering environmental, health and safety aspects in their criteria, thus assessing the sustainability of a selected product at an early stage of product development (Biddy et al., 2016, Posada et al., 2013; Patel et al., 2006).

In conclusion, the selection criteria of promising bio-based chemicals have also varied because of variations in industrial interest and international demand for certain chemicals. However, with the potential that lies in biomass conversion to numerous possible products, it is necessary to reliably select chemicals that have mature technologies (Posada et al., 2013). The maturity of a technology to produce a bio-based chemical is one main criterion used in most studies. The TRL should be coupled with factors such as a high selling price, market demand and reasonable capital and operation costs for biorefineries to be economically viable. Also, issues of policy support, environmental impacts and compliance with environmental requirements, should be considered. The present study is based on the STEP-Bio programme list of 13 shortlisted chemicals, with polyethylene, sorbitol, glucaric acid and levulinic acid biorefineries being investigated. The four bio-based products generated via chemical and catalytic means have production processes at near commercial to commercial phase, a high market demand and can be produced from lignocellulose feedstocks in biorefinery complexes.

2.3. Biorefinery concept

A biorefinery has been defined as a system analogous to a petroleum refinery, where biomass instead of petroleum is the feedstock processed to produce a wide range of marketable bio-based chemicals and energy products in an integrated approach (Van Ree et al., 2014). The term biorefinery usually refers to and is derived from the raw material feedstock used as well as the biomass-conversion processes applied to obtain these bio-based products (Kamm et al., 2005). However, some other classifications have been identified (de Jong et al., 2012a), and used in the early stages of the development of the biorefinery concept.

2.3.1. Biorefinery classifications

Early biorefinery classifications are available (Dyne et al., 1999; Kamm and Kamm, 2004; Gravitis et al., 2008; Demirbas et al., 2011; Reno et al., 2014) and were at times a source of ambiguity. To this end, these classifications have been refined over the years to eliminate uncertainties associated with describing them (Kamm et al., 2005). The most widely used classification has divided biorefinery facilities in four groupings. The first grouping was based on the type of feedstock used, leading to descriptions such as municipal solid waste (MSW) biorefineries, where the feedstock was organic residues or municipal solid waste. The second type describes the biorefinery by the treatment process used, giving rise to terms such as thermochemical biorefineries. The third grouping is based on the product type i.e. fuel carrier or chemical. Lastly, the fourth description is a detailed grouping that links the raw materials and final products using the order: Name of platforms/Feedstock/Products/Processes (de Jong et al., 2012a). This last group has been applied as a standardised system of classification used extensively by the International Energy Agency (IEA) Biorefinery Task 42 project (Van Ree et al., 2014).

Even though different classifications and descriptions of biorefineries were observed, most of the biorefinery classifications are based on the biomass feedstock used and this current study observed that the underlying biorefinery concept of producing an array of products was appropriately applied. The classification by the International Energy Agency is now extensively used to describe biorefinery complexes.

2.3.2. Growth of the biorefinery approach

The growth of the biorefinery approach has encouraged the sustainable production of chemicals in developed and emerging economies, with economic benefits being realised (Haro et al., 2013; Lunt, 2014). This has led to the production of numerous bio-based products with potential to replace or complement their fossil-based counterparts as bio-based chemicals have the same properties and functions as fossil resources (Taylor et al., 2015; de Jong et al., 2012b). With this similarity between properties, some bio-based chemicals are suitable for use in downstream processing technologies and infrastructure used for fossil-based feedstocks and hence have been termed “drop in” chemicals (de Jong et al., 2012b).

Biorefineries have started emerging in European countries during the last one to two decades, mainly because of concerns about global warming and climate change, depletion and inaccessibility of fossil reserves leading to national and regional legislation on bio-based economies being put in place (King, 2010). In developing countries, some penetration of biorefineries has taken place, especially for the production of bio-ethanol and bio-energy (Axelsson et al., 2012; King, 2010; Botha and von Blottnitz, 2006; Van Dam et al., 2005) (see Table 2-4). More recently, furfural has been produced in mass by South Africa, making it the third world's largest producer of this commodity (Biddy et al., 2016). Also, other advancements have included conceptualised research on biorefineries annexed to typical South African sugar mills conducted by researchers including Nieder-Heitmann et al., (2018); Mandegari et al., (2017a); Farzad et al., (2017); Petersen et al., (2014); Leibbrandt, (2010). These studies were mostly of bio-based chemicals produced via fermentative process routes at the exclusion of PE, sorbitol, glucaric acid and levulinic acid that follow a non-fermentative (chemical) route, which this study invetsigates.

Table 2-4: Some studies that have conducted techno-economic studies on biorefineries using varied feedstocks to produce chemicals and electricity

Feedstock	Country	Products	References
Sugarcane bagasse	Brazil	Methanol, ethanol, electricity	(Reno et al., 2014)
	South Africa	Ethanol, methanol, lactic acid acid, electricity	(Mandegari et al., 2018)
	Colombia	1G, 2G, 3G ethanol	(Moncada et al., 2014)
	South Africa	Lactic acid, methanol, ethanol, furfural, butanol, FT syncrude	(Farzad et al., 2017)
	Brazil	Ethanol (1G and 2G), electricity	(Dias et al., 2013)
	Brazil	Levulinic acid, furfural, formic acid, electricity	(van Benthem et al., 2002)
	Brazil	1G and 2G ethanol	(Furlan et al., 2013)
	Brazil	2G ethanol	(Dias et al., 2012)
	Australia	2G ethanol	(O'Hara, 2011)
	USA	Ethanol	(Kazi et al., 2010)
	South Africa	2G ethanol, electricity	(Petersen et al., 2014)
	South Africa	Succinic acid, Polyhydroxylbutyrate (PHB)	(Nieder-Heitmann et al., 2018)
	Argentina	Xylose, xylitol, furfural	(Clauser et al., 2016)
	South Africa	Xylitol, citric acid, glutamic acid, electricity	(Ozudogru et al., 2018)
Corn stover	Sweden	Ethylene	(Arvidsson and Lundin, 2011)
	China	Ethanol, succinic acid, acetic acid, electricity	(Luo et al., 2010)
	U.K	Glucaric acid, electricity	(Thaore et al., 2019)
Wood chips	Canada	Pulp and paper	(Marinova et al., 2009)
	USA	2G ethanol	(Huang et al., 2009)
	Germany	Ethylene, lignin and bio-methane	(Nitzsche et al., 2016)
Cereal and oilseed	Sweden	Ethanol, biogas, electricity and heat	(Ekman et al., 2013)
Waste glycerine	UK	Biodiesel and succinic acid	(Vlysidis et al., 2011)
Grain and straw	Sweden	1G and 2G ethanol	(Joelsson et al., 2016)

Traditionally, the feedstock for most biorefinery approaches was specifically 1st generation (1G) edible resources but with the further advancement of the biorefinery concept, 2nd generation (2G) inedible feedstocks such as agricultural residues (sugarcane bagasse, cereals, wood chips, corn stover etc.) are also being considered in developed and developing countries as shown in Table 2-4.

Second generation feedstocks do not compromise food security and have environmental benefits (which have mostly been measured as greenhouse gases (GHGs) in comparison to fossil fuels (Wolf et al., 2005; Paturska et al., 2015). However, 2G biorefineries' are not as technologically advanced as fossil-based technologies (and 1G technologies). More recently, 3rd generation (3G) biorefineries using algae (Moncada et al., 2014) have emerged (Table 2-4) although these studies are still in their infancy.

Therefore, biorefinery studies have been gaining ground globally from a conceptual basis to the actualisation of some into pilot and commercial plants. Apart from some of the biorefineries having positive economic returns, some studies have revealed that cleaner products are generated and thus have reduced greenhouse gas (GHG) emissions unlike fossil-based petrochemical sources.

2.4. Lignocellulose feedstock availability

The global plant biomass capacity is estimated at 200 x 10^9 t/y, of which 90% is lignocellulose (Saini et al., 2015). Sugarcane bagasse's global availability is the 3rd highest agriculture residue after rice straw (4-fold higher) and wheat straw (2-fold higher) (Saini et al., 2015). Lignocellulosic biomass can be converted into various bio-based chemicals in a biorefinery. These chemicals range from building blocks to derivative chemicals.

To give an indication of the global and local lignocellulose feedstocks from sugarcane bagasse and brown leaves, which also gives an idea of the global sugar demand, cane sugar global capacities are discussed in section 2.4.1 and 2.4.2.

2.4.1. Global capacities of cane sugar

The demand for sugar globally is high because of its extensive use in the food and beverage industries (FAO, 2018). The total global raw sugar production for 2019/20 is estimated at 174 million tonnes, which is 3.4% lower than the previous year's production due to expected lower yields from the top producers, Brazil and India (USDA, 2019). Despite this, market reports have forecasted a 2.1% steady growth of this commodity during the period 2020–2025 (FAO, 2018). Approximately 65-70 % of the total world's production is from sugarcane (George et al., 2010) and so 2019/20 cane sugar production stands at 117 million tonnes based on a 67.5% average value of the global production volume. Therefore, part of the agricultural residues generated after sugar production at conventional sugar mills can be valorised into bio-based chemicals and bio-energy.

Additionally, with changing eating habits and increased awareness of the health effects of excessive sugar consumption, the sugar market has seen an emergence of the sweetener market although cane sugar is still dominant. Figure 2-1 shows the % production volumes of sugar and sweetener markets where starch sweeteners (high fructose corn syrup, inulin and polyols such as sorbitol, xylitol and mannitol) stand at 22 %. Intense sugars (including saccharin, aspartame, sucralose and cyclamate) represent 3% of the global production volume (Bahndorf and Kienle, 2004) whilst raw sugar represents 75% of the combined production capacities.

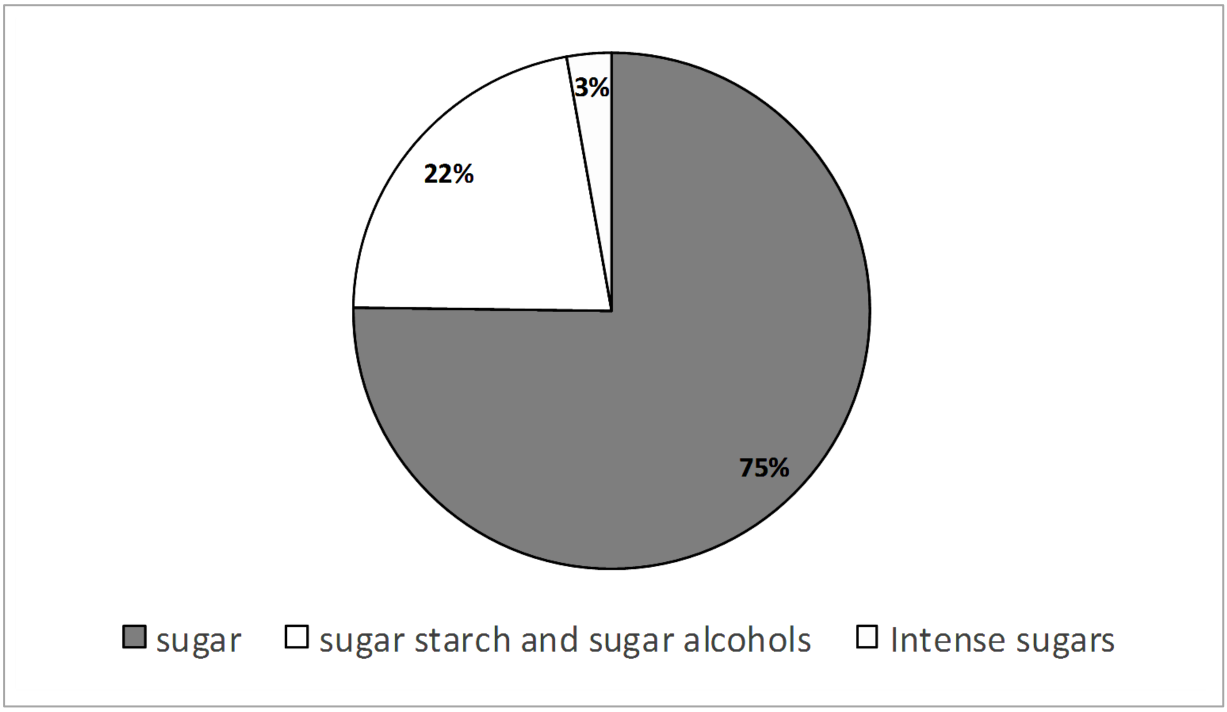
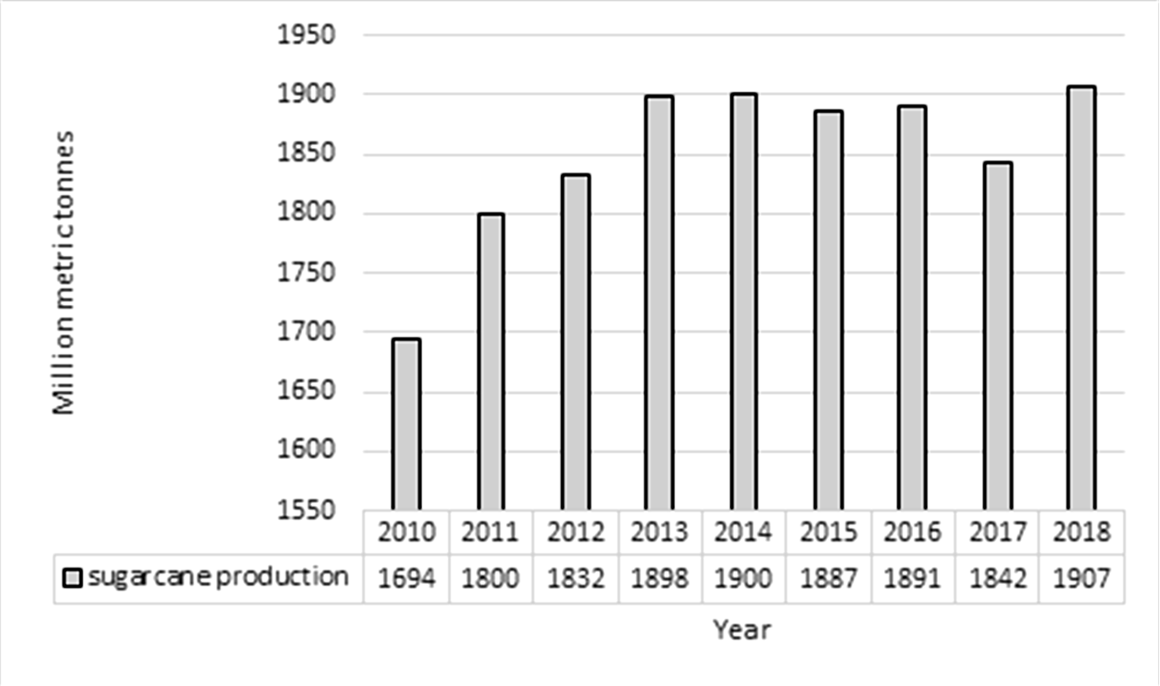


Figure 2-1: Sugar and sweetener production capacities in US$ billion market value (Bahndorf and Kienle, 2004)

2.4.2. Local and global sugarcane and bagasse production capacities

Material balance studies show that 1kg of sugar produced results in about 0.3 kg of molasses as a secondary product and 1.25 kg of bagasse (dry basis) (Botha and von Blottnitz, 2006). In addition, as reported by Garcia-Perez et al., (2002) 270 kg bagasse/t of cane milled are generated at sugar mills. Therefore, if the South African sugar industry crashed 13.8 million tonnes of sugarcane during the period 2018/2019 (South Africa Sugar Industry Directory, 2020), then 3.7 million tonnes of bagasse was generated. At most typical sugar mills, bagasse is currently burned inefficiently for energy production as discussed in chapter 1, but replacing inefficient boilers with efficient ones, would free more agricultural residues for bio-based chemicals' production (detailed discussion in section 1.1). Futhermore, if non-burn sugar harvesting practices are used, more biomass from fields (20 t/h dry mass brown leaves) is generated and part of it can be included in the bagasse feedstock mix (45 t/h dry mass) whilst some is left as a mulch in fields. On a global scale, the total sugarcane production capacities from 2010-2018 as shown in Figure 2-2 ranged from 1690 to 1907 million metric tonnes (Statista, 2020); therefore, sugarcane bagasse including brown leaves generated in fields practising non-burn harvesting techniques has potential as a lignocellulose feedstock.



	2010	2011	2012	2013	2014	2015	2016	2017	2018
☐ sugarcane production	1694	1800	1832	1898	1900	1887	1891	1842	1907

Figure 2-2: Global sugarcane production capacities from 2010 to 2018 (Statista, 2020)

Sugarcane thrives mostly in tropical and sub-tropical climates and Brazil is the world’s largest producer of sugar from sugarcane (scientific name: Saccharum officinarum) (Canilha et al., 2012) at 739 million t/y, followed by India, China, Thailand, Pakistan, Mexico, Colombia, Indonesia, Philippines and the United States of America. South Africa is the largest producer of cane sugar in Africa and is in the world’s top 15 leading suppliers of this product, having an estimated annual direct market of US$ 0.9 million from its local and international sales (SASA, 2017). The major cane-growing regions of irrigated and rain-fed plantations of South Africa comprise 14 mills; twelve factories are located in Kwa-Zulu Natal and two are in Mpumalanga (SASA, 2013).

In summary, biomass resources are readily available at times in generous amounts with lignocellulose being the most abundant of all biomass types. At local sugar mills, sugarcane bagasse and brown leaves are identified as potential feedstocks for value–addition to chemicals besides their main use as a source of energy.

2.5. Lignocellulose biomass composition

Producing bio-based chemicals from lignocelluloses requires a breakdown of the feedstock structure. Sugarcane is made up of fibrous stalks that are rich in sucrose sugar, the food component of the plant, which already has a niche in the market. The sucrose content of the sugarcane represents approximately 12-15% of the whole plant (mass basis) (Mutton, 2008). Approximately 11-16% is fibre, the starting material for the production of potential bio-based chemicals. The rest of the plant (> 70%) is water (Mutton, 2008). Hence, the whole sugarcane plant can be valorised into useful products. Figure 2-3 shows a general breakdown of the food and non-food components of sugarcane, including the available quantities of the possible products that can be extracted from it.

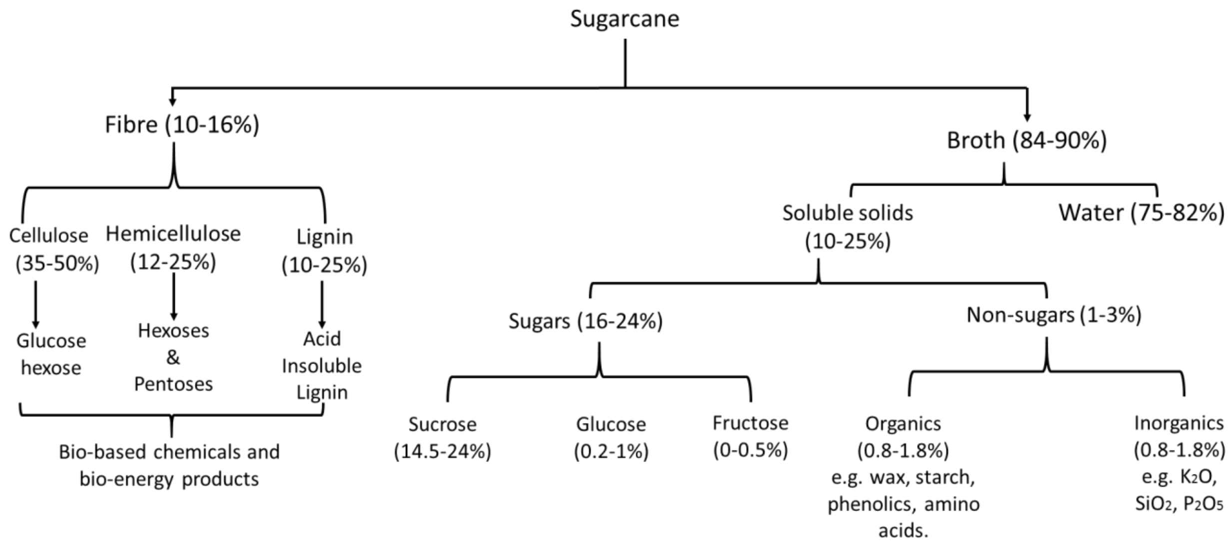


Figure 2-3: General composition of the food and non-food parts of sugarcane (Redrawn from (Mutton 2008))

Lignocellulosic biomass has three major fibre components (10-16%) namely cellulose, hemicellulose and lignin as shown in Figure 2-3. Also contained in the sugarcane structures are smaller amounts of organics (0.8-1.8%) such as proteins and starches, and inorganics including waxes and ash (Mutton, 2008).

The chemical diversity of the three major components exists in varying proportions not only in different types of lignocellulose material but also in one type of the same crop, whether naturally or selectively bred (Benjamin et al., 2013). These variations can be attributed to factors including climate, type of soils used and harvesting, collection and storage methods (Kenney et al., 2014; Solomon, 2009). Therefore, sugar yields from sugarcane per process are bound to vary regardless of the application of similar process conditions. Table 2-5 gives a summary of the variations in major components of sugarcane grown in different regions of the world.

Table 2-5: Feedstock composition (wt% dry mass basis) of sugarcane feedstocks from different regions (redrawn from (Canilha et al., 2012))

Country	**Cellulose**	**H.cellulose**	**Lignin**	**Ash**	**Extractives (free basis)**	**Reference**
Brazil	37.7	27.2	20.6	6.5	-	(da Silva et al., 2010)
Brazil	50	25	25	2-3	-	(Basso et al., 2013)
South Africa	40.6	22.8	25.5	3.6	7.5	(Nsaful et al., 2013)
South Africa	41.1	26.4	21.7	4.8	6.8	(Petersen et al., 2014)
South Africa (local and imported)	32.6-40.7	23.6-31.0	14.4-23.1	0.6-3.4	3.5-12.4	(Benjamin et al., 2013)
USA	43	24	22	4.8	-	(Kim and Day, 2011)
La Reunion France	45	26	20	2.1	9	(Boussarsar et al., 2009)

The primary platform molecule extracted from lignocellulose biomass is a simple monomer sugar and it is from this material that bio-based chemicals are produced. For instance in sugarcane hemicellulose, the main simple sugars present are xylose and arabinose with minute quantities of mannose and galactose. Xylose is the starting material for xylitol production. On the other hand, the main lignocellulose component with the highest glucose content is cellulose. Glucose can be processed in a number of different ways to produce bio-based chemicals such as ethanol, polyethylene, sorbitol, levulinic, glucaric, adipic and succinic acids. The three major lignocellulose components are described in sections 2.5.1, 2.5.2 and 2.5.3.

2.5.1. Cellulose

Cellulose is the most abundant and main component in cell walls of lignocellulose biomass. It consists of 40-50% of the feedstock and is the primary source of glucose used to produce the four shortlisted chemicals. It is a strong molecular crystalline structure with long chains of C6 glucose monomers. Cellulose is made of the polysaccharide glucan, which is depolymerised enzymatically or chemically to monosaccharide D-glucose, a hexose monomer (Hayes et al., 2006).

2.5.2. Hemicellulose

Hemicellulose is the second most prevalent component in lignocellulose biomass at 25-35%. It is a pseudo cellulose molecule, a carbohydrate polymer containing C5 and C6 sugars. Hemicellulose is relatively amorphous and interacts with cellulose and lignin. Its amorphous nature causes hemicellulose to easily hydrolyse into solution under milder pretreatment and hydrolysis conditions than cellulose. It mainly constitutes the polymers mannan and galactan (hexoses) and xylan and arabinan (pentoses), which, when hydrolysed, form monosaccharides D-mannose, D-galactose, D-xylose and L-arabinose, respectively (Lavarack et al., 2002).

2.5.3. Lignin

Lignin is a phenolic polymer described as essentially the “glue” that binds the whole plant structure together giving the plant structure rigidity and resistance to withstand environmental elements such as pest attacks and harsh weather and also transports water to the plant tissues (Liu et al., 2018). While cellulose and hemicellulose are polysaccharides that can be hydrolysed to simple sugars, lignin is the largest non-carbohydrate fraction of lignocellulose contributing 30% of the total weight of lignocellulose. Lignin holds about 40% of the energy content in lignocellulose (Chaturvedi and Verma, 2013), making it a potential source of heat and power. Other value added products from lignin i.e. macromolecules, polymers and oxidized products (vanillin and vanillic acid), are currently explored but not commercialized, due to high processing costs (Fache et al., 2015).

Feedstock composition plays a critical role in process design (Murat Sen et al., 2012). For lignocelluloses biorefineries, pretreatment and hydrolysis processes are a prerequisite as they assist in the breakdown of the lignocellulose structure for the easy release of targeted sugars (i.e. xylose, and glucose) that are processed further downstream. This leads to higher capital and processing costs for lignocelluloses than 1G feedstocks that are devoid of a pretreatment stage. These pretreatment and hydrolysis methods are at varying technological advancement ranging from laboratory to commercial level (Taylor et al., 2015).

2.6. Pretreatment of lignocellulose biomass

A lignocellulose biorefinery constitutes four main process stages: pretreatment, hydrolysis, conversion and purification further downstream. These process stages are discussed in this section and subsequent ones as they are unavoidable stages that are required in the production of the shortlisted chemicals from lignocellulose feedstocks.

Pretreatment technologies deconstruct the naturally resistant lignocellulose feedstocks, and increase the material's structural porosity, thus exposing the lignocellulose components of cellulose, hemicellulose and lignin for enzymatic digestion (Cherubini, 2010) into monomeric sugars xylose, glucose and arabinose. This makes the accessibility of targeted sugars by downstream processes less challenging. Figure 2-4 illustrates the effect which pretreatment has on the different components of lignocellulose biomass.

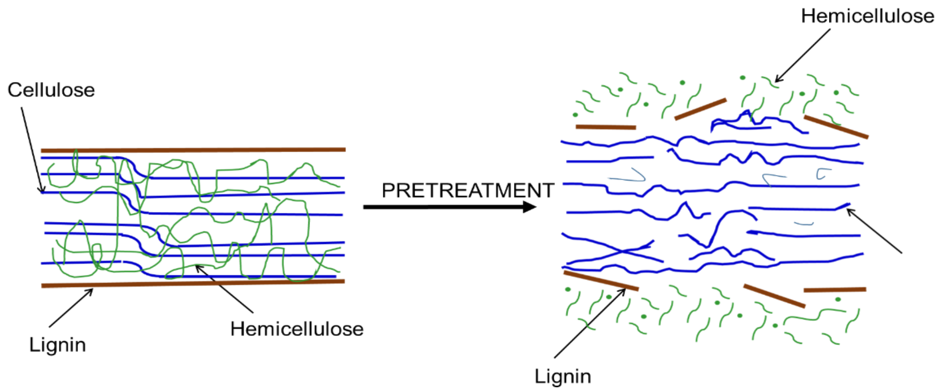


Figure 2-4: Schematic presentation of the effects of biomass pretreatment on the lignocellulose components (redrawn from (Mosier et al., 2005))

Depending on the raw material and nature of the target product, different pretreatment methods are used, namely physical, chemical, physico-chemical and biological, which induce different monomer sugar yields and improve the effectiveness of enzyme treatment techniques further downstream (Pedersen and Meyer, 2010).

2.6.1. Pretreatment technologies

Pretreatment technologies can be grouped as physical, chemical, physical-chemical and biological; however, despite the advancements made in these pretreatment technologies, most of them are still uneconomical, ineffective and in their nascent stages. Therefore, in pretreatment technology selection, a trade-off between process economics and sugar yields must be reached (Gnansounou and Dauriat, 2011; Kazi et al., 2010) including the environmental considerations of these pretreatments. Figure 2-5 shows some examples of the different pretreatment technologies and their possible effects on biomass. However, emphasis is given to milling (TRL 5-6), SO_2-steam explosion (TRL 6-8) and dilute acid pretreatment (TRL 5-7) technologies (Taylor et al., 2015) that were applicable to this current research:

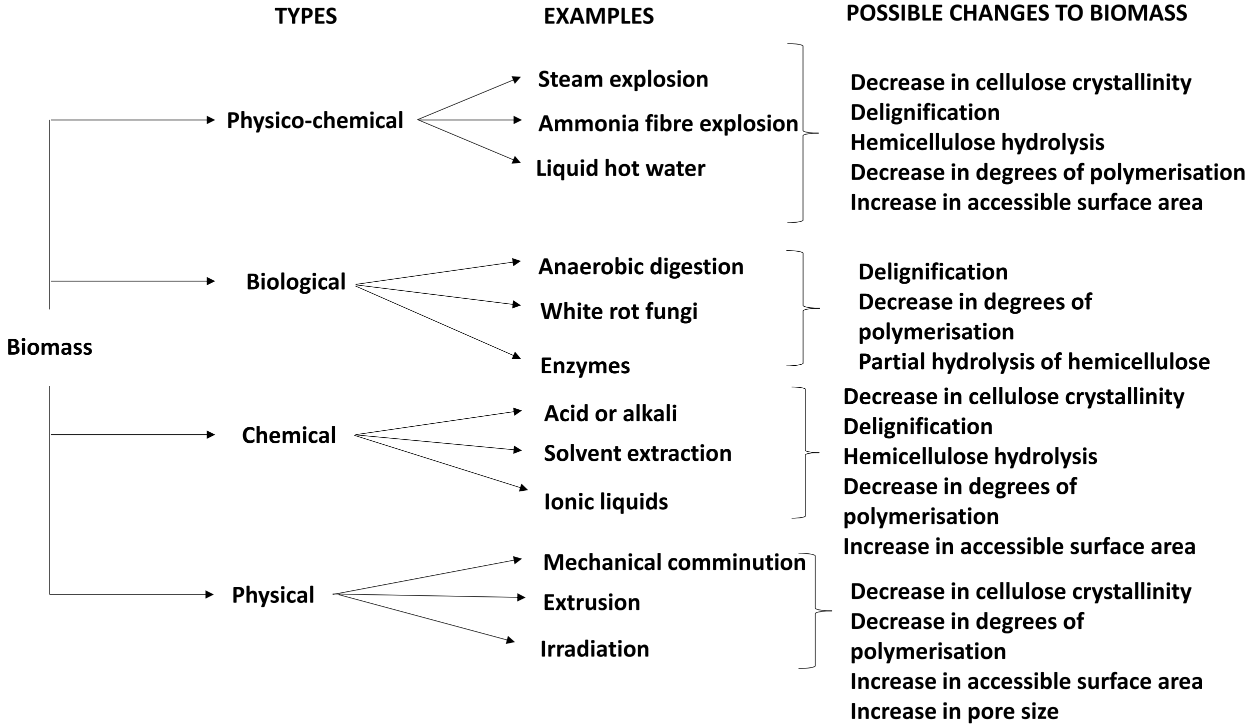


Figure 2-5: Examples of pretreatment technologies and possible effects on biomass (Brodeur et al., 2011; Kumar and Murthy, 2011)

2.6.1.1. Physical pretreatment-milling

Milling, a physical pretreatment, also referred to as a mechanical process, usually involves a reduction in particle size, cellulose crystallinity and degree of polymerisation as the surface area of lignocellulose increases with reduced particle sizes. Mechanical methods include chipping, milling/comminution and grinding of particles to the desired particle size (Alvira et al., 2010). This method tends to be energy intensive, costly and attains low sugar yields.

Milling, chipping, grinding have been used on materials including hardwood, straw, corn stover, alfalfa, cane and sweet sorghum bagasse (Saini et al., 2015). Milling of sugarcane to extract the juice, occurs in a conventional sugar mill and generates sugarcane bagasse as one of the residues, which is the main feedstock for the biorefineries. Most studies that have used sugarcane bagasse as feedstock in biorefineries did not include additional mechanical steps to further reduce the feedstock particle size after sugar juice extraction prior to biorefining (Farzad et al., 2017; Mandegari et al., 2017; Hermann et al., 2007; Lavarack et al., 2002). Milling is a technology being used at near commercial to commercial level, with a TRL of 5-7 (Taylor et al., 2015).

2.6.1.2. Chemical pretreatment–dilute acid pretreatment

Chemical pretreatment methods include alkali or acid based technologies. Acid-based treatments can either be diluted or concentrated (30-70 wt% concentrations), inorganic or organic acids that act as catalysts. Concentrated acids are avoided due to high maintenance and equipment costs associated with protecting process vessels from acid corrosion. Therefore, weak acid pretreatment is the conventional method for industrial applications, with dilute sulphuric acid (H_2SO_4) being the most used even though nitric and hydrochloric acids have also been used despite being more expensive than H_2SO_4 (Kumar et al., 2009).

Dilute acid (0.5-1.5 wt% acid concentration) pretreatment is one of the most researched pretreatment methods (Kazi et al., 2010) with operating temperatures of between 140–215 ^{o}C and residence times of 12-22 mins for sugarcane bagasse (Benjamin et al., 2013; Diedericks et al., 2012). However, process conditions are usually determined by the feedstock type and desired downstream products. Temperatures between 90–180 ^{o}C and 15-180 min residence times have been used on feedstocks including rice straw, wheat straw, sorghum and corn stover (Alvira et al., 2010). Dilute acid pretreatment is a technology currently applied at near commercial to commercial level, with a TRL of 5-7 (Taylor et al., 2015).

Dilute acid pretreatment mainly solubilises the hemicellulose fractions into pentose and hexose sugars (Agbor et al., 2011; Kazi et al., 2010) due to the hemicellulose's amorphous nature. Lignin is moderately or not hydrolysed in this pretreatment type but dilute acid pretreatment also leads to the formation of inhibitory products, which require a detoxification stage to remove them. Their removal aids in cellulose accessibility by enzymes in downstream processes (Agbor et al., 2011; Kazi et al., 2010). Examples of these inhibitors generated include acetic acid, formic acid, furan derivatives and phenolic compounds (Benjamin, 2014).

Table 2-6 makes a comparison of the composition of hemicellulose hydrolysates following dilute acid pretreatments of different lignocellulose feedstocks at acid concentrations of 1.9–3.8 w/v H_2SO_4. It shows some of the main inhibitors generated, which vary from one type of feedstock to another.

Generally, the hydrolysate yields of xylose, arabinose and glucose between bagasse and wheat straw were comparable even though bagasse's acid concentration was higher. Process optimisation is therefore useful in estimating the maximum reagents required for a process to achieve acceptable yields.

Table 2-6: Composition of hydrolysates from various feedstocks following dilute acid pretreatment

Feedstock	Bagasse	Sugarcane leaves	Wheat straw
Acid	3.8% w/v%H_2SO_4	2.90 w/v% H_2SO_4	1.85 w/v% H_2SO_4
Sugar concentration (g/l)			
Xylose	14.3	56.5 combined sugars	12.9
Arabinose	2.9		2.7
Glucose	2.4		1.9
Inhibitor concentrations (g/l)			
Acetic acid	4.1	3.19	2.9
HMF	0.04	0.15	-
Furfural	-	0.56	0.2
References	Sritrakul et al., 2017	Moutta et al., 2011	Canilha et al., 2008

2.6.1.3. Physico-chemical pretreatment–SO2-steam explosion

This pretreatment type combines physical and chemical techniques under mild chemical conditions but when carried out at elevated reaction conditions it is referred to as hydrothermal pretreatment (Brodeur et al., 2011). Steam explosion is one example of this pretreatment method, it is a widely used hydrothermal physical-chemical method (Taylor et al., 2015; Agbor et al., 2011) as it has the highest technology readiness level compared to other pretreatment methods at 6-8 (demonstration to commercial stage) (Taylor et al., 2015). Steam explosion can be used in the presence of acid (such as H_2SO_4) or gaseous catalysts such as SO_2 or CO_2 (Trajano and Wyman 2013). Inherent moisture in biomass reacts with the gas or inorganic acid creating an acidic environment and acetic acid from the acetyl groups both act as catalysts that partially hydrolyses hemicelluloses (Weil et al., 1997). In steam explosion, biomass is contacted with high-pressure steam (HPS) and after a short residence time, its contents are released into a flash drum, where a sudden drop in pressure causes an explosive breakdown of the biomass structure (Trajano and Wyman, 2013). Temperatures ranging from 160–230 ^{o}C and varying residence times (seconds to minutes) have been used (Bura et al., 2003; Ohgren et al., 2005; Sendelius, 2005).

Generally, SO_2-steam explosion temperature and pressure ranges (160-230 ^{o}C at 9–10 atm) are higher than in dilute acid pretreatment (90–215 ^{o}C at 1atm) whereas the residence times are lower in SO_2-steam explosion than dilute acid pretreatment. The elevated process conditions have cost implications because of the need to use pressure vessels and several vessels to contain pressurised reactions and accommodate mixtures for longer time periods respectively (FitzPatrick et al., 2010). Both SO_2-steam explosion and dilute acid pretreatments are subject to one or more of these cost implications. Moreover, steam explosion has high glucose yields (Taylor et al., 2015) but one key barrier of this process is the formation of inhibitors, which compromise the final product yields (Pandey, 2008) if not effectively removed. Therefore, trade offs are required between process costs and sugar yields or inhibitor formation and its effective removal. Table 2-7 gives a summary of the varied capital costs of some pretreatment studies from previous techno-economic studies. The dilute acid and SO_2-steam explosion pretreatment capital costs varied between 16–24% of the total installed cost.

Table 2-7: Capital investment costs for dilute acid and SO_2 -steam explosion pretreatments from various studies

Pretreatment technology	**Pretreatment capital cost (% of the total installed cost)**	**Reference**
Dilute acid	35%*	(Humbird et al., 2011)
Dilute acid	15.5%	(Hamelinck et al., 2005)
SO_2-steam explosion	16-20%	(Wingren et al., 2003)
Dilute acid	23.6	(Aden and Foust, 2009)
Dilute acid	19.5%	(Wooley et al., 1999)

*Combined dilute acid pretreatment and enzymatic hydrolysis

Steam explosion and dilute acid pretreatments as discussed in section 2.6.1.2 are effective technologies used in industry and are able to achieve comparable hemicellulose hydrolysis (% solubilisation) as summarised in Table 2-8, with minor differences arising from feedstock choice and process conditions. Significant differences in the two technologies therefore, could lie in the capital investment costs and possibly their environmental burdens but not in the effectiveness of pretreatment. Hemicellulose hydrolysis (solubilisation) improves the digestibility of cellulose during enzymatic hydrolysis and yields of between 14–23 g/100g hemicellulose (from the two processes) have been achieved in previous studies (see Table 2–8) for feedstocks (sugarcane bagasse, wheat straw, corn stover and spruce) with hemicellulose compositions of 21–28%. No comparative studies however, on the environmental impacts of the two technologies are readily available.

Table 2-8: Comparison of pretreatment technologies and their effect on hemicellulose hydrolysis

DILUTE ACID				
	% Hemicellulose	**% Hydrolysis**	**Yield (g/100 g)**	**References**
	28	72	20	(Lavarack et al., 2002)
	24	75	18	(Diedericks et al., 2012)
	26	62	16	(Canilha et al., 2008)
	21	92	19	(Aguilar et al., 2002)
STEAM EXPLOSION				
	% Hemicellulose	**% Hydrolysis**	**Yield (g/100 g)**	**References**
(SO_2-catalysed)	24	57	23	(Carrasco et al., 2010)
(SO_2-catalysed)	26	87	16	(Rudolf et al., 2008)
(CO_2-catalysed)	23	63	14	(Ferreira-leitão et al., 2010)

Despite the differences in the capital costs of the various pretreatment technologies, omitting this stage has implications for product yields and downstream processes for the removal and/or recovery of inhibitors and by-products (Trajano and Wyman, 2013) and so it is an unavoidable stage for most lignocellulose processing technologies.

2.7. Enzymatic hydrolysis

Enzymatic hydrolysis is one of the main technologies investigated up to commercial scale (Balat 2011) (TRL 7-8). During this process, cellulose liberated from pretreatment technologies is converted to glucose (hexoses) using cellulase enzymes, whilst minor portions of hemicellulose are catalysed to pentoses (xylose) as shown in the overall equations 2-1 and 2-2 (Nitzsche et al., 2016). This pocess occurs at mild process conditions (pH 4.8-5.0 and temperatures 45–50 ^{o}C) (Canilha et al., 2012).

Cellulose hydrolysis : $(\text{Glucan})_n + {}_n\, H_2O \rightarrow n$ Glucose Equation 2-1

Hemicellulose hydrolysis: $(\text{Xylan})_n + n\, H_2O \rightarrow n$ Xylose Equation 2-2

Cellulase enzymes are catalytic proteins that specifically target cellulose and break it down into a disaccharide called cellobiose, then hydrolyse it to glucose monomers (Humbird et al., 2011). Enzymatic hydrolysis of celluloses requires three groups of cellulolytic enzymes (cellulases). The first component is endo-β-1,4-glucanases, which attracts regions of low crystallinity in the cellulose fibres, creating free chain ends (Canilha et al., 2012). The second group of enzymes is exoglucanase or cellobiohydrolases that degrades the cellulose further by removing cellobioses from the free end-chains and the third β-glucosidase and then hydrolyses cellobiose into glucose (Canilha et al., 2012; Kumar et al., 2008), the precursor to the production of the shortlisted chemicals in the current study.

During enzymatic hydrolysis, degradation of products do occur and lignin can also react to form phenolics and polymeric materials (Balat, 2011). Degradation of hemicelluloses leads to the production of inhibitors such as acetic acid and furfural from xylose at high temperature and pressure whilst 5-hydroxymethyl-furfural (HMF) is produced from hexose (glucose) from celluloses (Balat, 2011).

Most enzymatic hydrolysis studies have been mainly conducted for the production of ethanol (Sun and Cheng, 2005; Cheng et al., 2008; Tsoutsos and Bethanis, 2011; Kim et al., 2014; Sritrakul et al., 2018). Hence, even their inhibitory effect has mainly been related to the ethanol producing enzymes used during enzymatic hydrolysis and organisms used in simultaneous saccharification and fermentation (SSF). However, with chemical processes using lignocellulose feedstocks, inhibitors produced only impact enzymes in the hydrolysis stage and not the downstream chemical environments. An opportunity therefore exists to explore alternative and cost-effective enzymes that are not linked to downstream SSF processes.

Some limitations of enzymatic hydrolysis (although an effective technology) include its slow process that takes hours to days (Canilha et al., 2012; Humbird et al., 2011) for the reaction to go to completion. Enzymes are also expensive and sensitive to temperature, which deactivates or denatures their proteins when operated outside their optimum temperatures leading to a drop in cellulose conversions (Humbird et al., 2011). Research is currently ongoing into commercial enzymes with high sugar yields at low enzyme loading doses and optimised enzymatic reaction temperatures (Humbird et al., 2011), which to some extent lowers process costs (Canilha et al., 2012). Furthermore, since enzymes are affected by inhibitors; cellulosic feedstocks require a wash stage (water–acetone wash) or an evaporation step where inhibitors such as furfural, acetic acid and xylo-oligomers formed during pretreatment are removed prior to enzymatic hydrolysis (Benjamin et al., 2013). Other inhibitor detoxification technologies exist (though not considered in this research) such as membranes, ion exchange chromatography, neutralisation, overliming, adsorption (on activated carbon) and solvent extraction (Canilha et al., 2012), which can also be applied as purification technologies as briefly discussed in section 2.8.

2.8. Purification techniques at commercial scale

After monomeric sugars like glucose are produced via enzymatic hydrolysis, they are converted to the desired products (polyethylene, glucaric acid, sorbitol and levulinic acid), which are then purified using different recovery and purification technologies. This section briefly considers purification technologies applied in industrial processes and highlights some of their advantages and disadvantages (see Table 2-9). This is followed by an overview of the conversion (and purification) processes for the shortlisted chemicals in section 2.9.

Second generation biorefineries incur high pretreatment and hydrolysis costs. Additionally, the product purification stage in biorefineries is also responsible for a large part of the total costs (Kiss et al., 2016; Huang et al., 2008) although this is not highlighted as much as the pretreatment and hydrolysis costs. High contributions to the total cost from purification technologies can be attributed to factors including the low feed concentrations (water based) in most biorefineries leading to low product yields, whilst some products form complexes and azeotropes with organic and inorganic components, thus, requiring further processing (Kiss et al., 2016). Therefore, high capital and operating costs are also unavoidable during separation and purification stages and usually a combination of simple to complex and capital intensive technologies are usually used including:

i. Distillation (TRL 8-9)

ii. Ion exchange chromatography

iii. Steam stripping (TRL 8-9)

iv. Solvent (liquid-liquid) extraction

v. Adsorption,

vi. Evaporation/ precipitation and

vii. Filtration, as summarised in Table 2-9 and their advantages and disadvantages, which are highlighted.

Table 2-9: Advantages and disadvantages of recovery and purification technologies

Recovery process	**Advantages**	**Disadvantages**	**References**
Distillation	Simple, commercial process	Energy intensive, by–products formation	(Kiss et al., 2016).
Ion exchange	Re-cyclable	Expensive	(Marques et al., 2016)
Steam stripping	High purity products attained	Energy intensive	(Rackemann and Doherty, 2011)
Solvent extraction	Fewer additional processing steps	Costly due to large solvent amounts, toxic	(Nhien et al., 2016)
Adsorption	Simple	Limited commercial use, low adsorption capacity	(Rackemann and Doherty, 2011)
Evaporation	Simple, less time consumed	Economically unattractive	(Obuli et al., 2013)
Filtration	Simple	High cost of filter	(Kiss et al., 2016).

2.9. Conversion (and purification) of lignocellulose feedstock to bio-based chemicals

An overview of the different catalytic conversion processes for the four chemicals used in industry (at demonstration to commercial level) are discussed in sections 2.9.1, 2.9.2, 2.9.3 and 2.9.4. Further discussed are the purification technologies applied, product purities, yields and global production capacities. The liberated sugar (glucose in this study) obtained after pretreatment and hydrolysis (sections 2.5 and 2.6) is the precursor to the production of sorbitol, glucaric acid, levulinic acid and polyethylene (Lee et al., 2016; Marques et al., 2016; Girisuta, 2007; Mun, 2004) via the processes and process conditions summarised in Table 2-10.

Table 2-10: Bio-based chemicals produced from glucose precursors using near-commercial to commercial chemical and catalytic processes (Lee et al., 2016; Marques *et al.*, 2016; Girisuta, 2007; Mun, 2004)

CHEMICAL	Polyethylene	Sorbitol	Glucaric acid	Levulinic acid
PRODUCTION PROCESS	Polymerisation	Hydrogenation	Oxidation	Biofine process
TRL	8–9 Commercial	8–9 Commercial	8–9 Commercial (niche)	7–8 Near commercial to commercial (niche)
PROCESS CONDITIONS	100ºC, 35atm	120ºC, 69 atm	80ºC, 14 atm	210ºC, 25 atm 190ºC, 15 atm
CATALYST	Ziegler-Natta	Raney Nickel	Platinum/carbon	Dilute H_2SO_4 acid
PRODUCT PURITY	99 wt%	70 wt %	70 wt%, 98 wt%	98 wt%
YIELD	97–99 wt%	65–80 wt%	50–60 and 74 wt%	45–60 wt%
PURIFICATION TECHNOLOGIES	Filtration, drying	Ion exchange, evaporation	Ion exchange, evaporation	Distillation
REFERENCES	Mun, 2004	Marques et al., 2016	Lee et al., 2016; Thaore et al., 2019	Girisuta, 2007

2.9.1. Polyethylene production and recovery overview

The commercial production of polyethylene (TRL 8–9) from ethanol (as the starting material) involves the conversion of ethanol to ethylene via a dehydration process followed by ethylene polymerisation to either low density polyethylene (LDPE), high density polyethylene (HDPE) or linear low density polyethylene (LLDPE), depending on the process conditions applied (Grau 2010). High density polyethylene is considered in this current study. Compared to the other chemicals under consideration in this study (Table 2-10), polyethylene production is one of the most established technologies operating at commercial level (Xie et al., 1994). It also has the highest number of alternative technologies operating at commercial scale though most of them operate at high temperature (140–300 ºC) and pressure conditions (600–3000 atm) (Xie et al., 1994). The most versatile processes for PE production that are able to produce HDPE at low capital costs and which are less energy intensive include the gas phase and slurry polymerisation processes (Xie et al., 1994).

2.9.1.1. Polyethylene conversion and purification technologies

Polymerisation involves the chemical combination of monomers to form long polymer chains (Icis, 2015). In gas or slurry polymerisation, pressurised ethylene is mixed with Ziegler-Natta solid catalyst suspended in 1-butene comonomer and hydrogen, for an enhanced ethylene consumption rate (Mun, 2004; Xie et al., 1994). The mixture is heated to 80-110 °C and pressures maintained at 30–35 atm leading to the formation of long polymer chains according to the following simplified exothermic reaction shown in Equation 2-3.

$$\text{Ethylene polymerisation reaction: } C_2H_4 \rightarrow (C_2H_4)_n \quad \text{Equation 2-3}$$

The product stream from the conversion reactor is filtered removing the catalyst and a degasser removes the hydrogen and comonomer. The polymer is then dried eliminating any moisture and leaving a polymer powder that can be extruded into films, sheets or pellets. Polyethylene yields of 97–99 wt% are attainable (Icis, 2015) at a 99 wt% purity (based on ethylene).

Figure 2-6 shows a simplified flow diagram of PE production. The ethanol dehydration to ethylene, an endothermic process occurs at 450 °C and 11 atm pressure over activated alumina or silica catalysts prior to polymerisation. The ethanol to ethylene process leads to about 98% of ethanol being converted to 99.7 wt% pure ethylene (Yan, 2013; Morschbacker, 2009) whilst a small part of the ethanol reacts to form by-products namely diethyl ether, acetaldehyde, ethane, methane, isobutene and carbon monoxide (de Lima et al., 2012; Arstad et al., 1997).

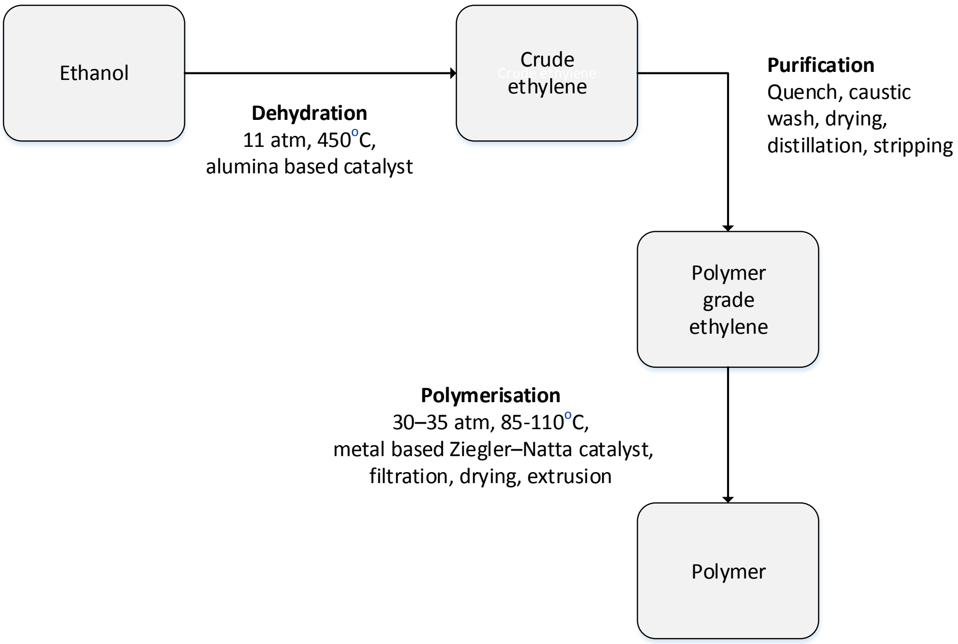


Figure 2-6: Polyethylene production process flow diagram including key process stages (Grau, 2010; Morschbacker, 2009; Mun, 2004; Xie et al., 1994).

2.9.1.2. Feedstock sources

Besides the bio-based (1G and 2G) feedstock source, PE can also be produced from ethylene obtained from fossil based resources that are processed using well-established technologies. The most common commercial scale fossil-based technologies used to produce ethylene, the starting material for polyethylene are steam cracking of naphtha (Morschbacker, 2009) and more recently shale gas fracking (Biddy et al., 2016), discussed briefly herein.

Steam cracking is a petrochemical process where saturated hydrocarbons are broken down into smaller unsaturated hydrocarbons (White, 2007). Light hydrocarbon feedstocks such as light naphthas, liquid petroleum gas or ethane are mixed with steam and heated to 850 ^{o}C in the absence of oxygen at short residence times (up to milliseconds in modern cracking furnaces for improved yields) (White, 2007). Once the high cracking temperatures are reached, the produced gas is quickly quenched to stop the reaction and obtain the ethylene and by-products namely propylene and butadiene (White, 2007). The quantities of the lighter alkenes produced are dependent on the feedstock used, feedstock to steam ratio, process temperature and residence times (White, 2007). Ethylene production capacities from steam cracking are approximately 45-fold more than amounts from biomass (Fan et al., 2013).

In recent years, a more cost-effective and simpler way of producing ethylene from shale gas has emerged, which has led to ethylene being cheap (Foster, 2018) although concerns have been raised over its potential environmental impacts to the air and water from gas and oil leaks (Leahy, 2019; Jackson et al., 2014) and its link to seismic activities (Auld, 2019). However, ethylene from low-cost natural gas feedstocks still incurs lower production costs than producing it from crude oil (Foster, 2018). Shale gas fracturing or fracking is a technique that recovers natural gas, including methane, ethane (from which ethylene is produced), propane, butane, iso-butane and oil from shale rocks by injecting a high pressure water, sand and chemicals mixture directly into a rock to release the natural gas inside the shale rocks (Stevens, 2012). The high pressured mixture is then pumped into drilled holes in the rock fractures enabling trapped gas to escape into engineered collection wells and transported for commercial use (Stevens, 2012). Ethane is isolated from the natural gas and can then be steam cracked to produce ethylene, the starting material for the polymerisation process.

2.9.1.3. Global polyethylene production capacities and key stakeholders

Braskem based in Brazil has been producing bio-based ethylene as a polyethylene precursor (since 2010) as shown in Table 2-11 and production capacities of about 200 kt/y are recorded (IAR, 2015b).

Table 2-11: Key stakeholders producing bio-based polyethylene (IAR, 2015b)

Stakeholder	Place	Business sector	Combined capacity (t/yr)
Braskem	Brazil	2010	200 000
Dow Chemicals	Netherlands	2015*	-

*The plant was expected to start operations in 2015, with a capacity of 350 kt/y, however, the project was postponed and no further information given on when it will resume (BioBiorefineries Blog, 2020)

2.9.2. Sorbitol production and recovery overview

2.9.2.1. Sorbitol conversion and purification technologies

D-sorbitol production process via the catalytic hydrogenation of glucose in terms of technology maturity is a commercially recognised process (TRL 8–9) (Taylor et al., 2015) similar to the PE technology. The main process reaction involved is shown in Equation 2-4.

Glucose hydrogenation to sorbitol reaction: $C_6H_{12}O_6 + H_2 \rightarrow C_6H_{14}O_6$ Equation 2-4

Sorbitol hydrogenation process has the highest pressure condition of 69 atm (70 bar) compared to the other chemicals' production processes as shown in Table 2-10, a requirement dictated by the catalyst for its effective operation (Marques et al., 2016).

After the conversion process occurring at 120 ^{o}C, sorbitol is purified using precipitation, filtration (to separate out the catalyst), ion exchange chromatography (to remove nickel and gluconate ions), followed by a decolourisation adsorption stage using activated carbon. The final commercial grade sorbitol solution at 70 wt% purity is achieved by vacuum evaporation of the crude sorbitol solution (Marques et al., 2016; Duflot, 2014). Higher purities of up to 98 wt% are also attainable using distillation and acetonitrile solvent (Gunukula and Anex, 2017). Sorbitol yields of 65–80 wt% have been reported by Ahmed at al., (2009). Figure 2-7 shows a schematic diagram of a sorbitol production process via the chemical route commonly used in industry. Included in the diagram are the reaction, purification and recovery units used in achieving desired product purity.

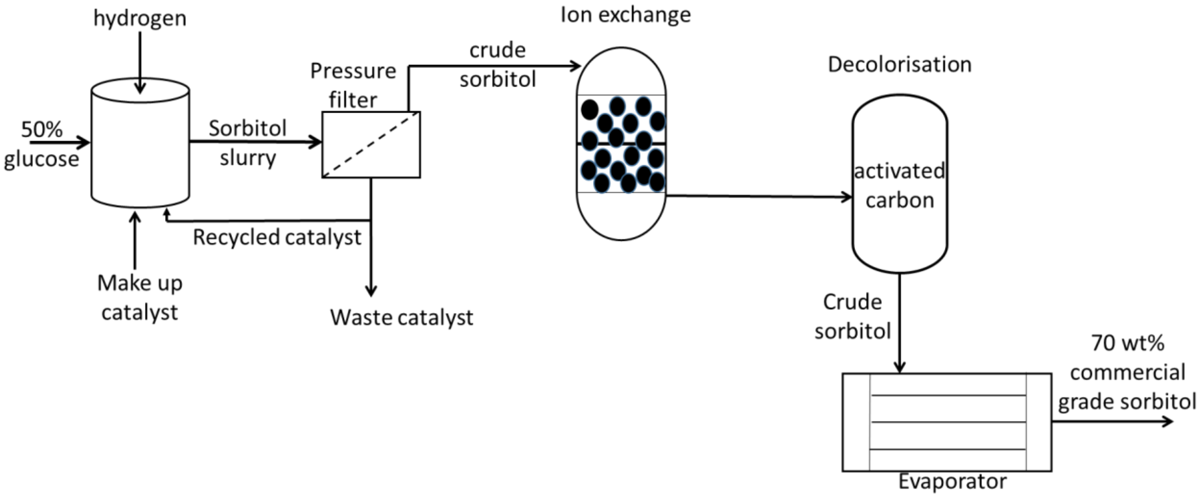


Figure 2-7: Simplified flow diagram for the production of sorbitol showing the hydrogenation of glucose, purification and recovery stages (Marques et al., 2016)

The hydrogenation of D-sorbitol is commonly carried out with transition–metal catalysts of Ni, Ru, Pt and Rh, supported on oxides, carbons, polymers and zeolites (Zhang et al., 2016). Commercial plants typically use Raney nickel (Marques et al., 2016) or carbon-supported Ru catalysts. Raney nickel is subject to low selectivity and prone to deactivation and product contamination, whilst carbon–supported Ru catalysts are expensive and easily poisoned by organic impurities and sulphur compounds (Zhang et al., 2016).

2.9.2.2. Feedstock sources

Sorbitol is mainly derived from 1G sources (Marques et al., 2016; Ahmed et al., 2009; Kusserow et al., 2003; Silveira and Jonas, 2002) and no studies have explicitly stated the feedstock as being 2G, apart from Zhang et al., (2013), who acknowledged the need to utilise what they termed “biomass” as feedstock. The batch method is used at commercial scale, to attain complete glucose conversions in the reactors (Silveira and Jonas, 2002) but investigations into continuous processes are underway as this would increase material throughputs (van Gorp et al., 1999).

2.9.2.3. Global sorbitol production capacities and key stakeholders

Global production capacities of sorbitol stand at approximately 1.3 million t/y with the main actors being Roquette Freres in the USA and China that contribute 27% to the overall global capacities as summarised in Table 2-12. Most of the production plants (40%) are in China and mostly benefit from the lower plant production costs in that region.

Table 2-12: Key stakeholders producing bio-based sorbitol (IAR, 2015b)

Stakeholder	Place	Business sector	Combined capacity (t/yr)
Roquette Freres	USA, China,	Agri-	347 500
Shandong Tianli	China	Pharmaceuticals	200 000
Sorini	Indonesia	Chemistry	195 000
Ingredion	USA, Brazil	Agri-	180 000
Archer Daniels Midland	USA	Agri-	162 000
Khalista Chemicals	China	Chemistry	120 000
Cargill	Germany	Agri	100 000
Global Nikken & Zhejiang Huakang	China	Chemistry & Biotechnology	120 000
Gulshan Polyols	India	Chemistry	45 000
Sama PT Satria Pacific & Budi PT Kimia	Indonesia	Chemistry	12 700
Shandong Longlive	China	Biotechnology	Not confirmed

2.9.3. Glucaric acid production overview

2.9.3.1. Glucaric acid conversion and purification technologies

Glucaric acid production process is also a commercial process (TRL 7–8), similar to the PE and sorbitol production processes, although it entered the market less than a decade ago. Glucaric acid production has recently been conducted by the catalytic oxidation of glucose (50 wt% glucose solution in water) (Colmenares et al., 2011) using Pt/C catalyst (Lee et al., 2016). The general chemical reaction is shown in Equation 2-5.

Glucose oxidation to glucaric acid reaction: $C_6H_{12}O_6 + 1.5\ O_2 \rightarrow C_6H_{10}O_8 + H_2O$ Equation 2-5

The oxidation process at times forms an intermediate product, gluconic acid (not depicted), which is then further oxidised to glucaric acid at pH 7.2, 14 atm and 80 ^{o}C (Lee et al., 2016) even though detailed reaction mechanisms for the intermediate product are not readily available (Isikgor and Becer, 2015). A 74 wt% glucaric acid yield has been recorded by Lee et al., (2016) whilst the Rennovia patent of a one pot oxidation process attained a yield of 50–60 wt% at 80–90 ^{o}C and elevated pressures of 35–40 atm (Thaore et al., 2019).

Purification techniques used include ion exchange chromatography, adsorption and evaporation (Thaore et al., 2019), similar to the sorbitol downstream processes. Limited data however, exists on the product purity at different purification stages including the chemical's market selling price.

A commercially available catalyst, platinum on activated carbon (Pt/C), has been identified as the most effective catalyst for glucose oxidation when compared to Pt/SiO_2 (platinum on activated silica) and Pt/Al_2O_3 (platinum on activated aluminium oxide), despite being the most expensive of the three catalysts (Saeed et al., 2017; Solmi et al., 2017). The Pt/C catalyst (with a glucose/catalyst ratio of 54:1) achieves better yields in neutral to basic pH conditions whereas in acidic conditions, gluconic acid is formed instead (Lee et al., 2016).

2.9.3.2. Feedstock sources

The traditional and commercial method of producing glucaric acid involves the use of glucose with nitric acid as the oxidising agent and solvent, however, data is not readily available (Grand View Research, 2017). This conventional technology is simple, which makes it attractive but, it has environmental concerns due to the nitrous oxide fumes (NO_x), which it emits (Grand View Research, 2017). To mitigate these concerns, a proprietary technology has been developed and recently commissioned by Rivertop Renewables consisting of a one-pot oxidation process processing glucose in an O_2 environment.

2.9.3.3. Glucaric acid production capacities and key stakeholders

Glucaric acid is currently being produced commercially by two main stakeholders in the USA and is serving a niche market. Current production capacities are not explicitly revealed but are projected to reach approximately 50.4 kt/y in the short term as shown in Table 2-13.

Table 2-13: Key stakeholders producing bio-based sorbitol (IAR, 2015b)

Stakeholder	Place	Date	Combined capacity (t/yr)
Rennovia	USA	2012	Not confirmed
Rivertop Renewables	USA	2014	50 400 (projection)

2.9.4. Levulinic acid production overview

2.9.4.1. Levulinic acid conversion and purification technologies

The United States of America (USA) Patent by Fitzpatrick, (1997) forms the basis of the Biofine continuous process, which is a dilute acid catalysed two-stage process operated at high temperatures and pressure. Unlike the other production processes using expensive solid catalysts, the Biofine process uses cheaper dilute acid catalyst and therefore, lowers the total production cost of levulinic acid via this process. The technology readiness level of the Biofine process is indicated as near-commercial to commercial (TRL 6-8) (Taylor et al., 2015).

In the first reactor, operated for 15 seconds at 210 ^{o}C and 25 atm, hemicellulose is hydrolysed into soluble hexose and pentose monomers, which further react leading to furfural gas formation (in most cases), as depicted in Figure 2-8. In addition, an intermediate product, 5-hydroxymethylfurfural (5-HMF), is also produced from the reaction of glucose (hexose sugars). The slurry from the first reactor is fed to a second reactor where 5-HMF is converted to levulinic acid and formic acid at 190 °C, 15 atm and 10-20 mins reaction time. Formic acid is evaporated from the bulk levulinic acid and purified via distillation whilst the crude levulinic acid is also distilled to 98 wt% pure product. Figure 2-8 shows the transition of the different biomass sugars in the Biofine process.

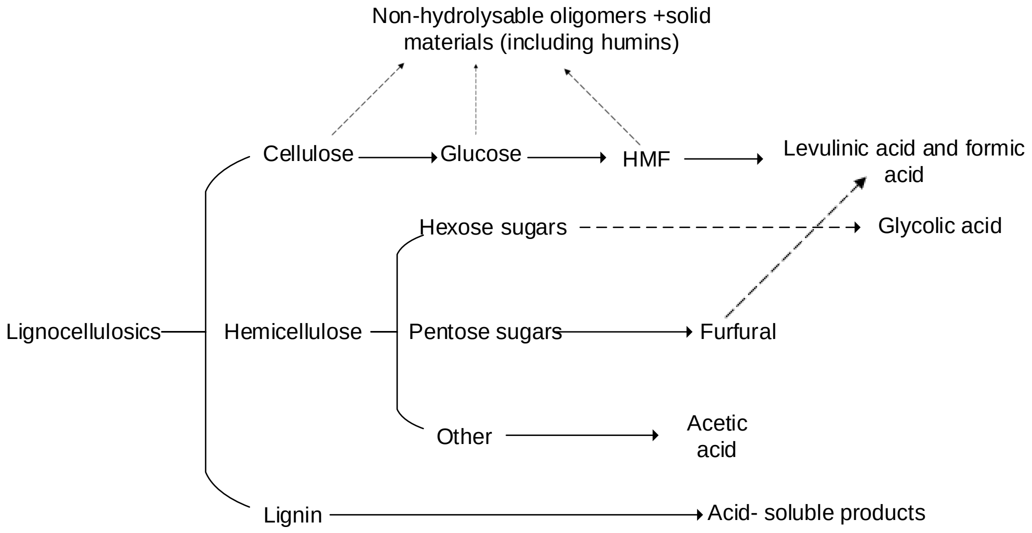


Figure 2-8: Liberated sugars and chemicals during levulinic acid production from biomass (redrawn from Girisuta, (2007); Rackemann and Doherty, (2011))

The Biofine process produces levulinic acid yields of 60–80% of the theoretical limit (approximately 43–58 wt% yield based on cellulose), in comparison to batch processes where yields are typically less than 50% of the theoretical limits (Rackemann and Doherty, 2011). Levulinic acid purification technologies mainly involve energy intensive distillation techniques where product purities of 98 wt% are attained.

In the last decade, research has been conducted on levulinic acid production and purification using different production processes, catalysts and feedstocks. These have included the hydrolysis of acetyl succinate ester, acid hydrolysis of furfural alcohol, oxidation of ketones and lead catalysed carbonylation of ketones (Patel et al., 2006; Mukherjee et al., 2015). Other processes have included thermo-chemical pretreatments (Elumalai et al., 2016; Kang and Yu, 2016; Joshi et al., 2014), thermal-enzymatic pretreatments (Schmidt et al., 2017), functionalised ionic liquids (Shen et al., 2015), acid hydrolysis (Jeong et al., 2017) and reactive extraction (Brouwer et al., 2017). On the other hand, purification techniques were based on liquid-liquid extraction (Brouwer et al., 2017), hybrid solvent screening (Nhien et al., 2016), extractive solvents and vacuum evaporation (Elumalai et al., 2016), however, all these processes are still at laboratory scale. Product yields were generally low at 13–21 wt% (Chen et al., 2017; Jeong et al., 2017; Elumalai et al., 2016) as LA production is based on the C-6 sugars in biomass.

2.9.4.2. Feedstock sources

Levulinc acid production via the Biofine process has used feedstocks including lignocellulose materials/carbohydrates such as maize and wheat (Hayes et al., 2008; Chang et al., 2007; Bozell et al., 2000). Other technologies have been based on feedstocks such as rice straw, cellulosic food waste, hybrid poplar, quercus mongolica, cotton straw, eucalyptus wood and sugarcane bagasse cellulose (Brouwer et al., 2017; Elumalaiet et al., 2016; Kang and Yu, 2016; Joshi et al., 2014).

2.9.4.3. Levulinic acid production capacities and key stakeholders

The main levulinic acid producers are in the USA and Italy serving a niche market, whilst several plants are in China however, their production capacities are unknown as shown in Table 2-14. The total levulinic acid production capacity stands at approximately 8.3 kt/y (IAR, 2015b).

Table 2-14: Key stakeholders producing bio-based sorbitol (IAR, 2015b)

Stakeholder	Place	Business sector	Combined capacity (t/yr)
Biofine	USA,	Chemistry	5199
The Calorie	Italy	Technology	3000
Segetis	USA	Chemistry	80*
Hebeil Langfang Triple Well Ltd., Hebei Shijiazhuang Worldwide Ltd., Jiangsu Yancheng China Flavour Ltd., Shan Apple Flavour & Fragrance Ltd.	China	Chemistry	Not confirmed
Ouyi Shajiazhuang Co. Ltd	China	Pharmaceuticals	Not confirmed

*An additional 9900 t/h levulinic acid projected in the future

In summary, technologies for the production of the four bio-based chemicals under consideration are at near commercial to commercial level. Though detailed data is still limited in some cases, sorbitol from biomass has the highest production capacities followed by PE, two of the most established technologies. Bio-based levulinic acid and glucaric acid are emerging technologies and currently serving niche markets. Variations were observed in the process conditions for the commercial technologies used, however the ranges in the product yields for sorbitol, glucaric acid and levulinic acid (based on cellulose) were comparable at 65–80 wt%, 50–74 wt% and 45–60 wt% respectively, whilst the PE yields were much higher (based on ethylene) at > 97 wt%.

2.9.5. Production of bio-energy in combined heat and power plants

Although electricity cogeneration produced in a combined heat and power plant is not one of the shortlisted chemicals, it is integrated into the biorefineries to provide the processes' energy needs by combusting biomass at 99% mass conversion of the biomass feedstock to CO_2 (Nsaful et al., 2003). A combined heat and power (CHP) plant combusts part of the feedstock and cellulignin residues from the process in a furnace operating at 870 °C and 1 atm in excess air to produce heat energy (Mandegari et al., 2017). The produced energy heats up the boiler feed water to 480 °C (at 64 bar) and generates superheated steam, which is then fed through a condensing extraction steam turbine (CEST) to make electricity (Colombo et al., 2014) and steam. The main waste stream of the CHP plant is solid ash, which is treated and disposed of or used/sold as a fertiliser. A second waste product is flue gas that is scrubbed to remove particulate matter before emission into the atmosphere. Figure 2-9 shows a block flow diagram of the CHP plant and its main input and output variables.

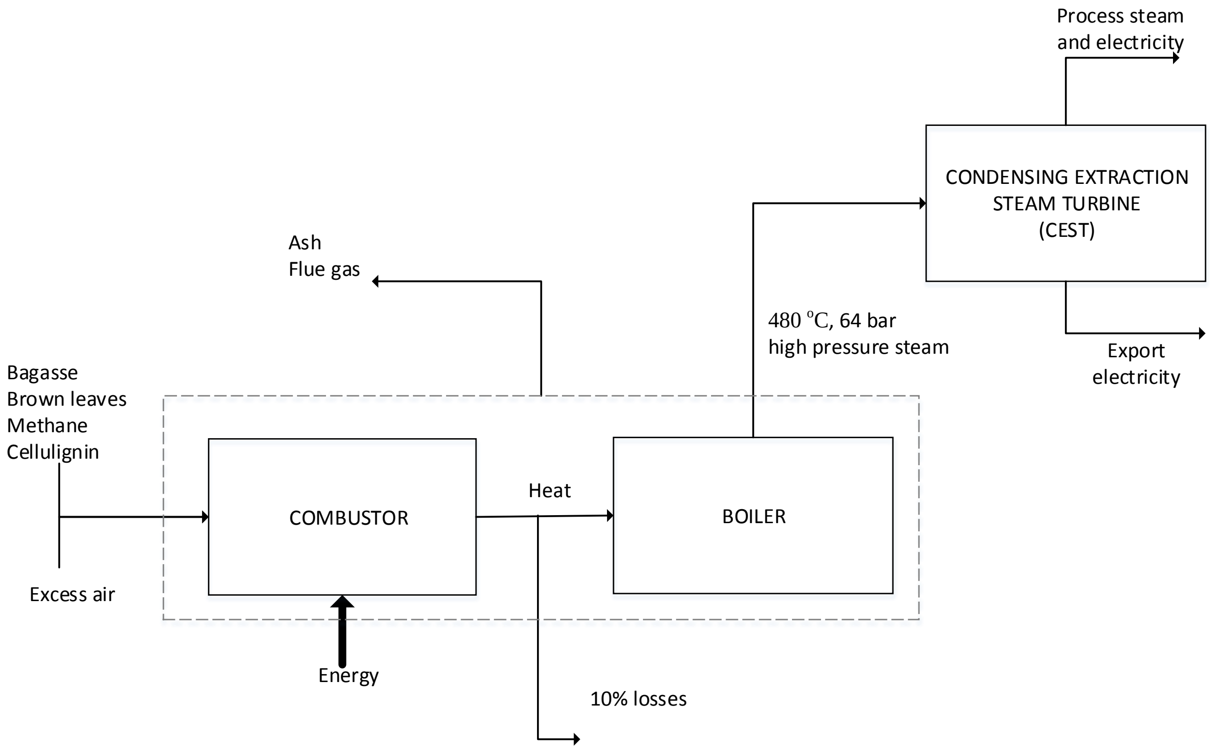


Figure 2-9: Schematic of steam and electricity production in a combined heat and power plant. Process details from Colombo et al., (2014).

Combustion of sugarcane bagasse is used to meet the energy needs of sugar mills in South Africa and many other sugar producing countries (Nsaful et al., 2013) but due to inefficiency and insufficient supply of bagasse at times, coal supplements energy supply, which has the environmental effects of increased greenhouse gas emissions. There is, therefore, potential to increase the efficiency of traditional cogeneration systems that have low pressure boilers and back pressure turbines (Alonso-Pippo et al., 2009; Mashoko et al., 2013) by replacing them with modern high temperature-pressure systems. Alternatively, in South Africa, the existing mills' back extraction turbines are maintained to produce electricity whilst the CHP plant with new boiler technologies generates steam (part of it for the sugar mill) and electricity (Nsaful et al., 2013) for biorefinery energy needs.

Over the years, there has been an advancement of cogeneration systems and turbine technology such as the already commercial steam-turbine Rankine system for electricity generation from sugarcane bagasse (Seabra and Macedo, 2011). These modern systems efficiently burn bagasse to supply energy directly to sugar mill operations and any excess electricity is sold to the grid for extra revenue (Humbird et al., 2011; Hassuani et al., 2005; Larson et al., 2001). Although, for improved CHP plant performances, these integrated systems should be situated close enough to the plants they serve to avoid energy losses.

The condensing extraction steam turbine (CEST) is one of the mature technologies widely used commercially in sugar factories to produce electricity from biomass (Seabra and Macedo, 2011; Alonso-Pippo et al., 2009). For example, in modernised Brazilian sugar mill processes, low pressure boilers have been replaced with medium to high pressure (>30 bar) boilers and condensing steam extracting turbines (CEST) equipped with either 32 bar/400 ^{o}C, 63 bar/450 ^{o}C or 82 bar/650 ^{o}C boilers.

The bigger, high pressure boilers have an advantage over the smaller, low pressure boilers used in traditional sugar mills because they efficiently produce steam and electricity, whereas the low pressure boilers (such as the 28 bar/360 ^{o}C) in traditional mills are mainly used for process steam production. Although, with the highly efficient CEST systems comes the demand for larger amounts of biomass to operate them. Hence, CEST plants are not recommended for small sugar factories processing around 7000 tonnes of cane/day (Alonso-Pippo et al., 2009) or less.

Other upcoming advanced technologies such as the biomass integrated gasifier/gas turbine combined cycle (BIG/GTCC) with the potential to be cost competitive with commercialised CEST systems have been developed (Larson et al., 2001; Eduardo et al., 1998). Some studies have shown that the BIG/GTCC systems promise high efficiency and lower electricity costs than CEST systems (Larson et al., 2001; Eduardo et al., 1998). A study by Eduardo et al., (1998), based on a 205 tons of cane per hour sugar mill, indicates that thermodynamically, the BIG/GTCC systems show better operation results with twice the amount of electricity produced than in a CEST system. Nevertheless, economically, the CEST system has been shown to have better financial results with lower electricity costs and pay-back periods (Eduardo et al., 1998).

Most traditional sugar mills, especially in developing countries, operate inefficient energy systems. Commercialised modern turbines such as condensing extraction steam turbines (CESTs) operate at 85% isentropic and 95% mechanical efficiency (Mandegari et al., 2017a) and thus are more energy efficient than traditional extraction back-pressure turbines used as prime movers at a typical sugar mill.

Conventional South African sugar mill steam turbines operate at 25-30% efficiency and are typically single stage impulse type (Mbohwa, 2013). Therefore, with the improved energy efficient cogeneration systems, some sugarcane bagasse is freed for valorisation into bio-based chemicals. The CEST plant and other types of combined heat and power plants have been commercialised with the CEST plant being the most common system used at sugar mills (Seabra and Macedo, 2011; Alonso-Pippo et al., 2009).

2.10. Heat integration and pinch analysis

Pinch analysis is a technique used in process design to minimise energy consumption and maximise heat recovery. Although not novel, it is a useful technique for minimising energy demands in energy intensive process equipment such as distillation columns. No formal heat integration by pinch analysis has been conducted on any biorefineries producing chemicals from South African mills and so limited data exists on the potential energy savings achieved following heat integration. Recovered heat after integration is used internally, making processes energy efficient. This, therefore, reduces total operating costs by minimising the utilities used in a process (Van der Westhuizen, 2013). However, trade-offs are necessary between factors such as the operating costs (utility use), capital costs for heat exchanger networks and the impact of control complexities associated with instrumentation and control systems (Towler and Sinnott, 2008), which affects plant stability, variability and product quality.

Several studies on heat integration (by pinch) in integrated (Modarressi et al., 2012; Fujimoto et al., 2011) and stand-alone (Singh and Crosbie, 2011; Liebmann et al., 1998) biorefineries using computer packages/simulations are available. Notable studies have been based on bio-ethanol biorefineries using starch, sugar crops, lignocellulose and woody biomass as feedstock (Julio et al., 2017; Abdelaziz et al., 2015; Martinez-Hernandez et al., 2013; Modarresi et al., 2012; Fujimoto et al., 2011). These studies applied computer software packages to conduct pinch analysis (Modarresi et al., 2012; García et al., 2011), whilst others, in addition to the use of technological means, have used consultants (Fujimoto et al., 2011). This demonstrates how this methodology can at times be complex, thus needing specialised attention supported by computer software packages that are also used to design heat exchanger networks.

It was established in these studies that energy savings and costs could be achieved in processes following pinch analysis and expressed as % energy savings, % savings in utility costs (Liebmann et al., 1998) and MW (Modarressi et al., 2012) or a combination of the different measures. Modarresi et al., (2012) in their simulation estimated 40% savings on a bio-ethanol production process' hot and cold utilities whilst Fujimoto et al., (2011) achieved 38% energy savings on a simulated bio-ethanol production process. Similarly, Marinova et al., (2009) attained 21 MW steam savings on a simulated forest biorefinery for bio-ethanol and acetic acid production following heat integration by pinch analysis when compared to a conventional kraft pulp mill. Energy optimisation through a technique such as pinch analysis is thus an integral part of any process.

2.11. Market projections of the shortlisted chemicals

A comparison made of the market projections for the four chemicals in terms of their market sizes, production capacities and projected compounded annual growth rates (CAGRs) is summarised in Table 2-15. The compounded annual growth rate (CAGR) has been defined as an investment's mean annual growth rate over a specified time frame longer than a year (Lunt, 2014). As earlier stated in section 2.9, most of these chemicals, apart from polyethylene (mostly from fossil sources), are produced from first generation (1G) feedstocks and are at demonstration to commercial level. To this end, limited data exists for their second generation (2G) counterparts as shown in Table 2-15 where most of the information is based on 1G or fossil-based sources.

Table 2-15: Projected market sizes and compounded annual growth rates for polyethylene, sorbitol, glucaric acid and levulinic acid

Feedstock	**Chemical**	**CAGR (%)**	**Market size (US$ million)**	**Production capacity (kt/y)**	**Refs***
Fossil	Polyethylene	3.9 (2019-2025)	143 000 (by 2026)	300000	a
1G				200 (in 2010)	b
1G	Sorbitol	5.3 (2016-2023)	2710 (by 2024)	1500 (in 2008)	c and d
2G				Not available	-
1G	Glucaric acid	9.1 (2016-2022)	1300 (by 2025)	50 (in 2015)	e
2G				Not available	-
1G 2G	Levulinic acid	14 (2020-2027)	72 (by 2027)	17.5 (in 2016)	f and d

***References:** a is (Globe News Wire, 2020), b is (Industry Arc, 2019), c is (Market Watch, 2020), d is (IAR, 2015b), e is (Grand View Research, 2017) and f is (Data Bridge Market Research, 2020).

The projections on the four chemicals under review show a positive market growth as summarised in Table 2-15 where the CAGRs were 3.9–14%. Their market sizes in the next 5–6 years are projected at US$ 0.1 billion-US$ 143 billion whilst their production capacities are about 18–300200 kt/y, with PE having the highest market size (US$ 143 billion) and production capacity (300200 kt/y), mostly from fossil sources as shown in Table 2-15. However, it should be noted that this analysis does not take into account the short and long term impact of the COVID-19 pandemic on different sectors.

Levulinic acid, with a US$ 72 million market size, currently produced from lignocellulose feedstocks and serving a niche market (with a market selling price of US$ 5000/t–US$ 8000/t), is predicted to have the highest compounded annual growth rate (CAGR) of 14% over a six year period from 2020 (Industry Arc, 2019). This is followed by glucaric acid with 9.1% CAGR (until 2022) (Grand View Research, 2017) as the chemical is currently also serving a niche market (though the market selling price is unavailable), whilst PE recorded the lowest CAGR of 3.9%. The high CAGR in the levulinic acid market can be attributed to its emerging "green" technology, multiple applications (over 60) and increasing demand in the pharmaceuticals industry (Grand View Research, 2017). On the other hand, glucaric acid's predicted growth can be associated with its high demand in the phosphates (detergents) industry. Detergents are a significant contributor of phosphates to the environment after agriculture and sewerage (Society of Chemical Industry, 2017), leading to eutrophication of water bodies; thus bio-based glucaric acid (that is devoid of phosphates), can mitigate eutrophication. Sorbitol's CAGR of 5.3% (from 2016 to 2023) may be attributed to its extensive use in the food, pharmaceuticals, polymer and polyester industries (van Ree et al., 2014; Taylor et al., 2015).

Concerning market sizes, polyethylene currently has the highest market size of US$ 174 billion (Globe News Wire, 2020) compared to other chemicals, mainly due to its versatility and well established and mature technologies. Polyethylene is extensively used in the plastics industry (soft and heavy duty plastics), automotive parts, cosmetics and toys (van Ree et al., 2014; Taylor et al., 2015). Sorbitol has the second largest market share (US$ 2.7 billion) driven mainly by high consumer demand for low calorific foods and the growing organic personal care market (Market Watch, 2020). Glucaric acid's market size (US$ 1.3 billion) is half that of the market size of sorbitol and levulinic acid's size is the smallest (US$ 72 million) because the two chemicals' technology readiness levels are at demonstration to commercial stage and serving niche markets.

As shown in Table 2-15, the total 1G PE production volumes are low compared to fossil based PE counterparts with capacities 1500-fold higher than the bio-based PE volumes (Fan et al., 2013). Since no fossil-based equivalents for sorbitol, glucaric acid and levulinic acid exist, the production volumes of the three bio-based chemicals (18–1500 kt/y) were also low compared to fossil-based PE (300000 kt/y). Despite this significant difference in the PE capacities, scope exists to increase production capacities from bio-based PE sources, considering that regulations concerning health hazards and emissions from fossil sources have been imposed on plastics (Research and Markets, 2020). Therefore, bio-based polyethylene production volumes would not only complement fossil sources, but also lead to environmental benefits compared to the fossil-based approach (Haro et al., 2013).

At a local perspective, Sasol (in Sasolburg) and Safripol are the main producers of PE (from fossil sources) with the latter producing most of the high-density polyethylene. A local market for the polymer exists but it is fragmented due to the array of grades and uses of PE on the market (Research and Markets, 2020). South Africa has in the last seven years exported between 35–75 kt/y of low-density polyethylene and 13–23 kt/y high-density polyethylene (Department of Trade and Industry, 2018) because of a competitive international market (Du Plessis, 2010) and existing trade agreements (Research and Markets, 2020). Regarding sorbitol, the South African Department of Trade and Industry market statistics have indicated that the country imports and exports 3.9 kt/y and 0.1 kt/y respectively (Department of Trade and Industry, 2016) whilst the DST does not explicitly state the import and export values of glucaric acid and levulinic acid, suggesting that these chemicals are not extensively produced or imported (Department of Trade and Industry, 2016).

2.12. Techno-economic analyses of biorefineries

If the biorefinery approach of chemicals from 2G sources is to advance, then there is need to conduct techno-economic assessments of these chemicals prior to any feasibility studies being undertaken by the sugar industry stakeholders. For example, an over production of a chemical that contributes above 10% (assumed) to global capacities, especially for niche products, floods the market and thus transitions a product from serving a niche to a commodity market (see chapter 5), which in turn lowers the market selling price of thatproduct.

A techno-economic assessment (TEA) is a useful cost-benefit tool used in justifying investment, especially in projects nearing or at commercialisation level as it helps quantify cash flows such as the fixed capital and operating costs to help determine the total cost of production of a given product (Humbird et al., 2011; Towler and Sinnott, 2008). It further helps in identifying areas where more research should be focused in order to achieve significant improvements in the economics of any given process.

Techno-economic assessment methodologies are well established and include capital and installed costs determination, adjustment of equipment purchase costs to the desired capacity and time, calculation of the fixed capital and total capital investments and operating costs (Humbird et al., 2011; Towler and Sinnott, 2008). The key cost and economic estimation parameters are discussed in brief hereunder.

2.12.1. Capital costs

The total plant cost can be determined from the summation of individual process unit costs of a plant done, either manually or using computer software. Since, the most reliable sources of obtaining equipment costs (from contractors on capital projects) (Towler and Sinnott, 2008) is a challenge due to the sensitive and confidential nature of this information, computer tools such as Aspen ICARUS TM technology are now used to reliably estimate equipment, installation and bulk costs (Towler and Sinnott, 2008). These computer packages are reliable as they are regularly updated using data from contractors and equipment manufacturers.

2.12.1.1. Purchased and installed equipment costs

Process modelling software including ASPEN Process Economic Analyser (incorporated in ASPEN Plus ® and which uses the Aspen ICARUSTM technology), are able to size and calculate the equipment and installation costs of most process equipment types. This is with the exception of non-standard units such as reactors, boilers, turbo-expanders, generators and wastewater treatment basins (Mandegari et al., 2017) that are sized and the costs determined using published price data (Humbird et al., 2011). The module (factorial) costing technique is one method used to estimate the purchase and installation costs in a given range of size parameters. The correlation used is in the form:

Module costing technique correlation: $Ce = a + b\,S^n$ Equation 2-6

where, C_e = purchased equipment cost based on a cost basis such as the US Gulf for a given year (i.e. Chemical Engineers Plant Cost Index (CEPCI) or NF refinery inflation index)

a, b = cost constants used with standard tables for purchased equipment costs of common plant equipment,

S = size parameter (units such as area, length, area, power etc.)

n = scaling exponent for the type of equipment, which are well documented (Humbird et al. 2011).

The installation cost ($C_{installed}$) is determined by applying a factor to the purchased cost (C_e), as shown in Equation 2-7 (that accounts for materials of construction and pressure) to the equipment cost such as the Lang factor. Installation factors for various pieces of equipment are also well documented (Humbird et al., 2011).

$$C_{installed} = C_e \times \textit{installation factor} \qquad \text{Equation 2-7}$$

The purchase costs were determined using historical data and the cost updated to current year (2016) prices using chemical engineering Price Cost Indexes (CEPCIs) (see list of CEPCI values in

Appendix A-3) according to the relationship:

$$\text{Cost in year A} = \text{Cost in year B x } \frac{CEPCI\ year\ A}{CEPCI\ year\ B} \qquad \text{Equation 2-8}$$

A preliminary CEPCI value of 536.5 was used.

2.12.1.2. Fixed Capital Investment

This is the total installed cost incurred during the design, construction and installation of a plant (Humbird et al., 2011). This investment cost comprises the inside battery limits (ISBL) investment, which is the actual cost of a plant (made up of direct and indirect costs) and the offsite battery limits (OSBL) that consist of modification costs such as engineering costs and contingency charges (Towler and Sinnott, 2008).

The fixed capital investment (FCI) is the sum of the total direct (TDC) and total indirect costs (TIC). The total working capital was estimated as 5% of the FCI of a project. It can also be calculated as the difference between the total indirect costs (TIC) and the fixed capital investment (FCI). In addition, the total capital investment (TCI) is described as the sum of the fixed capital investment (FCI), working capital (WC) and land, values used together with the total operating cost described in section 2.12.2 to assess the techno-economics of scenarios.

2.12.2. Operating Costs

Operating costs include revenues and profits of a process and can be variable operating costs (VOP) or fixed operating costs (FOC). The VOP is directly proportional to the production rate of a process and accounts for the cost of raw materials, utilities, consumables, effluent disposal, packaging and shipping. Consumables typically cost ≤ 3% of the capital cost of production (CCOP) (Towler and Sinnott, 2008).

On the other hand, the fixed operating cost (FOC) relates to operating labour, supervision, and salaries, including general plant overheads such as human resources, research and development (Towler and Sinnott, 2008). The fixed operating costs such as salaries of employees were based on rates in Mandegari et al., (2017a) that were adjusted according to the size of the plant being considered. Maintenance was set at 3% of the inside battery limit (ISBL) (of the plant) whilst the installed cost, property insurance and tax was 0.7 % of fixed capital investment (Mandegari et al., 2017a). The FOC also deals with maintenance of labour and materials, property taxes, insurance, rent of land or buildings, sales and marketing, environmental charges, capital charges associated with interest payments on debts and loans, licence fees and royalties (Towler and Sinnott, 2008).

2.12.3. Economic indicators

Economic indicators such as the discounted payback period (DPBP), net present value (NPV), internal rate of return (IRR), discounted cash flow rate of return (DCFROR), minimum product selling price (MPSP) and investment rate of return (ROR) are well established parameters that are extensively used in techno-economic assessments (Humbird et al., 2011; Towler and Sinnott, 2008). The DCFROR analysis applied makes use of the total capital investment (TCI) and total operating cost (TOC) to determine the profitability of a scenario.

Some techno-economic assessments and parameters for biorefineries based on developed and developing countries, are summarised in Table 2-16 for feedstocks including sugarcane bagasse, sucrose, vegetable oil, corn stover, switchgrass and wood. The plant life span range of lignocellulose biorefineries in developed and developing countries was comparable at 20–30 years as well as the hurdle rate (8–10%) and construction period (2–3 years) whilst the project start-up times significantly varied from between three months to two years, depending on the complexity of a process configuration determined by the product being generated. The biorefineries, which process sugarcane bagasse in South Africa and Brazil had the highest start-up times (Mandegari et al., 2017a; Dias et al., 2013) although another sugarcane bagasse biorefinery in South Africa had a six month start-up period for a process generating jet fuel as the final product from bagasse, 1G and vegetable oils. The working capital, which is a percentage of the fixed capital investment (FCI), varied significantly at 5–20% for developing countries and 5–18% for developed countries.

Table 2-16: Economic parameters used in different techno-economic studies based on different feedstocks

Reference	Mandegari et al., 2017a*	Tao et al., 2011	Humbird et al., 2011	Nitzsche et al., 2016	Dias et al., 2013	Diederichs et al., 2016
Feedstock	Sugarcane bagasse	Switchgrass	Corn stover	Wood	Sugarcane bagasse	Bagasse, 1G, vegetable oil
Country of study	South Africa	U.S.A	U.S.A	Germany	Brazil	South Africa
Yearly operating time (months)	9	-	11.7	-	5.5	11
Plant life span (years)	25	20	30	30	25	20
Income tax rate (%)	28	39	35	30	34	35
Hurdle rate (%)	9.7	10	10	8.27	-	10
IRR method	Real term	-		-	Real term	-
Inflation rate (%)	5.7	-	-	1.25	-	-
Working capital (% of FCI)	5	5	5	17.5	20	10
Construction period (years)	3	2.5	3	3	2	3
Start-up time (years)	2	0.5	0.25	-	2	0.5
Cost year of analysis	2016	2007	2007	2013	2010	2014

2.13. Case studies of techno-economic assessments

Concerning sugarcane biorefinery techno-economic assessments, studies in countries with tropical and sub-tropical climates including India, South America, South Africa, Australia and parts of America (Louisiana) among others, have emerged in recent years. These studies have used sugarcane agricultural residues incorporated into a sugar mill, producing various chemicals as outlined hereafter. South Africa has been carrying out research on the techno-economic studies of biorefineries annexed to a typical sugar mill, chemicals assessed include xylitol (Ozudugro et al., 2018), itaconic acid (Nieder-Heitmann et al., 2018), bio-ethanol (Petersen et al., 2014; Mandegari et al., 2017; Petersen et al., 2018) syn-crude, n-butanol, lactic acid and furfural (Farzad et al., 2017).

2.13.1. Biorefinery case studies for polyethylene production

Ethanol is a starting material in the production of chemicals such as ethylene, which can be polymerised to polyethylene, one of the chemicals being considered in this study. Several ethanol techno-economic assessments have been conducted (Mandegari et al., 2017a; Rezende and Richardson, 2015; Petersen et al., 2014; Moncada et al., 2014; O'Hara, 2011). Concerning ethylene, one detailed ethylene techno-economic assessment, where bio-ethanol is dehydrated to ethylene, is available (Haro et al., 2013), whilst several kinetic studies and reviews have been conducted (Kagyrmanova et al., 2011; Morschbacker, 2009; Banerjee et al., 1998; Arstad et al., 1997; Le Van Mao et al., 1989; Le Van Mao et al., 1987; Figueras Roca et al., 1969). However, no techno-economic assessments (TEAs) for ethylene polymerisation to polyethylene were found. Haro et al., (2013) have done extensive studies on ethylene production, using five different case studies that used different processing routes and applied first generation and/or second-generation feedstocks. The general finding was that ethylene production is only profitable when low-cost Brazilian ethanol is used, using thermo-chemical processing (case study 4). In addition, ethylene production from ethanol is highly dependent on the price of ethanol feedstock, which should be below €0.45/L (US$ 0.53/L) in order to achieve profitability regardless of the origin of the ethanol (case studies 1–4).

2.13.2. Biorefinery case studies for sorbitol production

Regarding sorbitol apart from kinetic studies and review articles on their production process where 1G feedstocks are used (no pretreatment and hydrolysis stages), no detailed economic studies of biorefinery set-ups were available. A study by Silveira and Jonas, (2002) identified a company called Companhia Lorenz (Blumenau, Brazil) during the period 1995–1997, it worked in partnership with the Centro de Desenvolvimento Biotecnológico (CDB) (Joinville, Brazil) on the biotechnological production process of sorbitol. Their pilot plant, producing sorbitol and ethanol, was considered economically feasible at a plant capacity of 5 kt/y; unfortunately, at the end of 1997, the company closed down due to financial challenges (Silveira and Jonas, 2002). More recently, Lorenz Company is in the process of producing sorbitol, gluconic acid and ethanol through a biotechnological process (Silveira and Jonas, 2002), probably based on the process previously developed by CDB. Production capacities of 10 kt/y sorbitol, 8 kt/y gluconic acid and about 7 kt/y ethanol, are projected (Silveira and Jonas, 2002). No further information on the economics is provided.

2.13.3. Biorefinery case studies for glucaric acid production

Information regarding glucaric acid production is limited. Glucaric acid is currently serving a niche market and has proprietary rights on its bio-based technology. Glucari acid has been considered indirectly in an economic assessment done in the United States of America (USA) by Gunukula and Anex, (2017) on four process pathways, where glucaric acid was generated in one of the scenarios then used to produce 80 kt/y adipic acid. This scenario achieved 98wt% pure glucaric acid by applying a distillation and solvent extraction stage, using a toxic but effective solvent, acetonitrile. The total capital investment of the adipic acid process via the glucaric acid route was calculated as US$ 81 million and the scenario was unviable (NPV not indicated) due to low catalyst selectivities and pH dependency of the glucose oxidation reaction.

A more recent study by Thaore et al., (2019) has produced glucaric acid using corn stover in a biorefinery with CHP plant. Natural gas was also used as a source of process energy. The two process options (glucose oxidation with O^2 and nitric acid) using steam and H_2SO_4 during pretreatment followed by enzymatic hydrolysis, were economically viable leading to US$ 2.53/kg and US$ 2.91/kg minimum selling prices for a 20 year project lifespan.

2.13.4. Biorefinery case studies for levulinic acid production

While case studies are limited, biorefineries producing levulinic acid (LA), regardless of the feedstock used, had positive economic assessments. This is possibly mainly due to the high LA selling price of US$ 5000/t-US$ 8000/t as it is currently serving a niche market (Grand View Research, 2017) and also the economic benefits from multiple products such as furfural and formic acid produced alongside LA. However, the one detailed techno-economic study (using ASPEN Plus ®) of an energy integrated biorefinery in Brazil producing LA (100 kt/y), furfural and formic acid from bagasse demonstrated that it was profitable. It used an LA selling price of US$ 313 /t based on the value of diesel at US$ 25/barrel because the LA product was used as a fuel additive (van Benthem et al., 2002), whereas the LA selling price for niche markets is currently about US$ 5000/t-US$ 8000/t. The electricity cost was stated as US$ 4 million. The process attained a net present value (NPV) of

US$ 202 million and a payback period of 4.5 years, mainly because of producing furfural alongside levulinic acid. The Brazilian plant was bioenergy self-sufficient because the tar and asphalt-like substances from the process were enough to generate power to support the whole plant.
The electricity selling price of the scenario by van Bentham et al., (2002) was significantly high (at US$ 93/kWh) and cannot compete favourably at a local context (with prices at US$ 0.08/kWh) or even in developed countries because consumer's willingness to pay price premiums on bio-based products has a threshold, which is low in developing countries (Bomb et al., 2007). If this scenario is to appeal to the local market, one possible adjustment would be to sell the levulinic acid, curretly serving niche markets at a higher price (US$ 5000-8000/t) and lower the electricity selling price to values close to US$ 0.08/kWh (which however, is also low considering the high capital investment costs of the CHP plant).

Due to levulinic acid's multiple applications, some TEAs have been conducted where LA has been the starting material for a process and not a final product; these were also profitable. The economic benefits from multiple products were also evident in these studies which were based on 20 year project lifespans. Murat Sen et al.,'s (2012) techno-economic studies, using ASPEN plus® on a novel catalytic strategy for loblolly pine for the reduction of LA to butene alkene, was economically attractive when the plant capacity was set between 1.5–2.5 kt/day (although the butene selling price used was not explicitly stated). A fixed capital cost of US$ 10 million/year was calculated and a US$ 2.94 million/y return on investment attained. The total annual operating costs were US$ 46.2 million. The plant produced levulinic acid and formic acid before undergoing a GVL production and recovery reaction. This was followed by GVL conversion and oligomerisation to butene. On the other hand, another techno-economic study based on ASPEN Plus ® and ICARUS process evaluator has been identified where LA was the starting material for the catalytic production of 5-nanonone including pentanoic acid, a by-product sold separately at a higher price than the mixed gaseous and liquid streams (Patel et al., 2010). Out of two scenarios studied, the plant using 99 wt% purity levulinic acid as feedstock, although having a higher total capital investment than the other option, was economically viable with an IRR of 15% compared to a minimum discount rate of return of 10%.

In summary, techno-economic assessments have been conducted for the chemicals using different feedstocks except for sorbitol and polyethylene, where such studies are not available. Levulinic acid is the only chemical where techno-economic assessments have been carried out to a greater extent because the chemical has multiple applications whilst one TEA has been conducted on glucaric acid using corn stover. The TEAs for levulinic acid production have shown economic viability but mostly have involved the use of levulinic acid as a precursor to the production of other chemicals. The general trend observed was that profitability of a biorefinery improved when a plant produced multiple products and was operated in a given plant capacity (economies of scale benefits).

2.14. Additional sustainability parameters for biorefineries

2.14.1. Social impact assessment

Social impact assessment (SIA) can be defined as the process of identifying and managing social issues of a project, including an effective participatory engagement of key stakeholders in the identification, assessment and management of these social impacts (Vanclay et al., 2015). Thus, social aspects are equally important in the sustainable assessment of a biorefinery. Unfortunately, most studies have focused on the economic and in some cases, economic-environmental assessments of biorefineries (Aristizábal-Marulanda et al., 2020).

The challenge with social impact assessments (SIAs) has been the lack or low availability of methodologies that are inclusive and permit the precise assessment of quantitative and qualitative social indicators (Aristizábal-Marulanda et al., 2020; Asah and Baral, 2018). Since social impacts also include qualitative indicators such as human rights, ethics, access to goods and services, crime, culture and politics (Nemarumane and Mbohwa, 2013), it poses a challenge to quantify some of these indicators despite being important social issues.

In recent years, reliable methodologies aimed at the holistic assessment and management of social impacts as well as their integration into economic and environmental impact assessments have emerged (Vanclay et al., 2015; Azapagic and Perdan, 2000), therefore, scope exists to expand and assess more social indicators, even in biorefinery complexes. Table 2-17 summarises some general measurable social impacts currently applied in different industries, including biorefinery case studies.

Table 2-17: Measurable social impacts applied in industry (Aristizabal-Marulanda et al., 2020; Nemarumane, 2013; Chester, 2010)

Issue	Indicator
Employment	Provision of employment
Child labour	Total children in employment
Access to material resources	Level of facility water use (relate to industrial sector and renewable resource) Extraction of biomass (relate to area)
Fair salary	Minimum wage/month, living wage/month
Health and Safety	Human toxicity potential (GHG, NO_x emissions)
Impact on local communities	Contribution to local economy, job creation
Energy security	Contribution to national energy security

It can also be seen from Table 2-17 that issues such as access to material resources, which can form part of the social impact, are similarly captured in as indicators (abiotic depletion (fossil fuels)) in methodologies such as life cycle assessments as discussed in section 2.13.2. Therefore, care should be taken not to double count some indicators that may overlap with other methodologies.

Research on sugar mill biorefineries annexed to typical sugar mills that has assessed the sustainability of biorefinery scenarios, have used the number of additional jobs created as a social indicator (Nieder-Heitmann et al., 2018; Mandegari et al., 2017a; Farzad et al., 2017). It has been observed that the number of additional jobs created when green harvesting techniques are adopted is higher than when fields are burned during harvesting, due to the labour needed to harvest, and collect the brown leaves in readiness for transportation (Mandegari et al., 2017b). But generally, the number of additional jobs created, which is dependent on the plant capacity (number of process areas), varied only slightly between different biorefineries, and so the social score in multi criteria decision assessments between scenarios is not significant (Nieder-Heitmann et al., 2019) and needs to be expanded to capture other indicators such as those summarised in Table 2-17.

A recent study, based on ethanol and electricity and electricity-only production from coffee cut-steams in biorefinery complexes conducted a social (and an economic) assessment, where 8 indicators were used to perform the social analysis (Aristizábal-Marulanda et al., 2020). The ethanol and electricity scenario was infeasible socially due to high resource requirements (but economically feasible only at a plant scale higher that 17 t/h feedstock). The electricity-only scenario on the other hand, had low social risks in most of the indicators used (but was economically infeasible at any processing scale). Therefore, potential now exists to explore more social indicators for sustainability studies, where multiple indicators in all sustainability areas are considered during the design stage of a biorefinery.

2.14.2. Environmental impacts recorded during life cycle assessments

Life cycle assessments estimate environmental burdens of a product, service or production process throughout its life cycle within a fixed boundary using several indicators; they also identify opportunities for effective environmental improvements (Julio et al., 2017). Even though life cycle assessments have limitations (Arodudu et al., 2017), measuring environmental benefits based only on reduced greenhouse gas emissions and energy requirements does not give a bigger picture of other potential environmental impacts (Gnansounou et al., 2015). To determine the environmental burden or gain of a process, indicators such as abiotic depletion potential (ADP), global warming potential (GWP_{100a}), acidification potential (AP), eutrophication potential (EP), ozone layer depletion potential (ODP), human toxicity, fresh water aquatic ecotoxicity, marine aquatic ecotoxicity, terrestrial ecotoxicity and photochemical oxidation are used. Life cycle assessment is therefore an important tool that captures complexities and interdependency of material flows in a process, product or system (Parajuli et al., 2015). These indicators have been used to make comparisons against their fossil-based equivalents where applicable.

With the advancement of the biofuels sector, several life cycle assessments (LCAs) have been conducted of biofuel production from 1G and 2G feedstocks (Cherubini and Strømman, 2011) as well as 3G sources (Pinilla, 2011) in some instances. However, comparative studies are usually complex because of differences in input data, functional units, allocation methods, reference systems and other assumptions used (Cherubini and Strømman, 2011).

Life cycle assessment studies on ethanol (and electricity) produced from sugarcane and its agricultural residues, are well documented (Galdos et al., 2013; Reno et al., 2014; Farzad et al., 2017) (see also Table 2-18), including recent LCAs on lactic acid, butanol, furfural, Fischer Tropsch syncrude and methanol biorefineries (Farzad et al., 2017). Table 2-18 summarises life cycle studies conducted in different countries using sugarcane and sugarcane bagasse as feedstocks. The most commonly used categories, with a significant impact in the sugarcane life cycle studies, have been GWP_{100a}, followed by energy analysis and lastly acidification, eutrophication and abiotic depletion (fossil fuels) potential (see Table 2-18). Being multi-product biorefineries with the exception of a few (Macedo et al., 2004; Kadam et al., 2002a), economic allocation was applied in these studies.

Furthermore, LCAs of sugarcane and sugar producing industries detailing emissions occurring during cultivation, harvesting, transportation and milling of the sugarcane, have received attention (Renouf, 2006; Mashoko et al., 2010), with cultivation and transportation to sugar mills having a major impact (Reno et al., 2014). In addition, LCAs of power generating technologies producing bio-energy (steam and electricity) from sugarcane residues, are also available (Mashoko et al., 2013; Lopes Silva et al., 2014; Eksi and Karaosmanoglu, 2018); some are shown in Table 2-18. However, no detailed LCAs have been conducted on lignocellulose biorefineries producing polyethylene (that was significantly unprofitable, therefore excluded), near-profitable and profitable sorbitol, glucaric acid and levulinic acid from sugarcane bagasse. A recent study by Thaore et al., (2019) has conducted an LCA on glucaric acid production from corn stover and used GWP100a as the impact category and calculated the total GHG emissions at 1675 kg CO_2 eq./kg glucaric acid. The main contributors to this impact were potassium hydroxide, corn stover, ammonia, cellulase enzymes and natural gas.

Table 2-18: Life cycle assessments on processes using sugarcane and sugarcane bagasse as feedstocks to produce various bio-based products

LOCATION	FEEDSTOCK	ALLOCATION	PRODUCTS	CATEGORIES															REFERENCES
				GW	En	OG	HT	AD-f	AD	AP	EP	OD	PS	FW	POCP	TE	ME	TP	
South Africa	SB	-	Bio-ETOH CHP	•				•		•	•							•	Botha and von Blottnitz, 2006
India	SB	n.a	Bio-ETOH	•	•	•		•		•	•							•	Kadam, 2002a
Mauritius	SB	EC	CHP	•	•			•		•	•	•	•					•	Ramjeawon, 2008
Brazil	SC	EC	Bio-ETOH	•	•			•		•	•	•	•					•	Luo et al. 2009a
Nepal	SC	EN/EC	Bio-ETOH		•														Khatiwada and Silveira, 2009
Brazil	SC	n.a	Bio-ETOH	•															Macedo et al., 2004
South Africa	SC	-	Sugar Elec	•	•	•		•				•							Mashoko et al., 2010
South Africa	SB	EC	Sugar Elec		•	•													Mashoko et al., 2013
South Africa	SB	EC	Bio-ETOH* Sugar CHP LA* BT* MT* FT Syn.* FF*	•		•	•	•	•	•	•	•		•	•	•	•		Farzad et al., 2017
Australia	SC	EC/SYS. EXP	Sugar	•	•	•				•	•								Renouf, 2006

* This study was based on 6 scenarios, each producing one of the chemicals and electricity cogeneration alongside sugar.

KEY

Feedstock

SB = Sugarcane bagasse
SC = Sugarcane

Allocation

EC = Economic
EN = Energy
SYS. EXP = System expansion

Products

Bio-ETOH = Bio-ethanol
CHP = Combined heat and power
LA = Lactic acid
BT = Butanol
MT = Methanol
FT Syn. = Fischer Tropsch syncrude
FF = Furfural
Elec = Electricity

Impact categories

GW = Global Warming potential
En = Energy analysis
HT = Human toxicity
OG = Other gases besides GHGs
AD-f = Abiotic depletion (fossil fuels)
AD = Abiotic depletion potentail
AP = Acidification potential
EP = Eutrophication potential
OD = Ozone layer depletion potential
PS = Photochemical smog formation potential
FW = Fresh water aquatic ecotoxicity
POCP = Photochemical oxidation potential
TE = Terrestrial ecotoxicity
ME = Marine aquatic ecotoxicity
TP = Toxicity potential (heavy metals, carcinogens etc)

2.15. Multi criteria decision assessments

Multi criteria decision assessment (MCDA) is a general framework that can be used in decision making and for planning purposes to evaluate problems involving several stakeholders and trade-offs between multiple and contradictory monetary and non-monetary objectives (Pohekar and Ramachandran, 2004; Kangas and Kangas, 2005; Martinez-Hernandez et al., 2014). This assessment tool is an alternative to cost benefit analysis methodology but in addition, MCDAs also consider non-monetary indicators. It is a mature tool rooted in Decision Analysis theory and can be applied to any field. Some examples of its application have been in energy planning (Pohekar and Ramachandran, 2004), ecosystem service valuations (Saarikoski et al., 2016), forest management (Kangas and Kangas, 2005), natural resource management (Mendoza and Martins, 2006), health care (Drake et al., 2017), environmental management (Kiker et al., 2005) and waste paper management (Hanan et al., 2013).

Multi criteria decision assessments basically evaluate the performance of alternatives/options with respect to criteria that capture value judgements on key decision making problems (Watrobski et al., 2019). Multi criteria decision assessments (MCDAs) assist in the making of decisions where multiple objectives exist using quantifiable or non-quantifiable, a combination of the two or relative weights (Watrobski et al., 2019). Earlier on in its development, MCDA was used as a single score criteria approach aimed at projecting future demands for example in energy management systems. However, with the growing environmental concerns in the last two to three decades, most MCDAs now incorporate environmental and social considerations, which led to an increase in the application of MCDAs to resolve their multiple objectives (Watrobski et al., 2019; Pohekar and Ramachandran, 2004). To this end, MCDAs have since been applied in sustainability assessments in biorefinery (biomass) value chains (Parajuli et al., 2015) and environmental projects (Kiker et al., 2005).

There are a variety of different MCDA methods and tools (software) available such as weighted averages, outranking, fuzzy principles and their combinations (Parajuli et al., 2015; Pohekar and Ramachandran, 2004). Regardless of the variations of MCDAs, they share some basic concepts, which all MCDAs should cover namely: objectives, criterion for evaluation, goals and attributes. Details of the different methods can be assessed in several literature sources (Wang et al., 2009; Mendoza and Martins, 2006). The value base method is one of the most widely used approaches in the sustainability studies of biorefinery value chains as it accommodates qualitative and quantitative information with respect to the selected criteria (Parajuli et al., 2015). It involves the use of assigned ratings (scores) to an alternative followed by rating using a scale whose range is arbitrary and which is selected based on the decision maker’s choices. Once this rating scale is defined, rating values assigned to each parameter per indicator should be carefully applied so that scores are appropriate and representative of the impact of each parameter relative to the other alternatives. For this reason, stakeholder involvement in the whole MCDA is key to obtain balanced views and ratings of the different parameters to eliminate bias.

Concerning sugarcane biorefineries, MCDAs have been extended to the production of itaconic acid, polyhydroxybutyrate (PHB) and succinic acid produced via biological processes with the most sustainable scenario being succinic acid, PHB and electricity in a multi-product biorefinery (Nieder-Heitmann et al., 2019). However, no multi criteria decision assessments (MCDAs) have been conducted to score and rank biorefineries at sugar mills where chemical and catalytic processeses are used to produce sorbitol, glucaric acid and levulinic acid. Though the MCDA exercise is consultative, involving stakeholders, it is used in this study as a preliminary assessment of the robustness of the profitable and marginally unprofitable biorefinery scenarios based on the combined sustainability indicator trade-offs used in the sensitivity study. Due to the variabilities that exist within MCDA methodologies in the sustainability indicators used and associated weightings, comparative studies become a challenge since solutions are diverse (Julio et al., 2017). However, changing the representative economic, environmental and social weightings over a range of weightings can help identify the most sustainable biorefinery for key sugar industry stakeholders (Nieder-Heitmann et al., 2019) to conduct feasibility in developing countries.

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Chapter 3

3.0 Techno-economic assessment of a polyethylene biorefinery using cellulosic ethanol as feedstock.

Objective of dissertation in this chapter and summary of findings

The objective of chapter 3 is to assess the techno-economics and social impact of a biorefinery producing high density polyethylene (labelled PE) from cellulosic ethanol as feedstock. The 11 t/h cellulosic ethanol feedstock used in the PE model was obtained from an existing ethanol biorefinery (labelled ETOH) with combined heat and power (CHP) plant that used sugarcane and bagasse as feedstock (Mandegari et al. (2017).

This chapter (including subsequent chapters 4 and 5) presents methodologies and results on the generated biorefinery scenarios (objective two) used for the techno-economic assessments (objective three) and social impacts (part of objective 4) of the polyethylene biorefinery. Objective 2 is firstly to develop discrete simulations of biorefineries producing the shortlisted chemicals, annexed to an existing sugar mill and secondly, to develop a utility supply system in the form of a combined heat and power plant (CHP). The CHP plant was however, not modelled for this case as the PE biorefinery in the current study was connected to an existing bio-based ethanol biorefinery with CHP plant modelled by Mandegari et al., (2017). The feedstock to this polyethylene (PE) model was cellulosic ethanol whereas the other scenarios discussed in chapters 4 and 5 used sugarcane bagasse and brown leaves as the starting material. The ETOH model to which the polyethylene biorefinery was connected was taken as a black box. This existing ETOH biorefinery was marginally profitable with a 10.2% IRR at a 9.7 hurdle rate for a 25 year project lifespan.

The third objective was to determine the techno-economic viability of producing polyethylene (whilst sorbitol and glucaric acid and levulinic acid were considered in chapters 4 and 5 respectively) in integrated biorefineries, and compare them to a base case scenario only producing electricity. The number of additional permanent jobs created with the establishment of the biorefineries formed part of objective four. The number of jobs was determined quantitatively by counting the number of personnel required per process plant based on a scenario’s complexity.

This current chapter focused on the production of polyethylene (PE) in a biorefinery using Aspen Plus ® v 8.6 and literature data. The second generation (2G) ethanol feedstock (11 t/h) required to produce polyethylene was obtained from an existing model (Mandegari et al., 2017) (taken as a black box) with a combined heat and power (CHP) plant annexed to a sugar mill. The 2G ETOH biorefinery met its energy needs by diverting 35% (bypass ratio) of the available 113 t/h (wet mass basis) bagasse and trash to the CHP plant where it was combusted for steam and electricity production for internal process use. To meet the additional energy needs of the bio-ethanol to ethylene (BETE) to PE process units developed in this current study, the electricity demand was obtained from the excess electricity produced in the CHP plant of the existing model and a cost allocation to the cooling water and steam utilities of 6.5% each of the inside battery limits (ISBL) was used (Mandegari et al., 2017). An alternative scenario (presented in Appendix B-6) was developed where the amount of biomass diverted to the CHP plant (termed bypass ratio) in the model by Mandegari et al., (2017) was adjusted upwards to 48% to meet the additional process units' energy demand. As a result of the reduced feedstock to the biorefinery due to the increased bypass ratio and subsequent reduction in design capacity, the fixed capital investments and operating costs were adjusted by a factor of 0.9.

In this study, 11 t/h cellulosic ethanol was converted to 6 t/h (36 kt/y) PE, which represents 0.01% of the current global fossil-based production capacities. The bio-based ethanol to ethylene (BETE) and ethylene to polyethylene (PE) process areas consumed 12 MWh cooling duty, 11 MWh steam and 4.2 MWh electricity. The whole biorefinery (ETOH-BETE-PE) termed PE-1 was unprofitable with a net present value (NPV) of -282 US$ million when PE was sold at an estimated fossil-fuel based price of US$ 886/t (Resource Recycling, 2016) based on a 9.7% hurdle rate in real terms for a 25 year project life. The total capital investment (TCI) cost was US$ 311 million whereas the annual variable and fixed operating costs were US$ 21 million and US$ 9.7 million respectively. About 52% of the fixed operating costs was from the labour costs for the 59 additional jobs created in PE-1. The annual total cost of production of PE (sum of the variable, fixed operating costs and annual capital charge, was US$ 31 million." The annual capital charge (ACC) refers to the equivalent annual costs of the total cost of capital assets extended over a process'lifespan. The ACC is used for accounting purposes to calculate the total cost of production of a process on an annual basis.". For the PE-1 scenario to attract private investors (at IRRs of >20%), the PE selling price should reach US$ 2956/t threshold, which represents a required price premium or increase of 233%.

Abstract

This study investigates the techno-economic viability of producing polyethylene using cellulosic ethanol feedstock from an existing biorefinery (ETOH) and CHP plant annexed to a conventional sugar mill. This scenario (PE-1) was then compared to a base case combined heat and power plant producing electricity only to determine which investment option is better for the sugar industry. Aspen Plus ® v 8.6 was used to generate mass and energy balances of the two scenarios. The base case scenario used 113 t/h sugarcane bagasse and brown leaves (wet mass basis) to produce electricity whilst the feedstock to the BETE and PE models was cellulosic ethanol from an ETOH biorefinery that used 113 t/h (wet mass basis) sugarcane bagasse and brown leaves as feedstock and combusted 35% of this feedstock for energy production. The base case scenario was profitable though only marginally with a 10.7% internal rate of return (IRR) and US$ 6.5 million net present value at a 9.7 discount rate over a 25 year project period. The PE-1 biorefinery, on the other hand, was unprofitable at –282 US$ million NPV. The PE-1 scenario can attract private investments at IRRs of 20% if its selling price was US$ 2956/t that is 233% higher than the current fossil fuels polyethylene price of US$ 886/kg used.

3.1. Introduction

Bio-based polyethylene (PE) has been recently shortlisted amongst the top 10 most promising chemicals for future bio-economies by the National Renewable Energy Laboratory (NREL), Department of Energy (DoE) of the United States of America (USA) (Taylor et al., 2015). The consideration of bio-based chemicals such as polyethylene produced in biorefinery complexes has been motivated by the global challenges of rising petroleum prices, the depletion of fossil reserves caused by an increased energy demand due to population growth and environmental burdens brought about by anthropogenic activities (Wolf et al., 2005).

Currently, the bulk of PE produced still originates from technologically well-established petrochemical sources with global capacities of 200000-350000 kt/y (Fan et al., 2013; IAR, 2015b). In comparison to fossil sources, the bio-based PE production capacities are negligible. For instance, the largest bio-based PE producer, Braskem in Brazil, followed by Dow chemicals, only produce about 0.1% of the global PE production capacities (190–200 kt/y) (IAR, 2015a; 2015b). Therefore, potential to expand the market share of bio-based PE exists, considering that fossil-based PE products are now regulated due to their associated hazards and emissions (Research and Markets, 2020).

Being termed a “drop in” chemical, bio–based polyethylene has the added advantage of being processed in existing infrastructure of mature technologies of their fossil fuel counterparts, with minimum process modifications required (Van Ree et al., 2014). Additionally, lignocellulose feedstocks (used to produce cellulosic ethanol feedstock), avoid the food-fuel association that is a major issue in developing countries where food security is a challenge. To this end, the value addition of lignocellulose materials such as sugarcane bagasse, produced after sugar juice extraction, and dried leaves, holds promise as it can provide additional revenue for conventional sugar mills and uplift social communities that rely on this industry. In South Africa, for example, if the inefficient burning of bagasse in old boilers was to be replaced with efficient boilers coupled with “green” non-burn harvesting techniques (Smithers, 2014), then approximately 113 t/h agricultural residues (wet mass basis) would be freed and valorised into bio-based chemicals and bio-energy (Mandegari et al., 2017). Therefore, scope exists for the production of bio-based polyethylene.

Fermentative processing of glucose and xylose sugars into ethanol, the precursor to bio-based polyethylene, has been extensively studied. Ethanol is then catalytically dehydrated to produce ethylene (Mohsenzadeh et al., 2017; Morschbacker, 2009) followed by its polymerisation. Polymerisation is typically a continuous process and earliest commercial plants operated at high pressures of up to 3000 atm (Xie et al., 1994); however, with research and development of variant technologies, polymerisation operations in the slurry and gas phase now occur at lower pressures of 30–100 atm (Grau, 2010).

Globally, polyethylene is the most widely manufactured polymer (Taylor et al., 2015), with a wide range of applications such as plastic bags, plastic films, geo-membranes and storage containers (bottles and tubes) (Taylor et al., 2015). It is also used in toys, engineering, agriculture, cosmetics, personal care products, automotive parts and water piping because of its good performance and low costs (Huang et al., 2009; Babu et al., 2013).

Bio-based polyethylene production from lignocellulose feedstocks, however, has not been widely researched in terms of sustainability (techno-economic, environmental, and social) whilst its precursor (ethanol to ethylene) has received some attention especially in techno-economics (Jernberg et al., 2015; Haro et al., 2013). Apart from kinetic studies on the polymerisation process, no detailed techno-economic assessments (TEAs) for polyethylene biorefineries have been identified to the best of the author's knowledge. Therefore, this study aims to determine the viability of producing PE in biorefinery complexes at conventional sugar mills using second generation, non-food feedstocks. Another contribution of this study is the comparison of PE production to a combined heat and power plant only producing steam and electricity from the available lignocellulose feedstock. The purpose is to assess which of the two is a better investment option at conventional sugar mills.

3.2. Materials and methods

3.2.1. Feedstock composition, specification and process configuration

The feedstock to the BETE-PE model was cellulosic ethanol. It was obtained from an existing ETOH biorefinery that processes sugarcane bagasse and brown leaves (Mandegari et al., 2017) (see Figure 3-1). The ETOH model was used as a black box and its capital investment costs and operating costs were incorporated into the current study to estimate the economic implications of extending the existing marginally profitable ETOH biorefinery (black box) and converting the ethanol to polyethylene as final product.

Approximately 11 t/h bio-ethanol was supplied to the BETE process, which was followed by ethylene (PE) polymerisation to 6 t/h polyethylene (Figure 3-1) (See Appendix B-1 for the Aspen Plus ® models). The excess electricity in the existing ETOH model was used to meet the BETE and PE process units' electricity demand, which left 2.9 MWh for sale to the grid. The steam and cooling demands were given a cost allocation of 6.5% each for the inside battery limits (ISBL) as was done for the cooling duty in Mandegari et al., (2017). An alternative model, where the by-pass ratio was adjusted to meet the additional BETE-PE energy needs and a 0.9 factor applied to the fixed capital investment and variable operating costs, is presented in Appendix B-6 (Table B6-2).

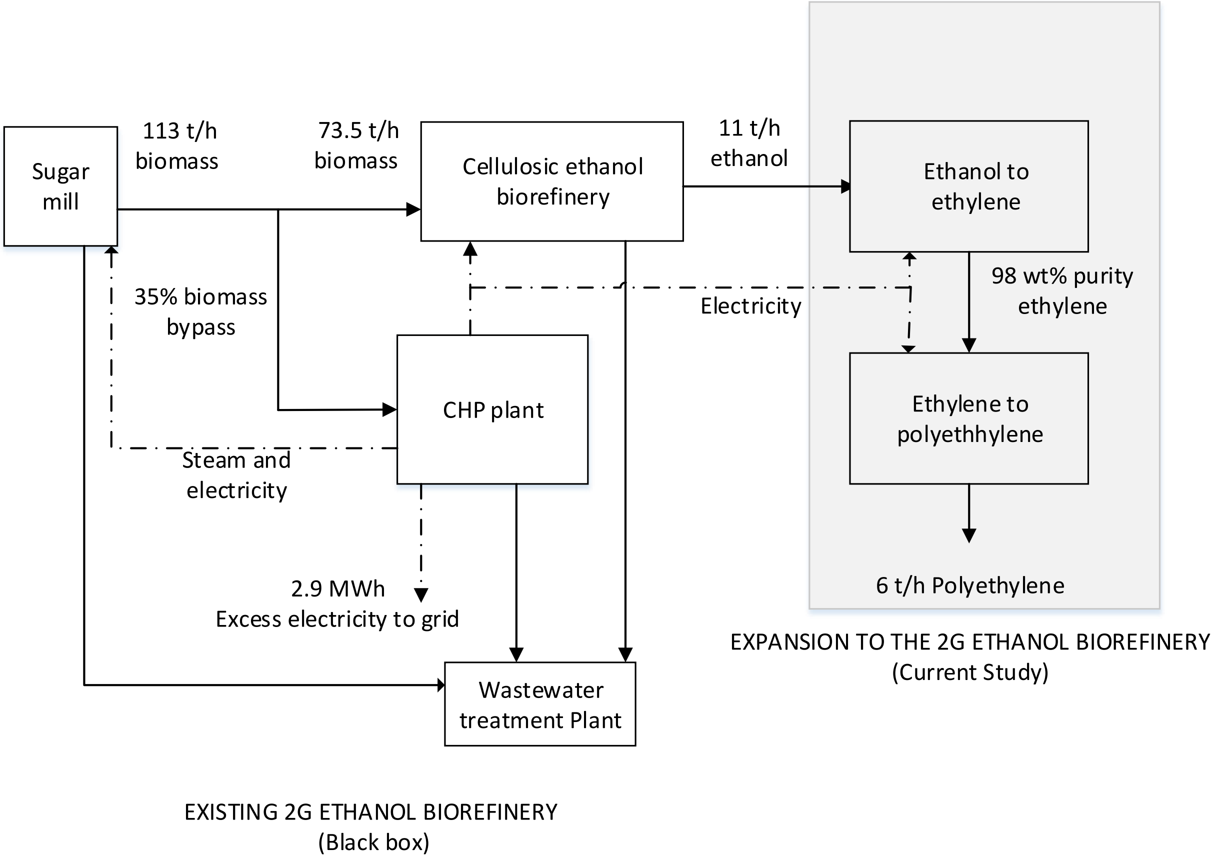


Figure 3-1: Simplified block diagram of the existing 2G ethanol simulation (black box) by Mandegari et al., (2017) and its expansion for polyethylene production

For the CHP base case scenario, the CHP plant's feedstock was 113 t/h sugarcane bagasse and brown leaves (wet mass basis) (65 t/h dry mass). The feedstock composition was based on mean mass compositions of 70% and 30% mixture of bagasse and brown leaves respectively on a dry mass basis. The feedstock included 40.7% cellulose, 27.1% hemicellulose, 21.9% lignin, 6.7% extractants and 3.5% ash (dry mass basis) and 42% moisture (Farzad et al., 2017; Benjamin et al., 2013) (see Appendix B-4 for the biomass equivalents for non–native Aspen Plus® components).

3.2.2. Thermodynamic model

The BETE-PE model and combined heat and power (CHP) plant were modelled in Aspen Plus® v.8.6, which generated mass and energy balances. The default coefficient property method selected (in chapters 3, 4 and 5) was the Electrolyte Non-Random Two-Liquid (ELECNRTL) activity model, used in the presence of polar components. This method has the capability of modelling aqueous electrolytes of any strength and solutions with multiple solvents and activity coefficients for ionic species (Mohsenzadeh et al., 2017). It uses the activity coefficient approach to calculate the liquid properties and equation of state to calculate the vapour phase (using the Peng-Robinson equation of state applied in pure and mixed components) (see Figure A3-4 in Appendix A-3 on guidelines for choosing property and activity coefficient methods). On the other hand, the NRTL property method was used (in chapters 3, 4 and 5) for liquid phase reactions and azeotropic alcohol separation such as in the distillation units and energy supply process areas. This property method describes phase equilibrium of strongly non-ideal solutions (Leibbrandt, 2010; Mohsenzadeh et al., 2017). In addition, POLYNRTL property method was used (in chapter 3), specifically for the polymerisation reactor, to calculate the polymer and solvent activity coefficients (Schefflan, 2011). The caustic wash stage (in chapter 3), where 50% sodium hydroxide (NaOH) was used to absorb CO_2 from the ethylene stream into the OH-ions was modelled using the amine property package (Schefflan 2011).

It was assumed in this chapter (and chapters 4 and 5) that the solid components in the process were water insoluble (WIS) and so do not disturb the liquid-liquid or vapour-liquid equilibriums. Therefore, to handle a stream with WIS and liquid components, two substreams were inputted into Aspen Plus® a vapour-liquid stream (MIXED) and a solid stream (CISOLID) (Gnansounou et al., 2015).

Due to the complex nature of lignocellulose materials, their specific physical properties are not defined in the ASPEN Plus property database. Therefore, lignocellulose components used in the CHP plant were defined based on the component definitions in Humbird et al., (2011) (see Appendix B-4). Aspen Plus® conventional components such as ash (calcium oxide), carbon dioxide, water, oxygen, nitrogen, methane, sulphur and sulphur dioxide are present in the native Aspen Plus® databank.

3.2.3. Process design of bio-ethanol to ethylene process (BETE)

The production of ethylene from bio-based ethanol undergoes a catalytic conversion stage followed by purification stages that include product quenching, caustic washing, drying and cryogenic distillation to produce 99.96 wt% polymer grade ethylene. The detailed process conditions are given in subsequent sections, namely 3.2.3.1 to 3.2.3.2. Figure 3-2 shows a schematic of the main processes in the bio-ethanol to ethylene (BETE) conversion and downstream purification processes. A detailed Aspen plus ® model of the BETE process area and its mass and energy balance, is given in Appendix B-1 and B-2.

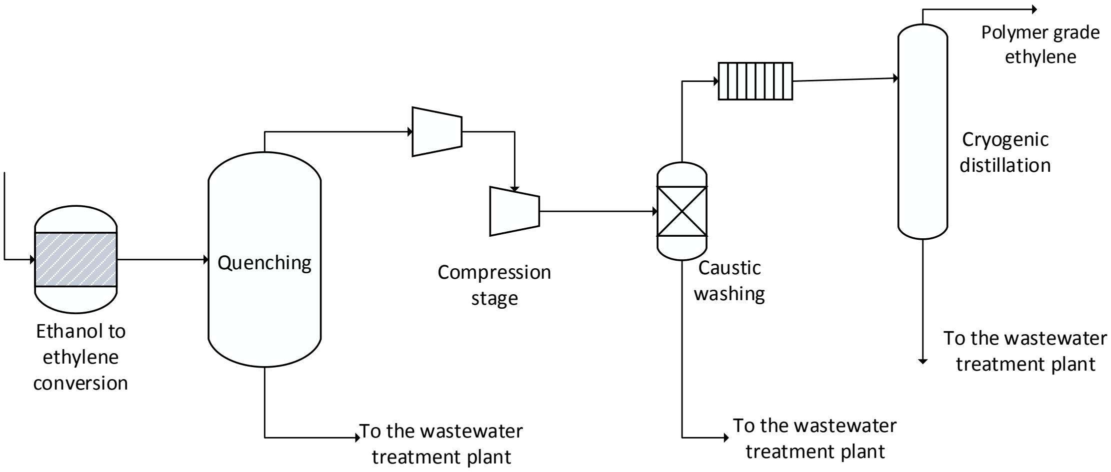


Figure 3-2: Simplified flow diagram of the bio-ethanol to ethylene (BETE) process area (Arvidsson and Lundin, 2011)

3.2.3.1. Feedstock preparation and conversion

Liquid cellulosic ethanol at 1 atm and 25 ^{o}C was conditioned prior to dehydration by pressurising it to 13 atm (Barrocas et al., 2007; Arvidsson and Lundin, 2011) and directly injecting it with medium pressure steam in an evaporator (heat exchanger) unit. This was done so as to raise the feedstock temperature to 450 ^{o}C and convert the liquid ethanol to a gas (Arvidsson and Lundin, 2011).

During the dehydration reaction process (stoichiometric reactor), ethanol in the presence of a syndol catalyst in a packed bed with a 0.9333 g/cm^3 bulk density and 0.4 void fraction (Karim, 2011) was converted to the main product ethylene and by-products diethyl ether, acetaldehyde, ethane, methane, isobutene and carbon monoxide (Arstad et al., 1997). The assumed reactions and conversions (wt %) occurring during ethanol dehydration to ethylene are summarised in Table 3-1.

Table 3-1: Ethanol dehydration reactions and conversions used in the stoichiometric reactor (RSTOIC) models (Arvidsson and Lundin, 2011; Kagyrmanova et al., 2011)

Reaction	Reactant	Wt % conversion
*Ethanol → Ethylene + H_2O	Ethanol	98%
2 Ethanol → Diethyl-ether + H_2O	Ethanol	0.05%
2 Ethanol → 1,2-Butadiene + $2H_2O$ + H_2	Ethanol	0.5%
Ethanol → Acetaldehyde + H_2	Ethanol	0.2%
2 Ethanol → Propylene + CO_2 + H_2	Ethanol	0.07%
Ethanol + H_2 →Ethane + H_2O	Ethanol	0.2%
Ethanol → Methane + CO + H_2	Ethanol	0.08%
Ethanol + H_2O → Methane + CO_2 + H_2	Ethanol	0.1%

* Assumed that some of the ethanol was unconverted or unrecovered.

3.2.3.2. Purification of ethylene

The outlet stream from the reactor containing mainly ethylene was compressed to 15 atm. Compressors used were assumed to operate at 72% isentropic efficiency (Arvidsson and Lundin, 2011) and a 95% mechanical efficiency (Mandegari et al., 2017). The compressed ethylene mixture was then cooled (in heat exchangers) to 145 ^{o}C for maximum water removal in a 20-stage quench tower (Kurukchi et al., 2001) with operating details summarised in Table 3-2(a).

Table 3-2: The operating conditions of the quench tank (Kurukchi et al., 2001), caustic wash tower (Arvidsson and Lundin, 2011) and cryogenic distillation columns (Arvidsson and Lundin, 2011) for ethylene purification

	(a) Quench tank*	**(b) Caustic wash***	**(c) Distillation**
Aspen block	**RADFRAC**	**RADFRAC**	**RADFRAC**
Number of stages	20	60	20
Condenser type	-	-	Partial vapour
Reboiler type	-	-	Kettle
Reflux ratio (mol)	2.8	3.7	0.8 (mass)
Distillate to feed ratio (mole)	0.45	0.96	0.96 (mass)
Condenser pressure (bar)	-	-	17
Reboiler pressure (bar)	-	-	17
Column pressure (atm)	1	1	2.5

*The quench and caustic wash columns were designed using DSTWU columns from which the reflux ratio vs the number of theoretical stages profiles were generated and used to design the RadFrac coumns to attain > 99 wt% ethylene recovery (see Table B1-4 in Appendix B for details of the DSTWU process conditions).

A water spray at 20 ^{o}C was introduced at the top of the quench tank column where another stream, a recycle stream at 20 ^{o}C containing 25% of the bottom stream was also fed (Arvidsson. and Lundin, 2011). The two top streams supply just sufficient spray water to cool the feed stream entering the quench tank without flooding the column as too much water in the process has cost implications when removing it downstream. The rest of the bottom product from the quench tank was sent to the wastewater treatment (WWT) plant.

The top product stream from the quench tower underwent further compressions up to 20 atm and was cooled to 35 ^{o}C (Kurukchi et al., 2001), then fed to a 60-stage caustic wash tower (see Table 3-2(b)) to ensure sufficient CO_2 removal from ethylene (Arvidsson and Lundin, 2011). A caustic stream of 50 mass % sodium hydroxide (NaOH) was supplied to the caustic tower.

Any remaining water in the ethylene stream from the caustic wash tower was dried using molecular sieves at 19 bar to avoid the formation of hydrates and ice during cryogenic distillation. Water trapped on the molecular sieves was recovered by heating and sent to the WWT facility. The ethylene rich stream from the molecular sieves was cooled to -37 ^{o}C using a refrigerant R-1270 (propylene) operating in a closed loop system prior to cryogenic distillation. The cryogenic distillation column process conditions are shown in Table 3-2(c). After distillation, polymer grade ethylene (99.96 wt%) (Mohsenzadeh et al., 2017) was produced as a top product and the bottom products of the cryogenic column (mainly made up of heavier carbons) were sent to a wastewater treatment plant.

3.2.4. Process design of bio–based ethylene to polyethylene

Figure 3-3 shows a simplified process flow diagram of the polyethylene production process and its downstream purification stages (see Appendix B-1 for the Aspen Plus® model). Polymerisation, although a complex process, involves the catalytic chemical combination of monomers to produce long chains of polymers (Bohm, 2003). The process stages included feedstock conditioning, polymerisation, hydrogen, catalyst and 1-hexene comonomer recovery stages, drying and extrusion.

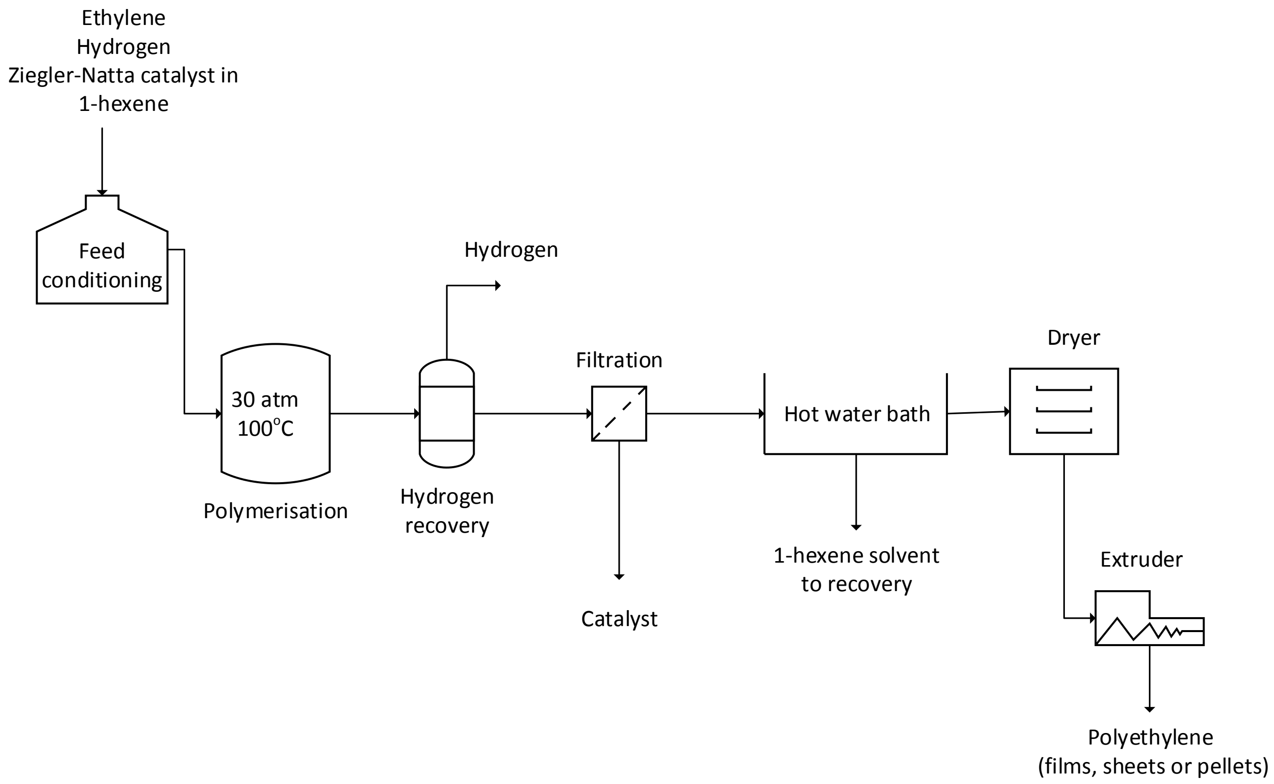


Figure 3-3: A simplified flow diagram of the bio - ethylene (BETE) polymerisation process area (Arvidsson and Lundin 2011)

The polymer grade ethylene was mixed with 1.35 t/h purchased hydrogen assumed to have been produced from natural gas and 0.3 t/h Ziegler-Natta catalyst was suspended in a dilute solvent of 1-hexene. A 5% Ziegler-Natta catalyst based on the ethylene feedstock was used (based on the ratio applied by Lee et al., (2016) due to limited information). The slurry temperature was adjusted to 100 °C and compressed to 30 bar prior to polymerisation (Xie et al., 1994). The polymerisation reactor (modelled as an RYIELD block) used polyethylene proximate and ultimate analyses values from Al Amoodi et al., (2013) for fossil-based PE as shown in Table 3-3. The RYIELD model uses input and output data to calculate yield distributions (Brown et al., 2012).

Table 3-3: Proximate and ultimate analyses of data used for polyethylene in Aspen Plus ® (Al Amoodi et al., 2013)

	Proximate analysis %				**Ultimate analysis %**						
Sample	Moisture	FC	VM	Ash	Ash	C	H	N_2	Cl_2	S	O_2
PE	0.02	0	99.85	0.15	0.15	85.81	13.86	0.12	0	0.06	0

A 70% molar yield was used in the (RYIELD) polymerisation reactor to attain a PE product yield of 95-100 %. Excess hydrogen was recovered from the process whilst the slurry generated was filtered to remove the Ziegler-Natta catalyst (using separator blocks). A hot water bath recovered the solvent from the slurry, leaving a hydrated polymer stream. The polyethylene was then dried to powder that can be extruded to films, pellets, or sheets (Bohm, 2003) (extruder not included in economics).

3.2.5. Process design of a combined heat and power plant

The PE-1 scenario was compared to a combined heat and power (CHP) plant, an investment option producing only steam and electricity. The CHP plant investment option supplied the sugar mill with 120 t/h steam for its process, assuming the mill's energy demand of 0.4-ton steam per ton of cane crushed (Mandegari et al., 2017). The configuration of the CHP plants in all scenarios is the same, although there is variation in the input variables for each scenario, depending on plant capacities. The CHP plant comprises a biomass combustor where the bagasse and dried leaves (at 50% and 15% moisture respectively), are burned. It also has a boiler unit, which generates steam using energy from the exothermic combustion reactions and lastly, a turbine to generate electricity.

3.2.5.1. Combustion unit

The CHP base case combusted 113 t/h sugarcane bagasse and brown leaves (wet mass) (Humbird et al., 2011) in 20% excess air (Mandegari et al., 2017) at 205 ^{o}C in a stoichiometric reactor (RStoic) at atmospheric pressure leading to 99.9% conversion of biomass to CO_2 (Arvidsson and Lundin, 2011) (See Appendix B (Table B1-3) for combustion reactions). In a typical biorefinery and CHP plant configuration, methane from the wastewater treatment plant, bypassed biomass and cellulignin filtered from the hydrolysate stream, are also combusted. The combustor was assumed to operate adiabatically at a net duty of zero (Nsaful, 2013) and pressure of 1 atm to ensure that the energy input to the reactor was from the bagasse alone.

3.2.5.2. Boiler unit

The flue gases (at 870 ^{o}C) generated, after combustion of biomass, was channelled through a series of heat exchangers). The energy recovered from these exchangers (with 10% heat losses) was used to supply heat to the boiler (Flash2 block) operating at 0 atm, and leading to the production of high-high pressure steam released at 480 ^{o}C and 64 bar (Colombo et al., 2014). The process steam demand calculated in Aspen Plus ®, determined the amount of boiler feed water. This boiler feed stream was assumed to have undergone deaeration to remove oxygen, and treated with chemicals, to minimise boiler fouling. The cost of the boiler chemicals has been accounted for in the economic assessments.

The flue gas stream, after heat integration, was cleaned in a gas scrubber (separator block) with a CISOLID split fraction of 0.99 (see Appendix B-1 for Aspen unit specifications in Tables B1-1 and B1-2). At this stage, ash and particulate matter were removed for environmental compliance. This stream was then cooled to 55 ^{o}C using a heat exchanger block and released into the atmosphere.

3.2.5.3. Turbine unit

The generated high- high pressure steam (HHPS) from the boiler was expanded in a CEST turbine to produce electricity and steam, so as to meet the energy needs of the biorefinery and the sugar mill (120 t/h of steam at 400°C and 30 bar). The turbine is modelled as an isentropic compressor with an efficiency of 85% and a generator mechanical efficiency of 95% (Mandegari et al., 2017). In order for the turbine to reach maximum power recovery from produced steam, a condensate turbine can be applied with an outlet pressure of 0.1-0.2 bar (Nsaful, 2013).

The three stage-extraction CEST also produced high pressure- and low pressure-steams (HPS and LPS respectively). Depending on the process plant requirements, the turbine was conditioned with a desuperheater that supplies steam at 104 °C and 1 atm to adjust process stream conditions to high pressure steam (HPS at 266 °C, 13 atm) and low pressure steam (at 233 °C, 9.5 atm). The HHPS, HPS and LPS were used in the CEST system to generate electricity (and steam) for its process needs and any excess electricity was sold off to the grid at US$ 0.08/kWh. The remaining low energy steam from the last stage is condensed (Exchanger block) to 90 °C, the desired boiler feed water temperature. After being cleaned, this water, together with fresh make-up water, is recycled back to the boiler

3.2.6. Heat integration by pinch analysis

Pinch analysis was applied to estimate and quantify the energy savings in biorefineries following heat integration. After the development of process flow diagrams, heat exchangers (hot and cold streams) are identified leading to the development of heat and mass balances around the exchangers. From this configuration, the inlet and outlet temperatures around a heat exchanger, flow rate and heat capacity data were used in pinch analysis. A temperature difference between hot and cold streams, ΔTmin, of 10 °C was selected, which is in line with chemical processes. Streams with less than 1000 kW heat flow were not considered for integration due to their low thermal integration potential (Dias et al., 2009). Also, according to expert advice, hot streams less than 150 °C were excluded (unless they were flue gas streams), to avoid the indiscriminate selection of hot and cold streams.

These temperature values, together with calculated enthalpies, were entered in a cascade problem table algorithm to determine the process pinch point and targets. Graphical composite curves (CC) were also constructed to determine the possible theoretical maximum (Q_{MAX}) heat recovery after heat integration and targets Q_{MINHOT} and $Q_{MINCOLD}$. These are the minimum hot and cold utilities, needed to be supplied and removed from the system respectively. A heat exchanger network grid, showing the arrangement of the exchangers to achieve the maximum heat recovery calculated, was not considered.

3.2.7. Plant sizing and economic assessment

The equipment costs for the BETE-PE model were estimated in Aspen Plus ® Economic Analyser except the reactors, boilers and turbogenerators that were sized and costed using literature data (Humbird et al., 2011). Their installed costs were adjusted for a given plant capacity and cost year using relevant sizing exponents and Chemical Engineering Plant Cost Indices (CEPCI) (see Appendix A-3 for the short-cut module (factorial) methods used and CEPCI indices).

The variable operating costs were calculated using mass balances of the feedstock, reagents and waste disposal flow rates from the simulations. The fixed operating costs, included insurance and maintenance costs; employee salary rates were based on values from literature (Mandegari et al., 2017) whilst the social indicator (skilled, semi and unskilled jobs) was based on a quantitative measure of the number of additional permanent jobs created with the establishment and operation of the biorefinery whilst the CHP plant had a constant work force of 89000 man-days per year (Farzad et al., 2017). The total production cost was calculated by the summation of the total variable and fixed operating costs and annual capital charge.

From the calculated capital and operating costs, a discounted cash flow rate of return methodology (DCFROR) on a real term basis was used to measure profitability for a project life of 25 years. The economic assumptions used reflected emerging economies' parameters as presented in Table 3-4. The overall project profitability was measured using the internal rate of return (IRR) and net present value (NPV) at a 9.7% hurdle rate (discount rate of 15.4 % less 5.7% inflation) (Nieder-Heitmann et al., 2018; Mandegari et al., 2017). Also determined was the selling price required by the scenario to attract private investors at an IRR of 20%. A sensitivity analysis of the plant's profitability (IRR) was conducted to determine the robustness of the economic results using a ± 30% variance from the baseline.

Table 3-4: Economic parameters used in this study for a 2016 cost year analysis (Mandegari et al., 2017; Humbird et al., 2011)

Parameter	**Value used**
Annual operating hours	6480 h
Project life (years)	25
Depreciation	Straight line over 5 years
Salvage value	0
% Spent in year -2	10
% Spent in year -1	60
% Spent in year 0	30
Start-up time (years)	2
First year new plant capacity (% design)	50%
Second year new plant capacity (% design)	75%
Working capital (% of FCI)[c]	5%
Income tax rate	28.0%
Cost year for analysis	2016
Chemical Engineering Plant Cost Index (CEPCI)-2016	536.5
Inflation rate[a]	5.7%
Cash flow calculations basis/ IRR method	Real term
Discounted rate (hurdle rate)	9.7%
Price of fossil based polyethylene (US$/t)*	886

*Average PE price of US$ 886/t used (Resource Recycling, 2016)

[a] Inflation rate of 5.7% from Mandegari et al., 2017 and Farzad et al., 2017, based on the 2016 average inflation rate of developing countries (BRICS (Brazil, Russia, India, China, South Africa)) (Statista, 2019).

[c] See Appenndix A-3 for details on how the working capital was determined).

3.3. Results and discussion

The Aspen Plus® input and output streams of the PE-1 biorefinery are discussed herein. The PE-1 biorefinery was also compared to a CHP base case scenario, which only produced electricity through the processing the available 113 t/h sugarcane bagasse and brown leaves (wet mass basis).

3.3.1. Amount of ethylene and polyethylene produced from ethanol

Mass and energy balances of the biorefinery producing ethylene (BETE) and polyethylene (PE) together with the CHP plant base case scenarios, are shown in Table 3–5. The mass and energy balances shown for the ETOH model (black box) were obtained from Mandegari et al., (2017) for context.4

Table 3-5: A summary of the material and energy balances for the polyethylene and CHP base case scenarios

		ETOH (Black box)*	**BETE - PE**	**CHP base case**
Parameter	Unit			
Feedstock (DM-dry mass)	t/h	65	-	65
Total feedstock (WT-wet mass)	t/h	113	-	113
By-pass to boiler	%	35	-	100
Feedstock to bio refinery (DM)	t/h	42.25	-	0
Cellulosic ethanol[b]	t/h	11[b]	11	-
Ethylene	t/h	-	6.3	-
Ethylene/ethanol yield	kg/kg	-	0.54	-
Ethylene yield (of theoretical max.)	%	-	94.6	-
Polyethylene	t/h	-	6	-
Polyethylene/ethylene yield	kg/kg	-	0.95	-
Steam demand	MWh	155	10.6	7
Electricity demand	MWh	11.2	4.2	0.9
Cooling demand	MWh	50.6	12.1	39
Electricity produced (excess)	MWh	7.1[c]	-	60.9

*Details from Mandegari et al., (2017).

[b] Feedstock to the BETE process.

[c] 4.2 MWh of the excess electricity (7.1 MWh) was used in the BETE-PE units leaving 2.9 MWh for sale.

In the BETE process, a yield of 0.54 kg ethylene/kg ethanol was attained. This was comparable to ethanol to ethylene simulation yield of 0.57 kg ethylene/kg ethanol obtained in a stand-alone biorefinery study by Arvidsson and Lundin, (2011) and a study of an integrated plant conducted by Jernberg et al., (2015) with a 0.53 kg ethylene/kg ethanol yield. The ethylene yield as a percentage of the theoretical maximum, was 94.6%.

A total of 6.3 t/h ethylene was produced from 11 t/h ethanol. The ethylene was polymerised to 6 t/h (36 kt/y) polyethylene attaining a yield of 0.95 kg polyethylene/kg ethylene, although no comparative studies are available. The 6 t/h PE produced represent about 0.02% of the global fossil-based market size (Fan et al., 2012). The PE plant production capacity in this study fits into the size of a small-scale polyethylene plant of 20–60 kt/y (Van Ree et al., 2014). Therefore, its production volume is too low to have an impact on the current polyethylene market selling price with production capacities of about 200 000-350 000 kt/y (IAR, 2015b).

The combined heat and power (CHP) base case plant, on the other hand, which does not have a biorefinery, combusted all its biomass (113 t/h) to produce 61 MWh of electricity as its only product, with 0.9 MWh being used for its own internal process units. Approximately 61 MWh excess electricity was sold to the grid (at US$ 0.08/kWh) as shown in Table 3-5.

3.3.2. Pinch analysis

Pinch analysis was conducted on the BETE-PE process area where 1 hot stream and 3 cold streams were used in a problem cascade table where a hot pinch point of 466 °C and cold pinch point of 456 °C were attained (see Appendix B-3 for input stream data and cascade table). The maximum theoretical heat recovery, Q_{MAX} (the range where the hot and cold streams overlap) was calculated as 2544 kW, the minimum cold utility that would be removed as cooling duty ($Q_{MINCOLD}$), was 1256 kW and the minimum hot utility needed to be added to the network was 0 kW as shown in Figure 3-4. This integration led to a 10% and 21% saving on the overall hot and cold utilities respectively.

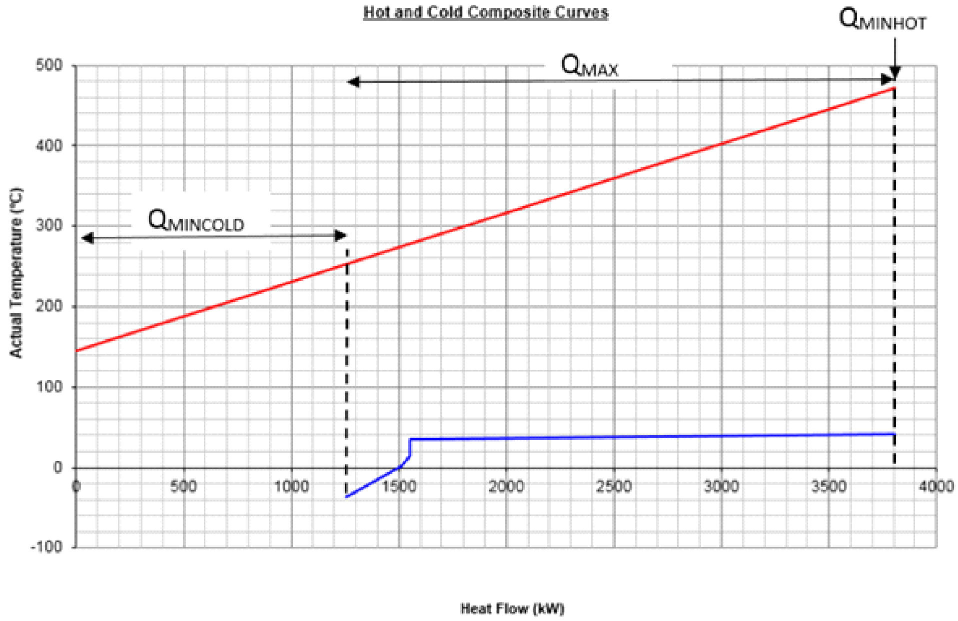


Figure 3-4: Hot and cold composite curve after integrating 1 hot and 3 cold streams for the BETE-PE process areas

3.3.3. Analysis of energy consumption

The energy demand for the ETOH-BETE-PE process units and CHP base case are presented in Table 3–5. The total steam demand generated in Aspen Plus for the BETE and PE was 11 MWh (44 t/h). The ethanol dehydration reactor in the BETE process area operating at 450 °C and 13 atm where ethanol was partially vapourised consuming 61% of the total steam demand followed by the caustic absorption tower (16%) and quench tank (13%). The polymerisation process area utilised 2% of the total steam demand because the polymerisation process is exothermic (Mun et al., 2011). In Mandegari et al.,'s (2017) study of the ETOH biorefinery, high steam demand originated from the purification stage and pretreatment processes that consumed 43% and 30% respectively of the total steam.

With regards to the cooling demand (12 MWh) in the BETE and PE process areas, 34% of the total cooling duty originated from the BETE product stage where the utility was used to cool the dehydration reactor outlet streams from 450 ^{o}C to 145 ^{o}C before its introduction to the quench tower. The condensers in the quench tank and caustic wash used 33% and 23% respectively of the total cooling duty to maximise water and CO_2 removal from the ethylene rich stream. Prior to cryogenic distillation of crude ethylene, the stream was cooled to -37 ^{o}C using a refrigerant in a closed loop system with a cooling duty of 0.8 MW. The CHP base case used 39 MWh of cooling duty on the flue gas stream after ash scrubbing.

Electricity usage in the BETE and PE process units was 3.3 MWh more than the consumption in the CHP base case that used 0.9 MWh electricity (see Table 3-5). This is because the biorefinery housed more pumps, fans and compressors than the CHP base case. The electricity demand in the ETOH model was also 3-fold more than that in the BETE and PE process areas and can be as a consequence of additional energy needed to power stirrers and pumps in the multiple enzyme production and fermentative units. Overall, a surplus electricity of 2.9 MWh and 60.9 MWh for the PE-1 biorefinery and CHP base case respectively was sent to the grid.

3.3.4. Economic evaluations

3.3.4.1. Total capital investment costs

Due to the numerous process areas in the PE-1 biorefinery, its total capital investment (TCI) cost was US$ 311 million, that is more than the TCI of the CHP base case scenario as shown in Table 3-6. The ETOH process areas had the largest contribution of 69% to the inside battery limits (ISBL), which excludes the waste water treatment (WWT) plant, boiler and CEST system, utilities and storage. The major capital investment costs according to Mandegari et al.,'s (2017) study on the ETOH biorefinery originated from the pretreatment stage (32% of ISBL and 13% of total installed cost) and conversion and purification stages (52% of ISBL). The pretreatment (SO_2-steam explosion) technology's capital cost in Mandegari et al.,'s (2017) study was close to values of percentage contributions to installed costs of 16-20% attained in other studies where SO_2-steam explosion was used (Wingren et al., 2003 and chapter 4 of this study).

Table 3-6: Total capital investment costs per scenario excluding feedstock handling costs

Total capital investment costs (US$ million)		
	PE-1	**CHP base case**
*Pretreatment	19.6	-
*Enzyme production	9.4	-
*Enzymatic hydrolysis and fermentation	9.7	-
*Recovery	12.4	-
*Evaporation	9.7	-
Ethanol to ethylene	1.8	-
Ethylene recovery	1.1	-
Ethylene purification	7.8	-
Ethylene to polyethylene	16.9	-
*Wastewater treatment	4.2	-
*Boiler and CEST	61.0	73.5
Utilities	11.5	4.0
Storage	4.4	-
Total inside battery limits (ISBL)	88.4	-
Total installed equipment costs	**169.5**	**77.5**
Total direct costs	184.9	77.5
Total indirect costs	111.0	46.5
Fixed capital investment	295.9	123.9
Total capital investment	**310.7**	**130.1**

*Values from Mandegari et al. (2017) at 35% bypass ratio of biomass for combustion in CHP plant

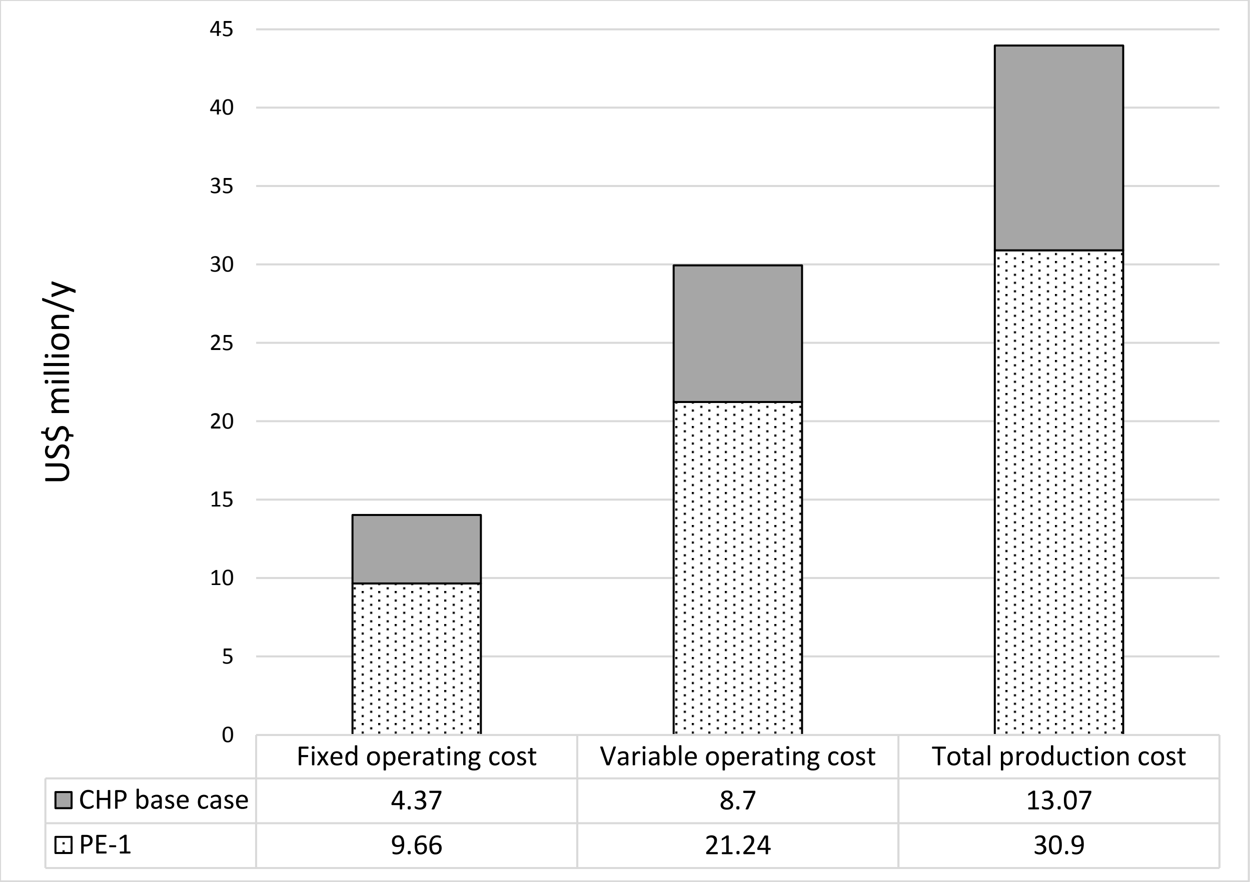
Conversely, the BETE process area contributed 12% to the biorefinery's ISBL. The ethanol dehydration process had a capital (installed) cost of US$ 10.6 million and was comparable to values attained by Haro et al., (2013) of € 8.9–13.6 million (US$ 10.5–16.1 million) for four biorefineries used in their study, operating at varying plant capacities and configurations.

The polymerisation process area's capital cost of US$ 17 million contributed 19% to the total ISBL of the PE-1 biorefinery, with the high pressure polymerisation vessels contributing 93% to the polymerisation TCI as a consequence of the cost of materials for construction of its high pressure reactors. The TCI of the polymerisation process area with a catalyst at 5% of the glucose feed (Lee et al., 2016) was comparable to values achieved for succinic acid fermentation process area. These were between US$ 19–25 million for sugarcane lignocellulose biorefineries with bypass ratios of 25–75% (Nieder-Heitmann et al., 2019).

The TCI of the CHP base case scenario was a third of the PE-1 biorefinery at US$ 130 million because it was devoid of a biorefinery. The TCI of the boiler and condensing extraction steam turbine (CEST) in the CHP plant contributed 36% to the total installed equipment costs attributed to the high capital cost of the CEST system (Humbird et al., 2011). The total capital investment cost of the PE-1 biorefinery (US$ 311 million) was comparable to TCI costs of bio-chemical biorefineries producing ethanol, ethanol and lactic acid, butanol and methanol that were in the range of US$ 233 million-US$ 321 million (Farzad et al., 2017; Mandegari et al., 2017).

3.3.4.2. Annual fixed and variable operating and production costs

The annual fixed operating, variable operating, and total production costs in the PE-1 biorefinery were higher than the CHP base case values by US$ 5.3 million, US$ 12.5 million, and US$ 17.8 million respectively, as presented in Figure 3-5. This was due to factors such as the larger amounts of reagents used, higher waste disposal costs and more personnel in the PE-1 scenario than the CHP base case.



	Fixed operating cost	Variable operating cost	Total production cost
■ CHP base case	4.37	8.7	13.07
⊡ PE-1	9.66	21.24	30.9

Figure 3-5: Annual variable and fixed operating costs and total production costs

The largest contribution of 52% to the total fixed operating costs was the labour cost as 59 skilled and unskilled employees were engaged in the PE-1 scenario compared to the CHP base case with 18. For the variable operating costs, the cost of the lignocellulose feedstock in ETOH, used to produce cellulosic ethanol, dominated the annual variable operating cost at 38% and this trend was observed in similar lignocellulose biorefinery studies annexed to sugar mills (Nieder-Heitmann et al., 2018; Mandegari et al., 2017) where the feedstock contributed 35-49% to the variable operating costs. This contribution was as a consequence of the cost allocation of US$ 10.72/t to the brown leaves for purposes of collection and transportation from the fields to the sugar mill in exchange for 120 t/h steam from the CHP plant to the sugar mill. Secondly, the catalysts used in the BETE-PE process areas contributed 23% of the total annual variable operating costs, although this cost would have been larger if the catalysts were not recyclable. For example, syndol catalyst used for ethanol dehydration to ethylene can go up to 24 months without regeneration (Chematur, 2018).

The annual total production cost, a summation of the variable operating costs, fixed operating costs and the annual capital charge of the PE-1 biorefinery, was US$ 31 million against US$ 13 million for the CHP base case scenario. This compared well with lignocellulose biorefineries annexed to sugar mills that used biochemical means (fermentation) to produce polyhydroxybutyrate (PHB) and succinic acid (SA) at US$ 35.7 million/y and US$ 32.7 million/y respectively (Nieder-Heitmann et al., 2019). Unit production costs of US$ 0.80/kg and US$ 0.03/kWh for PE and electricity respectively, were attained.

3.3.5. Economic viability

A biorefinery's profitability is determined by its ability to generate a return on investment. Table 3-7 summarises the economic results of PE-1 biorefinery in comparison to the CHP base case scenario. A high density polyethylene price of US$ 886/t was used (Resource Recycling, 2016).

Table 3-7: Economic viability of the PE and CHP base case scenarios[a]

	PE-1*	CHP base case
IRR (%)	-	10.3
Hurdle rate IRR (%)	9.7	9.7
NPV (US$ million)	-282	6.5
MPSP (US$/t) (NPV=0 at 9.7% hurdle rate)	1862	0.03
Product selling price (US$/t or US$/kWh) for20%IRR	2956	0.12

*An alternative biorefinery (option 2)'economic viability based on the approach of adjusting the bypass ratio as demonstrated in Appendix B-6 was also unprofitable (NPV of -221 US$ million)

[a]The economic viability options are based on a working capital of 5% of FCI. An economic assessment based on a working capital of 15% can be found in Appendix A-1 (Table A2-2)

The PE-1 biorefinery was unprofitable with a net present value (NPV) of -282 US$ million due to the high capital investment costs, low production rate (6 t/h PE) and relatively low polyethylene market price of US$ 886/kg. Therefore, bio–based PE from lignocellulose feedstocks cannot compete with fossil-based PE, which is dominated nowadays by even cheaper production methods using shale gas (Foster, 2018) that do not require pretreatment and hydrolysis stages. Additionally, polyethylene production from 2G feedstocks cannot compete with biorefineries using 1G ethanol feedstocks, which equally eliminates the pretreatment, hydrolysis and fermentation process areas and cuts down on the capital investments, variable and fixed operating costs. However, buying in 1G ethanol is equally unprofitable due to the high ethanol selling price. For instance, purchasing 11 t/h of 1G ethanol at an average price of US$ 0.50/l (Joelsson et al., 2016) was unprofitable (NPV of -34 US$ million). To this end, a 1G/2G biorefinery or 1G/2G/bio-ethylene scenario should be investigated as a way of improving the economics of the PE biorefinery.

For this scenario to be attractive to potential private investors, a minimum internal rate of return (IRR) of 20% is required; this can be achieved at a polyethylene selling price of US$ 2956/t, which is 233% higher than the average current market selling price of fossil-based PE (US$ 886/t). Bio–based PE would, therefore, require a substantial premium price (233%) above the current market prices for the bio-based route to be viable and attain a 20% IRR.

In developed economies, green premiums on bio-based chemicals, polymers and plastics do exist and are usually paid at different stages of the value chain (Carus et al., 2014). This is even though studies have shown that consumers are willing to pay 20-40% more on bio-based plastics (Carus et al., 2014). In developing countries, the willingness of consumers to pay a price premium on bio-based products is low, with the environmental reason for purchasing these products being overshadowed by price and availability (Bomb et al., 2007). Therefore, apart from green premiums, policy frameworks supporting bio-based polyethylene production are required, for instance through bio-based tax incentives, market introduction programs and consumer communications to improve perceptions of “green” products.

From Table 3-7, it was also seen that the CHP base case scenario, despite having lower total capital investment and production costs than the PE biorefinery was marginally profitable at 10.3% IRR and US$ 6.5 million NPV at a 9.7% hurdle rate, and hence not economically viable based on the 20% IRR requirement. An IRR of 10.3% for a CHP plant producing electricity only from sugarcane bagasse and brown leaves was calculated in studies by Nieder-Heitmann et al., (2019). One major contribution to this low profitability of the CHP plant was the low average regional selling price of electricity (US$ 0.08/kWh) (SAPP 2019) (see Appendix B-7 for the DCFROR spreadsheets).

3.3.6. Sensitivity analysis

A sensitivity analysis was carried out on the biorefinery’s profitability using nine economic variables and a ±30% variance.as shown in Figure 3-6. Four variables with a significant impact on the biorefinery’s profitability, and based on the minimum product selling price (MPSP) of US$ 1862/t, were the PE selling price, total annual production cost, fixed capital investment and process operating hours, as presented in Figure 3-6.

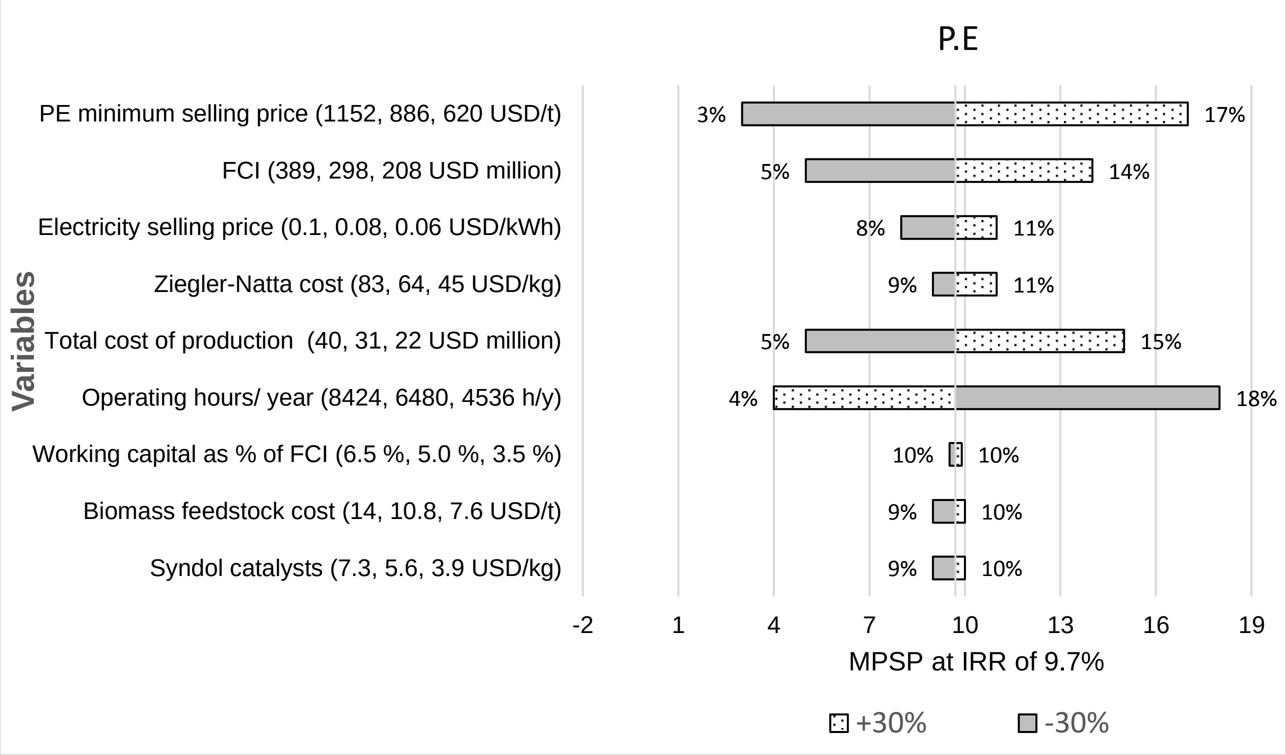


Figure 3-6: A sensitivity analysis of the PE biorefinery

Polyethylene selling price had a high impact on profitability with a 30% increase in the PE selling price, leading to an 7 % increase of the US$ 1862/t minimum product selling price (MPSP) (at IRR of 9.7%). Therefore, there is a need for supportive economic policies enabling the establishment of green premium prices for bio–based PE products from 2G feedstocks.

Increasing the operating hours of the biorefinery from 9 to 11 months without any significant change to the total capital investment, can increase the product rates and improve profitability by about 8%. A 30% increase in operating hours would require the processing of additional feedstocks, which creates an opportunity for the inclusion of first generation (1G) feedstocks considering that second generation feedstocks are constrained. Also, heat recovery from the polymerisation reactor can be used as a source of energy; this in turn lowers the steam demand and bypass ratios leading to more biomass being processed in the biorefinery for increased PE production rates.

The total annual production cost, followed by the fixed capital investment, also had an impact on the PE-1biorefinery's profitability as shown in Figure 3-6. The added unavoidable costs of the pretreatment and hydrolysis processing stages, including an *in-situ* enzyme hydrolysis production plant in the ETOH process area (Mandegari et al., 2017), raised the capital investment and production costs.

The catalysts, biomass feedstock costs, electricity selling price and working capital did not significantly impact the MPSP as demonstrated in Figure 3-6. The catalysts used can be regenerated and recycled and so this minimises the operating cost whilst the electricity selling price used in the region has a modest impact on profit margins.

3.4. Conclusions

A polyethylene biorefinery produced from cellulosic ethanol generated from a bio-ethanol biorefinery with a combined heat and power plant and annexed to a sugar mill, was investigated and compared to a CHP base case scenario producing electricity only. The polyethylene biorefinery was unprofitable at a -228 US$ million NPV. This was attributed to various factors including the high capital investments, low product rate (6 t/h) and polyethylene selling price based on the current fossil fuel market price of US$ 886/t. This scenario can only be viable if polyethylene is sold at a premium price, which is 223% higher than the market fossil based selling price. This is if it is to attract private investment and attain a threshold IRRs of 20%. The CHP base case, on the other hand, despite having a lower TCI cost than the PE biorefinery, was marginally profitable at 10.3% IRR at a 9.7% hurdle rate and US$ 6.5 million NPV due to the low regional electricity selling price of US$ 0.08/ kWh, which did not significantly increase the returns on investment.

Supplementary information: Polyethylene techno-economics in Appendix B

Appendix B includes the following details:

i. Aspen Plus models,
ii. Mass and energy balances,
iii. Pinch analysis
iv. Lignocellulose components as defined in Aspen Plus®
v. Equipment sizing data
vi. Alternative PE model
vii. Discounted cash flow rate of return flowsheets for PE–1 and CHP base case

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Chapter 4

4.0 Techno-economic analysis of chemically catalysed lignocellulose biorefineries at a typical sugar mill: sorbitol or glucaric acid and electricity co-production

The chapter presents techno-economic and social assessments of producing sorbitol and glucaric acid in biorefinery complexes annexed to a typical sugar mill. The chapter is presented in the form of a journal article in fulfilment of **objectives 2, 3** and part of **4** looking at the social impacts.

The techno-economic assessments of sorbitol and glucaric acid from lignocellulose materials has been published in the "Journal of Bioresource Technology 289 (2019), 1-10" and been reproduced in this dissertation with copyright permission from Elsevier publishers.

Title: "*Techno-economic analysis of chemically catalysed lignocellulose biorefineries at a typical sugar mill: sorbitol or glucaric acid and electricity co-production*"

Authors: *Kutemba K. Kapanji, Kathleen F. Haigh, Johann F. Görgens*

Objective of dissertation in this chapter and summary of findings

Chapter 4 builds on chapter 3 (techno-economics of polyethylene production) by considering biorefinery scenarios generated in Aspen Plus® producing sorbitol and glucaric acid. The chapter covers the techno-economic and social viability of lignocellulose biorefineries covering pretreatment (SO_2-steam explosion or dilute acid), enzymatic hydrolysis, hydrogenation and oxidation of glucose to produce sorbitol and glucaric acid respectively (objective three).

The aforementioned process stages were generated in Aspen Plus® (objective two) and the energy and material balances including literature data used to size and cost equipment followed by economic assessments based on a developing country's economic parameters at a 9.7% discount rate (real-term basis). No detailed techno-economic studies were identified for 2G integrated bioenergy self-sufficient biorefineries annexed to a sugar mill and producing sorbitol or glucaric acid with electricity cogeneration.

Biomass bypass ratios of 25-29.5% for the sorbitol and 35-37% for the glucaric acid scenarios were sufficient to meet the biorefineries' and sugar mill's energy demands, with surplus electricity sold to the grid. Product rates of 11.3-12.2 t/h and 10.3-11.1 t/h for sorbitol and glucaric acid respectively were attained based on bio-based product yields of 60.7-64.3 %.

The dilute acid pretreatment scenarios for sorbitol and glucaric acid were more economically viable than the steam exploded ones; however, profitability was generally marginal (1% above the 9.7% discount rate). This can be attributed to factors including the additional capital investment costs associated with the pretreatment and hydrolysis of second generation feedstocks in order to isolate glucose. For instance, sorbitol produced via dilute acid pretreatment attained a 10.7% IRR and US$ 15 million NPV, achieving a US$ 619/t minimum sorbitol selling price, which was 5% below the current market price. The sorbitol selling price should reach US$ 1283/t if the scenario is to reach an IRR of 20%, which is the threshold IRR that can attract private investors. The glucaric acid scenario via dilute acid pretreatment was also marginally profitable with an IRR of 10.7% and NPV of US$ 16 million, whereas the biorefinery using SO_2-steam explosion was unprofitable.

The results of the profitable (with IRR > 9.7%) and near-profitable scenarios from this chapter, chapters 3 and 5 will then be evaluated for environmental viability in chapter 6 to complete the sustainability assessment (economic, environmental and social impacts).

Summary of authors'contributions

Kutemba K. Kapanji designed and simulated the scenarios, costed them and assessed their economic viability. In addition, she analysed, interpreted the results and wrote the chapter. *Kate F. Haigh* contributed to the data interpretation and review of the chapter. *Johann F Görgens* assisted with interpretation of data and review of the chapter.

Abstract

Global concern about depletion of fossil reserves has driven countries towards bio-economies utilising mostly first generation feedstocks. The economic viability of bioenergy self-sufficient biorefineries processing sugarcane lignocelluloses into sorbitol or glucaric acid and electricity was investigated. Aspen Plus® simulations represented glucose conversion processes via SO_2-steam explosion or dilute acid pretreatment, followed by enzymatic hydrolysis. The most economically viable sorbitol scenario using dilute acid pretreatment with a capital investment cost per litre of US$ 3.96/L was marginally profitable having a selling price 5% below the US$ 655/t market price. To secure private investment, the sorbitol selling price should reach US$ 1283/t.

Key words: Biorefinery, Glucaric acid, Lignocellulose, Sorbitol, Techno-economic assessment

4.1. Introduction

Global concerns about the depletion of fossil fuel reserves, climate change impacts due to anthropogenic activities and a growing global population with its increased energy demand, have accelerated research into alternative renewable resources to replace fossil fuels. In recent years, a global shift towards greener economies has emerged characterised by biomass conversion in biorefinery complexes into an array of products (biofuels, bio- energy and bio-chemicals) (Mandegari et al., 2017). Biomass, more specifically lignocellulose, is inedible, readily available and cheap (Farzad et al. 2017) and has thus been identified as a potential renewable resource (Taylor et al., 2015).

Lignocellulose biomass includes agricultural residues such as sugarcane bagasse and leaves. The sugar industry in South Africa generates approximately 2.8 million t/y sugarcane bagasse after juice extraction. In addition, if “green” harvesting techniques that avoid burning were used, a further 1.35 million t/y leaves from fields would be gained (Smithers, 2014). Therefore, agricultural waste valorisation in biorefineries can bring about socio-economic benefits for typical sugar mills that have been plagued by fluctuating global sugar prices and so need to diversify their product range.

Two platform chemicals relevant to the sugar industry, sorbitol and glucaric acid, were identified in the 2004 and 2010 United States of America, Department of Energy, National Renewable Energy Laboratory reports as promising bio-chemicals for future bio-economies (Bozell and Petersen, 2010; Werpy and Petersen, 2004). Sorbitol is used in the food, cosmetics and pharmaceuticals industries (Isikgor and Becer, 2015). Glucaric acid is used in pharmaceuticals, concrete formulations, de-icing, anti-corrosion markets and as an adipic acid intermediate (Polen et al., 2013). It can also substitute phosphates in detergents, which mitigates eutrophication in water bodies (Edward de Jong et al., 2012).

Sorbitol is produced commercially from biomass via chemical pathways, while glucaric acid production also through chemical means is at demonstration to near commercialisation. Since no petrochemical feedstocks exist for these two chemicals (Taylor et al., 2015), they have been produced conventionally from monomeric sugar, glucose or starch precursors from 1st generation (1G), edible feedstocks. However, if food security and environmental concerns are to be lessened, then second generation (2G) non-food lignocellulose feedstocks should be considered.

One challenge, however, with using lignocellulosic biomass feedstocks for glucose production, is its recalcitrance to (bio)chemical conversion, which requires pretreatment and hydrolysis to release monomeric sugars, mostly glucose (Alvira et al., 2010; Yang and Wyman, 2007). For instance, an economic study on a cellulosic bio-ethanol plant by Humbird et al., (2011) determined that the combined pretreatment and hydrolysis stages accounted for about 35% of the total projected production cost.

Glucose from hydrolysis is hydrogenated to produce sorbitol using catalysts such as Raney nickel, Cu, Ru, Pt and Ru, supported on carbons, oxides, polymers, hydrotalcites and zeolites (Zhang et al., 2016; Ahmed et al., 2009). The typical glucaric acid production process involves oxidation of glucose with nitric acid (Saeed et al., 2017), although greener routes using pure oxygen or hydrogen peroxide have been explored (Lee, 2016; IAR, 2015) Catalytic studies for glucaric acid production included heterogeneous options such as Pt/C, Pt/SiO_2, Pt/ Al_2O_3, Au/TiO_2, Au/C, AuPt nanoparticles (Saeed et al., 2017; Solmi et al., 2017; van Gorp et al., 1999). On the other hand, milder biological routes using *Zymomonas mobilis* for sorbitol production and *Escherichia coli* for glucaric acid on 1G biomass have been investigated (Reizman et al., 2015; Moon et al., 2009), but most are in the early stages and presently unlikely to replace the technically mature chemical routes (de Jong et al., 2012).

Fifteen companies located in China, USA, South Korea, India, Brazil, Germany, and Indonesia produce sorbitol commercially (IAR, 2015). Roquette Freres is the largest producer with a capacity of 347.5 kt/y (70% of the global capacity) and the sorbitol selling price is about US$ 650/t (Taylor et al. 2015). Conversely, the global production capacity of glucaric acid is 50.5 kt/y (IAR, 2015), with Rennovia and Rivertop Renewables being the major producers. The glucaric acid selling price is unavailable.

Although the pretreatment and hydrolysis of sugarcane lignocelluloses to produce glucose (Benjamin et al., 2013; Rocha et al., 2012; Lavarack et al., 2002) and the conversion of glucose to sorbitol (Kusserow et al., 2003) or glucaric acid (Lee et al., 2016) have been reported separately, no integration of production processes from lignocellulose have been described, or assessed with regard to economic viability. Techno-economic studies on sugarcane bagasse biorefineries have focused on bio-ethanol and bio-energy (Rezende and Richardson, 2015; Petersen et al., 2014), although more recently, syn-crude, n-butanol, lactic acid, furfural and itaconic acid have been considered (Nieder-Heitmann et al., 2018; Farzad et al., 2017). The aim of this study is to assess the economic viability of using sugarcane lignocelluloses as feedstocks in bioenergy self-sufficient biorefineries, annexed to a typical sugar mill, to co-produce electricity and sorbitol or glucaric acid (from glucose) via chemically catalysed processes. If future feasibility studies on biorefinery complexes are to be conducted at typical sugar mills in emerging world economies, then detailed techno-economic assessments on biorefining is a prerequisite. In the present study, biorefineries producing the short-listed chemicals sorbitol and glucaric acid from lignocellulose feedstocks are studied.

4.2. Materials and methods

Feedstock composition plays a major role in the process design of a scenario. Whilst first generation feedstocks forego pretreatment and hydrolysis, lignocellulose materials require these two stages to alter the biomass structure thus exposing the components for more effective process conversions. Literature was the source of data for the biomass composition, reaction conditions and conversions used in the simulations.

The feedstock chemical composition, based on mean mass compositions of 70% South African sugarcane bagasse and 30% brown leaves (dry mass basis) (Mandegari et al., 2017), was 40.7% cellulose, 27.1% hemicellulose, 21.9% lignin, 6.7% extractants and 3.5% ash (dry mass basis) and 42% moisture (Frazad et al., 2017; Benjamin et al., 2013). The biorefinery feedstock was based on a 65 t/h biomass (dry mass basis) throughput that typifies a sugar mill operating for 9 months/year (see Appendix A-3, Table A3-1 for a detailed feedstock breakdown).

To minimise the carbon footprint, coal was not used in the scenarios. Thus, they were considered bioenergy self-sufficient as part of the biomass was combusted in a combined heat and power (CHP) plant to produce the required energy for the processes.

4.2.1. Process simulations

The biorefinery scenarios were modelled in Aspen Plus ® (Aspen Technology Inc., USA) v.8.6 process simulator, generating mass and energy balances including the utility (electricity, cooling water, air and steam) requirements. The Electrolyte Non-Random Two-Liquid (ELEC-NRTL) activity coefficient property method was used as a default method as reported in a similar study by Nieder-Heitmann et al., (2018) and the equation of state to calculate the vapour phase (Henry's law for vapour-liquid binary interactions). The Aspen Plus database and National Renewable Energy Laboratory (NREL) component definitions were used to define conventional chemicals and unconventional lignocellulose compounds respectively (Humbird et al., 2011).

Each biorefinery scenario was annexed to a conventional sugarcane mill. A block flow diagram representative of the scenarios including the pretreatment and hydrolysis options, conversion and purification stages, steam and electricity generation plant that have been considered in this study is shown in Figure 4-1.

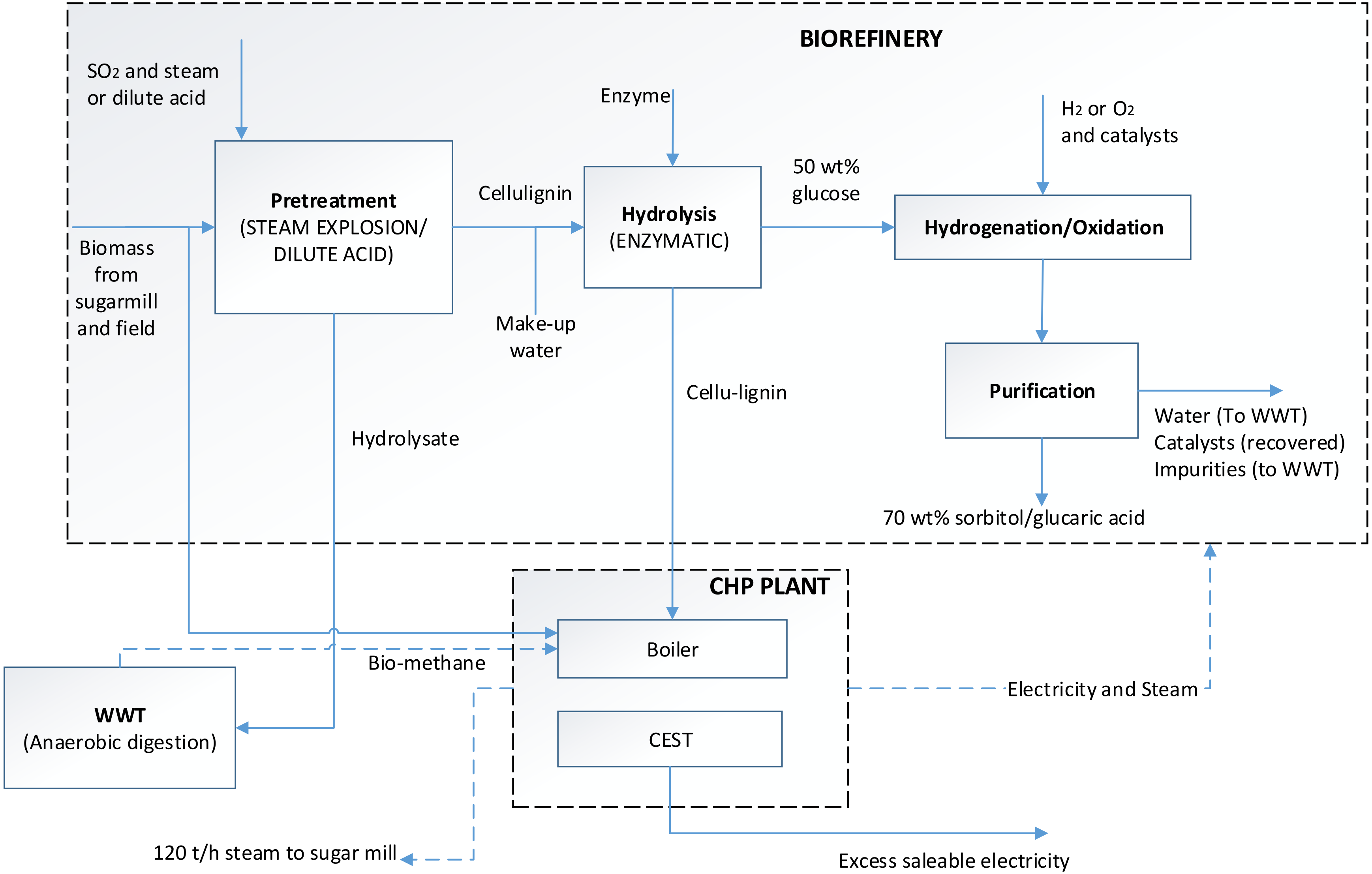

Figure 4-1: Sorbitol/glucaric acid biorefinery and CHP plant configuration with pretreatment and hydrolysis options used

Two common and mature pretreatment technologies, SO_2-catalysed steam explosion or dilute acid pretreatment followed by enzymatic hydrolysis were used to determine their combined effect on glucose yields and overall production costs. Sorbitol production involves the catalytic hydrogenation of glucose whereas oxidising glucose leads to glucaric acid being produced. To this end, the following configurations were assessed; $Sorbitol._{STEX}$, was a sorbitol biorefinery via SO_2-catalysed steam explosion and enzymatic hydrolysis, $Sorbitol._{DA}$, sorbital production using dilute acid pretreatment followed by enzymatic hydrolysis. Similarly, $Glucaric._{STEX}$ was a glucaric acid biorefinery involving SO_2-catalysed steam-enzymatic hydrolysis and lastly $Glucaric._{DA}$ was a conversion process via dilute acid pretreatment and enzymatic hydrolysis.

4.2.2. Pretreatment

Sulphur dioxide, for SO_2-catalysed steam explosion, was produced on-site by the reaction of elemental sulphur with excess air resulting in a 99.9% conversion of sulphur to SO_2 (3 wt% concentration) (Bura et al., 2003). The feedstock was impregnated with the SO_2 gas for 30 min and thereafter, batch fed to a steam explosion flash drum operating at 195 °C for 9 min (Bura et al., 2003) to alter the material structure. For the dilute acid pretreatment option, the dilute acid stream (1.1 wt% H_2SO_4) was heated to 158 °C and mixed with biomass in a pre-conditioning tank. Thereafter, the slurry was fed to a reactor operating at 6 bar for 30 min leading to the formation of monomer sugars and oligomers (Humbird et al., 2011; Bura et al., 2003).

The hydrolysate stream produced from steam explosion or dilute acid pretreatment, comprised xylose, extractants, acetic acid, furfural, xylo-and gluco-oligomers and cellubiose was filtered to remove the solids. The liquid hydrolysate stream was sent to the wastewater treatment (WWT) plant.

Prior to enzymatic hydrolysis, the filter cake was washed to remove inhibitors or dried to remove more water and inhibitors (Humbird et al., 2011). This was followed by the addition of make-up water to produce a slurry with 30 wt% solids (as defined in (Modenbach and Nokes, 2013;2012)), which was fed to a conditioning tank, where the slurry pH was adjusted to 6 using ammonia and heated to 48 °C. (A summary of the process units, conditions and conversions (mass basis) occurring during pretreatment where hemicelluloses hydrolyse is presented in Table 4-1).

Table 4-1: Summary of key equipment, process conditions, main reactions and conversions for steam explosion[a], dilute acid pretreatment[b] and enzymatic hydrolysis[a] used in Aspen Plus®

Process Area	**SO_2 catalysed steam explosion design specifications**	
Pretreatment (H.cellulose hydrolysis)	Cooler–EXCHANGER T_{out} = 220°C, P = 1 atm	Cools SO_2 stream from 800°C and heat recovered used in steam explosion
	Steam Explosion tank–FLASH 2 P = 9.5 atm, Duty = 0kW	Tank also supplied with steam at 195°C and 9.5 atm
	Steam explosion reactions and wt% conversions	
	Reactor–RSTOIC	Xylan + $H_2O \rightarrow$ Xylose; 57% Arabinan + $H_2O \rightarrow$ Arabinose; 57% Xylan + $H_2O \rightarrow$ Xylo-oligomer; 1% Acetate + $H_2O \rightarrow$ Acetic acid + 0.5H_2; 16% Xylan → furfural + H_2O; 2.7% Glucan + $H_2O \rightarrow$ Glucose; 5% Glucan + $H_2O \rightarrow$ Gluco-oligomer; 3% Glucan + $H_2O \rightarrow$ Cellobiose; 0.3% Lignin → Acid soluble lignin; 5%
	Dilute acid pretreatment design specifications	
	Evaporator–FLASH 2 T = 110 °C, P = 1 atm	Vapourises water and inhibitors from biomass
	Dilute acid reactions and wt% conversions	
	Reactor–RSTOIC P = 6 atm, T = 158 °C	Xylan + $H_2O \rightarrow$ Xylose; 50% Xylan → Furfural + H_2O; 7.9% Xylan + $H_2O \rightarrow$ Xylo-oligomer; 2% Glucan + $H_2O \rightarrow$ Glucose; 3% Xylan → furfural + H_2O; 7.9% Acetate + $H_2O \rightarrow$ Acetic acid + 0.5H_2 ; 13% Lignin → Acid soluble lignin; 5%*
Enzymatic Hydrolysis (Cellulose hydrolysis)	**Enzymatic hydrolysis reactions and wt% conversions**	
	Reactor = RSTOIC T = 40 °C, P = 1 atm	Glucan + $H_2O \rightarrow$ Glucose; 70% Glucan + $H_2O \rightarrow$ Cellobiose; 0.6% Glucan + $H_2O \rightarrow$ Gluco-oligomer; 4% Cellobiose → Glucose; 100% Lignin → Acid soluble lignin; 5%*
	Filter–SEPARATOR	Split of solids to solids stream = 1
	Evaporator–FLASH 2 T = 104 °C, P = 1 atm	Evaporates the gases and remaining water

[a] Steam explosion pretreatment and enzymatic hydrolysis conversions for xylose and/or glucose were based on Carrasco et al., (2010). The conversion of the minor hemicellulose arabinanose in steam explosion was assumed equal to that of xylan. Acetic acid, furfural and cellobiose were assumed and close to values used in Aguilar et al., (2002).

[b] Fractional conversions during dilute acid pretreatment was based on data from Koekemoer, (2018) and the lignin conversion of 5% used in the pretreatments and enzymatic hydrolysis was based on Humbird et al., (2011).

4.2.3. Hydrolysis

Enzymes were used to hydrolyse the pretreated cellulignin into glucose and other sugars as presented in Table 4-1 using experimental data from Carrasco et al., (2010). The glucose solution was filtered to separate any unconverted cellulose or unreacted lignin, assuming a split of solids to solids stream of 1. The filtered cellulignin solids were sent to the CHP plant as additional fuel. The glucose rich stream was concentrated by evaporation at 104 °C and 1 atm, to a 50 wt% glucose solution (Marques et al., 2016).

It was assumed that each scenario had an on-site enzyme production unit, which was sized and the cost based on a cellulase enzyme production unit by (Mandegari et al., 2017) and (Humbird et al., 2011). Ten percent (10%) of the concentrated glucose was diverted to the enzyme production plant and an enzyme loading of 20 mg/g cellulose was used (Humbird et al., 2011). This is in range with experimental results obtained by Mokomele et al., (2018), who determined that enzymatic hydrolysis of bagasse that underwent steam explosion required enzyme loadings of greater than 20 mg/g glucan to achieve xylose and glucose sugar conversions of greater than 75%.

4.2.4. Conversion

To produce sorbitol, the 50 wt% glucose solution was mixed with 5% Raney nickel catalyst (based on glucose) (van Gorp et al., 1999). Glucose hydrogenation occurred at 120 °C and 70 bar. It is desirable to use purchased bio-hydrogen gas to reduce the carbon footprint of the process, however, the use of “green” reagents has cost implications (Hosseini and Wahid, 2016) and currently it is challenging to find a suitable supplier mainly in developing countries. Therefore it was assumed hydrogen from natural gas was used. An 85% glucose to sorbitol conversion was assumed along with oxidation of glucose to gluconic acid (1%) during hydrogenation (van Gorp et al., 1999) as shown in Table 4-2.

Table 4-2: Conversions (wt %) of the hydrogenation and oxidation reactions of glucose for sorbitol and glucaric acid production

Process area	Conditions	Process Reaction	Conversion	Reference
Glucose hydrogenation to sorbitol	**Reactor–RSTOIC**	Glucose + H_2 → Sorbitol	85%	van Gorp et al., (1999)
	T = 120 ºC,	Glucose + H_2O → Gluconic acid + H_2	1%	“
	P = 70 bar			
Glucose oxidation to glucaric acid*	**Reactor-RSTOIC**	Glucose +1.5 O_2 → Glucaric acid + H_2O	74%	Lee et al., (2016)
	T = 80 ºC,	Glucose + 0.5 O_2 → Gluconic acid	20%	“
	P = 13 bar	Gluconic acid + O_2 → Glucaric acid + H_2O	40%	“

*Conversions used were assumed in order to obtain a glucaric acid final yield of 74 wt%.

For glucaric acid production, the 50 wt% glucose solution was mixed with pure oxygen at 80 °C and 13 bar. A platinum/carbon (Pt/C) catalyst at 5% of the glucose feed was used to give a 74% glucose to glucaric acid conversion (Lee et al., 2016). Some glucose is converted to gluconic acid, but the glucose to glucaric acid reaction is faster with the gluconic acid converted to glucaric acid in excess oxygen (Lee et al., 2016). The glucaric acid conversion reactions are specified in Table 4-2. The sorbitol and glucaric acid catalysts were regenerated using dilute sodium hydroxide and steam respectively after 770-1100 hrs of operation (Kusserow et al., 2003) and recycled with 10% fresh catalyst added. After an assumed time of 2 years (Dow, 2018), the catalysts are replaced totally due to irreversible damage caused by thermal degradation and poisoning (Bartholomew, 2001).

4.2.5. Purification and concentration

The downstream processing of crude sorbitol includes cooling, filtration, adsorption using synthetic resins and activated carbon, and concentration via vacuum evaporation to obtain commercial grade sorbitol at 70 wt% purity (Marques et al., 2016). After hydrogenation, the product stream was cooled to 80 °C and filtered to recover the catalyst. The sorbitol syrup was passed through a series of adsorption columns to remove nickel and gluconate ions. Amberlite resins were used as an adsorber with a 99% efficiency (Demirbas et al., 2005). Activated carbon acted as an acid filter to remove colour, odour and organic impurities. Thereafter, water and organic impurities were removed via vacuum evaporation at 103 °C to concentrate the sorbitol stream.

Due to limited data on downstream processing of glucaric acid, it was assumed that purification followed a similar pathway to sorbitol to achieve 70 wt% glucaric acid solution. Recent studies by Gunukula and Anex, (2017) who produce glucaric acid as a precursor to adipic acid production, show similar purification process units for glucaric acid production. However, Gunukula and Anex, (2017) included two further purification stages: distillation and solvent extraction using acetonitrile solvent to achieve 98% pure glucaric acid.

4.2.6. Combined heat and power (CHP) plant

The combined heat and power (CHP) plant is made up of a combustor, boiler and turbogenerator. In this system, sugarcane bagasse and dried leaves, cellulignin residues from enzymatic hydrolysis, and methane from the wastewater treatment bio-digesters (Humbird et al., 2011) were burned. Excess air was used to achieve 99.9% biomass conversion to CO_2 (Mbohwa, 2003) and the flue gas stream scrubbed of ash and particulate matter prior to atmospheric release.

Energy from the combustor was supplied to the thermal boilers producing high-high pressure steam

(HHPS) at 65 bar and 480 °C (Colombo et al., 2014). Electricity was generated from the condensing extraction steam turbine (CEST) operating at 85% isentropic and 96% mechanical efficiency and excess electricity was sold at US$ 0.08/kWh. Steam was extracted from the turbine at different conditions to meet the energy demands of the different biorefinery's process units. High pressure steam (HPS) at 266 °C, 13 atm and low pressure steam (LPS) at 233 °C, 9.5 atm was supplied to the biorefinery. The sugar mill was supplied with 120 t/h of high pressure steam (HPS) at 340 °C and 28 atm based on a mill with an energy demand of 0.4 ton steam per ton of cane crushed (Reid, 2006). Low energy steam from the final condensing extraction steam turbine stage was recycled back to the boiler together with make–up water following clean-up.

4.2.7. Wastewater treatment plant

The wastewater streams were sent to a wastewater treatment plant (not modelled) for anaerobic digestion of the organics into bio-methane (Naik et al. 2010) that was used as additional fuel for the boiler. Generic values of the chemical oxygen demand (COD) were used to determine the amount of biogas produced (1 kg COD = 0.23 kg methane) as described in Humbird et al., (2011). The wastewater treatment plant was accounted for in the economic assessment by allocating a volume based cost to the total wastewater stream (Humbird et al., 2011). The treated wastewater was assumed clean and recyclable back into the biorefinery and any short falls determined from the mass balance were met by make-up water.

4.3. Sizing and economics

Aspen Plus® Economic Analyser was used to size the process equipment and calculate purchase and installation costs for all equipment, except reactors, pressure vessels, boilers and the CHP plant, which were sized and costed using literature data (Humbird et al., 2011). Equipment purchase costs were adjusted to desired capacities and related time using the Chemical Engineering Plant Cost Index (CEPCI) of 536.5 for 2016.

4.4. Equipment cost analysis

The economic evaluation was based on the mass and energy balances from the models, market prices and economic assumptions summarised in Table 4-3, which reflect emerging world economies (Brazil, India, China and South Africa) where the bulk of sugarcane is grown. From the calculated capital and operating costs, a discounted cash flow rate of return (DCFROR) methodology was used. The cash flow for investment analysis was conducted in real terms, therefore all revenues and expenses were considered in current values with the exclusion of the effect of future inflation. The overall project profitability was measured using an internal rate of return (IRR), net present value

(NPV) and minimum product selling price (MPSP), a project break-even price (at which the net present value is zero) with a hurdle rate of 9.7%. The glucose for conversion into final product and used as seed in the enzymatic hydrolysis process was produced on-site. The cooling utilities (water or air) were accounted for as installed costs (6.5% of the total inside battery limit of the biorefinery's installed costs) (Mandegari et al., 2017). A sensitivity analysis of the minimum product selling price (MPSP), the price at which the project net present value (NPV) is zero, was conducted by varying economic parameters over a +30% and −30% variance from the baseline.

Table 4-3: Economic parameters used for a 2016 cost year analysis (Mandegari et al., 2017; Humbird et al., 2011)

Parameter	**Value used**
Annual operating hours	6480 h
Project life (years)	25
Depreciation	Straight line over 5 years
Salvage value	0
% Spent in year -2*	10
% Spent in year -1*	60
% Spent in year 0*	30
Start-up time (years)[a]	2
First year new plant capacity (% design)	50%
Second year new plant capacity (% design)	75%
Working capital (% of FCI)	5%
Income tax rate	28.0%
Inflation rate	5.7%
Cash flow calculations basis/IRR method	Real term
Discount rate (hurdle rate)	9.7%
Electricity price (US$/kWh)	0.08

* The percentage spent per year was based on the assumption used in Humbird et al., (2011) and Mandegari et al., 2017 (see Appendix A-3 for the detailed explanation of this assumptions)

4.5. Results and discussion

4.5.1. Material and energy balances

Following the modelling of bioenergy self-sufficient biorefineries, a summary of the material and energy balances is given in Table 4-4. It includes key stream flows on a dry mass (DM) and wet mass (WM) basis, bypass to boiler ratios and utilities.

Table 4-4: Material and energy balances for the bioenergy self-sufficient scenarios

Parameter		**Scenarios**			
		Sorbitol.STEX	**Sorbitol.DA**	**Glucaric.STEX**	**Glucaric.DA**
Feedstock	**Biomass to biorefinery (DM) (t/h)**	45.5	42.7	39.4	38.2
	Biomass to biorefinery (WM) (t/h)	84.8	79.7	73.5	71.1
Energy Source	**Biomass bypass to boiler (%)**	25.0	29.5	35.0	37.0
	Cellulignin + bio-CH_4 to boiler (t/h)	23.1	24.5	19.3	22.4
Energy demands	**Heating/Steam (MWh)**	65.1	74.3	70.6	88.9
	Cooling (MWh)	94.2	133.5	96.5	134.3
	Electric power (MWh)	2.0	1.9	1.9	1.9
	Steam to sugar mill (t/h)	120.0	120.0	120.0	120.0
Product	**Glucose yield after enzyme hydrolysis***	58.2	56.2	58.3	56.2
	Glucaric acid (t/h)	-	-	11.1	10.3
	Sorbitol (t/h)	12.2	11.3	-	-
	Bio-based product yield (%)*	61.3	60.8	64.3	60.7
	Electricity (MWh)	13.1	15.8	14.8	16.1
	Sellable electricity (GWh/y)	71.9	89.8	83.7	92.0

$$* \ \text{Yield} = \left(\frac{\text{Product (kg)}}{\text{Cellulose in feedstock (kg)}}\right) \times 100\%$$

From Table 4-4, it can be seen that the highest product flow rate is for sorbitol from the Sorbitol.$_{\text{STEX}}$ biorefinery, at 12.2 t/h, with a slight reduction for dilute acid pretreatment Sorbitol.$_{\text{DA}}$ at 11.3 t/h. The product flow rates were lower for the glucaric acid with 11.1 t/h calculated for Glucaric.$_{\text{STEX}}$ and 10.3 t/h for Glucaric.$_{\text{DA}}$. While the differences are relatively small the trend is in keeping with contributing factors discussed hereafter.

For both products it can be seen that the product flow rate is lower for the DA scenarios than the STEX scenarios due to higher bypass ratios which are a consequence of a higher energy demand for dilute acid pretreatment when compared to steam explosion. In addition, the lower conversion rate and higher by-product formation contribute to the drop in the glucaric acid flow rates relative to the sorbitol scenarios. Other factors that contribute to the product rate are discussed in sections 4.5.1.1 and 4.5.1.2. The sorbitol and glucaric acid product rates from the scenarios would contribute 5% and 130-144% respectively to the global sorbitol and glucaric acid annual production capacities (IAR, 2015).

4.5.1.1. Amount of glucose formed and its conversion to final product

The amount of glucose produced after hydrolysis of biomass is a function of the effectiveness of the pretreatment type and this is dependent on factors including feedstock type, process temperatures, catalysts used, solids loading and duration. Sorbitol and glucaric acid are produced from glucose and the difference in the glucose yields (56–58%), based on the theoretical maximum after enzymatic hydrolysis, of dilute acid and steam explosion pretreatment, was minimal at 2% (Table 4-4).

High glucose conversions of 85% and 74% (mass basis) for sorbitol and glucaric acid respectively as shown in Table 4-2 also contributed to the final product rates. In addition, low intermediate product formation during glucose hydrogenation to sorbitol increased product rates (Lee et al., 2016; van Gorp et al., 1999).

4.5.1.2. Amount of feedstock processed

The amount of final product (Table 4-4) is also affected by the amount of lignocellulose material available for conversion, which is determined by the production capacity of a sugar mill (a fixed value of 113 t/h bagasse and brown leaves) and the bypass ratio that is established by the biorefinery’s energy demand. Thus the bypass ratio is an indication of process energy demand, with a low demand meaning that higher flow rates are possible, which improves the economies of scale benefits (Mandegari et al., 2018). The % bypass of the scenarios beginning with the lowest to the highest was Sorbitol.$_{\text{STEX}}$ (25%), Sorbitol.$_{\text{DA}}$ (29.5%), Glucaric.$_{\text{STEX}}$ (35%) and Glucaric.$_{\text{DA}}$ (37%) as summarised in Table 4-4. An analysis of the energy consumption is discussed in Section 4.5.2 including the observed higher energy demands in the dilute acid pretreatment than in steam explosion. These bypass ratios were in range with ratios of between 19.5% and 33% obtained in biological and thermo-chemical biorefinery studies annexed to sugar mills conducted by Farzad et al., (2017). Nieder-Heitmann et al., (2018), however, obtained a 54% bypass ratio for a bioenergy self-sufficient biological itaconic acid biorefinery annexed to a sugar mill due to the process' energy intensity. The sorbitol scenarios had lower bypass ratios than the glucaric acid scenarios thus the higher biorefinery feedstock capacities (43-46 t/h greater than 38-39 t/h).

4.5.2. Analysis of energy consumption

A breakdown of the yearly energy consumption of the scenarios was given in terms of steam demand (or heating) (65–89 MWh), cooling demand (94–134 MWh) and electric power (1.9–2.0 MWh) as shown in Table 4-4 following heat integration by pinch analysis (see Appendix C-5). These utilities compare well with the magnitudes obtained in a similar study by Mandegari et al., (2017) with heating, cooling and power demands of 88–179 MWh, 50-108 MWh and 2-4 MWh respectively.

An energy distribution profile of the 4 scenarios is shown in Figure 4-2, where the utilities are identified for each process area including pretreatment, hydrolysis, conversion and purification and CHP. The utilities in the CHP process area are inclusive of 120 t/h of high pressure steam (HPS) supplied to the sugar mill.

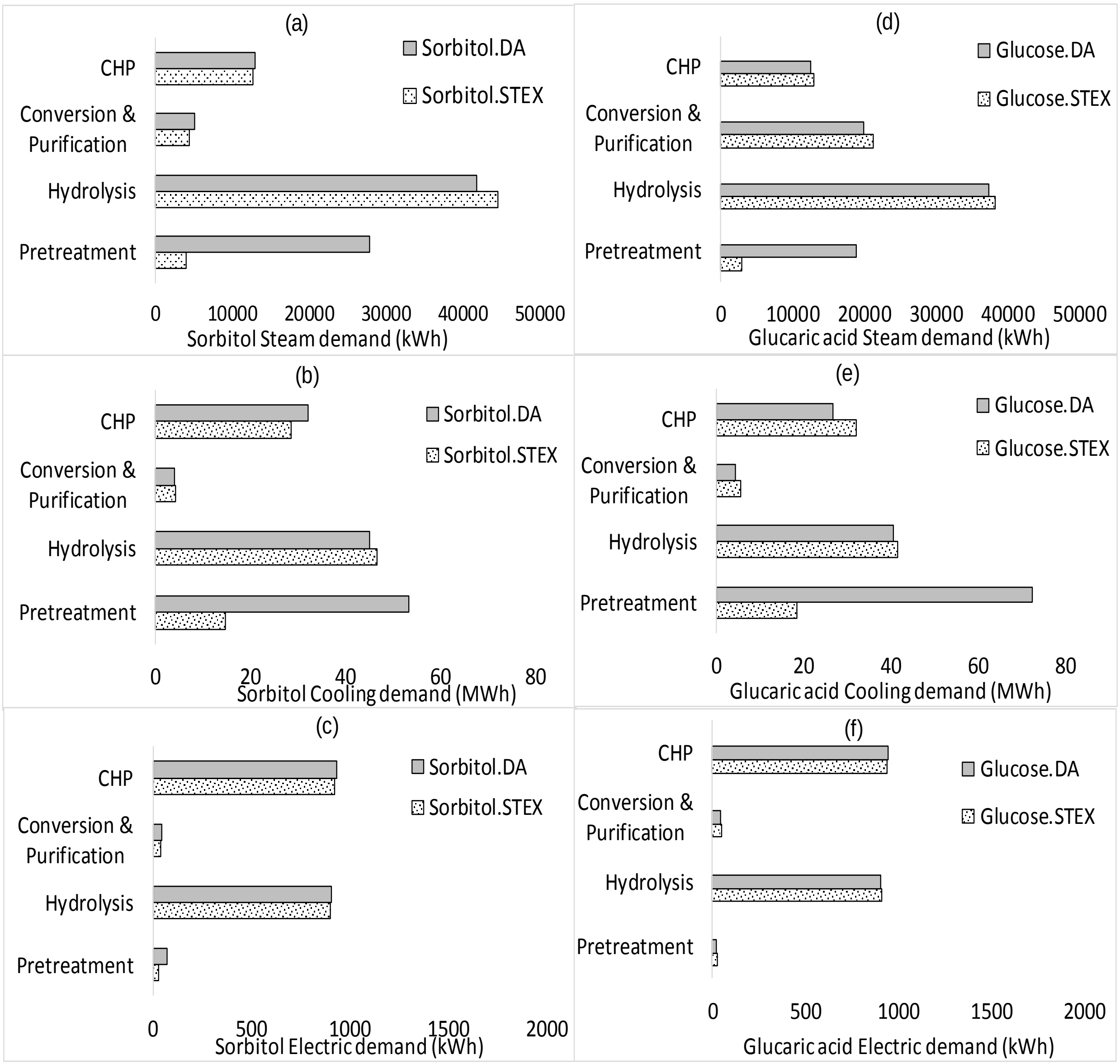

Figure 4-2: Annual energy distribution in various process areas for the bioenergy self-sufficient scenarios

Overall, it can be seen that the process areas with the highest steam, cooling and electricity demand were the hydrolysis, pretreatment and CHP plant respectively. The steam demand was between 65-69 MWh (Figure 4-2a) for the sorbitol scenarios and 74-89 MWh (Figure 4-2d) for the glucaric acid scenarios leading to the higher bypass ratios in the dilute acid pretreatment processes. This is to meet the high steam demand needed to maintain the dilute acid reactor temperature at 158 °C for 25-30 min, unlike in steam explosion where the reaction time is shorter (10 s) at temperatures of 195 °C.

The cooling demand in the dilute acid pretreatment scenarios was more than double that in scenarios with steam explosion (Figure 4-2b and 4-2e). With regard to the electric demand, the CHP plant electricity consumption was approximately 1 MWh for all the scenarios.

A large fraction of the steam, calculated as 68% in Sorbitol.$_{\text{STEX}}$, 45% in Sorbitol.$_{\text{DA}}$, 52% for Glucaric.$_{\text{STEX}}$ and 43% in Glucaric.$_{\text{DA}}$, was used to concentrate the glucose streams to 50 wt% (Marques et al., 2016) in flash drums. On the other hand, the high cooling demand (43 MWh) in pretreatment and in the hydrolysis process areas (42 MWh) in the dilute acid pretreated scenarios was required for cooling heated water and condensing vapour streams respectively. In addition, the electric demand (Figure 4-2c and 4-2f), was greatest in the CHP plant followed by the hydrolysis stage where pumps, agitators and compressors were used. The boiler feed water pump recorded the highest electric demand of between 26% and 29% of the total demand for all the scenarios, followed by the compressors. This high electric energy was due to pumping large quantities of feed water (221–233 t/h boiler feed water for the sorbitol and 232–247 t/h for the glucaric acid scenarios), which was heated in boilers prior to electricity production.

The conversion and purification stage steam duty in the glucaric acid scenarios (Figure 4-2d) (15-16 MWh) using oxidative processes was significantly higher than in the sorbitol process options (Figure 4-2a) (1.7-1.8 MWh), requiring a hydrogenation reduction process due to differences in process enthalpies. This high steam demand contributed to the higher bypass ratios in the glucaric acid than sorbitol scenarios as shown in Table 4-4.

4.5.3. Economic evaluation

4.5.3.1. Capital investment costs

A breakdown of capital investment costs for the various process areas for all scenarios, excluding feedstock handling costs (Mandegari et al., 2017), are presented in Figure 4-3. The CHP plant had the highest capital investment of all scenarios, as this equipment is expensive (Humbird et al., 2011). The CHP plant accounted for 47–56% of the total capital investment as shown in Figure 4-3, with capital costs in the range of US$ 64.9-68.4 million due the large boiler feed water quantities (221-247 t/h) needed to meet the process steam demand.

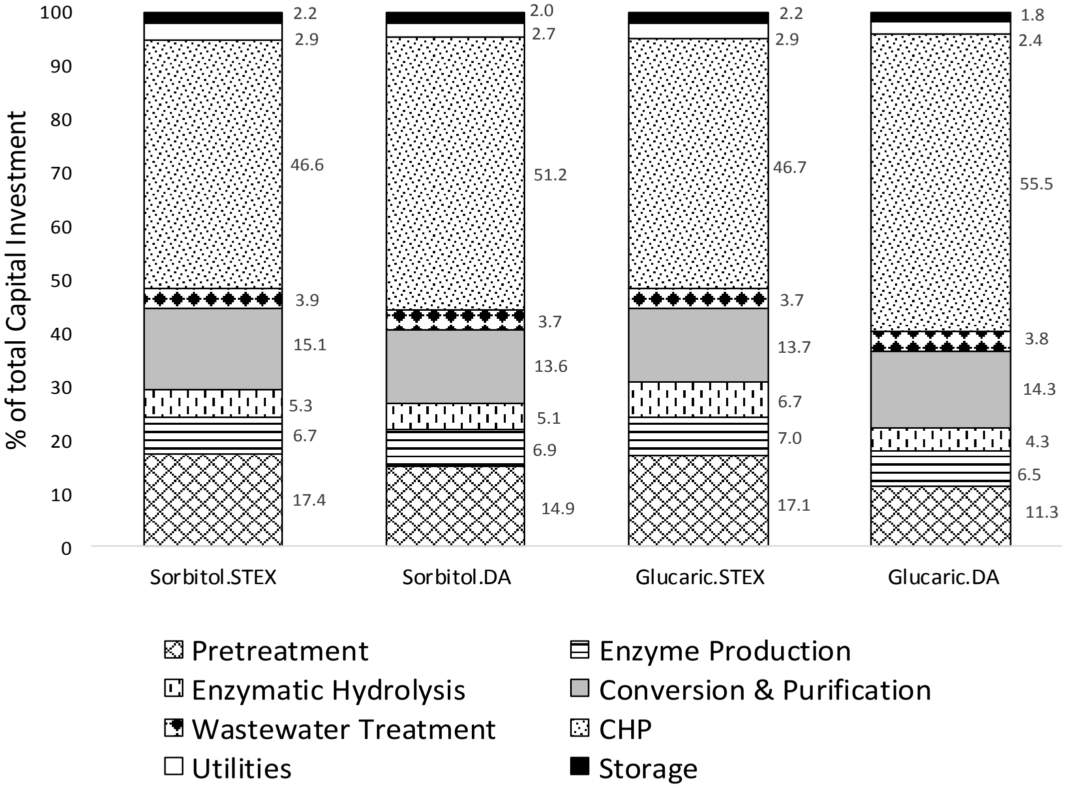

Figure 4-3: Percentage capital investment costs per process unit for the four scenarios

Pretreatment contributed 11-17% of the total capital cost as illustrated in Figure 4-3, with SO_2-steam explosion technology having a higher cost than dilute acid, mainly due to the larger amounts of biomass fed to the biorefineries in steam explosion than acid pretreatment. The pretreatment cost was US$ 19 million–US$ 26 million for the sorbitol and US$ 14 million–US$ 24 million for the glucaric acid scenarios. The combined pretreatment and hydrolysis capital cost were 23–32% of the total capital investment compared to 35% reported for a cellulosic ethanol plant (Humbird et al., 2011). The combined conversion and purification capital investment costs were between US$ 17 million–US$ 23 million. A major contribution to this cost is the materials of construction used to contain the hydrogenation (120 °C and 70 bar) and oxidation (80 °C, 13 bar) reactions.

A summary of the total capital investments, variable and fixed operating costs and costs of production for all the scenarios is outlined in Table 4-5. The inside battery limit's total capital investment costs were between US$ 44 million–US$ 66 million and the total installed equipment costs US$ 119 million–US$ 147 million (Table 4-5).

Table 4-5: Capital investments, variable and fixed operating and production costs for the four scenarios

	Sorbitol.$_{\mathrm{STEX}}$	**Sorbitol.$_{\mathrm{DA}}$**	**Glucaric.$_{\mathrm{STEX}}$**	**Glucaric.$_{\mathrm{DA}}$**
Total Capital Cost (US$ million)				
Installed cost (ISBL +OSBL)	147.5	126.6	141.7	119.2
Total direct costs (TDC)	159.0	135.4	152.8	127.0
Total indirect cost (TIC)	95.4	81.2	91.7	76.2
Fixed capital investment (FCI)	254.3	216.6	244.4	203.2
Total capital investment (TCI)	267.1	227.5	256.6	213.3
Variable Operating Cost (VOC) (US$ million/year)				
Raw materials and consumables	15.0	14.4	13.2	12.3
Waste materials costs	0.5	0.9	0.7	0.8
Total VOC	15.6	15.3	14.0	13.2
Fixed Operating Costs (FOC) (US$ million/year)				
Total labour costs (incl. salaries and labour overheads)	4.5	4.2	4.2	4.2
Maintenance cost (3% of FCI)	2.0	1.5	1.9	1.3
Property taxes and insurance (0.7% of FCI)	1.8	1.5	1.7	1.4
Total FOC	8.3	7.2	7.8	6.9
Total cost of production (TCOP) (US$ million/year)				
Total TCOP	23.8	22.5	21.8	20.1

4.5.3.2. Fixed operating, variable operating and manufacturing costs

Table 4-5 includes a summary of the total capital investment costs, plant overheads that include the direct and indirect costs, total fixed capital investment (FCI) and total capital investment (TCI). These values together with the variable operating (VOC), fixed operating (FOC) and total manufacturing/production (TCOP) costs were used to calculate the internal rates of return (IRRs).

The TCOP was US$ 20.1 million–US$ 23.8 million as shown in Table 4-5. Labour costs ranged from 42% to 61% of the total FOC for all the scenarios. The additional number of jobs created with the operation of a biorefinery and CHP plant for all scenarios was 46–58, which included skilled, semi-skilled and non-skilled labour.

The total VOCs were between US$ 13.2 million–US$ 15.6 million, with the sorbitol scenarios having higher costs than the glucaric acid process options due to the high plant capacity in the case of the Sorbitol.$_{\text{STEX}}$ and the high waste material disposal cost in Sorbitol.$_{\text{DA}}$ resulting from the additional disposal costs associated with lime sludge produced after neutralisation of the acidified wastewater.

The raw material and consumables contributed over 86% of the total VOCs in the four scenarios (Table 4-5). In particular, the feedstock, hydrogen and pure oxygen costs had contributions of between 51% and 59%, 17-18% and 12-15% in that order. The annual cost of the re-usable Raney nickel catalyst in sorbitol hydrogenation, Pt/C catalyst in glucaric acid oxidation and amberlite ion exchange resins used in the conversion and product purification stages was US$ 1.2 million-US$ 1.5 million Pt/C, US$ 1.3 million-US$ 1.4 million Ra-Ni and US$ 1.4 million-US$ 2.2 million resins respectively. Since glucose was produced *in-situ*, the enzyme production unit's operating cost, which includes enzymes, nutrients and glucose was lower than the cost incurred by Mandegari et al., (2017), where purchased glucose contributed 24% of the total variable operating cost (VOC) in a cellulosic ethanol biorefinery with onsite enzyme production.

4.5.3.3. Profitability

Table 4-6: Economic analysis of the sugarcane lignocellulose biorefineries[a]

	Sorbitol.STEX	**Sorbitol.DA**	**Glucaric.STEX**	**Glucaric.DA**
NPV (US$ Million)	-12.8	17.2	-12.3	16.0
IRR (%)	-	10.7	-	10.7
MPSP (US$/t)	679	619	681	618
Market Selling Price (US$/t)*	655	655	655	655
Payback period (yr)	-	19	-	19

*****Chemical price for 2016 adjusted using a 0.7% USA inflation rate from the 2015 base year sorbitol price of US$ 650/t (Usinflationcalculator, 2019).

[a] Alternative economic assessments of biorefineries in Appendix A-1, Table A2-2 based on a 15% working capital

The economic profitability of the biorefineries is based on their ability to produce a return on investment. Table 4-6 presents the calculated profitability economic parameters for sorbitol and glucaric acid scenarios. It was observed that while the steam explosion pretreated scenarios, Sorbitol.$_{\text{STEX}}$ and Glucaric.$_{\text{STEX}}$ had higher product flow rates than Sorbitol.$_{\text{DA}}$ and Glucaric.$_{\text{DA}}$, they were marginally unprofitable with NPVs in the same range at −12.8 million US$ and −12.3 million US$ respectively. Consequently, their minimum selling prices were 3.7-4.0% above the assumed current selling price of US$ 655/t (for glucaric acid's application as a food ingredient using the sorbitol selling price due to lack of data). A contributing factor to the non-viability included the higher capital investment costs in pretreatment for biorefineries using steam explosion than in dilute acid pretreated scenarios. Also a higher capital investment cost was observed in the separation and purification stage of the sorbitol scenarios using steam explosion than dilute acid pretreatment thus lowering profit margins.

From Table 4-6, it was observed that dilute acid pretreated scenarios Sorbitol.$_{\text{DA}}$ and Glucaric$_{\text{.DA}}$ were profitable with MPSPs of US$ 619/t and US$ 618/t respectively, which were below the sorbitol and glucaric acid selling price of US$ 655/t. However, profitability was marginal with IRRs that were 1.0% higher than the discount rate of 9.7% (15% less the inflation rate of 5%). The high capital investment costs and low product selling price were contributing factors. Net present values of US$ 17.2 million and US$ 16.0 million were obtained for Sorbitol.$_{\text{DA}}$ and Glucaric$_{\text{.DA}}$ respectively (Table 4-6). It should be noted that the IRRs of the economically viable lignocellulose biorefineries were not sufficiently high to warrant private investment in such new projects, which requires IRRs of at least 20-25%. For instance, to attain a 25% IRR, the sorbitol selling price in Sorbitol.$_{\text{DA}}$ should reach US$ 1283/t.

The total capital investment per litre of product, calculated from the total capital investment (Table 4-5) and chemical production tonnage (Table 4-4) revealed that the capital investment cost per litre via steam explosion of produced sorbitol (TCI$/L) was US$ 4.33/L and US$ 6.95/L for glucaric acid. This was 8.5% and 11.7% higher than for Sorbitol.$_{DA}$ (US$ 3.96/L) and Glucaric.$_{DA}$ (US$ 6.22/L) scenarios respectively. This is in agreement with the identified higher capital investment costs in the steam explosion than dilute acid scenarios despite the high product flow rates in steam explosion. A TCI$/L of US$ 3.03/L was calculated by Mandegari et al., (2017) for a biological biorefinery producing bio-ethanol fuel and annexed to a sugar mill.

Glucaric acid production process is nearing commercialisation. However, limited information is available in the public domain due to proprietary rights. Rivertop Renewables Inc. in the United States of America is the only plant that has commercialised production of glucaric acid, since 2015 (Saeed et al., 2017) with a recorded payback period of less than 2 years (Icis, 2013). The short payback time stated would suggest that this commercialised plant is a standalone process using 1G feedstock, which typically means lower capital investment and operating costs. In addition, glucaric acid may have a higher selling price than the US$ 655/t used because the product is currently serving a niche market. To achieve the 2 year payback time recorded in literature, a glucaric acid selling price for the Glucaric.$_{DA}$ scenario of US$ 3195/t is required, which gives a project IRR of 56.2% and NPV of US$ 1.1 billion.

Sorbitol production from biomass is based on mature technology. It is a less risky investment with the majority of process plants currently operating as stand-alone 1G fed plants, therefore, they have an economic advantage over 2G integrated plants. For instance, using data generated for the most profitable scenario Sorbitol.$_{DA}$, a 1G stand-alone system (not shown) using glucose feedstock and having the same plant capacity and operating period as Sorbitol.$_{DA}$ showed that the IRR and NPV increased from 10.7% to 17.5% and US$ 17 million to US$ 34 million respectively.

The bioenergy self-sufficient and economically viable scenarios Sorbitol.$_{DA}$ and Glucaric.$_{DA}$ at current economic parameters cannot therefore compete with existing stand-alone biorefineries. The 1st generation (1G) biorefineries operate for more than 9 months, do not incur expenses such as capital and variable operating costs associated with biomass pretreatment and hydrolysis and are not integrated with a CHP unit but purchase their electricity (produced from coal) and other utilities. The investigated economically viable scenarios, however, have potential to outweigh 1G systems on environmental benefits due to their non-use of fossil resources.

4.5.3.4. Sensitivity analysis

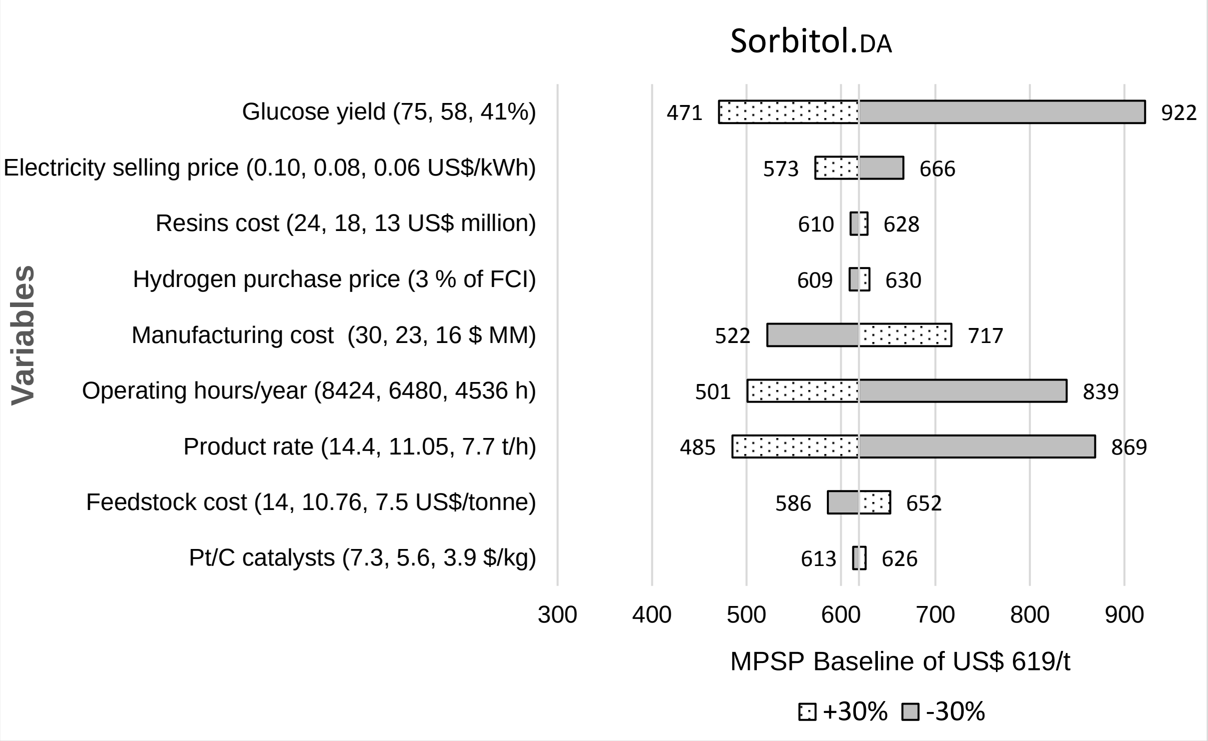

Figure 4-4: Sensitivity analyses for the most economically viable scenario Sorbitol.$_{DA}$

A sensitivity analysis of plant profitability for the most profitable and technologically mature scenario Sorbitol.$_{DA}$ is presented in Figure 4-4 using nine economic variables at a ± 30% variance. Four variables with a significant impact on the MPSP (US$ 619/t) were the glucose yield, prand the manufacturing cost as shown in Figure 4-4.

A 30% increase in glucose yield, operating hours, product rate and manufacturing cost led to a decrease in the MPSP from US$ 619/t to US $ 471/t, US$ 501/t, US$ 485/t and US$ 97/t respectively (Figure 4-4) which may be sufficient to justify an investment. A significant improvement of the glucose yield may be possible by increasing the solids loading of the feedstock. A 5% increase in the solids loading led to an 8% reduction in the process steam demand of the Sorbitol.$_{DA}$ scenario, which therefore can lead to a reduction in the bypass ratio and subsequent increase in biorefinery capacity. However, optimum solid loadings should be determined experimentally per feedstock as increasing solids loading will also have an effect of sugar yields and enzyme performance (Modenbach and Nokes, 2013, 2012).

Securing additional feedstock (1G or 2G) to operate the profitable Sorbitol.$_{DA}$ biorefinery for more than 9 months without any major change to the total capital investment would lower the MPSP, increase product rate and improve profitability. This coupled with the lower capital investment costs for dilute acid pretreated scenarios would increase profit margins.

Variables that do not impact the MPSP significantly include the ion exchange resins, catalysts, hydrogen purchase price, feedstock cost and electricity selling price as shown Figure. 4-4. This is mainly due to the recyclable nature of resins and catalysts, reasonable amounts of hydrogen needed for hydrogenation and the unattractive selling price of cogenerated electricity in biorefineries, which therefore does not increase profit margins significantly.

4.6. Conclusions

Four bioenergy self-sufficient lignocellulose biorefineries via chemical processes and annexed to a typical sugar mill were investigated. Dilute acid pretreated scenarios were more economically viable than the steam explosion pretreated models mainly due to lower production costs. Nonetheless, the high capital cost of the integrated CHP plant made them only marginally profitable. The most viable scenario Sorbitol._{DA} had a 10.7% IRR and US$ 17 million NPV, achieving US$ 619/t as a minimum sorbitol selling price that is 5% below the market selling price. To secure private investments, at an IRR of 25%, a sorbitol selling price of US$ 1283/t is required.

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Declaration of Competing Interest

The authors declare that they do not have any competing interests.

Supplementary information: Sorbitol and glucaric acid techno-economics

Appendix C includes the following details:

i. Supplementary data to this article (also at https:// doi.org/10.1016/j.biortech.2019.121635)

ii. Aspen Plus models and unit process conditions,

iii. Equipment sizing

iv. Mass and energy balances,

v. Pinch analysis results,

vi. Discounted cash flow rate of return flowsheets, for the profitable scenarios Sorbitol.$_{DA}$ and Glucaric.$_{DA}$.

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Chapter 5

5.0 Techno-economics of lignocellulose biorefineries at South African sugar mills using the Biofine process to co-produce levulinic acid, furfural and electricity alongside gamma valerolactone

Furthermore, under objectives 2, 3 and part of 4, apart from the selected chemicals, polyethylene (covered in chapter 3), sorbitol and glucaric acid (chapter 4) and the techno-economic and social impacts of biorefineries producing these chemicals, chapter 5 considers the fourth chemical shortlisted, levulinic acid (objective 2). In chapter 5, the techno-economic viability (objective 3) and social impact (part of objective 4) of biorefineries producing levulinic acid via the Biofine process together with furfural by-product and electricity co-generation are considered. In addition, a levulinic acid derivative, gamma valerolactone is also produced in one of the scenarios. The techno-economic and social impact studies will be followed by a life cycle assessment (in chapter 6) of the profitable and marginally unprofitable scenarios producing these shortlisted chemicals.

This chapter on levulinic acid production from lignocellulose biorefineries was prepared and has been submitted to the *“Journal of Biomass and Bioenegy”*.

Title: *Techno-economics of lignocellulose biorefineries at South African sugar mills using the Biofine process to co-produce levulinic acid, furfural and electricity alongside gamma valeractone*

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Objective of dissertation in this chapter and summary of findings

As a continuation and in addition to the considered bio-based chemicals polyethylene (chapter 3) sorbitol and glucaric acid (chapter 4), integrated biorefineries co-producing levulinic acid, furfural and electricity and levulinic acid, furfural, gamma valerolactone and electricity were assessed for their economic and social viability. The scenarios generated were also compared to a base case scenario (CHP base case) producing electricity only.

This work was novel in that the economic viability of levulinic acid was not assessed in isolation, but annexed to a typical sugar mill and in accordance with the expected impact of the levulinic acid production volumes on its selling price, as this chemical is currently serving a niche market. Also, the impact of producing multiple products on the economic feasibility of biorefineries was considered.

The results indicated that all levulinic acid scenarios were bioenergy self-sufficient following pinch analysis, with surplus of between 2–44 MWh electricity sold to the grid for additional revenue depending on the biorefinery configuration (as is detailed in Table 5-1 in Section 5.3.2). Scenario (A) producing a high volume, low value levulinic acid (7.2 t/h and selling at US$ 905/t), 3.4 t/h furfural and 13 MWh surplus electricity was profitable with a 17% IRR and US$ 139 million NPV at a 9.7% hurdle rate. Also, scenario (C) producing low volume, high value levulinic acid (0.15 t/h sold at US$ 6500/t), 0.1 t/h furfural, 6.8 t/h gamma valerolactone and 12 MWh electricity was profitable attaining an IRR of 23% and US$ 253 million NPV. On the other hand, scenarios (B1 and B2) producing levulinic acid for niche markets (0.14-0.16 t/h), 0.1 t/h furfural and electricity (9-44 MWh) for sale were unprofitable, due to the high total capital investment costs and low electricity selling price. This low electricity-selling price also negatively affected the CHP base case, which despite producing the highest amount of surplus electricity (60 MWh) was marginally profitable at 10.3% IRR and US$ 6.5 million NPV at a 9.7% hurdle rate.

Summary of authors' contributions

Kutemba K. Kapanji designed and generated the scenarios, costed them and assessed their economic viability. In addition, she analysed, interpreted the results and wrote the chapter. *Kate F. Haigh* contributed to the review of the chapter. *Johann F Görgens* assisted with data interpretation and reviewed the chapter.

Abstract

Lignocellulose biorefineries process biomass into 'green' chemicals and bio-energy and play a key role in sustainable bio-economies. Using sugarcane bagasse and trash as feedstock, biorefineries were simulated in Aspen Plus ® to generate mass and energy balances. Four scenarios with electricity and furfural as common products were generated. Scenario A in addition produced high volume, low value levulinic acid, whilst scenarios B1 and B2 generated low volume, high value levulinic acid. Scenario C produced low volume, high value levulinic acid and bulk gamma valerolactone. The four biorefineries were also compared to a combined heat and power plant that only produced electricity. Aspen Plus® Economic Analyser and a discounted cash flow rate of return methodology were used to determine the economic feasibility of the bioenergy self-sufficient biorefineries, annexed to a typical South African sugar mill. Levulinic acid production via the Biofine process makes economic sense when produced in small volumes for niche markets, due to the anticipated decreases in market prices when production volumes increase. Scenario (C) co-producing a low volume of levulinic acid (0.15 t/h) together with 3.3 t/h furfural, electricity (14 MWh) and 6.8 t/h gamma valerolactone, was the most profitable and viable. It attained an internal rate of return of 23% and a net present value of US$ 253 million at a 9.7% hurdle rate by matching chemicals' production volumes to market demands, to maintain high market prices for multiple revenue streams.

Keywords: Biorefinery, Bioenergy self-sufficient, Furfural, Gamma Valerolactone, Levulinic acid, Techno-economic assessments.

Declaration of interest

None

5.1. Introduction

The finite nature of fossil reserves and global warming concerns have advanced the global drive towards bio-economies (Zhang et al., 2016) including the establishment of biorefinery complexes, where different types of biomass are converted to an array of products using diverse technologies in a single facility (Cherubini, 2010). Integrated biorefineries with combined heat and power (CHP) plants that use part of the available biomass (so-called bypass) to generate energy, makes these facilities bioenergy self-sufficient, avoids the use of fossil fuels and has socio-economic and environmental benefits (Golecha and Gan, 2016). At a local context, second generation (non-food) sugarcane bagasse and trash present a promising feedstock option for valorisation into levulinic acid (LA) and electricity co-production to improve the revenue base of conventional South African sugar mills that have been affected by fluctuating global sugar prices (Mandegari et al., 2017).

Levulinic acid is one of the United States Department of Energy's top ten promising platform chemicals for bio-economies (Bozell and Petersen, 2010). Its production from biomass is associated with furfural by-product, formic acid co-product and bio-char waste. Due to levulinic acid's reactive functional groups, it has several applications and over 60 derivatives (Rackemann and Doherty, 2011), with one platform chemical of interest being gamma valerolactone (GVL) that finds use as a fuel additive and green solvent (Weingarten et al., 2012). Over the years, there has been an increasing demand for LA in the pharmaceuticals industry (Grand View Research, 2017). Furfural is used in the transportation, pharmaceutical and agrochemical industries and as a precursor to furan based chemicals and solvents (de Jong et al., 2012) whilst formic acid finds use in the food and leather industries. Bio-char, a solid waste is combusted for additional process energy (Morone et al., 2015).

Key stakeholders producing LA for niche markets are in the USA (Segetis and Biofine) and Italy (La Calorie) while other smaller plants are in China (IAR, 2015a, 2015b). The global LA production capacity stands at approximately 17.5 kt/y (IAR, 2015b) and has a market selling price of US$ 5000-8000/t (Grand View Research, 2015).Yet, a rapid growth of the market volume due to LA's high functionality is projected; hence, its market selling price may drop to as low as 0.00089-0.00092 US$/t (IAR, 2015a, 2015b). In this study, it is assumed that an LA production volume contributing more than 10% to the total global LA market supply will affect market prices (Chang, 2020). Locally, the Department of Trade and Industry (DST) does not explicitly state the import and export values of LA, suggesting that it is not extensively produced or imported (Department of Trade and Industry, 2016). Furfural's market value stands at 1200 US$/t (Taylor et al., 2015) and its annual global production volume is 146 kt.y^{-1} (IAR 2015b) with South Africa being the third world's largest furfural producer (Biddy et al., 2016). Formic acid, mainly produced by BASF, sells at US$ 0.00095/t (Gozan et al., 2018) and has a global production capacity of 305 kt/y. Levulinic acid's derivative, gamma valerolactone (GVL), has a selling price of about 1000 US$/t (Alonso et al., 2017) although its global production capacity is not readily available.

Levulinic acid was in the past mainly produced from fossil-based maleic anhydride (Mukherjee et al., 2015). However, the complex processes and the high cost of raw materials (Rackemann and Doherty, 2011) limit its mass production. Recently, research and development has been undertaken on LA production and purification using different techniques. Examples include hydrolysis of acetyl succinate ester, acid hydrolysis of furfural alcohol, oxidation of ketones and lead catalysed carbonylation of ketones (Patel et al., 2006; Mukherjee et al., 2015), thermo-chemical and thermal enzymatic pretreatments (Elumalai et al., 2016; Kang and Yu, 2016; Joshi et al., 2014; Schmidt et al., 2017), functionalised ionic liquids (Shen et al., 2015), acid hydrolysis (Jeong et al., 2017) and reactive extraction (Brouwer et al., 2017). Purification techniques considered include liquid-liquid extraction (Brouwer et al., 2017), hybrid solvent screening (Nhien et al., 2016), extractive solvents and vacuum evaporation (Elumalai et al., 2016). However, these processes are still at laboratory to early pilot scale and product yields are generally low at 13–21 wt% (Chen et al., 2017; Jeong et al., 2017; Elumalai et al., 2016) as LA production is based on the C-6 sugars in biomass. An effective method, the Biofine process, has been used to produce LA mainly from cellulose (glucose), hemicellulose C5 pentose and C6 hexose sugars including xylose and glucose, respectively (IAR, 2015b). Pentose (C5) sugars are reduced to furfural, which can undergo further reduction and acid hydrolysis to form LA (Morone et al., 2015; Rackemann and Doherty, 2010; Girisuta, 2007).

The Biofine process, at semi-commercial to commercial level, is a two-stage reaction technology in which biomass sugars undergo dilute acid (1-5 wt%) catalysed reactions to produce LA, furfural, formic acid and bio-char (Rackemann and Doherty, 2010; Girisuta, 2007). The first reactor operates at 210-230 ^{o}C, 20-25 bar and 15-30 secs. It hydrolyses and dehydrates cellulose to 5-hydroxymethylfurfural (5-HMF), whilst the hemicelluloses are first hydrolysed to hexose and pentose sugars, and subsequently dehydrated to 5-HMF and furfural gas, respectively. The second reactor operating at 190–220 ^{o}C, 10-15 bar for 10-20 mins, facilitates the reaction of 5-HMF to LA and formic acid (Fitzpatrick, 1997a).

The Biofine process is cost-effective (Bozell et al., 2000) with some economic projections indicating that the LA product cost per tonne (a ratio of the total cost of production to the product of the LA rate of production and its annual operating hours) can be below US$ 0.00022/t at plant capacities of > 1000 dry t/day (Fitzpatrick, 2002; Bozell et al., 2000). The low product cost per tonne LA produced coupled with its high selling price makes the process economically viable. This process also achieves high LA yields from cellulose of 70-80 wt% of the theoretical maximum (Hayes et al., 2008). However, how close to this value one gets is determined by the extent of the degradation of side reactions and effectiveness of hydrolysis (Hayes et al., 2008). Some limitations to the Biofine process include its energy intensive nature, the production of humins that clog equipment and lack of reproducibility from pilot trials to industrial scale (Morone et al., 2015).

Whilst some studies on LA production, even via the Biofine process have been conducted, most of them were stand-alone processes. Some economic study in Italy where the Biofine process was used to produce LA from paper sludge, tobacco and waste paper (Hayes et al., 2008) and another in Brazil using sugarcane bagasse processed in an extruder (mechanical means) and continuous stirred tank reactor have been considered (van Benthem et al., 2002), and scenarios were economically viable. However, the studies were not integrated bioenergy self-sufficient lignocellulose biorefineries. A TEA for the production of GVL only from loblolly was identified and the plant deemed viable at a capacity of 1500–2500 t/day (Murat Sen et al., 2012). Therefore, as an initial study, this research aims to conduct a techno-economic assessment (TEA) of LA production together with its associated products in integrated bioenergy self-sufficient lignocellulose biorefineries annexed to a conventional sugar mill. Secondly, the techno-economics of the developed scenarios will be compared to a base case electricity-only plant, which depicts the default option for investment, to establish which scenario should be preferred. In addition, the impact of LA production volumes on the overall market selling price, have not been reported and so the TEAs will be conducted LA prices for niche and commodity markets. If lignocellulose biorefineries annexed to conventional sugar mills are to be realised in future feasibility studies, then detailed TEAs on LA production are required.

5.2. Materials and methods

5.2.1. Simulation methodology

This was a conceptual study built using Aspen Plus® v 8.6 and used literature data to generate mass and energy balances. The Electrolyte Non-random Two-Liquid (ELEC-NRTL) activity coefficient property method was used as the default method. It uses the activity coefficient approach to calculate the liquid properties and the Peng-Robinson equation of state was used to calculate the vapour phase. Databases from Aspen Plus® and the National Renewable Energy Laboratory in-house defined components were used to name lignocellulose compounds and other components (Humbird et al., 2011).

5.2.2. Feedstock composition and process flow configurations

The feedstock chemical compositions for South African sugarcane bagasse and trash were assumed to be 40.7% cellulose, 27.1% hemicellulose, 21.9% lignin, 6.7% extractants, 3.5% ash and 42% moisture (dry base) (Farzad et al., 2017; Benjamin et al., 2013). The sugar mill operated for 9 months and supplied 113 $t.h^{-1}$ wet mass (65 $t.h^{-1}$ dry mass) of bagasse (70%) and trash (30%) dry mass basis (Mandegari et al., 2017) for the part production of chemicals in a biorefinery and a bypassed amount (bypass ratio, %) combusted in a combined heat and power (CHP) plant to generate electricity (see Table D1-1 for a detailed breakdown of the feedstock). In return, the sugar mill was supplied with 120 t/h of high pressure steam (400 ^{o}C, 30 bar) (Mandegari et al., 2017).

5.2.3. Process description of scenarios

A description of the scenarios considered in this study is shown in Table 5-1 and details of the process areas and conditions are given in subsequent sections.

Table 5-1: Description of 9 month operated biorefineries in this study

	Description of multi-product scenarios and their sellable products				
Scenario	**A**	**B1**	**B2**	**C**	**CHP**
Feedstock to CHP and biorefinery	113 t/h	113 t/h	49 t/h	113 t/h	113 t/h to CHP only (no biorefinery)
Products description	HV, LV levulinic acid (commodity)	LV, HV levulinic acid (niche product)	LV, HV levulinic acid (niche product)	LV, HV levulinic acid (niche product)	-
	Furfural	Furfural	Furfural	Furfural	-
	-	-	-	Bulk gamma valerolactone	-
	Adequate electricity for processes. Excess electricity sold to the grid.	(>90% biomass used to produce electricity). Large surplus electricity sold to grid	Just enough electricity for the processes. Excess electricity after process needs sold to the grid	Adequate energy for process needs. Excess electricity after process needs sold to the grid	Large amounts of electricity produced Large surplus electricity sold to grid

KEY:

LV, HV = Low volume, high value are specialty chemicals selling at > US$ 4400/t (National Academy of Science, 2000). An average levulinic acid market selling price of US$ 6500/t was used (from the range 5000-8000 US$/t (Grand View Research, 2015)).

HV, LV = High volume, low value are commodity chemicals selling at < US$ 2200/t (National Academy of Science, 2000) and a value of US$ 0.0009/t was used (from 0.00089-0.00092 US$/t) (IAR, 2015a, 2015b)).

5.2.3.1. Levulinic acid production

Figure 5-1 shows a simplified flow diagram of the Biofine process' main units for crude levulinic acid production, including process conditions used in this study prior to the separation and purification stages.

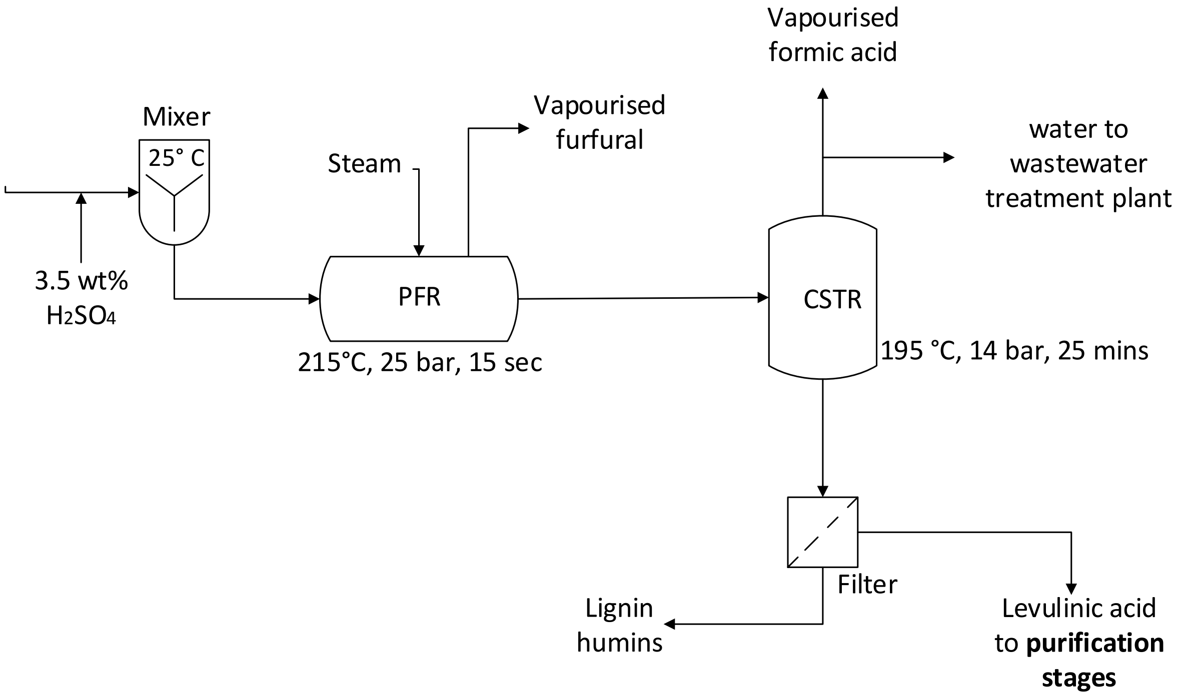

Figure 5-1: Schematic of the Biofine process for levulinic acid production (Adapted from Girisuta (Girisuta, 2007))

The Biofine process, as patented by Fitzpatrick, (1997), was the basis for the production of LA and furfural in all four scenarios. A 3.5wt% sulphuric acid catalyst (84-100 t/h for the different scenarios) was mixed with the lignocellulosic biomass to make a slurry (at 30% solids content) and the mixture sent to the first reactor operating at 215 ^{o}C and 25 bar, where 5-hydroxymethyfurfural and gaseous furfural are produced at 98 wt% purity are produced with the gas recovered, cooled and stored. The slurry from the first reactor was fed to reactor 2 operating at 195 ^{o}C and 14 bar, leading to the formation of LA and formic acid (Rackemann and Doherty, 2010). Formic acid was not reclaimed due to its high processing costs (Fitzpatrick, 2002) and low selling price.

Insoluble solids from reactor 2, comprising cellulignin and humins, were filtered out from the liquid stream, neutralised, washed (2:1 water to solids ratio) and combusted as additional process fuel (Morone et al., 2015). Key reactions and conversions of the main Biofine products occurring in reactors 1 and 2 to obtain 50-55% LA mass yields (Hayes et al., 2008) are shown in Table 5-2.

Table 5-2: Key assumed reactions and wt% conversions used in reactors 1 and 2 of the Biofine process (Rackermann and Doherty, 2010; Hayes et al., 2008*) to attain levulinic acid mass yields of 50–55%

Raw material	**Reactor 1 (RSTOIC Model)**	**Reactant**	**wt % conversion**
*H.C	Xylan + H_2O → Xylose	Xylan	70%
H.C	Xylose → Furfural + 3 H_2O	Xylose	99%
H.C (hexose)	Glucan + H_2O → Glucose	Glucose	68%
H.C (hexose)	Glucose → 5 HMF + 3 H_2O	Glucose	99%
H.C (other)	Acetate → Acetic Acid	Acetate	100%
	Reactor 2 (RSTOIC Model)	**Reactant**	**wt % conversion**
C/H.C	5 HMF+ 2 H_2O → Levulinic acid + Formic acid	5 HMF	99%
lignin	Lignin → $\text{Lignin}_{\text{acid insoluble}}$	Lignin	99%

*Assumed that H.C (hemicellulose) being amorphous is hydrolysed first (in reactor 1) followed by the crystalline cellulose (C) and any remaining H.C in reactor 2

5.2.3.2. Gamma-valerolactone production

For scenario C, crude levulinic acid was hydrogenated over a 15% RuRe (3:4) carbon catalyst and converted to gamma valerolactone (GVL) and carbon dioxide (160 kg/h) at 150 ^{o}C and 5 bar, resulting in 99% conversion of LA to GVL (Murat Sen et al., 2012). The product stream was fed to a flash tank operating at 98 ^{o}C and 1 atm, to remove CO_2 and the GVL rich stream sent for product recovery and purification further downstream (see Figure 5-3).

5.2.3.3. Recovery and purification technologies used in the models

The conventional method of LA purification in the Biofine process is via distillation (Morone et al., 2015). Furfural gas produced in scenarios A, B1, B2 and C was vaporised from the bulk solution at 2 bar and 106 ^{o}C (Fitzpatrick, 1997a), producing a 98wt% pure product. Levulinic acid was purified via vacuum distillation at 0.1 atm and steam stripped at 1 atm. to produce a 98 wt% pure commercial grade LA as a bottom product (LEV-ACID), as shown in Figure 5-2 and process conditions shown in Table D1-2 of Appendix D. The top product (TOPS2) containing a dilute acidified water and formic acid was cooled, neutralised and sent to the wastewater treatment (WWT) plant.

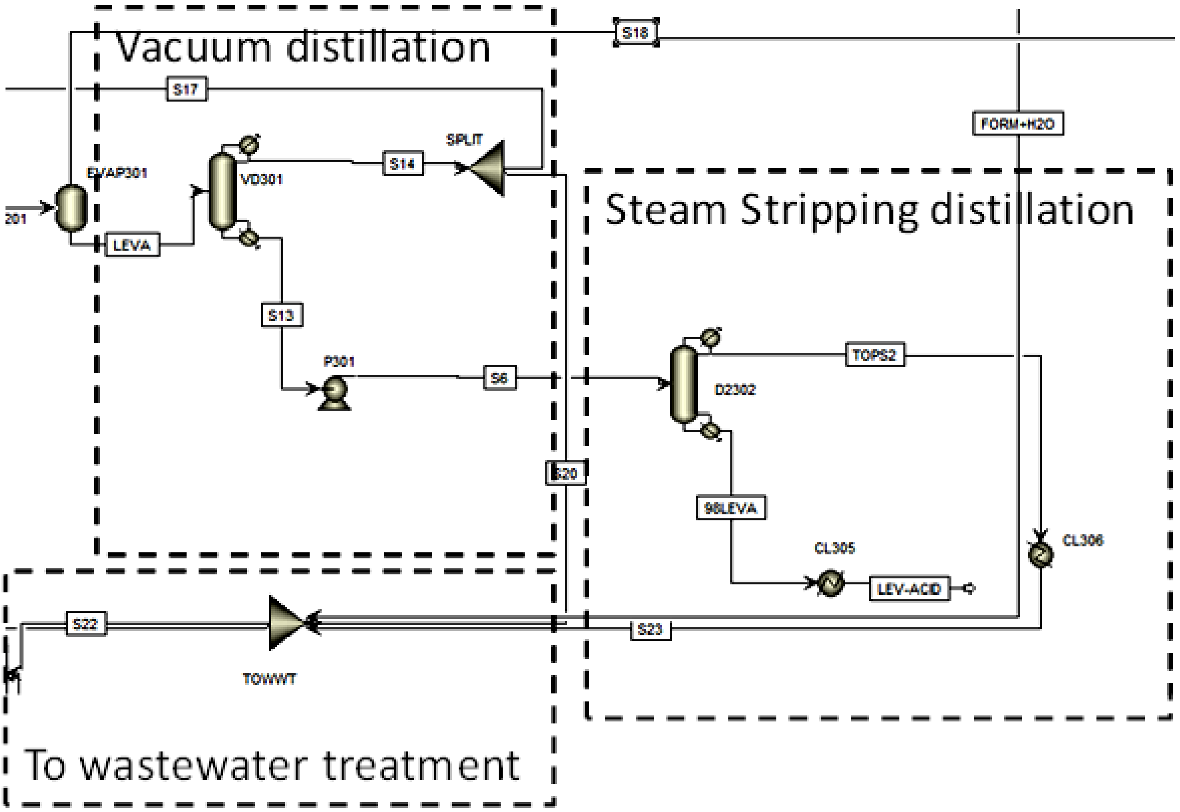

Figure 5-2: Distillation techniques used in scenarios A, B1, B2 and C for the separation and purification of levulinic acid (Fitzpatrick 1997a)

For the recovery and purification of GVL in scenario C, the crude GVL stream was sent to a series of liquid-liquid extractors operating at 3 atm and using 32 t.h^{-1} recyclable n-butyl acetate solvent (Braden et al., 2011) to attain a 98% GVL extraction efficiency into the solvent (Murat Sen et al., 2012). The solvent n-butyl acetate was then distilled from the GVL leaving a 98 wt% pure gamma valerolactone bottom product (Murat Sen et al., 2012) and the solvent recovered and recycled back to the process (see Table D1-3 for the process conditions). A 1.7 t.h^{-1} make-up stream of solvent was determined from Aspen Plus®. Figure 5-3 shows the modelled GVL production, recovery and purification processes.

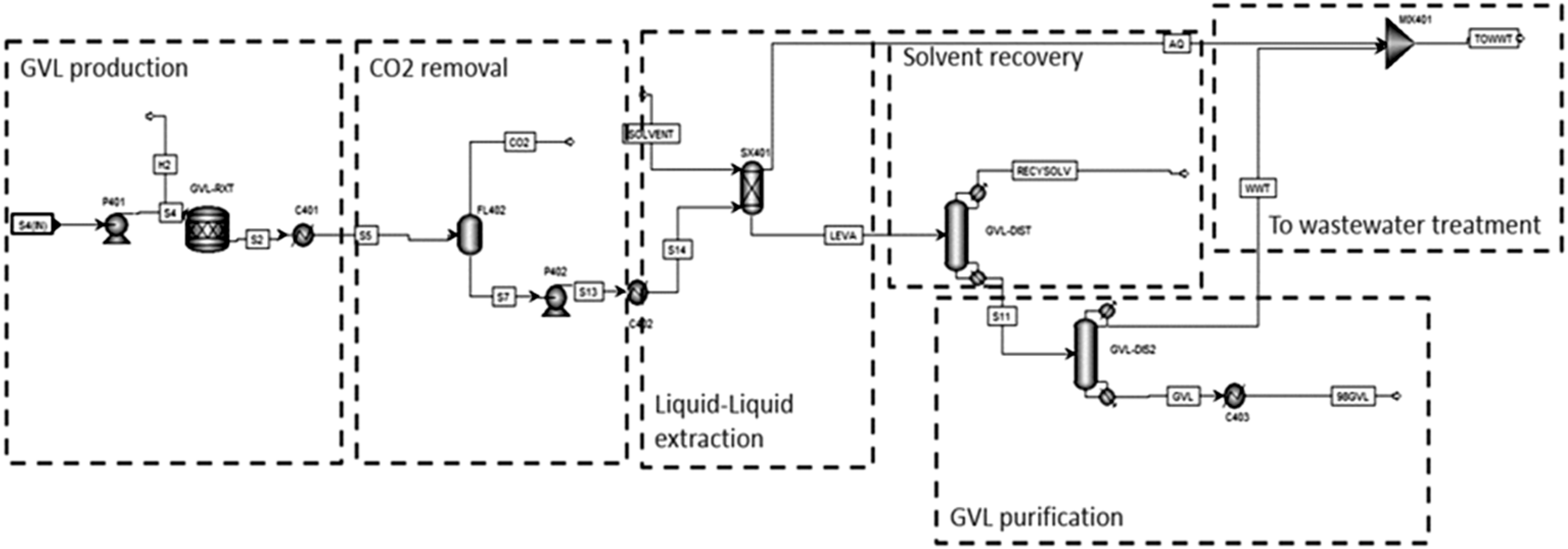

Figure 5-3: Modelled process for gamma valerolactone production using levulinic acid as feedstock (Adapted from (Murat Sen et al. 2012))

5.2.3.4. Electricity production

Electricity was produced in the CHP plant by combusting biomass, cellulignin and methane from wastewater treatment bio-digesters. The bypass ratio was determined by each scenarios' energy demand, with the exception of the CHP base case and scenario B1 as described in Table 5-1. A condensing extraction steam turbine (CEST) produced electricity based on an isentropic and mechanical efficiency of 75% and 98%, respectively (Mandegari et al., 2017). The CHP plant provided high pressure steam (at 266 ^{o}C and 13 atm) and low pressure steam (233 ^{o}C and 9.5 atm) to the different process units and excess electricity was sold (see the process flow diagrams and mass balances in Figures D1-1 and D1-2 and Table D1-4 of Appendix D-1).

5.2.3.5. Wastewater treatment plant

Wastewater streams were sent to a wastewater treatment plant (not modelled) for anaerobic digestion of the organics into bio-methane that was used as additional fuel for the boiler (Humbird et al., 2011). A volume based cost was assigned to the total wastewater stream in the economic assessment (Humbird et al., 2011) and a 1 kg COD = 0.23 kg methane generic chemical oxygen demand (COD) and biogas relationship used (Humbird et al., 2011). The treated wastewater was assumed clean and recyclable and any shortfalls determined from the mass balance were offset by make-up water.

5.2.4. Parameters for economic evaluation

Equipment sizes and costs were estimated by Aspen Plus® Economic Analyser, apart from specialised units such as reactors, boilers and turbo-generators, which were sized using the short-cut module (factorial) method (Humbird et al., 2011) (see Appendix D-4). The variable operating expenditures (OPEX) were calculated using data from the Aspen Plus® material balances. The operational chemical costs common to the LA scenarios were sulphuric acid catalyst, feedstock, make-up water, boiler and cooling tower chemicals and effluent disposal costs for ash and lime sludge. Scenario C in addition also utilised n-butyl acetate solvent and RuRe (3:4)/C catalyst.

The fixed operating costs were based on rates that reflect an emerging economic environment (Mandegari et al., 2017), with labour overheads at 90% of the total operating labour costs, a maintenance fee of 3% of the inside battery limits (ISBL) and insurance or property taxes at 0.7% of the FCI.

The discounted cash flow rate of return (DCFROR) methodology was used to assess profitability based on the internal rate of return (IRR) and net present value (NPV) on a real term basis, where inflation

(5.7%) was not accounted for. Also considered was a product's required selling price to achieve desired IRRs of 20% (EBRD, 2016) that could attract private investors. Other applied factors for economic evaluation are defined in Table 5-3.

Table 5-3: Economic parameters used for a 2016 cost year analysis (Mandegari et al., 2017; Humbird et al., 2011)

Parameter	**Value used**
Annual operating hours	6480 h (9 months)
Project life (Years)	25
Depreciation	Straight line over 5 years
Salvage Value	0
% Spent in year -2	10
% Spent in year -1	60
% Spent in year 0	30
Start-up time (Years)	2
First year new plant capacity (% design)	50%
Second year new plant capacity (% design)	75%
Working capital (% of FCI)	5%
Income tax rate	28.0%
Inflation rate	5.7%
Cash flow calculations basis/IRR method	Real term
Discount rate (hurdle rate)	9.7%
Electricity price (US$/kWh)*	0.08
LV, HV Levulinic acid market selling price (US$/t)	6500
Gamma valerolactone market selling price (US$/t)*	0.00091
Furfural market selling price (US$/t)*	1207

* Electricity, gamma valerolactone and furfural selling prices were adjusted at a 0.7% inflation rate from their base years to 2016 (USInflationcalculator, 2019).

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5.3. Results and discussion

5.3.1. Summary of the biorefinery capacities, bypass ratios and main products

Table 5-4: Mass and energy balance of all scenarios

			Levulinic acid scenarios				**Baseline**
		Units	A	B1	B2	C	**CHP**
Available feedstock	**To boiler and biorefinery (Wet Mass)**	**t/h**	113	113	49.4	113	113
Feedstock to boiler	**Biomass (Wet Mass)**	**t/h**	49.7	111.8	48.1	44.1	113
	Bypass ratio	**%**	44	97*	97*	39	100
Biorefinery feedstock	**Biomass (Wet Mass)**		63.3	1.2	1.4	68.9	-
Products rates	**Levulinic acid**	**t/h**	7.2	0.14	0.16	7.7[a]	-
	Levulinic acid yield (on cellulose)	**Mol %**	67	67	61	68	-
	Percentage of theoretical max (on cellulose)	**%**	63	63	58	64	-
	Furfural	**t/h**	3.4	0.067	0.075	3.3	-
	Gamma valerolactone	**t/h**	-	-		6.8	-
	Electricity	**MWh**	13.7	45.8	10.1	14.6	61.4
	Electricity to the grid	**MWh**	12.2	44.3	8.5	13	59.6

[a] 98% of the levulinic acid produced was converted to gamma valerolactone

*Although not technically viable due to the small biorefinery capacity, scenarios B1 and B2 were used to demonstrate a plant that produced 0.01% of the global LA volumes.

All scenarios were bioenergy self-sufficient as shown in Table 5-4, with A and C having bypass ratios in the same range at 39-44%, whilst B1 and B2's had a 97% bypass ratio because the scenarios only required 1.2-1.4 t/h feedstock to produce 0.14-0.16 t/h LA for niche markets (Table 5-4). Also see Appendix D-5 for detailed mass and energy balances.

5.3.1.1. Scenarios A and C mass balances

Scenarios A and C had LA product rates of 7.2-7.7 t/h, although 98% of the LA initially produced in scenario C was converted to GVL (6.8 t/h), leaving 0.15 t/h specialty LA whilst A produced LA for a commodity market (47 kt/y), which led to a decline in the LA selling price to 0.00091 US$/t as its production volume was 228% above the current global production capacity of 17.5 kt/y. Similarly, approximately 3.3-3.4 t/h furfural was produced in A and C (see Table 5-3), equivalent to about 22 kt/y, contributing 15% to the global furfural production capacities of 146 kt/y (IAR, 2015b) and assumed not to affect market selling prices. As shown in Table 5-4, the LA molar yields based on cellulose (61–68 mol%) were comparable to the 70 mol% LA yields from paper sludge cellulose based on the Biofine process (Fitzpatrick, 2002), with the minor variances emerging from the different biomasses and cellulose properties (Rackemann and Doherty, 2011).

5.3.1.2. Scenarios B1 and B2 mass balances

Scenarios B1 and B2 (including C) produced 0.14–0.16 t/h LA for niche markets translating to 5.2-5.9% of current global LA capacities (17.5 kt/y) (IAR 2015b), which was assumed not to affect the high LA market selling price. Due to the low LA volumes converted in B1 and B2, only 0.1 t/h of furfural by-product was produced (see Table 5-3).

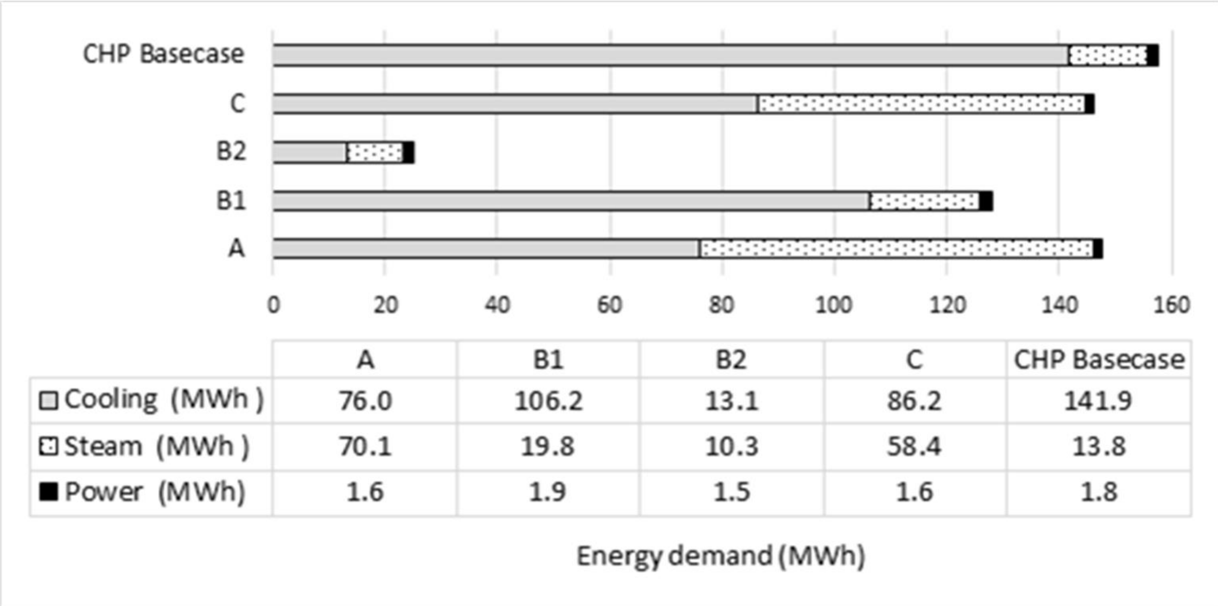
Scenario B1 produced the second highest excess electricity (44 MWh) after the CHP base case as shown in Table 5-3 because B1 combusted 1.2 t/h less feedstock than the CHP base case scenario. The excess electricity in B1 was 26% lower than what the CHP base case supplied to the grid and B1 only used 1.5 MWh electricity for energy needs thus, the high excess electricity generated (44 MWh). On the other hand, scenario B2 was only different from B1 in the amount of electricity produced (10 MWh) as shown in Table 5-4 because instead of using 113 t/h available feedstock, B2 only utilised 49 t/h of the available feedstock to just supply sufficient energy to meet the biorefineries' steam and electricity needs and produce low volume, high value LA, which B1 similarly produced.

5.3.2. Total energy needs per scenario compared to the base case

Figure 5-4 summarises the total energy consumed per scenario compared to the base case combined heat and power (CHP) plant following heat integration by pinch analysis (see Appendix D-6). The cooling demand was highest in all scenarios at 13-142 MWh, followed by steam then electricity.

5.3.2.1. Cooling duty

The trend observed in section 5.3.2 compares well with lignocellulose biorefineries producing sorbitol and glucaric acid (in chapter 4). This large cooling demand was generally due to the energy required to cool the flue gas streams (1-29 MWh), vacuum distillation condensers (1.3-51 MWh) (excluding the CHP base case) and an additional 2.3 MWh used in the distillation columns for GVL production in scenario C. Scenario B1 had the largest cooling demand (106 MWh) and B2 the lowest (13 MWh) among the LA scenarios. Although B1's cooling demand was 34% lower than the CHP base case, their cooling demands were comparable because they had similar CHP plant capacities and bypass ratios, leading to B1 and the CHP base case generating 46 MWh and 61 MWh electricity, respectively (see Figure5-4).



	A	B1	B2	C	CHP Basecase
□ Cooling (MWh)	76.0	106.2	13.1	86.2	141.9
▨ Steam (MWh)	70.1	19.8	10.3	58.4	13.8
■ Power (MWh)	1.6	1.9	1.5	1.6	1.8

Figure 5-4: Total utility demands per scenario excluding 120 t/h sugar mill steam demand

5.3.2.2. Steam demand

Steam demand in scenarios B1 and B2 was comparable to the CHP base case at 10.3-19.8 MWh, whilst that in scenarios A and C was 64-80% higher than the CHP base case due to their larger biorefinery capacities of 63-69 t/h compared to that of scenarios B1 and B2 (1.2-1.4 t/h), which were negligible. Besides the steam requirements in the CHP boiler for all scenarios that accounted for 22-69% of the total demand, scenarios A and C's high demand was as a consequence of the steam demand of the first Biofine process reactor, which consumed 30% of the total steam.

5.3.2.3. **Electricity demand**

Electricity usage in the scenarios was between 1.5-1.9 MWh mainly used to power pumps, compressors and fans. Approximately 149-326 t/h steam (produced from boiler feed water as shown in Table D1-3 of AppendixD-1) was used in the condensing extraction steam turbine in all the scenarios to generate 10-61 MWh electricity as shown in Figure 5-4.

5.3.3. Economic evaluation

5.3.3.1. Capital investment, annual operational and production costs

The total installed cost, fixed capital investment and total capital investment per scenario, excluding feedstock handling are presented in Table 5-5.

Table 5-5: Installed costs, fixed capital investments and total capital investment costs per scenario

Total Capital Investment (US$ million)					
Process Area	**A**	**B1**	**B2**	**C**	**CHP Baseline**
BIOFINE PROCESS					
Feedstock conditioning	9.3	0.7	0.7	8.6	-
Process conversions (Reactors 1 and 2)	10.2	8.9	8.9	10.1	-
Separation and purification	23.6	1.7	1.7	10.9	-
GVL production	-	-	-	17.5	-
Wastewater treatment plant	5.2	0.4	0.4	5.0	-
Boiler + CEST	69.4	70.1[a]	65.4[a]	66.1	73.5
Utilities (6.5% of ISBL)	2.8	0.7	0.7	3.1	4.0*
Storage (5 % of ISBL)	2.2	0.6	0.6	2.4	-
ISBL (Total biorefinery)	**43.2**	**11.3**	**11.3**	**47.1**	
Totals	**122.7**	**83.1**	**78.5**	**123.0**	**77.5**
Total direct costs (TDC)	**130.3**	**85.1**	**80.4**	**131.3**	**77.5**
Total indirect costs	**78.2**	**51.1**	**48.3**	**78.8**	**46.5**
Fixed capital investment (FCI)	**208.4**	**136.2**	**128.7**	**210.1**	**123.9**
Total capital investment (TCI)	**218.9**	**143.0**	**135.2**	**220.6**	**130.1**

*The CHP base case utility cost was the highest because the ISBL was based on the capital investment cost of the Boiler.

[a] Although the bypass ratio of scenarios B1 and B2 were comparable to the CHP base case, their Boiler + CEST capital investments were lower than the CHP base case because the latter used more boiler feed water than B1 and B2 regardless of its energy needs to attain a boiler outlet temperature to 480 °C (64 bar). This therefore, increased the boiler feed water resulting in a larger boiler size and capital cost.

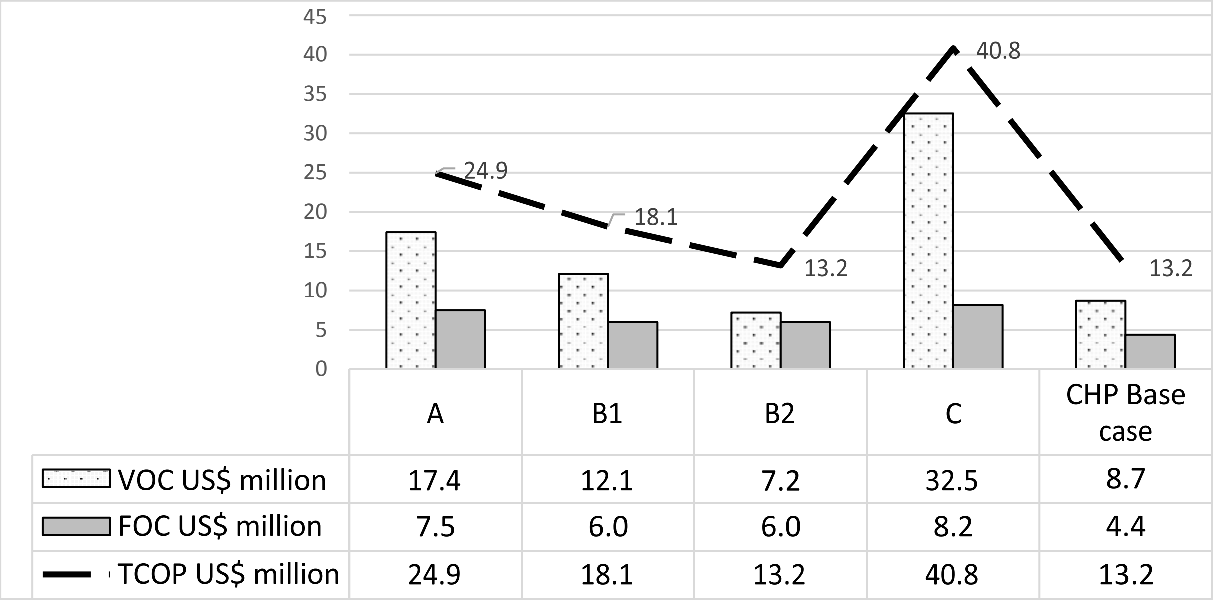
5.3.3.1.1. Total capital investment for scenarios A and C

The total capital investment (TCI) was highest in scenario C at US$ 221 million and A (US$ 219 million) than in B1 and B2 due to the larger reactor and column sizes in A and C designed to accommodate large biomass quantities (Table 5-4). In addition, scenario C also had a GVL process area (Morone et al., 2015) thus attaining the highest TCI. Generally, the TCIs for scenarios A and C were US$ 70-130 million less than other multi-product biorefineries with similar bypass ratios (36-40%) that used biological processes (Nieder-Heitmann et al., 2019; Farzad et al., 2017). This lower TCI can be attributed to the configuration of the Biofine process that is devoid of discrete pretreatment, enzymatic and fermentation units found in biological processes (Nieder-Heitmann et al., 2019; Farzad et al., 2017).

5.3.3.1.2. Total capital investments for scenarios B1 and B2

The order-of-magnitude of the TCIs in scenarios B1 and B2 was similar to the CHP base case owing to their large CHP plants and small sized biorefineries producing LA for niche markets only. Also, as was expected, the CHP plants in all scenarios had the highest capital costs at 30-56% of the total TCI because the condensing extraction steam turbine (CEST) is expensive (Humbird et al., 2011).

5.3.3.1.3. Variable operating costs for all scenarios



	A	B1	B2	C	CHP Base case
▨ VOC US$ million	17.4	12.1	7.2	32.5	8.7
■ FOC US$ million	7.5	6.0	6.0	8.2	4.4
— TCOP US$ million	24.9	18.1	13.2	40.8	13.2

Figure 5-5: Annual variable operating, fixed operating and manufacturing costs for all scenarios

Figure 5-5 summarises the annual variable operating costs, fixed operating costs and total cost of production of the different scenarios. The Biofine process requires minimal raw materials to operate, which mainly comprise biomass feedstock, dilute acid catalyst and a neutralising agent. Lignocellulose feedstock had the largest contribution to the total variable operating costs (VOCs) at 45-65% in scenarios A, B1 and B2. The lignocellulose cost used (US$ 10.79/t) was allocated to the trash only. This was based on the collection and transportation expenses incurred from the fields to the biorefinery and in exchange for this, the sugar mill was provided with 120 t/h steam. For scenario C, n-butyl acetate solvent had the largest contribution of 30% to the total VOC (US$ 33 million/y), a value that would have been higher had the solvent not been purified and recycled.

5.3.3.1.4. Fixed operating costs for all the scenarios

With regards to the fixed operating costs, scenario C had the highest value of US$ 8.2 million/y compared with US$ 6.0-7.5 million calculated for scenarios A, B1 and B2, whilst the CHP base case was at US$ 4.4 million/y as represented in Figure 5-5. Scenario C’s total labour cost was US$ 5.3 million/y since it engaged the largest number of employees (60) than scenarios A, B1, B2 (52) and the CHP base case (13) owing to the GVL production process area.

5.3.3.1.5. Total cost of production and cost per unit product generated

The annual total cost of production, defined as the sum of the variable operating coats, fixed operating costs and annual capital charge, which covers costs for items bought periodically during the year, was highest in scenario C at US$ 41 million/y. This was followed by scenario A at US$ 25 million/y, then B1 at US$ 18 million/y and lastly B2 and the CHP base case with US$ 13 million/y. The CHP base case however had the lowest fixed operating cost because it was devoid of a biorefinery thus, had the lowest labour costs and subsequently lower maintenance, property taxes and insurance costs.

Bozell et al., (2000) and Fitzpatrick et al., (2002) have projected a product cost per unit LA produced via the Biofine process for a 1000 t/day dry feedstock biorefinery to reach 0.00009–0.00022 US$/t. The LA production costs for the integrated scenarios A, B1, B2 and C were US$ 0.00053/t, US$ 0.01964/t, US$ 0.01312/t and US$ 0.00082/t, respectively. Despite similar process configurations and reagents used, the discrepancy can be attributed to economies of scale benefits for the 1000 t/day biorefinery that used dried paper mill waste with an 80% cellulose content (Fitzpatrick, 2002) and may have had a higher operating time. Scenarios A, B1, B2 and C on the other hand, had 16–935 t/day plant capacities for the integrated biorefineries that used bagasse and trash with 41% cellulose content. Additionally, scenarios B1 and B2’s product costs per unit LA generated were significantly higher than the LA selling price of US$ 0.00091/t and the furfural products rates were too low to have a positive impact on profit margins, thus B1 and B2's remained unviable.

5.3.3.2. Profitability of scenarios

A biorefinery's profitability is assessed on its ability to generate a return on investment The economic feasibility of the scenarios are shown in Table 5-6, indicated by the internal rate of return (IRR) and net present value (NPV). The required LA selling price at which a scenario would attract private investment (at IRRs of above 20%) (EBRD, 2016), was also determined.

Table 5-6: Economic analysis of bioenergy self-sufficient levulinic acid scenarios and CHP base case*

	Energy self-sufficient scenarios				
	A	**B1**	**B2**	**C**	**CHP base case**
Total Capital Investment (TCI) (US$ Million)	219	143	135	221	130.1
Net Present value (NPV) (US$ Million)	139	-52	-149	253	6.5
IRR based on adjusted selling prices (%)	17.4	-	-	23	10
Hurdle rate (%)	9.7	9.7	9.7	9.7	9.7
Payback period (years)	8	-	-	6	21

*An economic assessment of the LA-F-E and LA-GVL-F-E scenarios using a 15% working capital (instead of the 5% used in the current study) can be found in Appendix A-2, Table A2-2

5.3.3.2.1. Scenario A's economic viability

Producing LA in large quantities as in scenario A would flood the market leading to a decrease in the selling price to less than US$ 0.00089/t for a continued demand of the product (IAR, 2015a, 2015b). Scenario A produced 47 kt/y LA, 266% of the global production capacities thus transitioned the chemical to serving a commodity market assumed at US$ 0.00091/t selling price (IAR 2015a; 2015b). At US$ 0.00091/t, scenario A was still profitable with an IRR of 17.4%, a net present value (NPV) of US$ 139 million at a 9.7% hurdle rate (see Table 5-5). Its profit margins were increased by the bulk sale of furfural and electricity. Nonetheless, for scenario A to attract private investors (at an IRR ≥ 20%) (EBRD, 2016), an LA selling price of US$ 1080/t (19% above the commodity price) should be attained.

5.3.3.2.2. Scenarios B1 and B2's economic viability

To maintain LA production for a niche market, scenarios B1 and B2 only produced 0.91 kt/y LA and contributed 5.1% of the current global capacities, which was assumed not to affect the current market price. However, scenario B1 and B2 were unprofitable (see Table 5-6) due to the relatively low electricity selling price (US$ 0.08/kWh) (SAPP, 2019), low furfural product rates, high capital investment and production costs of US$ 143 million and US$ 19.6/kg for B1 and US$ 135 million and US$ 13.1/kg for B2 in relation to their low product volumes (0.91 kt/y).

5.3.3.2.3. Scenario C's economic viability

Scenario C was the most profitable and attractive scenario (Table 5-6), attaining a 23% IRR and US$ 253 million NPV at a 9.7% hurdle rate. Scenario C produced 0.14 t/h high value, low volume LA plus 3.3 t/h furfural (15% of current global capacities) and the rest of the LA was converted to bulk gamma valerolactone (6.8 t/h) sold at US$ 993/t, a price more than 50% below the selling price of conventional solvents (de Jong et al., 2012). The revenues from GVL and furfural contributed to scenario C being profitable. Scenario C compares well to a multi-product biorefinery that attained a 25% IRR for producing levulinic acid (US$ 5000/t), succinic acid (US$ 7500/t) and ethanol (US$ 750/t) by processing a 50 t/h mixture of soft woods and wheat straw for an operation time of 7200 h (10 months) (Giuliano, 2016).

5.3.3.2.4. The scenarios' profitability with respect to production volumes

When the global market size of a chemical is limited or market expansion is hindered by the maturity of a technology such as the Biofine process, high volume chemicals for such markets are not desirable. Instead, to increase profit margins, the co-production of a low-volume, high-value chemical besides a high-volume, low-value chemical such as electricity (Nieder-Heitmann et al., 2019) or gamma valerolactone (GVL) is key, as was the case with scenarios B1 and C that produced 44 MWh electricity and 6.8 t/h GVL, respectively, as the high-volume, low-value products. However, the low electricity selling price (US$ 0.08/kWh) compared to the price of GVL (US$ 993/t) led to an unfavorable economic outcome for scenario B1 (-52 US$ million NPV) as well as a low NPV of US$ 6.5 million in the CHP base case. Despite the CHP base case producing 7-12 times more electricity (see Table 5-3) and having the lowest capital investment cost (US$ 130 million) than the LA scenarios, it was marginally profitable with a 10.4% IRR, US$ 6.5 million NPV at a 9.7% hurdle rate and 21 year payback period (Table 5-5). Therefore, currently in a developing country context, a biorefinery‘s profitability lies more in the sale of chemicals sold at international prices rather than in electricity, which has a low regional price. Hence, a scenario must produce just enough electricity for internal consumption with minimal amounts for sale whilst producing multiple bio-based chemicals.

5.4. Conclusions

The impact of levulinic acid production volumes (based on the LA product rates in scenarios A, B1, B2 and C) on its market selling price and economic viability of multi-product lignocellulose biorefineries has been investigated assuming that an LA production volume contributing 10% or more to the total global production capacities would affect the LA market selling price. Increasing LA production volumes has potential to lower the selling price of this niche product; however, producing LA for either niche or commodity markets alongside bulk amounts of furfural and/or gamma valerolactone improves profit margins. This however, is not the case when large amounts of electricity are produced alongside levulinic acid for niche or commodity markets due to the low regional electricity selling price (SAPP, 2019). To this end, scenarios B1 and B2 producing low volume levulinic acid for niche markets, low furfural product rates and saleable electricity (44 MWh and 9 MWh, respectively) were unprofitable, whilst the CHP base case, despite producing the highest amount of saleable electricity (60 MWh), was marginally profitable. But multi-product scenario C producing 0.15 t/h levulinic acid for niche markets, 12 MWh excess electricity plus 6.8 t/h and 3.4 t/h bulk gamma valerolactone and furfural, respectively was the most economically viable investment at 23% IRR and US$ 253 million NPV at a 9.7% discount rate. Scenario A was also profitable at 17% IRR and US$ 139 million NPV for producing 7.2 t/h commodity levulinic acid, 3.4 t/h furfural and 13 MWh surplus electricity although it should sell LA at US$ 1080/t (19 % above the commodity price) to attract private investors at a 20% IRR.

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Supplementary information: Levulinic acid techno-economics in Appendix D

The following data is in Appendix D:

i. Supplementary data regarding this article.

ii. Sensitivity analysis of the LA-F-E and LA-GVL-F-E scenarios

iii. Aspen Plus ® models and unit process conditions

iv. Equipment sizing

v. Mass and energy balances,

vi. Heat integration by pinch analysis of scenarios LA-F-E and LA-GVL-F-E.

vii. Purchased costs and discounted cash flow rate of return spreadsheets

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Chapter 6

6.0 Life Cycle and Sustainability Assessments of Biorefineries Producing Glucaric acid, Sorbitol or Levulinic acid Annexed to a Sugar Mill

Following the techno-economic and social impact assessments of the biorefinery scenarios in chapters 3, 4 and 5, this chapter presents the environmental impacts of these biorefineries in fulfilment of objective 4, which was to conduct environmental and social impact assessments (already covered in chapters 3, 4 and 5) on the profitable scenarios (with the exception of two marginally unprofitable sorbitol and glucaric acid scenarios used for comparative purposes on pretreatment technologies).

This chapter was prepared as a manuscript and has been submitted to the “Journal of Cleaner Production” based on profitable scenarios (with an IRR above 9.7%) or marginally unprofitable scenarios (with IRR below but close to the 9.7% hurdle rate).

Title: *“Life Cycle and Sustainability* Assessments *of Biorefineries Producing Glucaric Acid, Sorbitol or Levulinic acid Annexed to a Sugar Mill”.*

Authors: *Kutemba K. Kapanji, Somayeh Farzad, Johann F. Gorgens*

Objective of dissertation in this chapter and summary findings

Having determined the additional jobs created and the economic viability of different biorefineries configurations in chapters 3-5, the environmental assessment was conducted on the scenarios, to complete the sustainability assessment in fulfilment of objective 4. Presented in this chapter are the environmental impacts of the profitable and marginally unprofitable scenarios for the production of the shortlisted chemicals (sorbitol, glucaric acid and levulinic acid). Polyethylene was significantly unprofitable, therefore, it is excluded from this assessment.

The SO_2-steam explosion pretreated gluacric acid and sorbitol biorefineries had 3–21% more environrmentl loads in abiotic depletion, photochemical oxidation, acidification and eutrophication than those via dilute acid pretreatment due to the associated emissions from the insitu SO_2 production unit. The levulinic acid biorefinery producing levulinic acid, gamma valerolactone, furfural and electricity cogeneration despite having the highest profitability (23% IRR) than the glucaric acid and sorbitol complexes significantly underperformed environmentally as a consequence of the use of hydrogen from natural gas and solvents. A sustainability (economic, social and environmental) assessment of the scenarios revealed that the most sustainable biorefinery was the glucaric acid biorefinery via dilute acid pretreatment followed by the levulinic acid scenario with furfural and electricity cogeneration.

Summary of author's contributions

Kutemba K. Kapanji compiled the data from SimaPro PhD 8.5.2.0 and used it together with literature data to conduct the life cycle assessment, interpret the results and write the chapter. *Somayeh Farzad* assisted in data interpretation and review of the chapter. *Johann F. Gorgens* assisted in data interpretation and reviewed the chapter.

Abstract

To advance the 'green' economy agenda aimed at mitigating environmental impacts, a holistic approach assessing sugarcane biorefineries is vital in establishing their sustainability (economic, environment and social matters). This study evaluates the environmental impact of six (bio)energy self-sufficient biorefineries (S1-S6), annexed to a sugar mill and using sugarcane residues to produce sorbitol, glucaric acid and levulinic acid, along with electricity. Different pretreatment technologies, i.e. SO_2-steam explosion and dilute acid, were investigated for sorbitol and glucaric acid production (S1-S4). Scenario S5 investigated levulinic acid and furfural production via the Biofine process, whereas S6 added the manufacture of gamma valerolactone to S5. Life cycle assessments evaluated using SimaPro PhD 8.5.2.0 and together with inventory data from previous Aspen Plus® v 8.6 models on economic and social impacts were used to evaluate the scenarios' sustainability. Results revealed that dilute acid pretreatment applied in S2 and S4 exhibited 23%-92% lower environmental impacts across most impact categories, compared to S1 and S3 via SO_2-steam explosion, mainly due to reduced SO_2 emissions. With respect to sustainability, S4 producing glucaric acid via dilute acid pretreatment was the most favourable, attaining a US$ 6 million NPV, 10.7% IRR at a 9.7% hurdle rate and created 49 jobs. It was followed by S5, the levulinic acid and furfural biorefinery that provided 52 jobs, attained a 17% IRR and US$ 139 million NPV, whilst S6, despite attractive socio-economic outcomes was the least desirable due to high environmental loads from gamma valerolactone production, associated with the manufacture, transportation and use of n-butyl acetate solvent and hydrogen from natural gas.

Key words: Life cycle assessment, Bio-energy, Glucaric acid, Sorbitol, Levulinic acid, Lignocellulose biorefinery

6.1. Introduction

The growing global environmental concerns including fossil fuels depletion, increased greenhouse gas (GHG) emissions and global warming have led governments to move towards a bio-based "green" economy, one of the key areas identified for sustainable development (Van Dam et al., 2005). Bio-economies have stimulated the advancement of the biorefinery concept, where a range of bio-based chemicals and bio-energy are produced in a single integrated approach (Cherubini, 2010). This approach has received support from governmental initiatives at a local, regional and international level. A local level example has been the formulation of the bio–economy strategy by the South African government in response to this new economy (Department of Science and Technology, 2013). Therefore, with the economic challenges being faced at conventional sugar mills due to fluctuating global sugar market prices, an opportunity exists to revitalise this industry by valorising part of the sugarcane bagasse into chemicals and (bio)energy. This can be realised if inefficient burning of biomass to produce low pressure steam for the mills is mitigated. Additionally, brown leaves can be added to the feedstock mix by adopting green cane harvesting techniques, devoid of burning, which liberates more biomass, part of which is further processed to chemicals and energy (Leibbrandt et al., 2011) and the rest used as a mulch, for water retention in fields.

Whilst biorefineries process different feedstocks including agricultural residues, woody materials, municipal solid waste and food crops (corn, oily seeds, sugar beet and cane) into valuable bio-based chemicals and fuels (Larson, 2006), the use of food crops bring about food-fuel competition (Aden and Foust, 2009). This is despite food crops having environmental benefits over fossil fuels (Soam et al., 2018). To this end, valorisation of non-food second generation (2G) lignocellulosic feedstocks in biorefineries holds promise (Soam et al., 2018), with glucaric acid, sorbitol and levulinic acid selected as examples in the present study. These chemicals have been prioritised as promising products for bio-economies by various studies (Biddy et al., 2016; Bozell and Petersen, 2010; Werpy and Petersen, 2004).

Glucaric acid is used in the pharmaceuticals and detergent industries, as a corrosion inhibitor, de-icing agent and precursor to adipic acid production, a key nylon-66 polymer (Polen et al., 2013). Glucaric acid's market size is growing and projected to exceed US$ 1.3 billion by 2025 (Grand View Research, 2017), due to its demand in the phosphates industry. Its' current production capacities from monomeric sugars (e.g. glucose) are estimated at 50 kt/y, with Renewables Inc. and Rennovia being the key players, based on limited information in the public domain. Sorbitol's market size is expected to reach US$ 2.7 billion by 2024 (IAR, 2015). Sorbitol, with a market selling price of US$ 655/t (Taylor et al., 2015), finds use in the food, cosmetics and pharmaceuticals industries (Isikgor and Becer, 2015) and the current production capacities stand at approximately 1500 kt/y (IAR, 2015). Levulinic acid's global production capacities stand at 18 kt/y and it has over 60 applications because of its several functional groups that enable it to react and transform into different products (Rackemann and Doherty, 2011). Currently, it is a specialty chemical with a US$ 33 million market size and 5000-8000 US$/t selling price (Grand View Research, 2017).

Life cycle assessment (LCA) is a useful management tool that is currently being used increasingly to measure environmental impacts (Eksi and Karaosmanoglu, 2018). Recently, LCAs on biorefineries have emerged including those using sugarcane bagasse as feedstock to produce, bio-ethanol (Botha and von Blottnitz, 2006), n-butanol, furfural, lactic acid and ethanol, with electricity (Farzad et al., 2017), although uncertainty analysis has been omitted. Regarding LCAs for 2G (bio)energy self-sufficient integrated biorefineries producing glucaric acid, sorbitol and levulinic acid, few in depth studies have been conducted as summarised hereafter.

A sustainability study on a glucaric acid biorefinery from corn stover, which partly used natural gas to meet energy needs has been undertaken, but only focused on CO_2 emissions (1675-2150 kg/t glucaric acid CO_2 emissions) and water mass balance (Thaore et al., 2019). An LCA by Akmalina, (2019) on a standalone biorefinery producing sorbitol from first generation (1G) glucose used six impact categories with a global warming potential of 3.55 kg CO_2 eq./kg sorbitol being reported as the most significant impact. Moreno et al., (2020), also conducted an LCA on sorbitol production from corn starch (1G), using six impact categories. Significant carbon footprints were attributed to starch production and sorbitol purification. Also, levulinic acid LCAs have been conducted on standalone processes by Isoni et al., (2018) and Hafyan et al., (2020), where the starting material was palm oil/rice straw and palm oil's empty fruit bunch, respectively. Environmental impacts were reported in terms of GHG emissions, with Hafyan et al., (2020) recording 6.3 kg CO_2 eq./kg levulinic acid. Lastly, an LCA on levulinic acid conversion to GVL using a solvent free method has been reported based on generated laboratory scale data (Van Slagmaat et al., 2019).

Against this backdrop, the present study's contribution is to use eleven impact categories and compare the environmental impacts of bio(energy) self-sufficient biorefineries on glucaric acid, sorbitol (chapter 4) and levulinic acid production using 2G feedstocks and annexed to a conventional sugar mill (chapter 5), as no such detailed studies including uncertainty analysis exist. Two lignocellulose pretreatment methods, i.e. SO_2-catalysed steam explosion and dilute acid pretreatment, prior to enzymatic hydrolysis and product conversion, were compared on an environmental basis for the sorbitol and glucaric acid scenarios. The combination of LCAs with published techno-economic and social impacts of the chemicals under consideration will determine which scenarios are preferred in terms of sustainability, a holistic approach not extensively conducted on the shortlisted chemicals.

6.2. Materials and methods

Mass and energy balances of the scenarios used in this study were based on data generated in Aspen Plus® v 8.6 used in previously-published techno-economic assessments (TEAs) for sorbitol, glucaric acid and levulinic acid production (chapters 4 and 5). Tables E1-1(a) and (b) of the supplementary information (Appendix E-1) have summarised the TEAs, job creation potential (social impact), mass and energy balances of the various scenarios from chapters 4 and 5.

This LCA study was based on the International Organisation for Standardisation (ISO) 14040 (ISO 2006a) and 14044 (ISO 2006b) guidelines that account for the energies and material input and outputs of a product's life (USA Environmental Protection Agency, 2006).

6.2.1. Description of scenarios

The environmental impact assessment was conducted for six integrated biorefinery complexes based on data from Aspen Plus models producing platform chemicals glucaric acid, sorbitol and levulinic acid (produced with furfural by-product and derivative gamma valerolactone) (chapters 4 and 5). Figures 6-1 and 6-2, show simplified flow diagrams of the different configurations including their major inputs and outputs.

A feedstock capacity of 113 t/h (wet mass basis) comprising sugarcane bagasse (70%) and brown leaves from fields (30%) was applied in the current study (chapters 4 and 5) at sugarcane biorefineries where green harvesting techniques were practiced and the burning of sugarcane fields avoided.

6.2.1.1. Sorbitol and glucaric acid scenarios

The techno-economic and social assessments of the sorbitol and glucaric acid scenarios (in chapter 4) used in this LCA study, included two pretreatment procedures. Scenario 1 (S1) and 3 (S3) applying SO_2-steam explosion (Sorbitol.$_{\mathrm{STEX}}$ and Glucaric.$_{\mathrm{STEX}}$) (Bura et al., 2003) whilst scenarios 2 (S2) and 4 (S4) were via dilute acid (Sorbitol.$_{\mathrm{DA}}$ and Glucaric.$_{\mathrm{DA}}$) (Humbird et al., 2011) prior to enzymatic hydrolysis (see Figure 6-1). Glucose produced in the Aspen Plus® models after enzymatic hydrolysis was then hydrogenated or oxidised to commercial grade sorbitol or glucaric acid (at 70 wt% purity) (Marques et al., 2016) respectively (see Figure 6-1). The economic allocation and environmental impact was only based on the final sorbitol and glucaric acid amounts and other components not considered. From the Aspen models, excess electricity in S1-S4 was between 11-14 kWh, values that were reduced to ensure that minimal amounts were sold as electricity sales did not significantly improve profit margins (chapter 4).

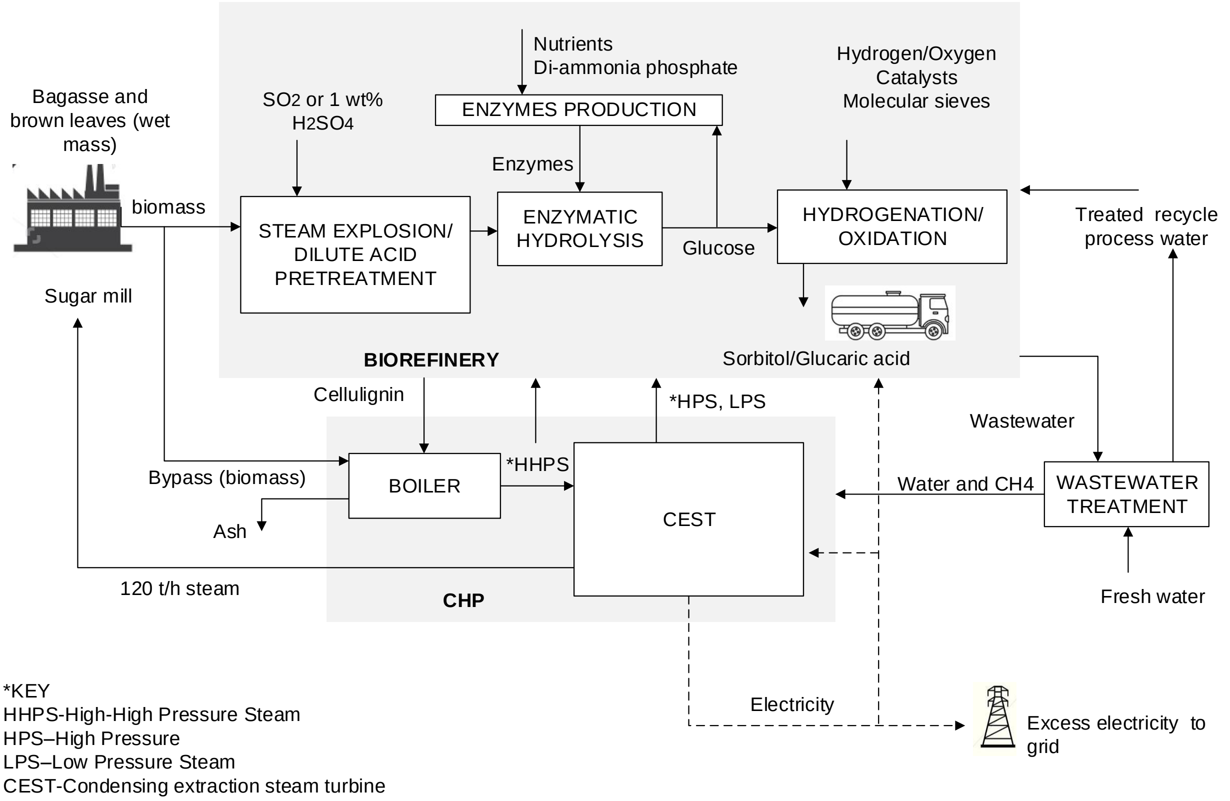


Figure 6-1: Generalised process flow diagram showing an integrated biorefinery with two different pretreatment options for the sorbitol (S1-S2)/glucaric acid (S3-S4) biorefineries along with electricity (chapter 4)

According to chapter 4 results, S1 (Sorbitol.$_{\mathrm{STEX}}$) and S3 (Glucaric.$_{\mathrm{STEX}}$) were marginally unprofitable with NPVs of -12.8 and –12.3 US$ million respectively, whereas S2 (Sorbitol.$_{\mathrm{DA}}$) and S4 (Glucaric.$_{\mathrm{DA}}$) were marginally profitable with NPVs of US$ 16-17.2 million, 10.7% IRR at a 9.7% discount rate and created 49 jobs, based on a sorbitol and glucaric acid (assumed) selling price of US$ 655/t (see chapter 4 and Table E1-1(b) of Appendix E1).

6.2.1.2. Levulinic acid scenarios

The techno-economic and social assessments of the levulinic acid scenarios 5 (S5) and 6 (S6) (chapter 5) used in the LCA were based on the Biofine process (Girisuta 2007). Distillation was used to purify levulinic acid (to 98 wt% purity) and 13.9-14 kWh sellable electricity generated. As shown in Figure 6-2(a), S5 (LA-F-E) produced bulk levulinic acid (7.2 t/h) for commodity markets, furfural by-product and electricity. Scenario S6 (LA-GVL-F-E) outlined in Figure 6-2(b) produced levulinic acid (0.15 t/h) for a niche market, furfural, electricity and bulk gamma valerolatone (GVL) (6.8 t/h) from > 95% of the diverted levulinic acid crude stream (see mass balances in Table E1-1(a)). Crude levulinic acid was hydrogenated to GVL and its process involved the use of hydrogen from natural gas and solvent extraction using n-butyl acetate, together with distillation techniques (Murat Sen et al., 2012). On a techno-economic and social perspective, S5 and S6 outperformed S1-S4, attained IRRs of 17% and 23% respectively and created 52-60 jobs, with NPVs of US$ 139-253 million at a 9.7% discount rate (chapter 5) as shown Table E1-1(a).

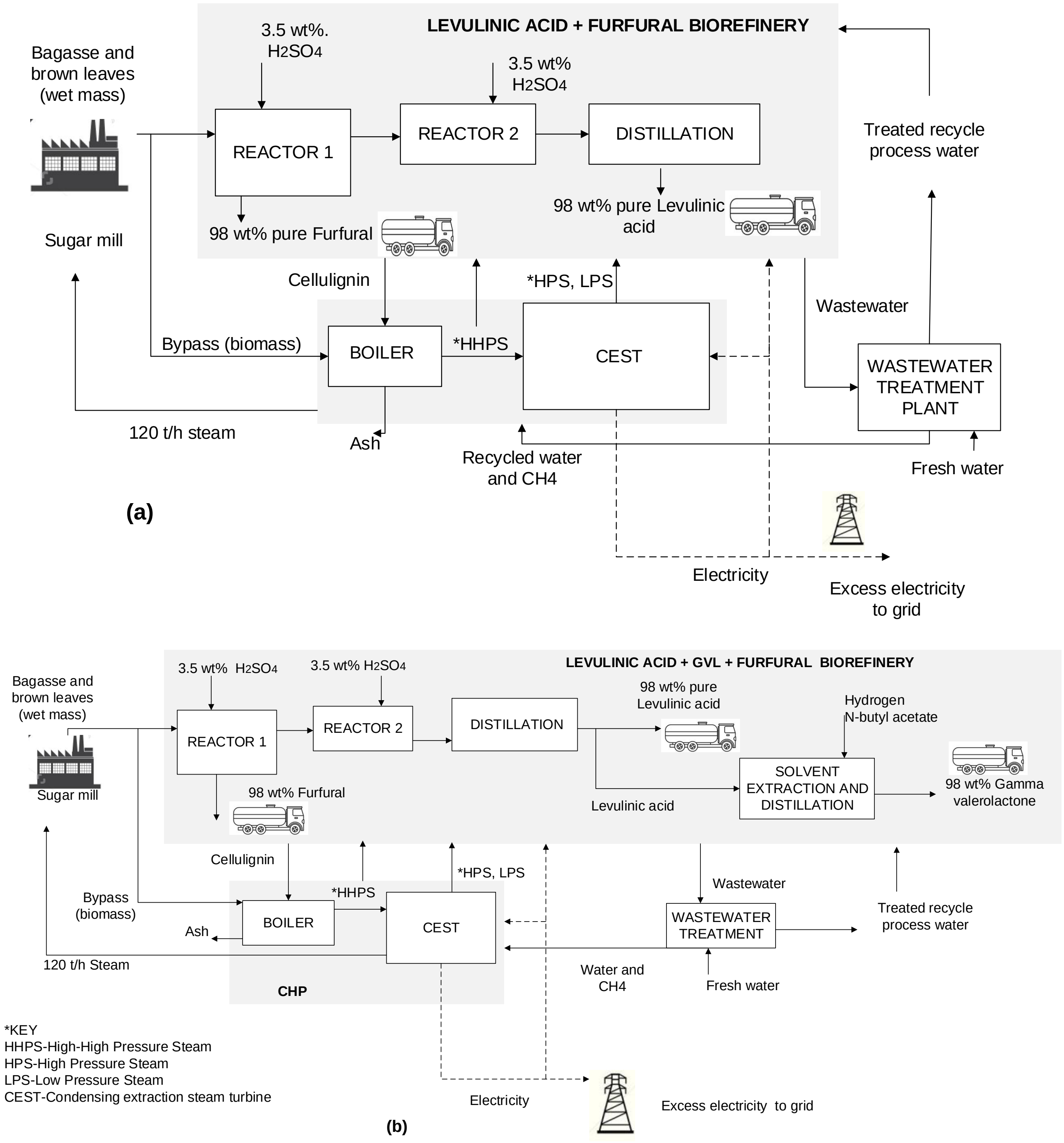


Figure 6-2: Integrated biorefineries producing sellable electricity with a) levulinic acid and furfural (S5) and b) levulinic acid, gamma valerolactone and furfural (S6) (from chapter 5)

6.2.1.3. Combined heat and power plant

The scenarios met their energy needs by cogenerating steam and electricity simultaneously in a condensing extraction steam turbine (CEST) that forms part of a combined heat and power (CHP) plant (see Figure 6-3). Figure 6-3 summarises the energy interactions of the biorefinery, sugar mill and CHP plant plus the fuel sources used. The CHP plant was integrated to each biorefinery and fed with a bypass stream (a ratio expressed as a %) of part of the brown leaves and bagasse (with 50% inherent moisture, wet mass basis) (D) to meet the processes energy needs. Cellulignin from the processes and bio-methane from the wastewater treatment (WWT) plant (H) were additional fuel sources used, thus eliminating fossil fuels and making the scenarios (bio)energy self-sufficient (see Table E1-2 in supplementary information) for the quantitative energy (A-H) process inputs). The integrated biorefineries were annexed to an existing sugar mill and supplied the mill with 120 t/h of high pressure steam at 340 °C and 28 bar (chapters 4 and 5), whilst excess electricity (C) was sold off.

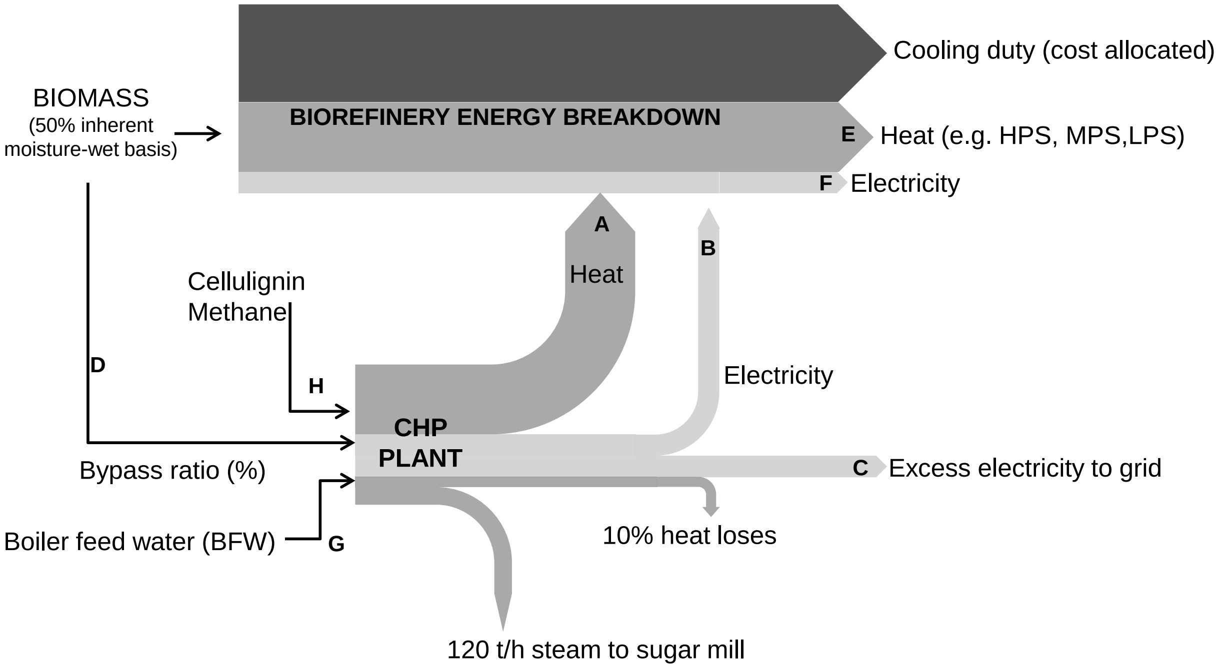


Figure 6-3: Energy flow system of the biorefinery, sugar mill and combined heat and power plant

6.2.2. Purpose, scope and functional unit

The purpose of this study was to evaluate the environmental viability of six (bio)energy self-sufficient lignocellulosic biorefineries annexed to a conventional sugar mill, producing sorbitol, glucaric acid or levulinic acid (as well as furfural and gamma valerolatone) with electricity cogeneration. An attributional life cycle assessment approach was applied for comparative purposes of scenarios to avoid complexities associated with consequential analysis where environmental impacts become responsive to potential policy decisions (McManus and Taylor, 2015).

The scope of this LCA was a “cradle” to “factory gate” system boundary (Figure 6-4), which comprised sugarcane cultivation, greencane harvesting, transportation, sugar milling, biorefinery, wastewater treatment unit receiving all waste streams and a combined heat and power (CHP) plant.

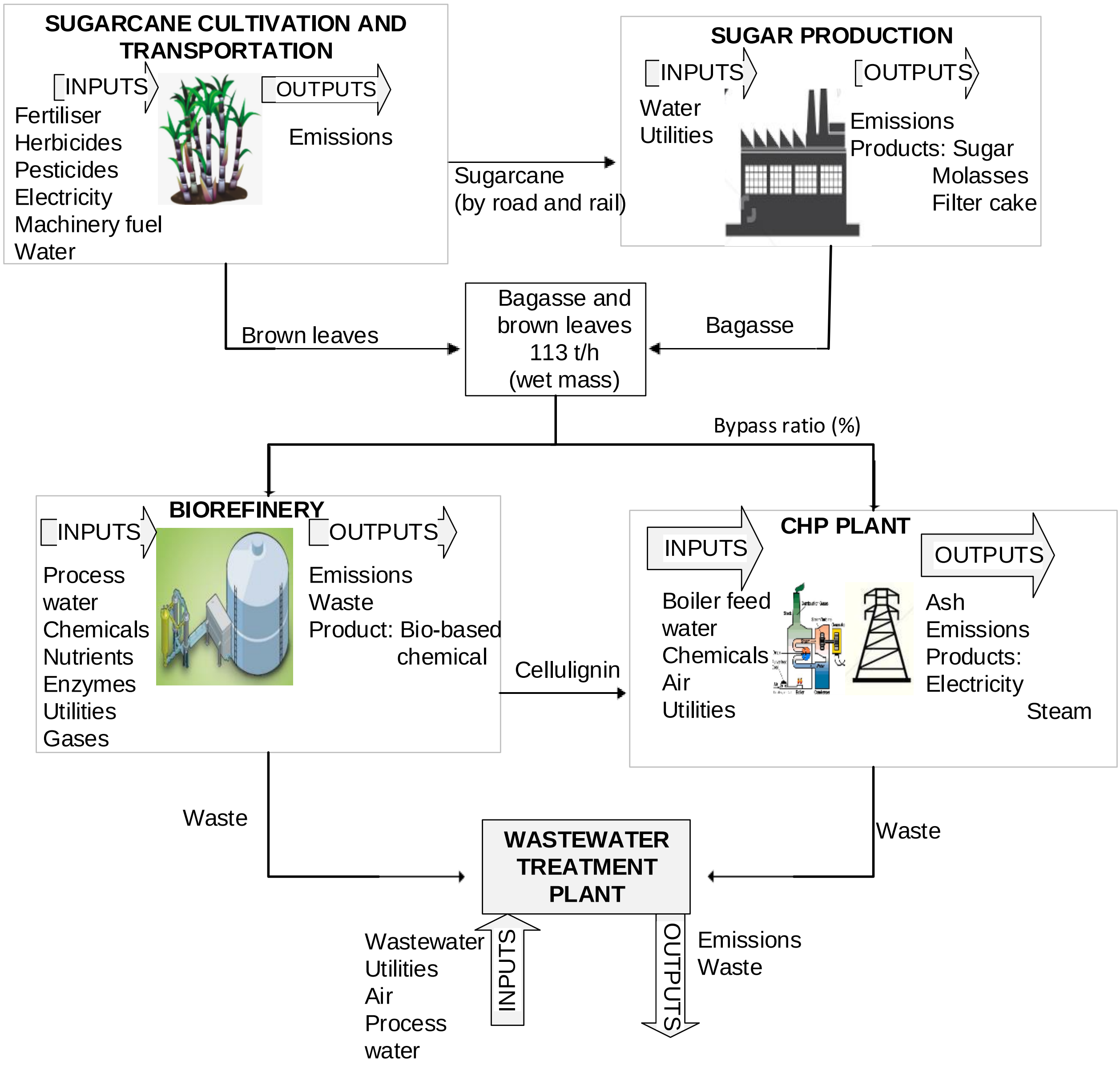


Figure 6-4: The “cradle” to “factory gate” system boundary used in this study

The functional unit was “a biorefinery processing 113 t/h (wet mass basis) of sugarcane bagasse and brown leaves into bio-based chemicals and bio-energy” while results of the environmental loads were given for 1 kg product or 1 kWh electricity.

6.2.2.1. Life cycle inventory, impact assessment method

The process network was built on the Eco-invent v.3-allocation, cut off by classification-unit library, to generate the life cycle inventory assessments and water footprints. The life cycle impact assessment (LCIA) and default characterisation method CML-IA baseline V3.05/EU25 were applied. The CML-IA midpoint approach comprising 11 impact categories has also been used in previous biorefinery studies (Farzad et al. 2017). The categories are abiotic depletion potential (ADP), abiotic depletion on fossil fuels, global warming potential (GWP_{100a}), eutrophication potential (EP), photochemical oxidation potential (POCP), acidification potential (AP), ozone layer depletion (ODP), marine aquatic ecotoxicity, terrestrial ecotoxicity, fresh water aquatic ecotoxicity and human toxicity (HT).

The water footprint was based on Eco-Indicator 99 v1.02 (Pfister et al., 2009), a damage-oriented approach defining an endpoint level, with single characterisation scores on human health, eco-system quality and resources. Conversely, AWARE v1.01 method, an environmental problem-oriented (midpoint) indicator was used to assess water usage. It assesses water depravity potential per area following usage by humans and ecosystems (Boulay et al., 2017) assuming that the less water remaining available per area, the more likely another consumer will be deprived (Boulay et al., 2017).

6.2.2.1.1. Life cycle inventory data source

Sugarcane cultivation and sugar production were based on input data from Mashoko et al., (2010), Mashoko et al., (2013) and Farzad et al., (2017) and adjusted to a conventional South African sugar mill processing 300 t/h sugarcane over a 9 month crushing period (Mandegari et al., 2017) (see Appendix E1, Table E1-3). Data for the biorefinery, CHP plant and WWT unit (based on the chemical oxygen demand (COD) measure and methane produced) were derived from Aspen Plus® v 8.6 (chapters 4 and 5) and Mandegari et al., (2017).

The following assumptions were applied to the life cycle assessment for all scenarios (where applicable):

i) Green harvesting techniques were applied, whereby sugarcane burning during harvesting was avoided leading to a reduction of particulate matter and air emissions. Part of the preserved leaves from the field was used as a mulch and the other combined with sugarcane bagasse as biorefinery feedstock (113 t/h wet mass) (Farzad et al., 2017).

ii) Collection of 25 t/h brown leaves from the field was 100 % by road. A 25 km in-field and 25 km average distance from the plantation to the biorefinery was considered, based on 1.08 MJ/tkm energy requirement per truck (Farzad et al., 2017).

iii) Steam and electricity requirements of the sugar mill were considered intermediate streams supplied by the CHP plant, since high pressure steam is also used for electricity generation at the mills and biorefineries.

iv) There was no coal supplementation in S1-S6 although hydrogen gas assumed to come from natural gas was used in S1, S2 and S6.

v) The uptake of CO_2 during cultivation was not included in the agriculture economic systems (Renouf et al., 2010) as ReCiPe methods account for this. The S1-S6 and CHP plant's CO_2 emissions from biomass to air were biogenic as they came from a renewable feedstock.

6.2.2.1.2. Allocation factor

The economic allocation factor applicable to processes with multiple products was implemented to partition the input-output flows and environmental burden according to the value and quantity of co-products (see Table E1-4 in Appendix E1). This was done because the physical allocations (by mass or energy) cannot reflect the basic relationships between co-products in economic-value driven multi-product biorefinery complexes (Farzad et al., 2017).

6.2.2.1.3. Sensitivity and uncertainty analysis

A sensitivity analysis on the characterisation model, available in the supplementary information (Figure E1-2), was used to establish the robustness of the LCA findings to the LCIA choice of methodology (CML-IA) used in this study, which was compared to IMPACT 2002+ V2.14 method used in LCAs on sorbitol (Akmalina, 2019) and levulinc acid (Isoni et al., 2018) production. Additionally, the effects of process water on energy needs was briefly discussed.

To increase the transparency of the LCA data and results for the support of policy and decision making, an uncertainty analysis using scenario analysis was conducted on the biorefinery based mostly on uncertainties in input parameters due to the non-availability of quantitative uncertainty studies on variables used. It was followed by a propagation of uncertainties to the Aspen Plus® model outputs (details in Tables E1-12-E1-14) by determining the uncertainty using a worst and best case from the baseline.

6.3. Results and discussion

Environmental profiles of the investigated biorefineries including contributions of each product stage to the impact categories, are presented in Figure 6-5. A summary of each scenario's environmental burdens are tabulated in Table E1-5 to E1-10 of the supplementary information. The environmental contributions of sugarcane cultivation and milling were common to all scenarios and dominant across all scenarios except in S6. Since all scenarios processed 113 t/h bagasse (wet mass) and the unit of bagasse processed was defined as the functional unit, agricultural inputs were broadly similar. Therefore, major differences in the environmental impacts originated from the biorefinery, CHP and WWT plants. Without considering the environmental burden of sucrose production (outside the scope), which had the highest economic allocation of 88% (see Table E1-4 of Appendix E-1), it was observed that generally, environmental loads in sugarcane cultivation, milling and combustion (flue gas emissions and ash) significantly contributed to the impacts. The exception was S6, where GVL production dominated as shown in Figure 6-5(f). Sugarcane cultivation and milling's environmental impacts have been attributed to excessive consumption of herbicides, N/P fertilisers and diesel used in machinery and transportation (Cherubini & Strømman, 2011; Mashoko et al., 2010). Therefore, good management of agricultural activities can mitigate some of these impacts.

Environmental profiles of the investigated biorefineries including contributions of each product stage to the impact categories, are presented in Figure 6-5. A summary of each scenario's environmental burdens and uncertainties is shown in Table E1-5 to E1-10 of the supplementary data. Environmental contributions from sugarcane cultivation and milling were common to S1-S6 and dominant across S1-S5 except in S6. Since all scenarios processed 113 t/h bagasse (wet mass) and the unit of bagasse processed was defined as the functional unit, agricultural inputs were broadly similar. Therefore, major differences in the environmental impacts originated from the biorefinery, CHP and WWT plants. Without considering the environmental burdens of sucrose production (outside the scope) that had the highest economic allocation of 88% (see Table E1-4), it was observed that generally, environmental burdens in sugarcane cultivation, milling and combustion (flue gas emissions and ash) significantly contributed to the impacts, except in S6 where GVL production dominated (see Figure 6-5(f)). Sugarcane cultivation and milling's environmental impacts have been attributed to excessive consumption of herbicides, N/P fertilisers and diesel used in machinery and transportation (Mashoko et al., 2010). Therefore, good management of agricultural activities can mitigate some of these impacts.

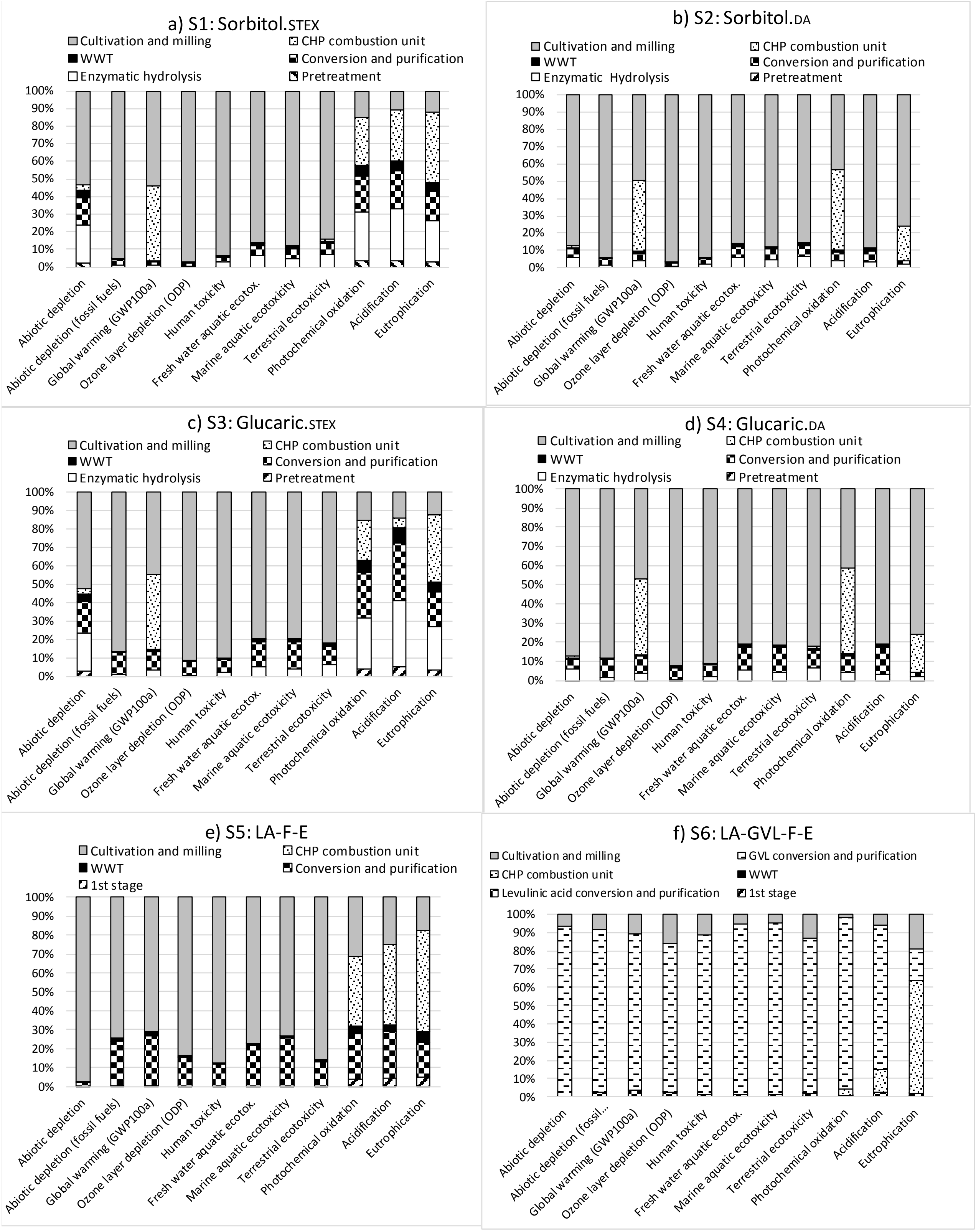


Figure 6-5: Characterised LCIA biorefinery profiles for S1-S6

As demonstrated in Figure 6-5(a), for S1 (Sorbitol.$_{\text{STEX}}$), sugarcane cultivation and milling contributed about 53-97% to all impact categories except in POCP, AP and EP where it delivered

11-14% of the environmental impacts. The main contributor (> 90%) to the ODP, ADP, ADP fossil fuels and GWP_{100a} was air emissions of sulphur dioxide (SO_2), nitrous oxides (NO_x) and carbon dioxide (CO_2) from fossil fuels consumption during cane harvesting and transportation. Impacts from sugarcane harvesting were minimised because of avoided emissions from green cane harvesting practices. Human exposure to metal ions such as antimony found in ash landfills was the main cause of HT. On the other hand, the combustion unit in S1 (Figure 6-5a) contributed 26-40% to GWP_{100a}, EP, AP and POCP as a consequence of CO_2, N_2 and SO_2 gas emissions, whilst it delivered less than 5% of the impacts across the other categories. Enzymatic hydrolysis contributed 21-29% to ADP, POCP, AP and EP and less than 8% to the ecotoxicities and HT. A major contributor to AP and POCP was SO_2 emitted to the air, whereas EP originated from the release of di-ammonium phosphates to water and N_2 to air during enzyme production and hydrolysis. This contribution to eutrophication from enzymatic hydrolysis in the current study is comparable to the 18-20% in a sugar mill biorefinery producing ethanol (Mandegari et al., 2017). Furthermore, glucose conversion and purification to sorbitol contributed 17-22% to ADP, POCP, AP and EP as demonstrated in Figure 6-5(a) and 3-8% across other impact categories. The utilisation of raw sulphur to produce SO_2 for the gas catalysed steam explosion was the main cause of ADP whilst flue gas emissions of SO_2 and N_2 caused POCP, AP and EP. The contribution of N_2 to POCP, EP and AP is mainly as a result of its conversion to NO_x and NH_3

Biorefinery S2 ($Sorbitol._{DA}$) demonstrated in Figure 6-5(b), showed similar trends to S1 in most of the impact categories (ADP fossil fuels, ODP, HT and ecotoxicities). However, when compared to S1, significant differences (24% increase) in the CHP unit's impact on POCP and a 22-27% decrease in the AP and EP were observed. The increase in POCP could be attributed to an increased in the total N_2 in the flue gas. The reduction in AP and EP from the CHP unit in S2 was due to a decline in the N_2 gas emissions and insignificant SO_2 amounts in the flue gas, due to the absence of an *in situ* SO_2 production unit. Additionally, the absence of sulphur and an SO_2 production unit in S2, which led to less SO_2 and N_2 gas emissions reduced the ADP, POCP, EP and AP. It was generally observed that the conversion and purification stage, enzymatic hydrolysis and SO_2-steam explosion pretreatment (though the overall pretreatment contributions were less than 5%) led to higher impacts in ADP, POCP, AP and EP for S1 than S2, whilst the ecotoxicities, HT, ADP fossil fuels and ODP were similar in the two scenarios. The total GWP_{100a} in S1 was 6.7 kg CO_2 eq./kg sorbitol ± 0.5 kg CO_2 eq./kg sorbitol and 12.6 kg CO_2 eq./kg ± 0.2 kg CO_2 eq./kg sorbitol for S2, which was the third highest impact after marine aquatic ecotoxicity and abiotic depletion fossil fuels.

Although LCA comparisons with other studies pose challenges due to variations in methods, allocations and scope, the environmental impacts in a stand-alone sorbitol production process from 1G glucose conducted by Akmalina, (2019) reported a total GWP_{100a} of 3.55 kg CO_2 eq./kg sorbitol. The lower GWP_{100a} of that study compared to S1 and S2 can be justified by a larger system boundary of the current study (comprising pretreatment, hydrolysis, CHP and WWT). The other impact categories EP, AP, POCP, ADP and ODP in comparison to the GWP_{100a} were minimal in the research by Akmalina, (2019) but similar orders of magnitude of these impacts were obtained in this current study. Furthermore, an LCA on sorbitol production by Morone et al., (2020) based on the ReCiPe methodology and Gabi 7.3 LCA software reported that starch usage (cultivation) was the main contributor to HT, AP and particulate matter formation, with contributions to cultivation from HT and AP being in agreement with this current study. Both studies also acknowledged a significant environmental impact of using hydrogen from fossil fuels and the high energy demand from the conversion and evaporation units in the hydrogenation process (chapter 4).

As demonstrated in Figure 6-5(c), the environmental burdens for S3 ($Glucaric._{STEX}$) were mostly attributed to cultivation, milling, CHP combustion, conversion, purification and enzymatic hydrolysis. The CHP unit contributed about 22-40% to GWP_{100a}, EP and POCP whilst it delivered less than 5% across other categories. The major cause of GWP_{100a} and POCP in the CHP unit was the release of biogenic CH_4 gas to the atmosphere, whereas EP was attributed to N_2 gas emissions. Glucaric acid conversion and purification accounted for 15-32% of the burdens across fresh water and marine aquatic ecotoxicities, ADP, POCP, AP and EP though it delivered 7-11% across the other categories. This was attributed to nickel, selenium, cobalt and vanadium discharged to waste streams including metal ions originating from ion exchange resins, activated carbon and catalysts (Pt/C) that contributed to the ecotoxicities. Additionally, hydrogen fluoride (HF) and beryllium emissions to air significantly impacted marine-and fresh water-aquatic ecotoxicities. Sulphur used in SO_2 production was the major contributor to ADP whereas POCP, AP and EP were as a consequence of SO_2 and N_2 emissions to air. Conversely, enzymatic hydrolysis contributed 20-34% to ADP, POCP, AP and EP with the highest impact of 35% being in AP caused by nitrous oxides and ammonia flue gases including SO_2 air emissions mostly originating from the *in situ* SO_2 production plant.

Considering S4 ($Glucaric._{DA}$) demonstrated in Figure 6-5(d), apart from sugarcane cultivation and milling contributions, 20-45% of the environmental impacts (GWP_{100a}, POCP and EP) were from the combustion unit. The conversion and purification stage delivered 10-17% across all categories except in ADP, ODP, HT, POCP and EP, where the impacts were less than 5%. Glucaric acid scenarios S3 and S4, despite having similar trends across most impacts, showed significant differences in ADP, POCP, AP and EP for the CHP combustion unit, enzymatic hydrolysis as well as the conversion and purification stages. This could be attributed to a higher bypass ratio required in S4, due to increased process energy demands. Similar to S2, an absence of sulphur in the production stages of S4 resulted in lower contributions from the conversion and purification stage and enzymatic hydrolysis to ADP, POCP, AP and EP. The overall GWP_{100a} for the glucaric acid scenarios was comparable, with S3 and S4 emitting 14 kg CO_2 eq./kg glucaric ± 0.8 kg CO_2 eq./kg glucaric acid and 13.3 kg CO_2 eq./kg glucaric acid ± 0.4 kg CO_2 eq./kg glucaric acid, respectively.

An LCA conducted by Thaore et al., (2019) on glucaric acid production from corn stover estimated the total GHG emissions at 1675 kg CO_2 eq./kg glucaric acid, with the main contributors being potassium hydroxide, corn stover, ammonia, cellulase enzymes and natural gas. Besides the differences in allocations, scope and process configurations, the use of biomass only as a source of energy (except in the sugar mill) in the current study significantly reduced GWP_{100a} impact. Also studies have indicated that sugarcane cultivation consumes less fertilisers and herbicides than corn agriculture, which therefore mitigates some environmental impacts in sugarcane cultivation (Luo et al., 2009).

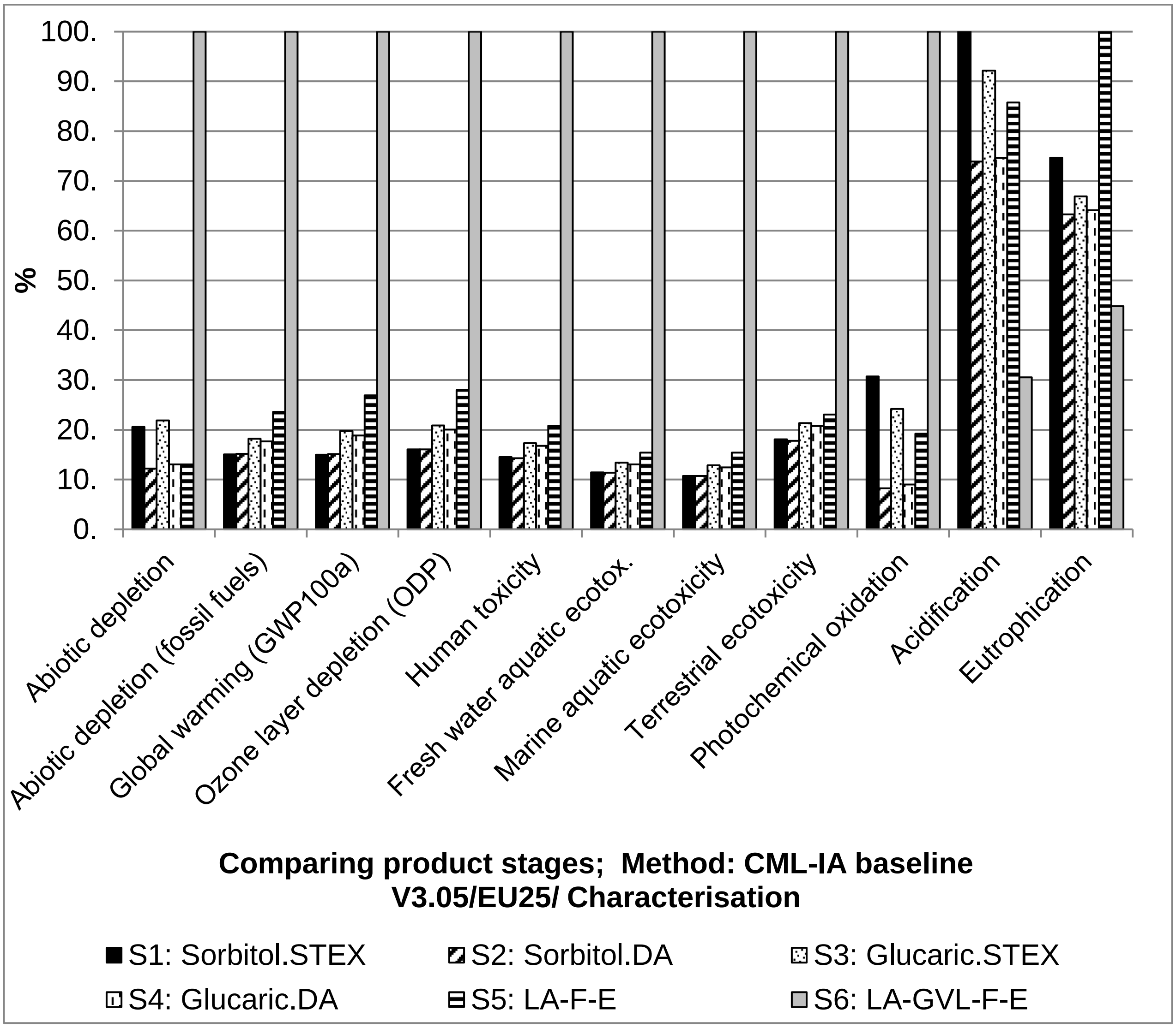
For the levulinic acid scenario S5 (LA-F-E) shown in Figure 6-5(e), the major environmental burdens apart from cultivation and milling impacts originated in part from biomass combustion contributing 37-52% to POCP, AP and EP due to flue gas emissions (CO_2, CH_4, SO_2 and N_2). This was followed by levulinic acid conversion and purification that contributed about 22-27% to ADP fossil fuels, fresh water aquatic and marine aquatic ecotoxicities, POCP, AP, EP and GWP_{100a}. The impact on ADP fossil fuels was due to the usage of natural gas, crude oil, coal and energy (oil) from the associated processes whereas the POCP and AP impacts were as a consequence of SO_2 emissions to air. Flue gases N_2 and CO_2 were mainly responsible for AP and GWP_{100a} respectively. The total GWP_{100a} in S5 was 8.8 kg CO_2 eq./kg levulinic acid ± 0.4 kg CO_2 eq./kg levulinic acid. An existing LCAs by Hafyan et al., (2020) on levulinic acid production from empty fruit bunch calculated a GWP_{100a} of 6.3 kg CO_2 eq./kg levulinic acid, with the largest impact attributed to the levulinic acid process itself where heat consumption was a major cause of GWP_{100a}. Based on their process configuration, acid hydrolysis, enzymatic production and saccharification stages had minimal contributions to GWP_{100a} (Hafyan et al., 2020). Eliminating sugarcane cultivation and biomass combustion in our study, then the 1st acid hydrolysis step of the Biofine process, a two-stage dilute acid production process would have minimal GWP_{100a} contributions and thus be in agreement with findings by Hafyan et al., (2020).

Biorefinery S6 (LA-GVL-F-E)'s major environmental burdens as shown in Figure 6-5(f) were derived from gamma valerolactone (GVL) production and purification with 78-93% contributions across all impact categories except in EP, where the impact was below 18%. The CHP unit's only significant contribution of 61% was in EP caused by phosphates discharged to water. A major contributor to ADP in GVL production was the release of cadmium and lead, whilst ADP fossil fuels' impact was from crude oil, natural gas and coal usage in the indirectly associated processes. The POCP at 89% was attributed largely to propene gas, 1-butanol and SO_2 emissions to air, whereas about 84-93% of contributions to the ecotoxicities were as a consequence of nickel, beryllium, vanadium, cobalt, barium and chromium VI discharged to water bodies and mercury to air. The ODP was attributed to methane, bromotrifluoro- and halon 1301 (from associated processes) air emissions, while AP resulted from SO_2 gas emissions. A major cause of EP was phosphates discharged to water and 85% of GWP_{100a} in the GVL production and purification stage was attributed to CO_2 gas emissions associated with the production and transportation of n-butanol (Pereira et al., 2014), a reagent used in manufacturing n-butyl acetate (Bories et al., 2018). The bulk of the crude levulinic acid product (> 95%) was converted to GVL, and a minimal amount reserved for a niche market (chapter 5) thus the higher contributions in the GVL production and purification stage. The GWP_{100a} from the production and purification stage was insignificant as demonstrated in Figure 6-5(f).

A study by Isoni et al., (2018) investigated LCAs of levulinic acid production from rice straw and palm oil in three Southeast Asian countries (using mass allocation and IMPACT 2002+) and attributed 25-52% of GWP_{100a} to agriculture. In this current study, cultivation and harvesting (agriculture)'s contribution to GWP_{100a} in S5 and S6 was 12-52%. Scenario 6's main impact was from the GVL conversion and purification stage leading to an 84% contribution to the total GWP_{100a} (40.3 kg CO_2 eq./kg levulinic acid ± 0.7 kg CO_2 eq./kg levulinic acid). Additionally, a recent laboratory study has determined a 7% reduction in GWP_{100a} of a GVL production process from levulinic acid under solvent free conditions using Shvo catalyst (Van Slagmaat et al., 2019). Therefore, potential exists to mitigate GHG emissions from the GVL production and purification stage in S6 once such technologies mature.

6.3.1. LCA comparisons

As sorbitol, glucaric acid and levulinic acid have no fossil-based equivalents, a comparison was done on the six scenarios as demonstrated in Figure 6-6 to show the distribution of impacts and most environmentally sound biorefineries relative to each other. The results of the life cycle impact assessment (LCIA) comparisons revealed that the impacts of S1-S5 were comparable, whereas S6 recorded the highest impacts across most categories.



* Environmental loads of all scenarios including the CHP base case is given in Figure E4-1 (Appendix E-4)

Figure 6-6: Characterisation LCIA profiles of all biorefinery processes using CML-IA method

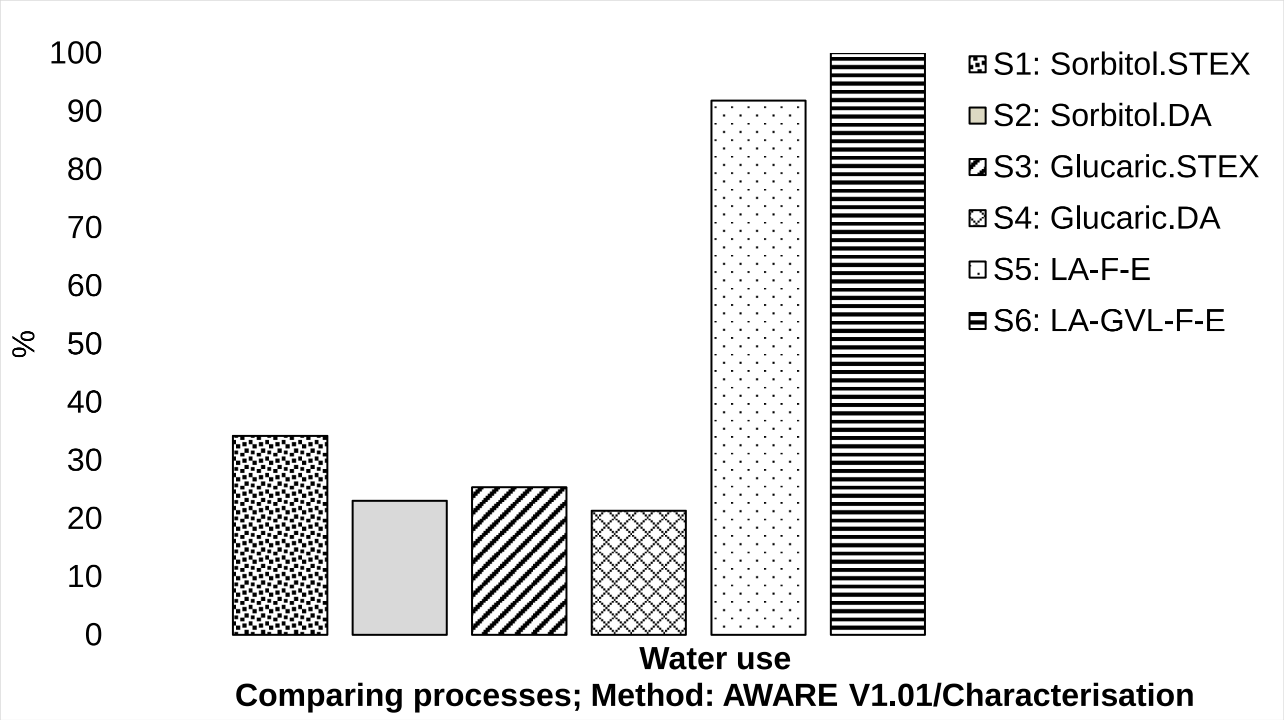
Despite being the most economically viable scenario, S6 delivered an inferior environmental performance and dominated nine impact categories, except AP and EP (see Figure 6-6). This was attributed to impacts associated with the use of H_2 from natural gas (Murat Sen et al., 2012) and n-butanol, a key reagent used in the production of n-butyl acetate solvent (32 t/h) for levulinic acid conversion and purification to GVL (Bories et al., 2018). Scenario S5 contributed the highest impact to EP due to N_2 emissions to air. It generally had fewer chemical inputs than S6 leading to more favourable environmental loads that were comparable to S1-S4.

Dilute acid pretreated biorefineries (S2 and S4) performed better environmentally than the S1 and S3 that applied SO_2–steam explosion. For the sorbitol biorefineries, it was observed that S1 had 9-21% higher environmental impacts than S2 and similarly the glucaric acid biorefinery S3 had 3-16% higher environmental loads than S4 mainly in ADP, POCP, EP and AP (Figure 6). Scenarios S1 and S3 dominated AP (followed by S5) then S2 and S4. The AP impact recorded in scenarios S1-S5 was above 73%.

Overall, S2 performed better environmentally (Figure 6-6), although S3's performance was also comparable to S2 in ADP (fossil fuels), GWP_{100a}, ODP, HT and the ecotoxicities. One hot spot reported in biochemical processes is the indirect emission from chemicals consumption (Reno et al., 2009). To this end, S2 and S4 largely benefitted from their lower chemical inputs in comparison to S1 and S3, whereas S1 and S3 suffered high environmental burdens in AP and EP caused by associated emissions to air of heavy metals (nickel and lead), SO_2 and N_2.

6.3.2. Water footprint

South African has been hit by dry spells in recent years and so water scarcity is a real challenge (Hoekstra et al., 2011). Thus, irrigation water (8000 m^3/Ha) was used at conventional sugar mills (see Table E1-3 of Appendix E1) and this calls for measures to ensure water intensive processes manage their water resource efficiently and minimise wastage of its available resource. The water footprints are presented in Figure 6-7*.



*Water use in Figure 6-7 was based on the initial total water requirements per process. The complexes then operate as closed loops and only process make up water (the difference between boiler feed water and waste water generated as shown in TableE1-1 (a) and (b)) is added to the scenarios.

Figure 6-7: Water use characterisation profiles for all scenarios

Following heat integration by pinch analysis in all biorefineries, levulinic acid scenarios S5 and S6's water footprint was 70-85% more than the glucaric acid and sorbitol complexes S1-S4 that used less energy intensive processes including ion exchange, adsorption and evaporation (chapter 4). The purification of levulinic acid and GVL via distillation is an energy intensive process requiring large steam and cooling duties (chapter 5), so a proper water management regime is essential, including heat integration (used in these scenarios) to reduce water consumption.

Similarly trends in the water footprint along with the process cause-effect chain were observed when the Eco-Indicator 99 (though not a recent methodology) was applied to determine additional damages caused by the biorefineries at the end of the life cycle on human health, ecosystem quality and resources as shown in Figure 6-8.

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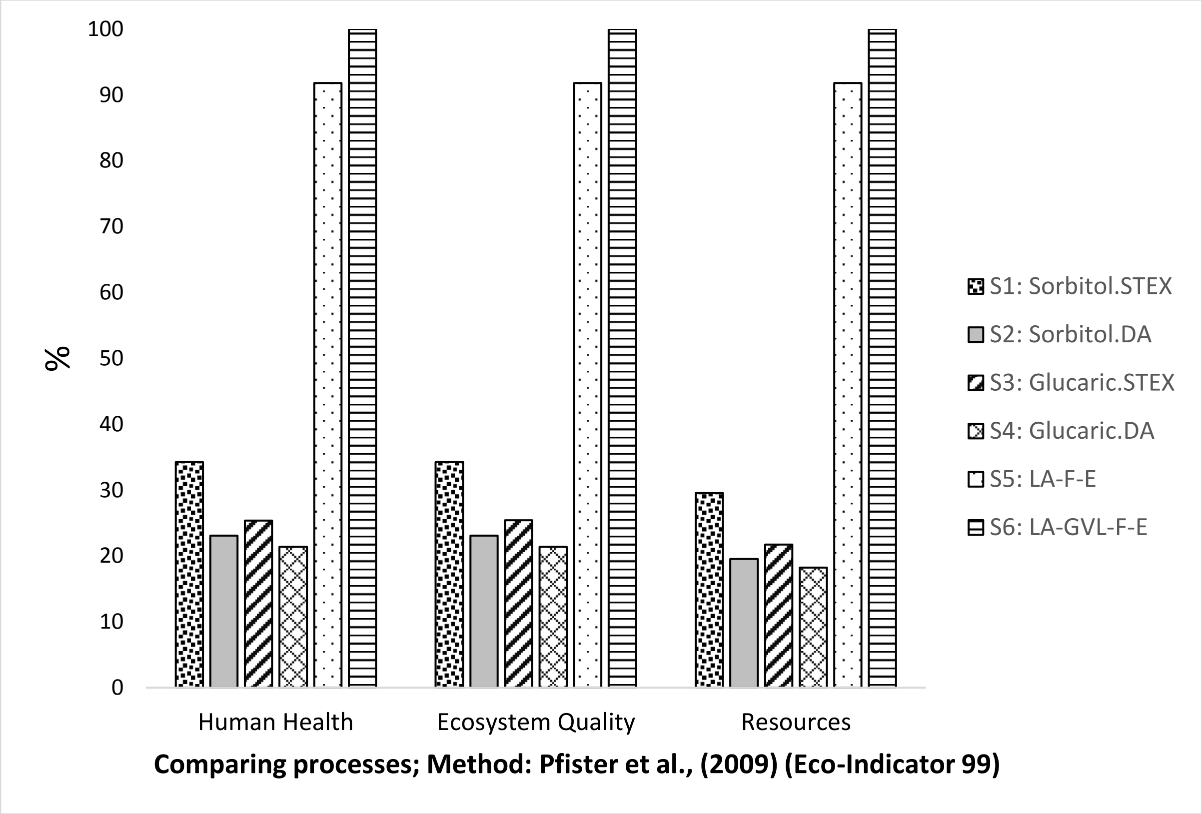

Figure 6-8: A characterised comparison of the human health, ecosystem quality and resource usage for all scenarios using Eco-Indicator 99

As demonstrated in Figure 6-8, levulinic acid scenarios generally used more dilute sulphuric acid, neutralising chemicals, n-butyl acetate solvent and hydrogen (for scenario 6) as the main reagents, besides additional emissions from the integrated CHP plants, which significantly impacted the three indicators by 70-85% more than S1-S4.

Conversely, the impact on human health, ecosystem quality and resources in S1 and S3 complexes using SO_2-steam explosion was about 2-11% more than that in S2 and S4 via dilute acid pretreatment. Besides the impacts from cane cultivation and harvesting earlier discussed, impacts from the biorefinery and CHP plant to human health and the ecosystem were caused by flue gas emissions (CO_2, SO_2 and NO_x) that led to acidification, which also has potential to increase material corrosion. Resource depletion was attributed to transportation fuels, use of hydrogen from fossil sources, water, catalysts (Spath and Mann, 2002) and quicklime for the neutralisation of waste streams.

6.3.3. Sustainability assessment of profitable scenarios

The establishment of biorefineries has potential to increase the revenue base of sugar mills, create jobs for harvesting brown leaves, including the operation of these complexes (chapters 4 and 5) and this should be done in an environmentally friendly way. The techno-economic, social impacts (number of jobs created) obtained from literature (chapters 4and 5) (also detailed in Tables E1-1 and E1-2) and LCAs from this study (for profitable scenarios S2, S4, S5 and S6) were combined into a sustainability mapping on a normalised chart using eight indicators (shown in Figure 6-9). Scenarios with the largest mapped area represented the inferior sustainable system and vice-versa.

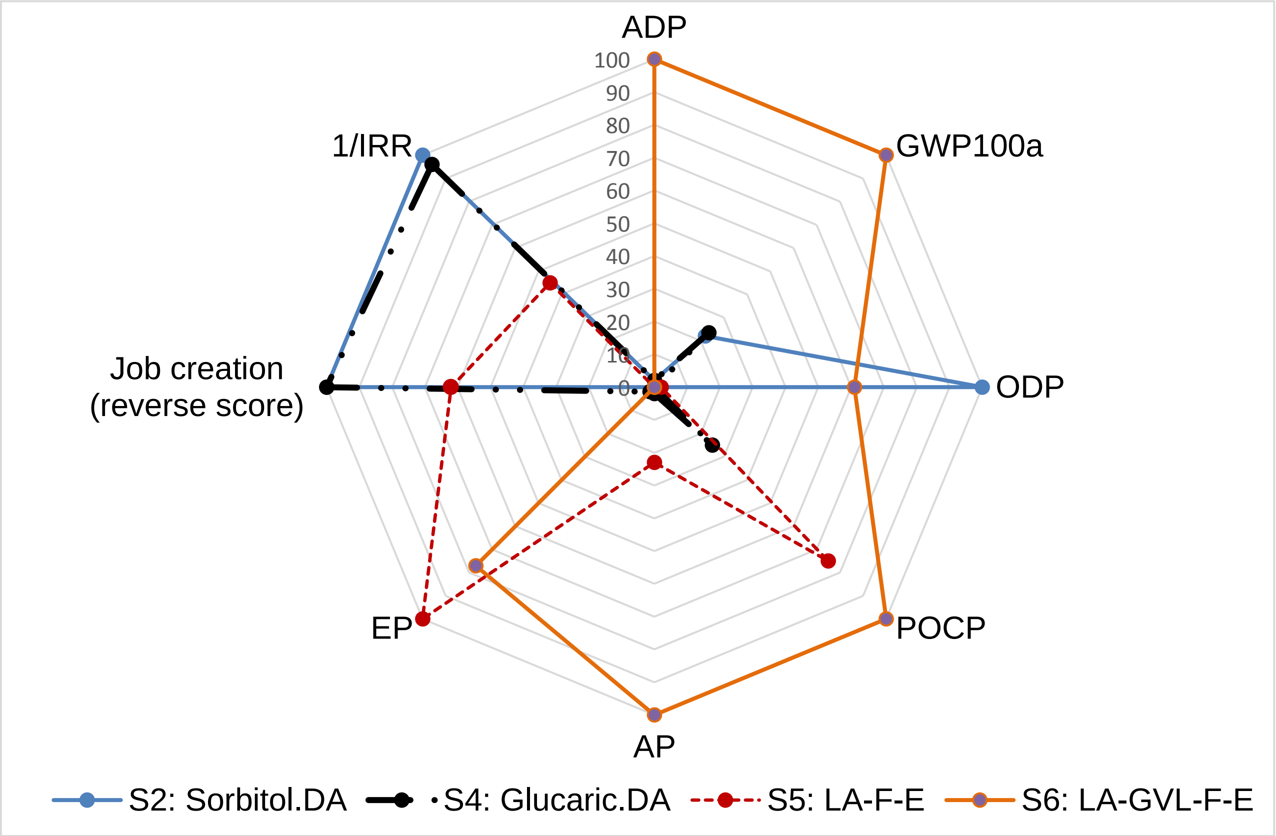

Figure 6-9: A sustainability analysis of the profitable scenarios using eight indicators

A sustainability study of biorefineries is essential to the establishment of the bio-based economy as this can inform policy, potential investors and communities on means of contributing towards it. Generally, the environmental and economic methods exist and are well-stablished, however, the social impact, which can be assessed with categories such as jobs created, gender issues, health impacts and land availability, is still in the development phase because of the complexity associated with qualitative measures. Job creation has been used as a key measure in other biorefinery studies (Mandegari et al., 2017; Farzad et al., 2017).

Generally, trade-offs are unavoidable in sustainability studies. For instance, from Figure 6-9, S4, was the most sustainable scenario, having the least environmental burdens, creating 49 additional jobs, although it was marginally profitable with a 10.7% IRR at a 9.7% hurdle rate) using an assumed glucaric acid selling price of US$ 655/kg (chapter 4). In addition, S5 (although comparable to S2) was sustainable with an IRR of 17% at a 9.7% hurdle rate and benefited from its minimal chemical inputs and low production costs whilst creating 52 additional jobs (chapter 5). Sorbitol scenario S2 was mostly disadvantaged by its utilisation of H_2 from natural gas, on-site SO_2 production coupled with a low market selling price and high capital investment costs.

In contrast, S6 was the least desirable scenario despite attaining the highest IRR of 23% and creating the most jobs (60) (chapter 5), due to its significant environmental burdens from the bulk GVL production and purification stage. Its sustainability status could be improved by minimising solvent consumption, efficiently managing solvent recycling, implementing alternative purification techniques and using hydrogen from renewable sources, although this may incur additional costs and negatively affect process economics (Hosseini and Wahid, 2016).

6.4. Conclusions

Detailed life cycle analyses of bioenergy self-sufficient biorefineries were conducted on complexes annexed to a sugar mill that produced sorbitol, glucaric acid and levulinic acid with electricity cogeneration. It was generally observed that S1 and S3 using SO_2-steam explosion pretreatment had 3-21% higher contributions to abiotic depletion, photochemical oxidation, acidification and eutrophication impacts than S2 and S4 via dilute acid pretreatment due to the added emissions from the SO_2 onsite production unit. However, the total GWP_{100a} in the sorbitol biorefinery S2 was 88% higher than S1, whilst this impact was comparable with a 5% difference in the glucaric acid scenarios S3 and S4. The most profitable levulinic acid biorefinery S6 (LA-GVL-F-E) significantly underperformed environmentally as a consequence of the associated burdens from the production, transportation and use of solvents and hydrogen derived from fossil sources. Applying a sustainability measure to the four profitable scenarios (S2, S4, S5 and S6) revealed that the glucaric acid biorefinery S4 ($\text{Glucaric}_{\text{DA}}$) was the most sustainable followed by S5 (LA-F-E), whereas S6 (LA-GVL-F-E) was the least sustainable. The life cycle and sustainability assessments of sugar mills coupled with uncertainty analysis offer guidance on potential bio-based chemicals for future biorefinery feasibility studies and environmental management practices industries can implement.

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Supplementary information: Life cycle assessments of profitable scenarios in Appendix E

Appendix E consists of:

i. Supplementary data regarding this article, which also includes
  - Flow diagram for the product stages and their life cycle inventories
  - Environmental loads of all scenarios including the CHP base case
  - Uncertainty studies using Scenario Analysis

ii. Appendix E-2: Life cycle inputted inventory data for all the profitable biorefineries including the CHP base case scenario.

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Chapter 7

7.0 Multi criteria decision assessment

Objective of dissertation in this chapter and summary of findings

This chapter presents the methodology and findings of the multi-criteria decision assessment conducted on the profitable scenarios. This is in fulfilment of objective five, which is to score and rank the biorefinery scenarios based on weighted economic, environmental and social (sustainability) indicators.

When equal representative weightings (RWs) of 33.33% on the economic, environmental and social indicators were applied, the biorefineries' rankings (and scores), starting with the most favourable to the least, was in the order: LA-F-E (3.79), Glucaric.$_{\mathrm{DA}}$ (3.46), Sorbitol.$_{\mathrm{DA}}$ (3.44), LA-GVL-F-E (3.42) and CHP base case (1.92). These results were to a large extent in agreement with the sustainability assessment conducted in chapter 6 on the life cycle assessment of the profitable scenarios. The robustness of the scenarios was assessed in a sensitivity analysis by varying the representative weightings on the sustainability indicators and determining the combined overall score of the biorefineries. The most robust scenario with the least change in the overall score after variations in the indicators following a sensitivity analysis was the scenario producing levulinic acid, furfural and electricity (LA-F-E) with a 15% overall change. This was followed by the sorbitol (Sorbitol.$_{\mathrm{DA}}$) and glucaric acid (Glucaric.$_{\mathrm{DA}}$) scenarios with a change of 20% and 21% respectively. The most profitable scenario, LA-GVL-F-E, producing levulinic acid, gamma valerolactone and furfural, with electricity cogeneration followed by the CHP base case, attained low scores and were the least robust due to the high environmental loads in both scenarios and the low social impact in the CHP base case.

7.1. Introduction

Multi criteria decision assessment (MCDA) is a broad framework used by stakeholders to resolve complex decision making situations where multiple and conflicting problems exist (Saarikoski et al., 2016). It is useful in that it enables decisions to be made transparently, using a systematic approach, about issues valued differently by stakeholders.

This framework has been used in various disciplines including energy management, health care systems, forest ecology and management, natural resource management and waste paper management (Drake et al., 2017; Saarikoski et al., 2016; Sureeyatanapas, 2016; Hanan et al., 2013;). More recently, due to global environmental concerns, most MCDAs now include environmental and social aspects (Watrobski et al., 2019; Pohekar and Ramachandran, 2004). No MCDAs, however, have been conducted on glucaric acid, sorbitol and levulinic acid biorefinery complexes. To this end, this study aims to conduct a MCDA on profitable biorefineries (with IRR > 9.7% hurdle rate), producing glucaric acid, sorbitol and levulinic acid. The MCDA is done by scoring and ranking the biorefineries based on varied representative weightings (RWs) of sustainability (economic, environmental and social) indicators. The three indicators are based on the rationale of sustainable development goals, namely that economic development should be undertaken in an environmentally friendly manner and at the same time uplift the social livelihoods of the citizens (Blodgett et al., 2012). Five scenarios (S1–S5) with electricity cogeneration (except in scenario 5), were assessed namely:

S1: Sorbitol biorefinery using dilute acid pretreatment (Sorbitol.$_{\text{DA}}$).

S2: Glucaric acid biorefinery via dilute acid pretreatment (Glucaric.$_{\text{DA}}$).

S3: Biorefinery that produced bulk levulinic acid and furfural (LA-F-E).

S4: Multi-product biorefinery producing levulinic acid for niche market, bulk gamma valerolactone and furfural (LA-GVL-F-E).

S5: CHP base case scenario only producing electricity.

7.2. Materials and methods

Since MCDA is a process where wider stakeholder consultation is key to capturing and aligning the assessment with their interests (Julio et al., 2017), this assessment is a preliminary step in establishing the general trend observed when a certain criterion is used in the scoring and ranking of biorefineries. The MCDA process used the rating approach where appropriate weightings are given to key sustainable development goals namely, economic, environmental and social and their sub-indicators, which are not exhaustive, but can be expanded upon. Generally, MCDA tools have five basic components applied herein (from section 7.2.1) although preference methods differ (Saarikoski et al., 2016):

7.2.1. MCDA Decision context

This involves defining the objectives of the MCDA. In this current study the objective of the MCDA was to score and rank the biorefinery scenarios based on weighted sustainability indicators. This was a preliminary step to inform key sugar industry stakeholders of potential biorefinery scenarios for future feasibility studies. Secondly, the MCDA was used as a sensitivity study to determine the most robust scenario following variations in the sustainability weightings.

7.2.2. Defining of criteria

A second component is the defining of criteria that measures for success or consequences of each alternative; this component usually involves stakeholder consultations. In this current study, the criteria measured under each indicator are described in Table 7-1 where four economic criteria were used. Eight environmental indicators were assessed, based on those parameters with a significant contribution after normalisation as noted in the life cycle inventory assessment (LCIA) results in chapter 6. The number of jobs created was the only criterion used under the social indicator (as discussed in chapters 3, 4 and 5).

Table 7-1: Criteria used per indicator for the profitable scenarios assessed using a rating scale of 1–5.

	DESCRIPTION OF NORMAL RATINGS ON A 1-5 SCALE*
ECONOMIC INDICATORS	
Internal rate of return	An IRR of 9.7 % scores 1. The higher the IRR, the higher the score[a]
Net present value	The higher the NPV, the higher the score
Total capital investment	A higher capital investment is unfavourable leading to a lower score
Total cost of production	Similarly, a higher cost of production receives a low score
ENVIRONMENTAL INDICATORS	
Ozone layer depletion	Based on LCIA results. The higher the impact, the lower the score
Abiotic depletion	The higher the impact, the lower the score and vice versa
Eutrophication	“
Human toxicity	“
Global warming potential	“
Acidification	“ “
Photochemical oxidation	“
Water demand	AWARE method. The higher the H_2O demand the lower the score
SOCIAL INDICATOR	
Number of additional jobs created	The higher the number of additional jobs created the higher the score and vice versa.

* An internal normalisation of indicators was done relative to the other scenarios. If a parameter was favourable at high values such as profitability then results were normalised against the highest value. If a low value was favoured in a parameter (e.g. water footprint, capital investment costs etc.) then normalisation was relative to that lowest figure.

[a] The scaling and scoring methodology is given section 7.2.4 and 7.2.5.

7.2.3. Weighting criteria

Thirdly, another component that relies on value judgement of key stakeholders is the weighting of criteria, where a percentage is given to each criterion to reflect the relative importance for the final decision. The initial economic, environmental and social indicators used were based on the national sustainable development using equal weightings, with initial representative weightings (RW) of 33.33% (Blodgett et al., 2012). The economic, environmental and social indicators' representative weightings were then varied in a sensitivity analysis to determine the most robust scenarios. But since the driver in any project is the economic benefit, the environmental and social representative weightings did not exceed the economic value.

7.2.4. Rating of options

The rating of listed options in MCDA use scales to achieve this. A qualitative measure such as low, medium, high with a corresponding numerical value to indicate the impact of each option is generally applied. In this current study, a 1–5 normal rating scale was used with 1 indicating a less favourable outcome and 5 the most favourable effect. The range of rating scales (e.g. 1–5, 1–9) is arbitrary, and its selection is adjusted to meet the needs of decision makers (Parajuli et al., 2015).

7.2.5. Scoring

The last component of a MCDA involves scoring a product using the weighting and the rating of each option, which are summed up to give the overall score for each decision option relative to the alternatives. Table 7-2 gives an example of the normal ranking methodology using a 1-5 rating scale.

Table 7-2: An example of normal ranking methodology for assessing sustainability criteria using rating scale of 1-5

Factors	**Weightage**	**Resource A**	**Resource B**	**Resource C**
		Score in a scale of 1-5		
Capability	40%	Value of 3 from 1–5 scale Score is 1.2 (0.4*3)	4 (0.4*4 = 1.6)	2.5 (0.4*2.5 = 1.0)
Experience	20%	4 (0.8)	3 (0.6)	4 (0.8)
Cost	15%	2 (0.3)	4 (0.6)	4 (0.6)
Availability	15%	4 (0.6)	5 (0.75)	5 (0.75)
Attitude	10%	3 (0.3)	4 (0.4)	5 (0.5)
Total score	**100%**	**3.2**	**3.95**	**3.65**
Priority/Ranking		3	1	2

7.3. Results and discussions

7.3.1. Equal representative weighting

Table 7-3: Normal ranking results for the biorefinery scenarios

			S1: Sorbitol.DA		**S2: Glucaric.DA**		**S3: LA-F-E**		**S4: LA-GVL-F-E**		**S5: CHP base case**	
		Weightage	**Scale (1 - 5)**	**Score**	**Scale (1 - 5)**	**Score**	**Scale (1 - 5)**	**Score**	**Scale (1 - 5)**	**Score**	**Scale (1 - 5)**	**Score**
ECONOMIC	1. Profitability	8.3	1	0.08	1	0.08	4	0.33	5	0.4	1	0.083
	2. Net present value (NPV)	8.3	1	0.08	1	0.08	4	0.33	5	0.4	1	0.083
	3. Total capital Investment cost	8.3	5	0.37	4.5	0.37	2.5	0.21	1	0.1	5	0.417
	4. Total cost of production	8.3	5	0.37	4.5	0.37	2.5	0.21	1	0.1	5	0.417
	Total economic	**33.3**		**0.9**		**0.9**		**1.1**		**1.0**		**0.9**
ENVIRONMENTAL	1. Marine Aquatic ecotoxicity	4.2	5	0.21	5	0.21	4	0.17	3	0.12	1	0.042
	2. Abiotic depletion (fossil fuels)	4.2	5	0.21	5	0.21	5	0.21	1	0.04	2	0.083
	3. Eutrophication	4.2	5	0.21	5	0.21	4.5	0.19	5	0.21	1	0.042
	4. Fresh water aquatic ecotoxicity	4.2	5	0.21	5	0.21	4.5	0.19	2	0.08	1	0.042
	5. Global warming potential	4.2	4	0.17	4	0.17	5	0.21	1	0.04	2	0.083
	6. Acidification	4.2	5	0.21	5	0.21	3	0.12	3	0.12	1	0.042
	7. Photochemical oxidation	4.2	5	0.21	5	0.21	5	0.21	2	0.08	1	0.042
	8. Water demand	4.2	3	0.10	3	0.12	2	0.08	1	0.04	5	0.208
	Total environmental	**33.3**		**1.5**		**1.5**		**1.4**		**0.7**		**0.6**
SOCIAL	1. No. of additional jobs created	33.3	3	1.00	3	1.0	4	1.33	5	1.67	1	0.3333
	Total social	**33.3**		**1**		**1**		**1.33**		**1.67**		**0.33**
	TOTAL Weightage/Score	**100.0**		**3.44**		**3.46**		**3.79**		**3.42**		**1.92**
	RANKING		**3**		**2**		**1**		**4**		**5**	

Five profitable scenarios, S1–S5, were ranked based on the normal ranking methodology on a 1–5 rating scale; the breakdown of the ratings and scores per indicator are summarised in Table 7-3. Each indicator (economic, environmental and social) had a 33.3% weighting (see Table 7-3). Appendix F summarises the TEAs, social and environmental impacts of S1–S5.

Using equal representative weightings (RW) of 33.33% per indicator as shown in Table 7-3, led to S3 (LA-F-E) attaining the highest aggregate score of 3.79 (also shown in Figure 7-1), due to its high IRR (17%), social impact (52 jobs) and low environmental impacts. This was followed by S2 (Glucaric.$_{DA}$) and S1 (Sorbitol.$_{DA}$) scoring 3.46 and 3.44 respectively as demonstrated in Table 7-3 and Figure 7-1. Biorefinery S4 (LA-GVL-F-E) scored a total of 3.42, attributed to its high capital investment costs and environmental burdens whilst S5 (CHP base case) attained the lowest value of 1.92. The main contributors to the underperformance in S5 were its high environmental impacts (low environmental score) in acidification, eutrophication, photo-chemical oxidation, marine and fresh water aquatic ecotoxicities and low economic and social contributions (see Table 7-3). Therefore, based on equal representative weightings, the scenarios were ranked as follows, beginning with the scenario that attained the highest score: S3 (LA-F-E), S2 (Glucaric.$_{DA}$), S1 (Sorbitol.$_{DA}$), S4 (LA-GVL-F-E) and S5 (CHP base case). This order is generally in agreement with the sustainability results discussed under the life cycle assessments in chapter 6.

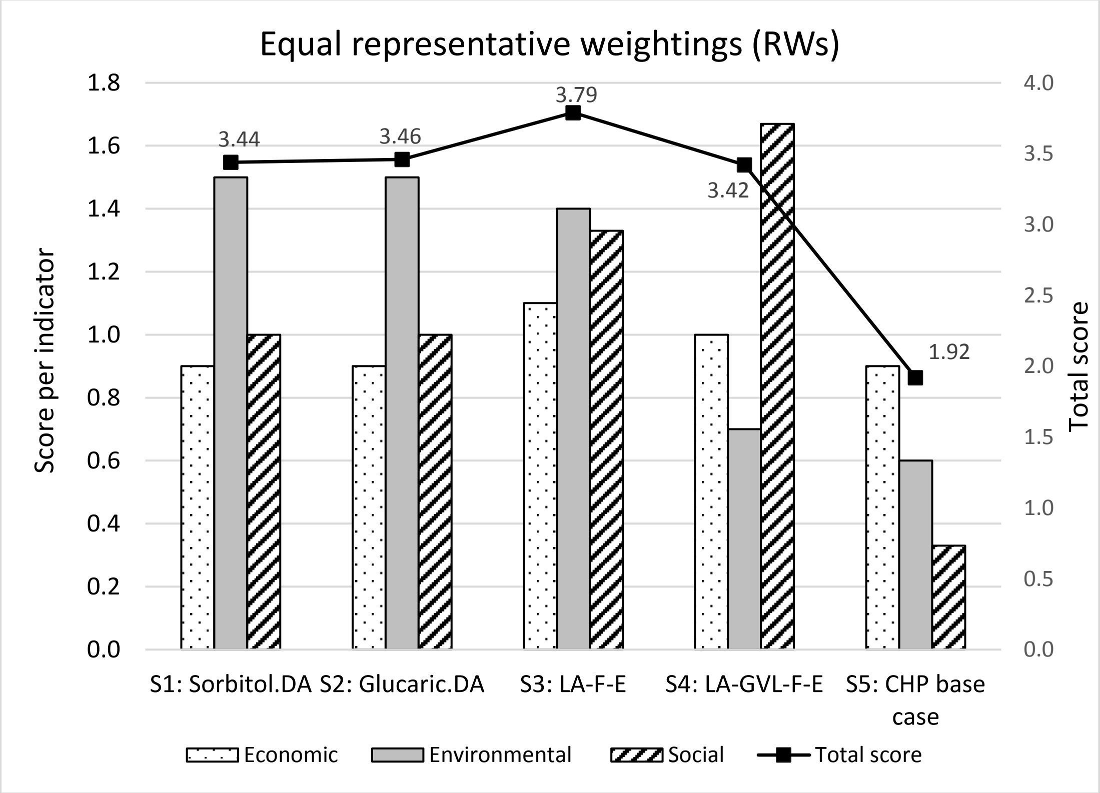

Figure 7-1: Graphical representation of the scores per scenario based on equal representative weightings of 33.33% for the three sustainability indicators

7.3.2. Sensitivity analysis

A sensitivity analysis was conducted of the scenarios by varying the sustainability representative weightings (RWs) as shown in Figure 7-2. However, since economic benefits are what drive any business, the economic RW was given the highest priority (had the highest representative weighting) in all sensitivity variations.

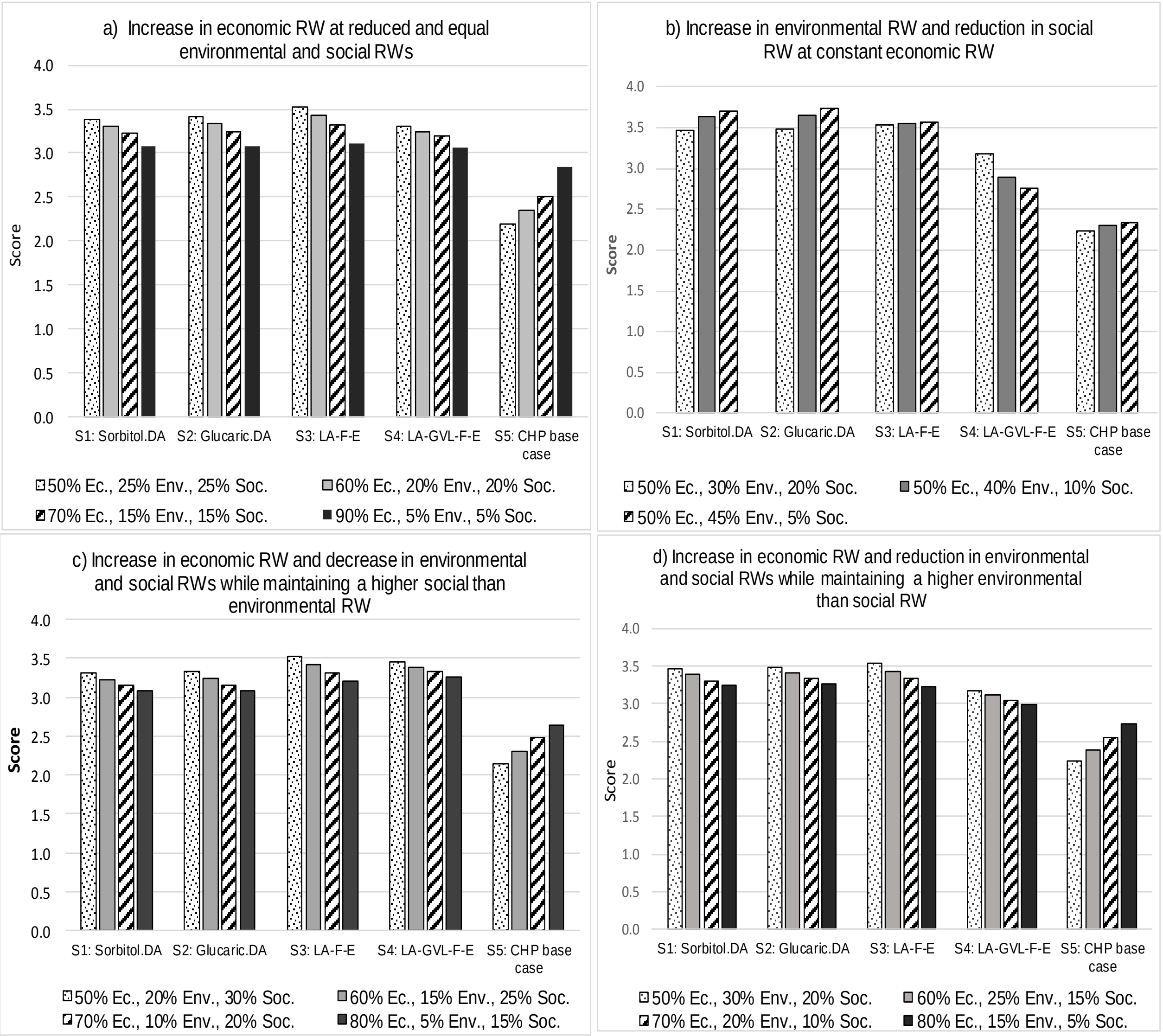

Figure 7-2: Sensitivity analysis of all profitable scenarios

From Figure 7-2 (a), it was observed that increasing the economic RW (from 50% to 90%) while reducing the environmental and social RWs by the same value of 25%, 20%, 15% and 5%, led to a 27% improvement in the score of S5 (from 2.2 to 2.8), due to its low capital investment cost, total cost of production, environmental and social impacts as a consequence of their reduced allocations. In scenarios S1–S4 on the other hand, an 8–14% reduction in the scores was observed. This was attributed to the reduction in environmental and social RWs for sorbitol and glucaric acid and high capital investment costs and total cost of production for the levulinic acid biorefineries. Therefore, an increase in economic RW from 50% to 90% at the expense of the environmental and social indicators that were reduced from 25% to 5%, improved S5's overall score, however, S3 still attained the highest overall scores at 3.1–3.6.

In Figure 7-2(b), the overall scores of the biorefinery scenarios 1-5, apart from S4, increased when the environmental RW was increased and the social RW decreased at a constant economic RW of 50%. Scenarios S1, S2 and S3's overall scores increased by 6.6%, 6.9% and 1% respectively, when the environmental RW was increased by 15% and the social RW reduced by 15%. Scenarios S1, S2 and S3 had an advantage (high overall scores) over S4 and S5 attributed to their low environmental burdens. Scenario S4 performed poorly with a 15% reduction in the overall score as the environmental RW increased. This was due to its high global warming, photochemical oxidation and abiotic depletion (fossil fuels), impacts attributed to chemicals used in the process and associated emissions from using H_2 produced from natural gas.

Increasing the economic RW (from 50-80%) whilst keeping the social RW higher than the environmental RW as shown in Figure 7-2(c), led to a 6-10% decrease in the overall scores of S1–S4 and a 23% increase in the total score of S5. However, S3 and S4 attained the highest total scores due to their high IRRs and number of additional employees engaged with the establishment and operation of the biorefineries. Conversely, S5 scored the lowest value because it underperformed in the economic and social assessments as a result of the low regional selling price of its main product, electricity (US$ 0.08/kWh) (SAPP, 2019) and small plant size, which entails a smaller workforce.

Similarly, increasing the economic RW and keeping the environmental RW higher than the social RWs as shown in Figure 7-2 (d) favoured S1, S2 and S3, which scored highly (3.25–3.54) due to the low capital investment costs, total cost of production and environmental impact in S1 and S2 and high profitability and low environmental loads in S3. It was observed that S3 attained the highest score following these variations.

Generally, it was observed that no scenario performed well in all indicators after variations in the RWs, therefore, a trade-off is required amongst the indicator weightings. Generally, S3 attained the highest sustainability scores at varied RWs with its aggregate scores in the range 3.1–3.6 as shown in Figure 7-2. Biorefineries S1 and S2 attained high scores when the economic and environmental RWs were higher than the social weighting whilst S4 had higher scores when the economic and social weightings were higher than the environmental RWs. Scenario S5 was the most underperforming biorefinery with scores of 1.9–2.9 because of low scores in all indicators when compared to S1–S4.

The most robust scenario after the sensitivity analysis, with the least change in its aggregate score following variations in the representative weightings was S3 (LA-F-E), which achieved a 15% change. Therefore, even in the near future when the levulinic acid production volumes increase, this scenario will be sustainable as it is based on bulk levulinc acid production, furfural and electricity, when compared to S1, S2, S4 and S5. Other robust scenarios included S1 (Sorbitol.$_{DA}$) and S2 (Glucaric.$_{DA}$) with a comparable overall change of 20% and 21% respectively. The most profitable scenario was S4 (LA-GVL-F-E) while the CHP base case was the least robust.

7.4. Conclusions

In this study, a multi criteria tool was developed and used as a preliminary exercise to compare and rank the performance of profitable scenarios based on varied weighted economic, environmental and social indicators. This is to inform decision makers and key stakeholders on the most sustainable biorefineries at typical sugar mills. Based on 33.33% equal representative weightings of the economic, environmental and social indicators, the order of ranking and scores obtained was LA-F-E (3.79), Glucaric.$_{DA}$ (3.46), Sorbitol.$_{DA}$ (3.44), LA-GVL-F-E (3.42) and CHP base case (1.92). The most robust scenarios, following variations in the weightings (based on a sensitivity analysis), were: the LA-F-E biorefinery producing levulinic acid for commodity markets, furfural and electricity, followed by Sorbitol.$_{DA}$ together with Glucaric.$_{DA}$ that produced sorbitol and glucaric acid respectively with electricity cogeneration. Since this is an initial study, there is still scope for improvement involving a wider stakeholder engagement and the inclusion of more assessment criteria.

Supplementary information

The scenarios' economic, environmental and social indicators used in the MCDA in Appendix F.

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Chapter 8

8.0 Summary, conclusions and recommendations

8.1. Summary of conclusions

The purpose of this study was to investigate the sustainability in terms of the economic, environmental and social impacts of adding value to lignocellulose feedstocks (sugarcane bagasse and dried leaves) in biorefinery complexes, annexed to a sugar mill to either produce shortlisted chemicals polyethylene, sorbitol, glucaric acid and levulinic acid or just electricity. The generated research findings provide key stakeholders with relevant information needed prior to feasibility studies. It also informs policy formulators on these bio-based products compared to fossil-based (where applicable) or first generation feedstocks and factors required to make second generation biorefineries competitive and sustainable. A summary of the techno-economic assessments of different scenarios discussed in this thesis for the production of the four chemicals is presented in Table A2-1 of Appendix A.

This was a conceptual study that was based on the application of literature data to Microsoft Excel spreadsheets, Aspen Plus® v.8.6 and Sima Pro® software packages to determine the techno economics, environmental and social impacts of producing the four shortlisted chemicals in different biorefinery configurations.

Following the introduction given in chapter one, chapter two was an overview of the biorefinery concept, how the classification of biorefineries has evolved and been standardised, the growth of this approach, short-listing of chemicals and techno-economic, environmental and social assessments of biorefineries producing the respective short-listed bio-based chemicals. Even though a global shift towards bio-economies has taken place, most techno-economic studies have been on bio-ethanol production. It is in recent years where there has been an emergence of techno-economic assessments of bio-based chemicals produced via thermochemical and biochemical means such as n-butanol, methanol, jet fuel, lactic acid, succinic acid, xylitol, polylactic acid, poly-hydroxyalkanoates, butanediol and butadiene. Although polyethylene, sorbitol, glucaric acid and levulinic acid have been identified by the Department of Energy (DoE), National Renewable Energy Laboratories (NREL) studies as potential chemicals for future bio-economies, to date, no detailed sustainability assessments have been done on such biorefineries, annexed to a typical sugar mill.

Therefore, based on the literature reviewed, this research aimed to answer the following questions:

- Why were the chemicals polyethylene, sorbitol, glucaric acid and levulinic acid selected for the biorefinery studies?
- Would annexing a bioenergy self-sufficient biorefinery and CHP plant to a typical sugar mill to produce a chemical alongside sugar bring about sustainable (economic, environmental and social) gains for the sugar mills or would it be more beneficial to invest in a simpler system that will burn all the biomass and produce surplus electricity?
- How would the biorefineries perform if scored and ranked based on weighted economic, environmental and social indicators that reflect the sugar industry's interests and what are the trade-offs between these indicators?

Apart from polyethylene, sorbitol, glucaric acid and levulinic acid having been identified as promising bio-based chemicals, these chemicals have technology readiness levels at near commercial to commercial stage. In addition, the shortlisted chemicals are termed "drop in" as they can be manufactured using existing technologies with limited modifications to infrastructure. The characteristics of these second generation bio-based chemicals are also similar to their first generation and fossil-based counterparts, in some instances (i.e. polyethylene). Therefore, they can complement and even replace existing products.

In addressing the second research question, chapter 3, considered the *techno-economic assessment of a polyethylene biorefinery using cellulosic ethanol as feedstock* and generated a biorefinery producing polyethylene (PE). The polyethylene biorefinery was an extension to an existing bio-ethanol biorefinery that was annexed to a sugar mill and supplied the cellulosic ethanol feedstock required to produce PE. Techno-economic assessments showed that this scenario was unprofitable when bio-based polyethylene (PE) was sold at a fossil equivalent market selling price of US$ 886/t. It attained a net present value (NPV) of -282 US$ million at a hurdle rate of 9.7% due to its high capital investment cost (US$ 311 million) relative to the low PE production volume (0.01% of global production capacities) and market selling price based on fossil sources.

The **novel contributions** of this chapter include the conceptual design, simulation and techno-economic assessment of a polyethylene biorefinery using lignocellulose feedstocks, a model (ethylene to polyethylene process area) that was not identified in any other study either from fossil resources or first generation feedstocks.

The **key findings** were that the bio-ethanol biorefinery (existing model by Mandegari et al. (2017a)) contributed 69% to the inside battery limits (ISBL), which excludes the waste water treatment (WWT) plant, boiler and condensing extraction steam turbine (CEST) system, utilities and storage. This can be credited to the nature of the processed feedstock that requires pretreatment, hydrolysis and fermentative stages (including enzyme production) prior to bio-ethanol feedstock production.

As there are no detailed techno-economic PE studies on first generation or fossil-based feedstocks in literature, a comparison of the PE scenario to the base case producing electricity alone revealed that the CHP base case is more profitable (although just marginally and not viable) than the PE biorefinery, attaining a 10.3 % IRR and US$ 6.5 million NPV at a 9.7% hurdle rate. Despite the CHP base case producing 61 MWh for sale, its economic outcome was unfavourable due to the low current regional electricity selling price of US$ 0.08/kWh.

One way to make the whole PE biorefinery attractive to private investors (at a 20% threshold IRR) is to sell the bio-based PE at a premium price that is 233% more than the assumed fossil PE price of US$ 886/t, a premium value consumers in developing countries may not be willing to pay. The environmental impact assessments covered in chapter 6 did not include the PE scenario because it was a highly unprofitable biorefinery.

As a further build up to the sustainability assessment of the shortlisted chemicals, chapter 4, *Techno-economic analysis of chemically catalysed lignocellulose biorefineries at a typical sugar mill: sorbitol or glucaric acid and electricity cogeneration,* considered the techno-economics and social impacts of sorbitol and glucaric acid biorefineries. Here, two sorbitol scenarios and two glucaric acid scenarios were generated where the pretreatment process were altered (via SO_2-steam explosion and dilute acid pretreatment). The sorbitol and glucaric acid scenarios using dilute acid pretreatment and enzymatic hydrolysis (Sorbitol.$_{DA}$ and Glucaric.$_{DA}$ respectively) were marginally profitable, both with a 10.7% IRR and NPVs of US$ 17.2 million and US$ 16.0 million respectively at a 9.7% hurdle rate. However, from a sensitivity analysis point of view, it was seen that the profitability of the 2G sorbitol and glucaric acid biorefineries can be improved by increasing the solids loading in the biorefinery feedstock (see chapter 4), which reduces steam demand and increases biorefinery capacities and product rates. However, a realistic maximum solids loading must be determined empirically. Additionally, securing extra feedstock to operate the profitable scenarios for more than 9 months (to 11 months) would also improve profitability.

The **novel contributions** of chapter 4 include the design and simulation, and detailed techno-economic evaluations of sorbitol and glucaric acid biorefineries for 2nd generation feedstocks, which entails the inclusion of pretreatment and hydrolysis stages required to process lignocelluloses and release glucose sugars. Two process pathways were considered for comparative purposes. This work also includes a first detailed life cycle assessment (using 11 impact categories) and water footprint of two sorbitol and two glucaric acid biorefineries from "cradle" to "factory gate" covered in chapter 6.

The **key findings** are that dilute acid pretreatment had a lower total annual production cost (US$ 20-22 million/y) than steam explosion at US$ 23-24 million/y (even though their yields were comparable). Therefore, sorbitol and glucaric acid biorefineries using dilute acid pretreatment followed by enzymatic hydrolysis were marginally profitable (10.7% IRR for both) whilst scenarios using steam explosion were unprofitable. However, all four scenarios at current configurations are not viable enough to attract private investors (reach IRR of ≥ 20%). This is because lignocellulose biorefineries cannot presently compete with existing first generation stand-alone biorefineries due to their high capital and annual variable operating costs associated with lignocelluloses' pretreatment and hydrolysis and the capital costs of an integrated CHP unit. The marginally profitable sorbitol and glucaric acid scenarios via dilute acid pretreatment should sell their second generation bio-based products at US$ 385/t and US$ 400/t respectively more than the current selling price of US$ 655/t if they are to be competitive and attract private investments.

Life cycle assessments were covered in chapter 6, based on 1 kg of product and 1 kWh electricity. The sorbitol and glucaric acid scenarios using dilute acid pretreatment (Sorbitol.$_{DA}$ and Glucraic.$_{DA}$) had a lesser environmental burden than producing the two chemicals using SO_2-steam explosion pretreatment, which involves onsite SO_2 production. The environmental loads in sorbitol and glucaric acid scenarios via SO_2-steam explosion were 9–12% and 3–16% respectively, higher than the Sorbitol.$_{DA}$ and Glucaric.$_{DA}$ in abiotic depletion, photochemical oxidation, eutrophication and acidification potentials. This is due to the added emissions from the SO_2 onsite production unit used in steam explosion. The global warming potential in Sorbitol.$_{DA}$ was 88% higher than in the sorbitol biorefinery using SO_2-steam explosion whilst this impact was comparable (5% difference) in the glucaric acid scenarios.

Lastly, another shortlisted chemical assessed for its techno-economic and social viability was levulinic acid covered in chapter 5 titled *"Techno-economics of lignocellulose biorefineries at South African sugar mills using the Biofine process to coproduce levulinic acid, furfural and electricity alongside gamma valerolactone"*. Four levulinic acid biorefineries using the Biofine process were generated. Two scenarios producing low volume, high value levulinic acid (B1 and B2) were not technically or economically viable. Levulinic acid production currently seems attractive because of the high market selling prices of up to US$ 8000/t as it is a niche product. However, it is foreseen that an over-supply of the chemical will flood the market and drastically drop its price to as low as US$ 905/t. Therefore, the biorefineries were generated to respond to the change in selling prices caused by the volumes produced. It was assumed that a levulinic acid production volume contributing 10% or more to the total global production capacities would affect the overall levulinic acid selling price. The most profitable scenario that achieved a 23% IRR and US$ 253 million NPV at a 9.7% hurdle rate was a multi-product biorefinery coproducing low volume levulinic acid (0.15 t/h) for niche markets, 3.3 t/h furfural, 14 MWh electricity and 6.8 t/h bulk gamma valerolactone. The second most profitable scenario produced bulk levulinic acid (7.2 t/h) for commodity markets, furfural and electricity co- generation and attained a 17.4% IRR against a 9.7% hurdle rate and a net present value (NPV) of US$ 139 million at 9.7% hurdle rate , a levulinic acid selling price of US$ 1080/t (and not the current US$ 905/t) was required to achieve a 20% threshold IRR. A total of 52-60 jobs were created in the levulinic acid scenarios.

The **novel contributions** of chapter 5 were the design and modelling of integrated levulinic acid biorefineries, using the Biofine process and annexed to a typical sugar mill. Also the techno-economic evaluations were conducted based on the impact levulinic acid production volumes would have on the selling price of this chemical, such that selling prices ranged between US$ 6500/t–US$ 905/t depending on whether it was a niche or commodity product. In addition, the life cycle assessment was the first detailed study (using 11 impact categories) of levulinic acid biorefineries at typical sugar mills (chapter 6).

The **key finding** was that producing levulinic acid via the Biofine process, whether for niche or commodity markets alongside bulk chemicals such as furfural and gamma valerolactone led to profitable scenarios due to the low annual production cost of the Biofine process (US$ 0.52/kg and US$ 0.83/kg), economies of scale effects and profit gains from the multiple products generated. This led to the LA-GVL-F-E scenario producing levulinic acid for niche markets, bulk gamma valerolactone, furfural and electricity cogeneration being the most profitable and viable scenario (23% IRR). The regional electricity selling price of US$ 0.08/kWh is so low that even when the CHP base case produced the largest amount of electricity (61 MWh), it remained marginally profitable.

Concerning the life cycle assessments of levulinic acid covered in chapter 6, it was observed that the most profitable biorefinery (IRR of 23%) producing levulinic acid, gamma valerolactone and furfural with electricity cogeneration underperformed environmentally due to the environmental loads associated with the production and use of n-butyl acetate solvent and hydrogen gas from natural gas in the process. On the other hand, the biorefinery producing levulinic acid, furfural with electricity cogeneration generally had fewer chemical inputs than the former scenario leading to more favourable environmental loads.

Following the sustainability assessment of the four chemicals, chapter 7 then considered the scoring and ranking of profitable and marginally unprofitable scenarios based on representative weightings of the economic, environmental and social indicators assessed in previous chapters using a multi criteria decision assessment (MCDA) tool. The economic criteria was obtained from the techno-economic results (in chapters 3, 4 and 5), the environmental impacts based on results from the life cycle assessment (in chapter 6), while the social criteria used the number of additional jobs created (assessed in chapters 3, 4 and 5). A sensitivity analysis was used to determine the robustness of the biorefineries when the representative weightings per indicator were varied in order to inform stakeholders of which biorefineries are most sustainable and can be used in future feasibility studies.

When an equal weighting of 33.33% on the economic, environmental and social indicators was used, the levulinic acid scenario producing furfural by-product with electricity cogeneration (LA-F-E) scored the highest mark with 3.79 due to its high IRR (17%), social impact (52 jobs) and low environmental impacts. It was followed by Glucaric.$_{\mathrm{DA}}$ and Sorbitol.$_{\mathrm{DA}}$ scoring 3.46 and 3.44 respectively. The most profitable scenario LA-GVL-F-E scored a total of 3.42 attributed to its high capital investment costs and environmental burdens whilst the CHP base case attained the lowest value of 1.92. This was as a result of the CHP base case's low social contribution and high environmental burdens in acidification, eutrophication, photochemical oxidation, marine and fresh water aquatic ecotoxicities. However, in any business, the representative weightings for the economic indicator are given priority. Therefore, when the representative weightings were varied, with the economic being the highest, the most sustainable and robust biorefineries were the levulinic acid scenario LA-F-E followed by Sorbitol.$_{DA}$ and Glucaric.$_{DA}$ that produced sorbitol and glucaric acid and sorbitol respectively, with electricity cogeneration.

The **novel contribution** was that this was the first multi criteria assessment study conducted on sorbitol, glucaric acid and levulinic acid biorefineries from lignocellulose feedstocks based on economic, environmental and social impacts generated from the novel biorefinery complexes.

The **key finding** is that a trade-off usually exists mostly between the economic and environmental indicators in biorefineries. It was observed that the most techno-economically viable scenario LA-GVL-F-E (23% IRR) did not score highly when assessed for sustainability due to their low score on the total capital investment costs and mainly because of low ratings in the environmental indicators. The most robust (sustainable) scenarios were LA-F-E mainly as a result of its high rating on profitability and net present value because of its multiple products followed by Glucaric.$_{DA}$ and Sorbitol.$_{DA}$ that scored highly for their low total production costs for dilute acid pretreated scenarios.

8.2. Recommendations for future research

The following recommendations were put forward based on the sustainability assessments conducted on the biorefinery scenarios generated:

- Validate the developed simulations and techno-economic assessments using pilot scale studies considering that data was limited on most scenarios (PE and glucaric acid). Some factors to explore further include:
    i. Determining the maximum solids loading at which these biorefineries should operate. Increasing the solids loading leads to an increase in yields, as there is a reduction in energy demand leading to reduced bypass ratios and larger biorefinery capacities and product rates.

    ii. In addition, the Biofine process is stated to have a challenge of reproducibility of laboratory scale results to pilot scale, therefore this should be considered and possible modifications done to the process to achieve high yields.

    iii. Experimentally explore any other type of enzymes that can be used for enzymatic hydrolysis alone followed by chemical processing downstream as available studies are based on enzymes that perform enzymatic hydrolysis and fermentative reactions downstream. This might be a cost-saving measure for chemical processes.

- Sorbitol, glucaric acid and levulinic acid were produced from glucose and so there is scope to add value to the monomer xylose (which is sent to wastewater treatment plants) and develop multi-product biorefineries. However, a biorefinery's profit margin significantly improves if commodity chemicals are produced with specialty chemicals, hence valorisation of part of the lignin to high-value products such as vanillin can also be investigated.
- In addition, research into the production of sorbitol and glucaric acid scenarios that were marginally profitable by introducing 1G or 1G/2G feedstocks should be conducted and the combined feedstocks' impact on the profitability and environmental impacts for stand-alone and integrated bioenergy self-sufficient biorefineries assessed. In addition, research into 1G/2G and even with a combination of 1G/2G/ethylene should be investigated as a way of improving the PE economics.
- Look into the extension of the social impact indicators to include even some qualitative indicators, which would help make the MCDA tool more robust and use the MCDA as a preliminary tool and build upon it by carrying out wider stakeholder consultations that will lead to the inclusion of more criteria to use.

APPENDIX A

A-1: Shortlisting of bio-based chemicals

.1.1. IDENTIFICATION AND SELECTION OF BIO-BASED CHEMICALS FOR PRODUCTION IN A LIGNOCELLULOSE BIOREFINERY ANNEXED TO A TYPICAL SOUTH AFRICAN SUGAR MILL

The following criteria was used and a chemical was eliminated if it was:

i. Under consideration on other projects at Stellenbosch University or other collaborating universities, in order to avoid duplication of work.

ii. At a technology readiness level (TRL < 6) below demonstration stage, to eliminate chemicals that are decades away from industrial implementation.

iii. Can be produced from lignocellulose materials

iv. Having a low product to raw material ratio based on the feedstock and final product prices; a relationship used at this early stage to evaluate the economic potential of a product (Gobina, 2014).

It should be indicated that although ease of production is one criteria highlighted in the SMRI technical report (No.2215, 2015) as a criteria, it was only used at this stage of the study to suggest the mode of production of the different chemicals thus give an indication of the simplicity or complexity of a process route (e.g. high temperature, high pressure), which has cost implications.

Due to the high number of chemicals identified, it was a challenge to thoroughly find detailed information in a limited time on the production methods of different chemicals and determine whether experimental data exists on which to base the simulations. But generally, the non-availability of articles and reports on the subject chemical was also to some extent used to eliminate a chemical.

The flow diagram shown in Figure A1-1 outlines the steps taken in shortlisting the identified long list of potential bio-based chemicals that can be produced from lignocellulose feedstocks.

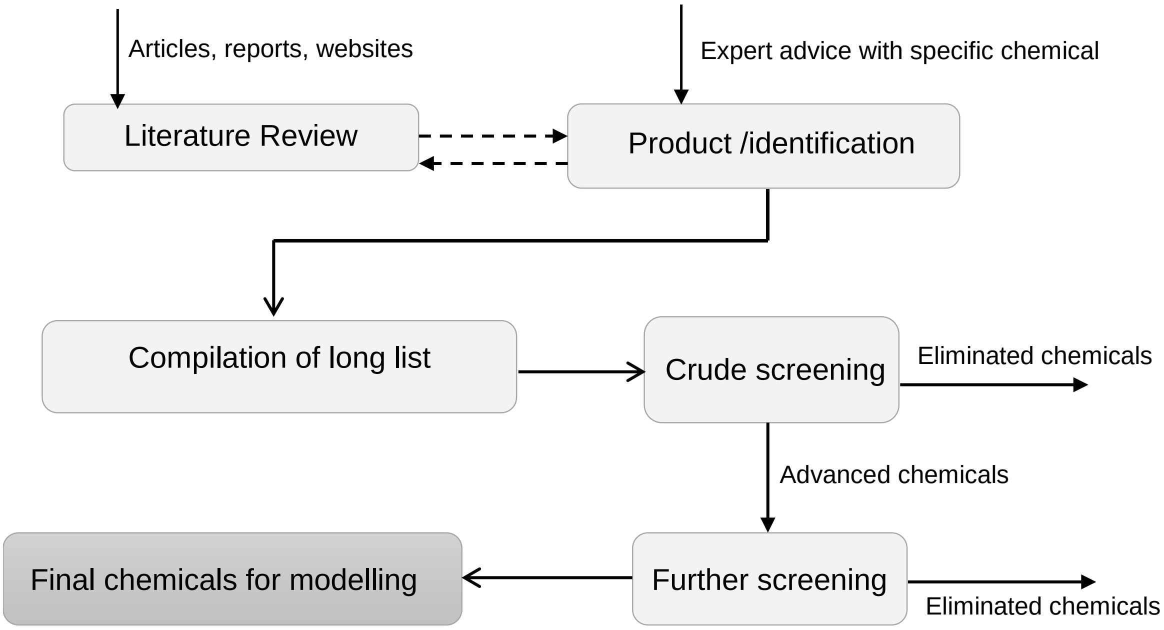


Figure A1-1: An outline of the steps taken in identifying and screening bio-based potential chemicals.

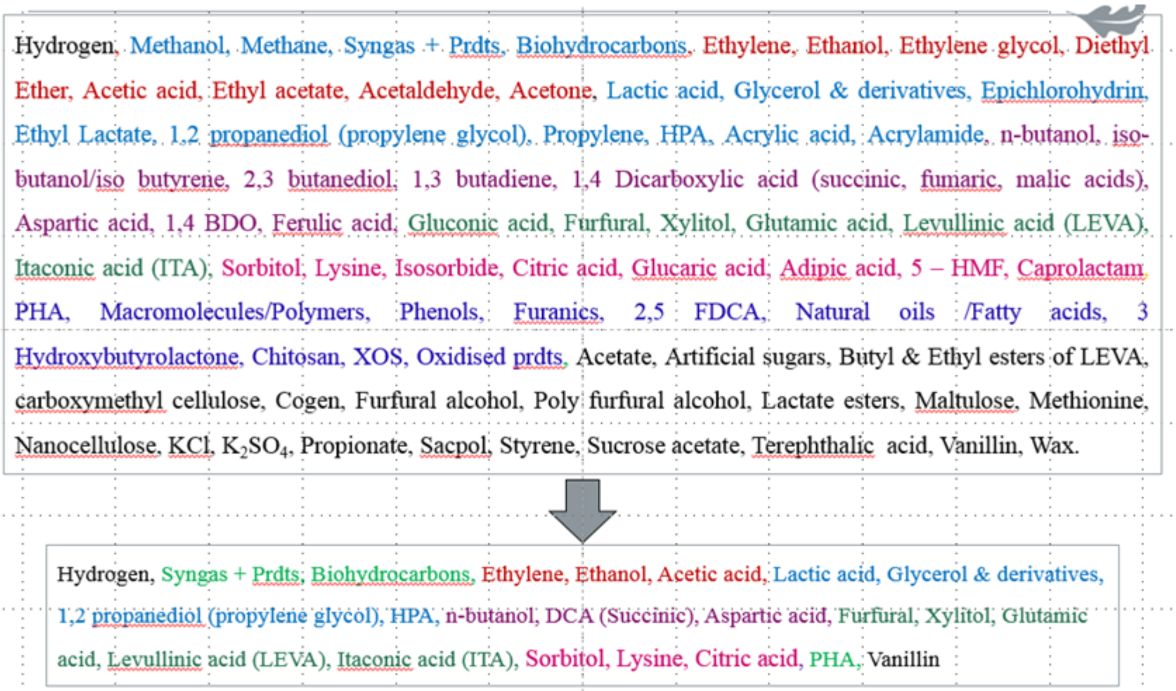
.1.2. TOTAL CHEMICALS CONSIDERED

Seventy-six (76) bio-based chemicals were compiled from 8 sources using a crude screening criteria. Table A1-1 shows the authors and the different sources of information used in this study. Thereafter, a long list of 76 identified chemicals was further reduced to 23 chemicals as shown in Figure A1-2 and further screened to 13–15 chemicals.

Table A1-1: A list of the main literature sources from where bio-based chemicals were drawn

Authors	Document type	Description
(Werpy and Petersen, 2004)	Company report	12 platform chemicals
(Patel *et al.*, 2006)	Company report	21 bio-based chemicals
(Bozell and Petersen, 2010)	Company report	10 platform chemicals
(Biddy et al. 2016)	Technical report	12 chemicals
(Menon and Rao, 2012)	Peer reviewed article	22 chemicals
(Posada *et al.*, 2013)	Peer reviewed article	12 bio-ethanol platform chemicals
Consultants (NNFCC, 2015)	Company website	48 chemicals
(Van Ree et al. 2014)	Company report	45 (based on 7 platform chemicals)
(SMRI, 2015)	Technical report	47 chemicals

From this list of 76 chemicals assessed, a further crude screening led to the selection of 23 chemicals as presented in Figure A1-2.



Hydrogen, Methanol, Methane, Syngas + Prdts, Biohydrocarbons, Ethylene, Ethanol, Ethylene glycol, Diethyl Ether, Acetic acid, Ethyl acetate, Acetaldehyde, Acetone, Lactic acid, Glycerol & derivatives, Epichlorohydrin, Ethyl Lactate, 1,2 propanediol (propylene glycol), Propylene, HPA, Acrylic acid, Acrylamide, n-butanol, iso-butanol/iso butyrene, 2,3 butanediol, 1,3 butadiene, 1,4 Dicarboxylic acid (succinic, fumaric, malic acids), Aspartic acid, 1,4 BDO, Ferulic acid, Gluconic acid, Furfural, Xylitol, Glutamic acid, Levullinic acid (LEVA), Itaconic acid (ITA), Sorbitol, Lysine, Isosorbide, Citric acid, Glucaric acid, Adipic acid, 5 – HMF, Caprolactam, PHA, Macromolecules/Polymers, Phenols, Furanics, 2,5 FDCA, Natural oils /Fatty acids, 3 Hydroxybutyrolactone, Chitosan, XOS, Oxidised prdts, Acetate, Artificial sugars, Butyl & Ethyl esters of LEVA, carboxymethyl cellulose, Cogen, Furfural alcohol, Poly furfural alcohol, Lactate esters, Maltulose, Methionine, Nanocellulose, KCl, K_2SO_4, Propionate, Sacpol, Styrene, Sucrose acetate, Terephthalic acid, Vanillin, Wax.

Hydrogen, Syngas + Prdts, Biohydrocarbons, Ethylene, Ethanol, Acetic acid, Lactic acid, Glycerol & derivatives, 1,2 propanediol (propylene glycol), HPA, n-butanol, DCA (Succinic), Aspartic acid, Furfural, Xylitol, Glutamic acid, Levullinic acid (LEVA), Itaconic acid (ITA), Sorbitol, Lysine, Citric acid, PHA, Vanillin

Figure A1-2: List of identified and shortlisted chemical colour coded based on their carbon numbers

It was observed that the 23 chemicals were all referenced by 2 or more sources and 8 of the 23 chemicals were building blocks whilst 14 were common to Stellenbosch University (SU) and University of Cape Town (UCT), who have embarked on the similar studies but using first generation (1G) feedstocks.

Table A2 shows a further reduction of the long list of chemicals. Chemicals marked in grey were eliminated based on any one of the elimination point. The chemicals not shaded (in white) including acetic acid, succinic acid, levulinic acid, glutamic acid, xylitol, itaconic acid, sorbitol, citric acid and poly hydroxyalkanoate (PHA) met the minimum requirements and were shortlisted.

Table A1-2: Criteria used in eliminating (marked in grey) or qualifying (in white) them (author's own selected screened chemicals)

Carbon No.	**Product**	**TRL**	**Raw mat./ Prdt. ratio**	**Other descriptions/ mode of production**
2	1G/2G	C	-	Sucrose/bagasse, lactic acid/bagasse etc.
	Ethyl acetate	C	-	Ethanol dehydrogenation and acetic acid reaction
	Ethylene glycol	C	0.01	Catalytic sorbitol hydrogenolysis or ethylene (mono ethylene glycol)
3	Acrylic acid	R-P*	0.01	Fermentation of carbs to 3 HPA & further dehydration or via Levulinic acid route.
	Propylene glycol/1,2 propanediol	-	0.02	Derived from glycerol (oil-based platform) or lactic acid or sorbitol
4	Butyric acid	P*	0.01	Commodity chemical from 1st phase methane production
5	5-hydroxybutyrolactone	P-D*	0.01	Starch is main feedstock. Isomerisation of glucose to fructose and dehydration of fructose to HMF
	5-Hydroxy methyl furfural	R-P*	0.01	-
6	2,5 - FDCA	R-P*	Very low	Chemical dehydration of C6 carbs. Oxidation of HMF gives FDCA
	Glucaric/Gluconic acid	D-C	0.03	Larger quantity (via nitric acid route). Aerobic fermentation of glucose with O_2 to gluconic/glucaric acid (catalytic oxidation)
	Adipic acid	R-P*	0.01	Fermentation and catalytic hydrogenation of glucose
	Xylo-oligosacharides	-	0.004	Specialty chemical*–with prebiotic properties but not fully established.
	Arginine	-	0.002	Specialty chemical*. Fermentation of non-essential amino acids
	p-xylene	P*	0.01	Production from HMF via hydrodeoxygenation
	Cellulose acetate	-	0.02	Acetylation of cellulose before sacharifying to glucose. Main feedstocks are rice husks and cotton
	Ethyl & butyl esters of LevA	-	0.02	From levulinic acid, High ecotoxicity (Lomba et al., 2011)
	Ferulic acid	-	0.001	Specialty prebiotic chemical*
n	Riboflavin	D	0.001	Specialty chemical via microbial fermentation*
	Poly butylene	C	<1	Microbial production of succinic followed by

	succinate			condensation
	Poly lactic acid	C	<1	Polymerisation of lactic acid or via sorbitol route
	Poly ethylene	C	<1	Dehydration of bioethanol
	Poly hydroxyl butyrate	-	<1	Fermentation of hemicellulose
	Poly trimethylene terephthalate (PTT)		<1	From 3 HPA , which has been excluded*
	Poly acrylic acid	-	<1	Catalytic thermal dehydration of acrylic acid (TRL of R-P)*
	Poly acrolonitrile		<1	Acrylic acid polymer*
	Poly acrolein		<1	Acrylic acid polymer*
	Poly acrylamide		<1	Acrylic acid polymer but TOXIC*
	Poly itaconic acid		<1	ITA derivative by fermentation of carbs
	Poly diphenolic acid	-	<1	Levulinic acid reaction with 2 Phenols
	Vanillin	C	0.02	Oxidised product from lignosulfonates

Carbon no.	Product	TRL	Production mode / Elimination points	Raw material to product ratio
0	Hydrogen		* insignificant market growth	0.33
2	Ethanol	C	* Research already done on another project	0.02
	Ethylene		* Research already done on another project	0.02
	Acetic acid	C	Byproduct of succinic acid production via bacteria fermentation (LT,LP)	0.02
3	1,3 propanediol	-	*Glycerol derivative-microbial conversionof glycerol	0.02
	3 HPA	P	Anaerobic fermentation of glucose to lactate (LT,LP)	0.02
	Lactic acid		* Research already done on another project	0.01
	Glycerol	C	*Mainly from the oil based platform	0.02
4	Succinic acid	D-C	Anearobic fermentation (LT,LP) or via levulinic acid oxidation	0.01
	Aspartic acid	-	Anaerobic fermnetation (LT,LP)	2.00
	n-butanol	-	* Research already done on another project	0.01
5	Levulinic acid	D	Acid hydrolyses reactions via Biofin eprocess (HT, HP)	0.003
	Glutamic acid	D-C	Anaerobic fermentation (LT,LP)	0.01
	Xylitol	C	Catalytic hydrogenation of C5 carbs (HT, HP)	0.01
	Itaconic acid	C	Baterial/fungal/anaerobic fermentation (LT,LP)	0.01
	Furfural	C	* Research already done on another project	0.02
	Isoprene	R-P	* Research already done on another project	0.007
6	Sorbitol	C	Catalytic hydrogenation of C5/C6 carbs (HT,HP)	0.03
	Citric acid	D-C	Microbial fermentation (LT,LP)	0.03
	Lysine (amino acid)	D-C	*Specialty chemical	0.01
n	PHA	D	Direct fermentation (LT,LP)	0.00

KEY
C-COMMERCIAL
R-P -RESEARCH TO PILOT
P -PILOT
LT - LOW TEMPERATURE
HT - HIGH TEMPERATURE
LP - LOW PRESSURE
HP - HIGH PRESSURE

Finally, the list was shortened to 13–15 bio-based chemicals for future modelling into lignocellulose biorefinery scenarios in this study and by two extra researchers (Ozudogru et al., (2018) and Nieder-et al., (2018)). The shortlisted chemicals were acetic acid, succinic acid, levulinic acid, glutamic acid, xylitol, itaconic acid, sorbitol, citric acid, PHAs, vanillin, glucaric acid, cellulose acetate, polyethylene; 8 building block chemicals and 5 derivatives.

In summary, the rapid screening approach was useful in identifying potential bio-based chemicals when time was constrained (Van Ree et al. 2014). Using a rapid and flexible screening approach, 13 bio-based chemicals were shortlisted for production in lignocellulose biorefineries for future economic and feasibility studies in South Africa. Four of the 13 chemicals namely polyethylene, sorbitol, glucaric acid and levulinic acid were considered in this research.

This study selects chemicals that can be a starting point for a SMRI database of potential bio-based chemicals that can be produced in lignocellulose biorefineries annexed to a sugar mill. The identification and selection of bio-based chemicals therefore, contributes towards South Africa's support and advancement of a bio-based economy.

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A-2: Summary of the techno-economics of scenarios for the four chemicals

Table A2-1: A summary of the techno-economic parameters for each biorefinery at a 9.7% hurdle rate in real terms[a]

Scenario	PE	Sorbitol.$_{\text{STEX}}$	Sorbitol.$_{\text{DA}}$	Glucaric.$_{\text{STEX}}$	Glucaric.$_{\text{DA}}$	LA-F-E[b]	LA-GVL-F-E[b]	CHP Base case
IRR%	-	-	10.7	-	10.7	17.4	23.7	10.3
NPV (US$ million)	-282	-12.8	17.2	-12.3	16.0	139	253	6.5
Market selling rice (US$ /t)	886	655	655	655	655	905	6500	0.08($/kWh)
Comment	Unprofitable	Unprofitable	Profitable but not viable	Unprofitable	Profitable but not viable	Profitable and almost viable	Profitable and viable	Profitable but not viable
Selling price (US$/t) required to reach viable IRR of 20%	2956	1140	1040	1166	1055	1080	-	0.12 ($/kWh)
Minimum Product selling price (US$/t where NPV=0)	1872	679	619	681	618	1079		0.077 ($/kWh)

* Furfural selling price of US$ 1207/t

[a] The TEA based on a 5% working capital

[b] Market selling price, MPSP in multiproduct biorefineries are based on the main product, which was levulinic acid in the LA-F-E and LA-GVL-F-E scenarios

Table A2-2: A summary of the techno-economic parameters for each biorefinery in this at a 9.7% hurdle rate in real terms (using 15% working capital)

Scenario	PE	Sorbitol.$_{\text{STEX}}$	Sorbitol.$_{\text{DA}}$	Glucaric.$_{\text{STEX}}$	Glucaric.$_{\text{DA}}$	LA-F-E	LA-GVL-F-E	CHP Base case
IRR%	-	-	-	-	-	15.7	20.6	-
NPV (US$ million)	-315	-38.0	-4.2	-36.5	-4.1	118	226	-5.6
Market selling rice (US$ /t)	886	655	655	655	655	905	6500	0.08($/kWh)
Comment	Unprofitable	Unprofitable	Marginally unprofitable but not viable	Unprofitable	Marginally unprofitable but not viable	Profitable and almost viable	Profitable and viable	Marginally unprofitable but not viable
Selling price (US$/t) required to reach viable IRR of 20%	3215	1241	1117	1273	1148	1218	-	0.132 ($/kWh)
Minimum product selling price (US$/t where NPV=0)	1989	728	664	732	665	515		0.082 ($/kWh)

A-3: Key process assumptions and CEPCI indices

Key Assumptions

1. FEEDSTOCK

Table A3:1 Feedstock composition and brown leaves (Mandegari et al., 2017)

	Bagasse[1]		Harvesting residues[1]		Mixture (Feedstock)	
Mass Component	Fraction %	Flow (t/h)	Fraction %	Flow (t/h)	Fraction %	Flow (t/h)
Cellulose	41.1	18.5	39.8	7.96	40.7	26.5
Hemicelluloses	26.4	11.9	28.6	5.7	27.1	17.6
Lignin	21.7	9.8	22.5	4.5	21.9	14.3
Ash	4	1.8	2.4	0.48	3.5	2.3
Extractive	6.8	3.1	6.7	1.34	6.7	4.4
Sum (Dry Mass)	100	45	100	20	100	65
Water*		45		3.5		48.5
Total (Liquid + Solid)		90.0		23.5		113.5

[1]: Average of measurements for South African bagasse (Petersen et al. 2014)

Table A3:2: Sugarcane bagasse and brown leaves supplied to the biorefinery (Mandegari et al., 2017)

Material	**Percentage**	**t/h**
Sugarcane		300
Wet bagasse	30% of sugarcane	90
Dry bagasse*	50% of wet bagasse	45
Ttotal harvesting residues-brown leaves and green tops)	15 % of Sugarcane	45
Brown leaf available to biorefinery	50% of total harvesting residues	22.5
Dry Trash	15% of wet	20
Total Dry feedstock*		65

*: extract is included in the dry base

- The biorefinery operated for 9 months (6480 hrs/y).

- All biorefineries were bioenergy self- sufficient. No coal was used except in the sugar mill for electricity generation.

- The sugar mill's steam demand of 0.4 ton of steam per ton cane crashed (120 t/h HP steam at 400 °C and 30 bar) was supplied by the biorefinery.

- There is a high level of **AUTOMATION** in the biorefinery complexes, thus, the relatively low number of jobs created.

2. SIMULATION

- Default property method was the ELEC-NRTL
- Feedstock solids loading (S.L) of 30% was applied to all biorefinery scenarios.

S.L = [Dry material/(Total mass of material + water added to material)]

(Modenbach et al., 2012).

- All reactors were modelled as RSTOIC blocks except for the P.E reactor that was a YIELD block.
- All reactors, ion exchange and adsorption columns were modelled as HIGH PRESSURE VESSELS (Towler and Sinnot, 2008)

Table A3-3: Calculating installation costs of pressure vessels*

Inlet flow rate to vessel (kg/h)	From Aspen
Vessel diameter	Estimate
Vessel cross section area	$A = \Pi D^2/H$
Find Vessel height (H)	$V = \Pi R^2 H$
Vessel Volume	Flow rate (m^3/h) x (Reaction time)
Extra head	30% for reactors, 20% for ion exchange, adsorption columns
Height to Diameter (H/D)ratio	1-10
Vessel diameters	3.05 m-4.57 m
Pressure vessel shell weight formula (steel vessels)	$W_V = 240\ C_W\ D_M(H_V + 0.8\ D_M).t$ (Units: N convert to kg) C_w is a factor accounting for weight of nozzles (1.08), D_M is vessel diameter, H_v is the height of the vessel and t is the wall thickness
Vessel D(m) and minimum wall thickness (t) (mm)	1 m–5 mm, 1 to 2 m–7 mm, 2 to 2.5 m–9 mm, 2.5 to 3 m-10 mm, 3 to 3.5 m–12 mm
Costing of vessel	$a + b.S^n$, where S is W_v(kg)
cost projected to 2016[a]	Cost in year A = Cost in year B x $\frac{CEPCI\ year\ A}{CEPCI\ year\ B}$
Installed cost	(installation factor of 2) x (projected cost)

*Final values in the equipment sizing tables.

[a] CEPCI values used in table A3-4

Table A3-4: CEPCI indices used for equipment sizing

year	CEPCI value
1995	381
1997	386.5
1998	389.5
1999	390.6
2000	392
2001	394
2002	396
2003	402
2005	468
2006	500
2007	525
2008	575
2009	551
2010	551
2011	585.7
2012	584.6
2013	567.3
2014	576
2015	654.9
2016	536.5

3. KEY PROCESS VARIABLES USED IN ASPEN PLUS

Table A3-4: Key input variables used in Aspen Plus®

Boiler unit		
3	Boiler feed water pressure	64 bar
4	Boiler feed water temperature	176 ^{o}C
5	High high pressure steam pressure	64 bar
6	High-high pressure steam temperature	480^{o} C
7	Average burner temperature	870^{o}C
8	Combustion conversion	99.9%
9	Inlet economizer temperature	278^{o}C
10	Air preheat temperature	185^{o}C
11	Stack temperature	149^{o}C
12	Boiler heat loss	10%
13	Compressed air pressure	1.014 atm
Steam and power unit		
1	Number of extractions	3
2	Turbine isotropic efficiency	85%
3	Mechanical efficiency	96%
4	Sugar mills steam extraction	30 bar
5	Min condensate turbine pressure	0.1 atm
6	Sugar mill energy consumption	120 t/h
Wastewater treatment unit[a]		
1	Wastewater temperature	35^{o}C
2	Chemical Oxygen Demand	16 g/L
3	Biological Oxygen Demand (BOD)	70%
4	Organic component $\rightarrow 3CH_4 + CO_2$	0.23 kg/kg
5	Nutrient (per COD)	37 g/kg
6	COD of treated water	0.1 g/L
	Enzymatic hydrolysis[b]	
	Enzymes loading	20 mg/g
	% glucose from enzymatic hydrolysis diverted for enzyme production*	10%

[a, b] The wastewater treatment plant and enzyme production plants were not modelled by economically assessed by allocating a volume based cost to the total feedstream (Humbird et al., 2011)

b. ECONOMICS

1. Depreciation rate is a straight line depreciation over 5 years (i.e 20%)

2. Exchange rate ZAR 13 to 1 US$

3. **No loan interest and payment** , 100% financing equity
   Net revenue = [total annual revenue] – [total operating costs] – [depreciation] – ~~[loan interest]~~
   Annual income = [total annual revenue] – [total operating costs] – [income tax] – ~~[loan payment].~~

4. Economic parameters for developing countries

Table A3-5: Economic parameters used for developing countries (2016 base year)

Parameter	**Value used**
Project life (Years)	25
Depreciation	Straight line over 5 years
Salvage Value	0
% Spent in year -2*	10
% Spent in year -1*	60
% Spent in year 0*	30
Start-up time (Years)	2
First year new plant capacity (% design)	50%
Second year new plant capacity (% design)	75%
Working capital (% of FCI)[a]	5%
Income tax rate	28.0%
Inflation rate	5.7%
Cash flow calculations basis/IRR method	Real term
Discount rate (hurdle rate)	9.7%
Electricity price (US$/kWh)	0.08

*,See notes on the assumptions made (Table A3-6)

Table A3-6: Assumptions for the construction activities and cash flow (Humbird et al., 2011)

Project month	Activity	% of Project cost
0	Project plan and schedule established; conceptual and basic design engineering, permits completed. Major engineering started on selected sub-packages, P&IDs complete, preliminary plant and equipment arrangements complete	10%
12	All detailed engineering including foundations, structure, piping, electrical, site, etc. complete; all instrument components, piping and electrical materials on site; all site grading, drainage, sewers, rail, fire pond, foundation, and major structural installation complete; all field fabricated tanks built.	60%
24	Complete process equipment setting, piping, electrical wiring and instrumentation installation complete, all building finishing and plumbing complete; all landscaping complete; pre-commissioning complete; and commissioning, start-up, and initial performance test complete.	30%

[a]Working capital assumptions (Humbird et al., 2011)

“Working Capital is defined as money available to cover issues including raw materials/ inventory supplies, storage goods, accounts receivable, cash on hand for monthly payments including wages and maintenance fees and taxes. The working capital is usually 10%–20% of the fixed capital investment. This flow of money is required over the plant’s project life, from the start-up phase to revenue generation from products. For this project, 15% working capital is approximately $30 million. Feedstock is available within the vicinity (no significant shipping/ transportation cost or storage. One month’s raw materials, labour, maintenance, taxes and overheads is approximately US$ 4.5 million (for 9 months operation). Therefore, a lower working capital is reasonable. Garret, 1989 has suggested that using a fraction of the yearly operating cost, typically 10%–35%, is more appropriate. Using this range of percentages gives a working capital of about US$ 8 million-US$ 31 million. Therefore, 5% of FCI as working capital is reasonable, giving values of working capital in the range of US$ 10 million-US$ 14 million.

[Garrett, D.E. Chemical Engineering Economics. New York: Van Nostrand Reinhold, 1989.]

c. MATERIALS UNIT COSTS (US$/KG) IN 2016

Table A3-7: Variable operating costs for most materials used in the DCFROR

Material	2016 Unit Cost (US$/kg)	Reference
Biomass feedstock	0.01	**Dias et al. 2011**
Syndol catalyst	60	Dow,2018
Hexene solvent	166	Icis, 2017
R-1270 Refrigerant	2	Lindus, 2017
Ziegler-Natta catlyst	64	Meltzer, 1990
Sulphur	0.12	Mandegari et al. 2017
Sulphuric acid (93%)	0.09	Tao et al. 2011
Raney nickel catalyst[a]	5.14	Brown et al. 2012
Pt/C catalyst[a]	4.73	Brown et al. 2012
Hydrogen[b]	2.89	Brown et al. 2012
Pure O_2[c]	0.05	Chandler et al. 2016
Activated carbon[a]	2.69	Activated Carbon, 2018
Amberlite ion exchange resins[d]	242.5	Dow, 2018
Caustic	0.09	Humbird et al. 2011
Host Nutrients	0.76	Mandegari et al. 2017
Glucose	0.58	Humbird et al. 2011
Ammonia di-sulphate	0.46	Mandegari et al. 2017
Boiler chemicals	3.70	Mandegari et al. 2017
Cooling tower chemicals	2.20	Mandegari et al. 2017
Make-up water	0.0022	eThekwini Municipality, 2011

[a] Catalysts annual cost (Activated Carbon,2017; Riogen, 2018; Brown et al., 2012) were divided over the material effective years and this cost included a refurbishment cost of 10% of the material

d. SCHEDULES FOR REACTOR VESSELS (IN HOURS)

Figure A3-1: Filling, reacting, emptying (+cleaning) schedule for steam explosion tanks and the 2nd levulinic acid reactor vessel

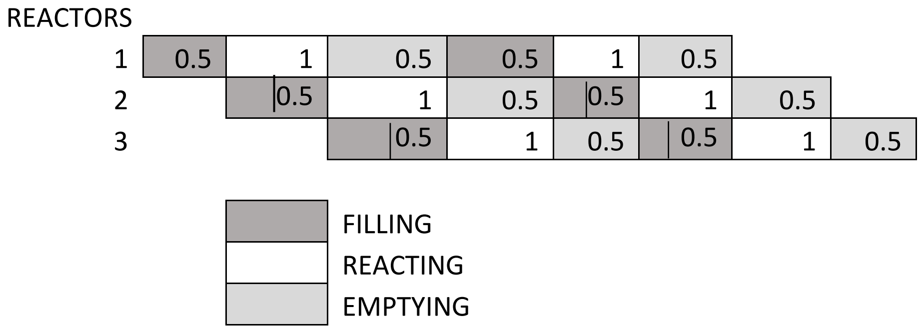


Figure A3-2: Feeding, reacting, emptying (+cleaning) schedule for ion exchange and adsorption columns.

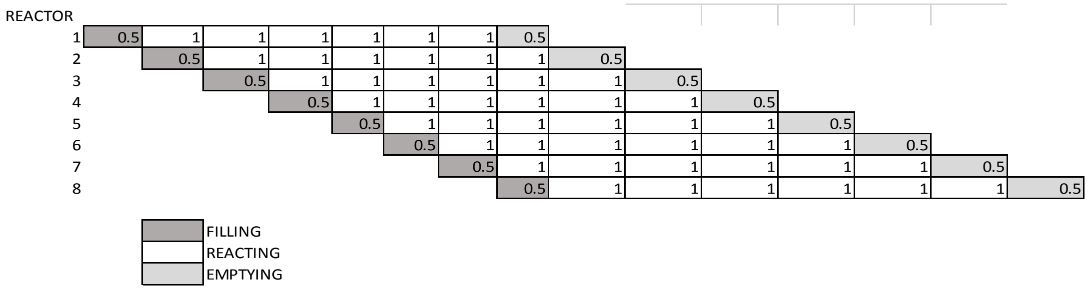
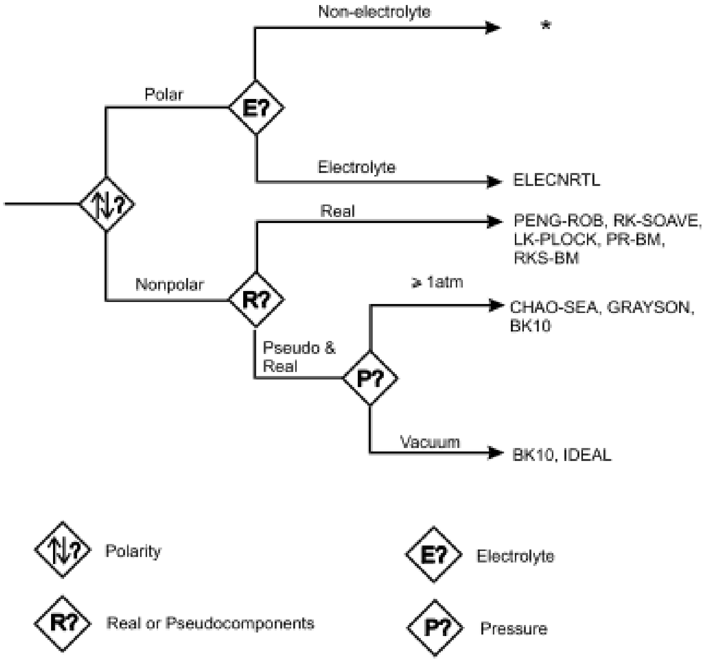


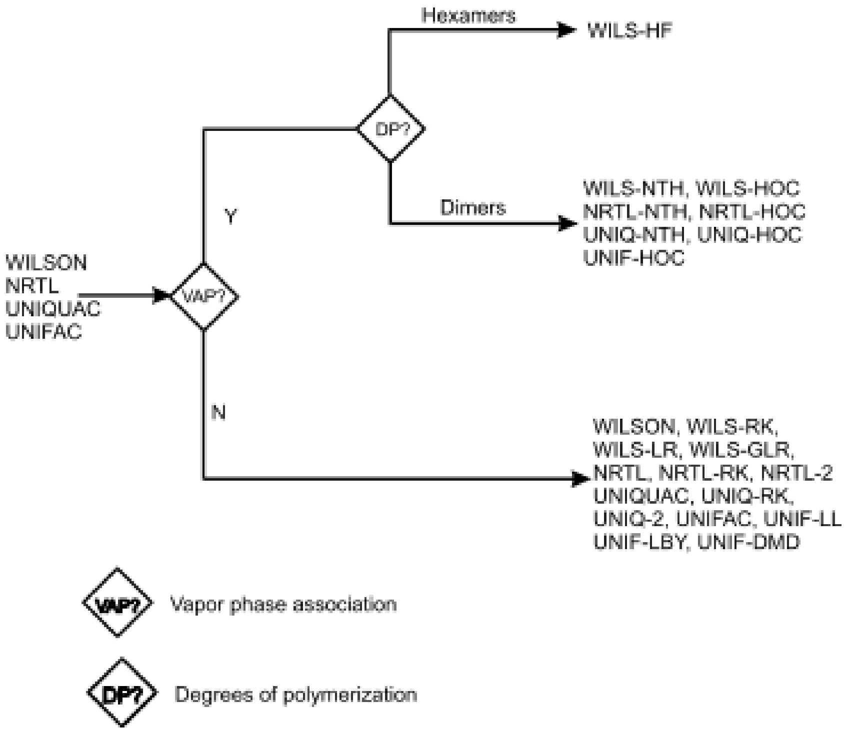
Figure A3-3: Filling, reacting, emptying (+cleaning) schedule for sorbitol and glucaric acid reactor vessels.

Note: Total number of vessels for all the columns are summarised in the equipment sizing tables.

e. GUIDELINES FOR CHOOSING PROPERTY METHODS IN ASPEN PLUS



(a)

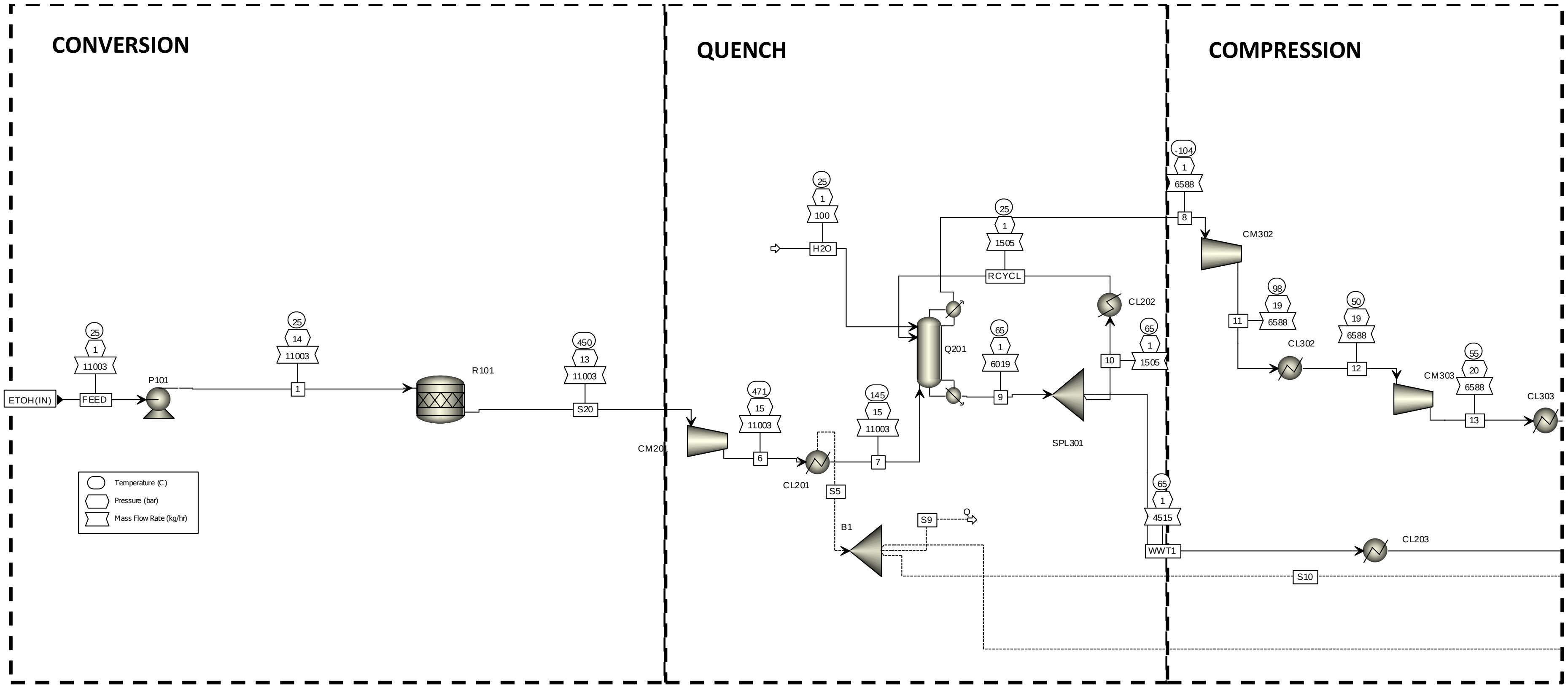


(b)

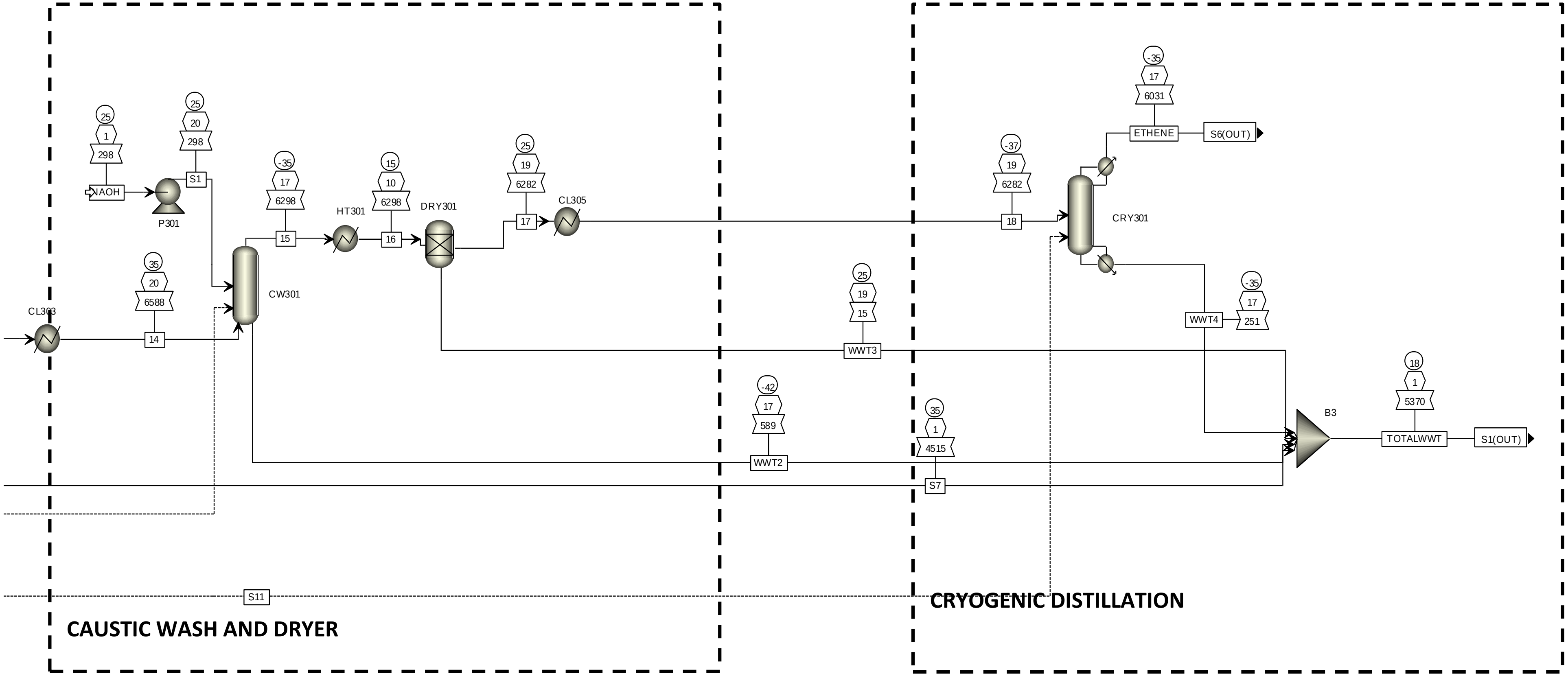
Figure A3-4: Guidelines for choosing (a) a property method and (b) coefficient activities for a property method (Redrawn from AspenTech, 2001)

APPENDIX B

B-1: Polyethylene production and CHP base case Aspen Plus ® models including process conditions



(a)



(b)

Figure B1-1: Ethanol to ethylene process flow diagram from Aspen Plus® including (a) conversion, quench and compression stages and (b) caustic wash, dryer and cryogenic distillation stages

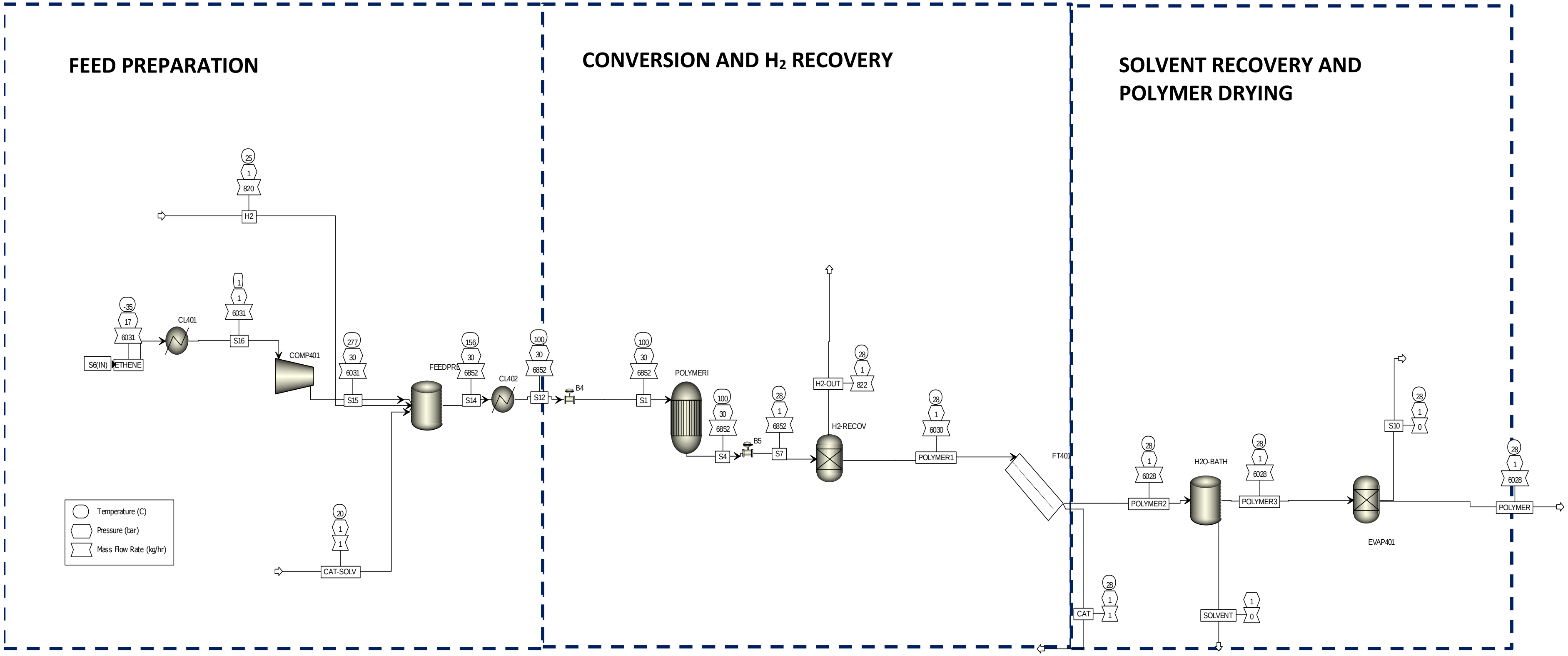


Figure B1-2: Ethylene polymerisation to polyethylene Aspen Plus® model

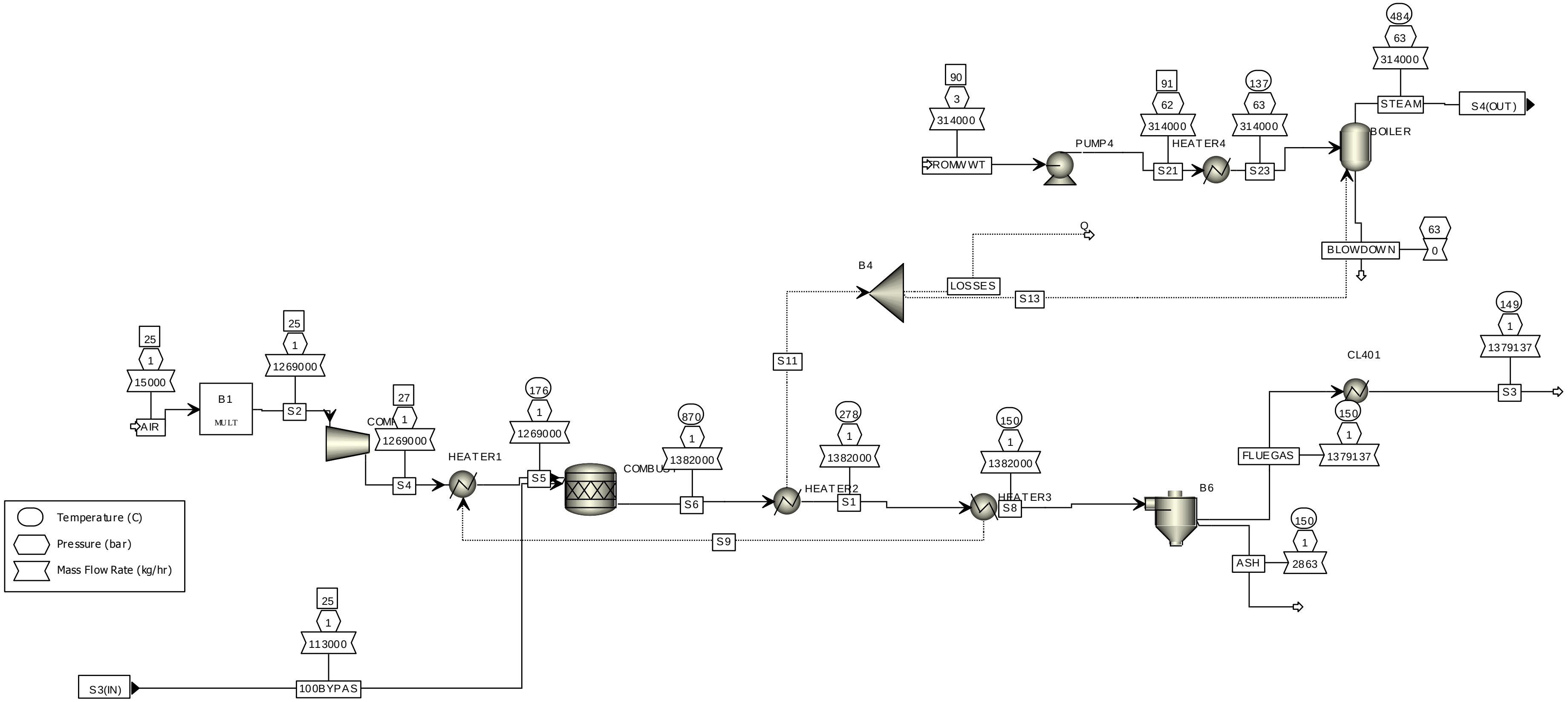


Figure B1-3: Boiler unit of the CHP base case Aspen Plus ® flow diagram

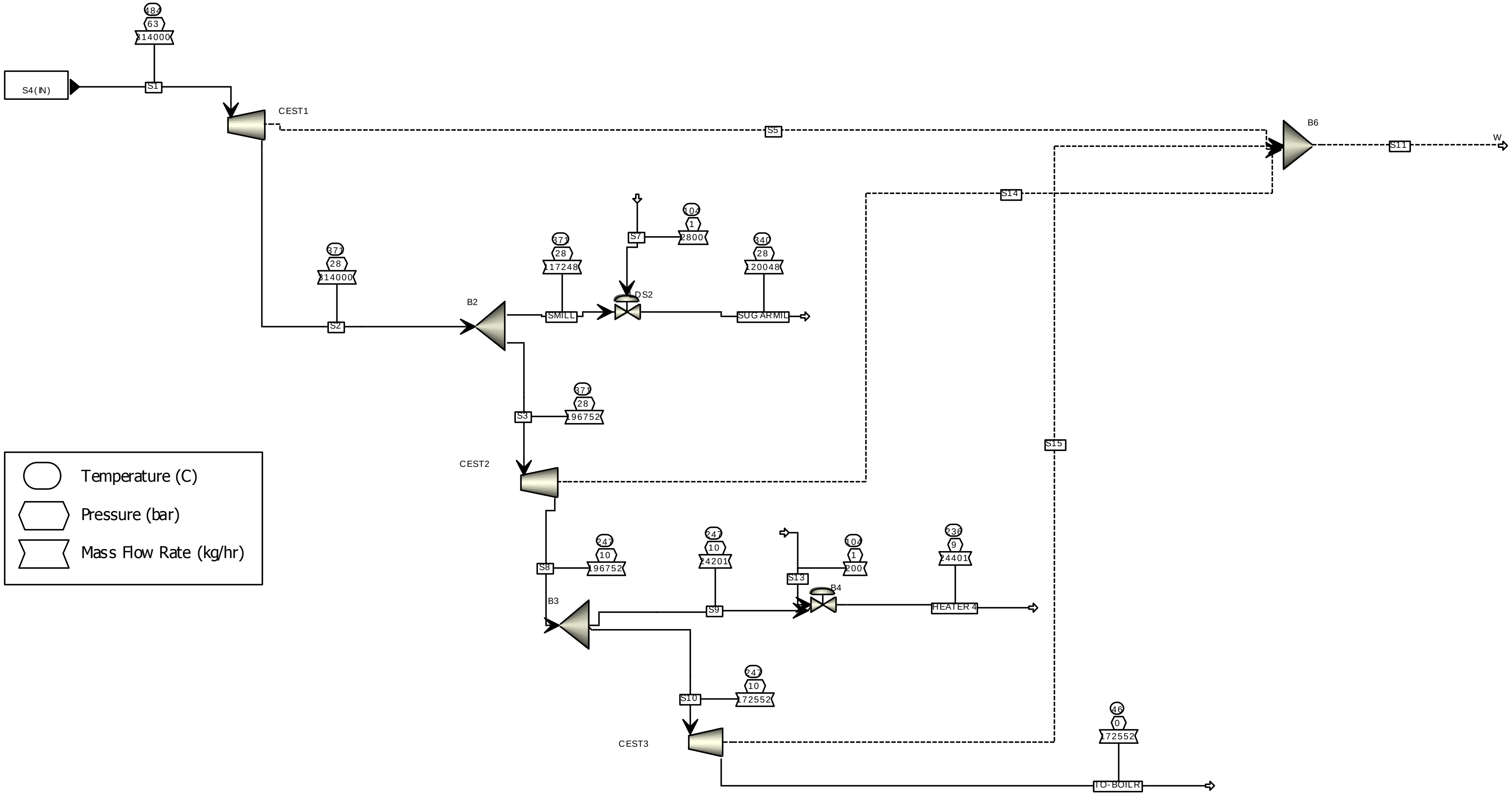


Figure B1-4: Condensing extraction steam turbine unit of the CHP base case

Table B1-1: Process conditions for Aspen models used for BETE and PE processes areas

	Aspen Unit	**ASPEN MODEL**	**Aspen Plus Process conditions**	**Other comments**
BETE	R 101	RSTOIC	Temp. = 450^{o}C, pressure = 13 atm	
	P101	PUMP	Pressure = 14 atm	Pump efficiency 75%, driver efficiency 95%
ETHYLENE PURIFICATION	CM201	PRESSURE CHANGER	Outlet pressure = 15 atm	Compressor
	CL201	HEAT EXCHANGER	Temp. = 145^{o}C, pressure = 15 atm	
	Q201	RADFRAC	Temp. = 195^{o}C, pressure = 19 atm	Used to model hemicellulose hydrolysis
	SPL301	SPLITTER	Temp. = 123^{o}C, pressure drop = 0	10% of product stream recycled back to Q201 (Quench)
	CL202	HEAT EXCHANGER	Temp. = 25^{o}C, pressure = 1 atm	
	CL203	HEAT EXCHANGER	Temp. = 35^{o}C, pressure = 1 atm	
	CM302	PRESSURE CHANGER	Outlet pressure = 19 atm	Compressor
	CL302	HEAT EXCHANGER	Temp. = 50^{o}C, pressure drop = 0	
	CM303	PRESSURE CHANGER	Outlet pressure = 20 atm	Compressor
	CL303	HEAT EXCHANGER	Temp. = 35^{o}C, pressure = 20 atm	
	CW301	RADFRAC	Pressure = 17 atm	
	P301	PUMP	Pressure = 20 atm	NaOH feed pump, pump efficiency 75%
	HT301	HEAT EXCHANGER	Temp. = 15^{o}C	
	DRY301	SEPARATOR (Dryer)	Temp. = 25^{o}C	
	CL305	HEAT EXCHANGER	Temp. = -37^{o}C	Cryogenic closed loop system
	CRY301	RADFRAC	Temp. = -35^{o}C, pressure = 17 atm	Cryogenic distillation, process conditions in chapter 3
	P101	PUMP	Pressure = 1 atm	Pumps hydrolysate to enzymatic hydrolysis, 75% efficiency
POLYMERISATION AND PURIFICATION	CL401	HEAT EXCHANGER	Temp. = 1^{o}C, pressure drop = 0	
	COMP401	PRESSURE CHANGER	Outlet pressure = 30 atm	Compressor
	FEEDPREP	MIXER	-	Assume 1% of solution reported to the solids stream
	CL402	HEAT EXCHANGER	Temp. = 100^{o}C, pressure drop = 0	
	POLYMERI	RYIELD (polymerisation)	Temp. = 100^{o}C, pressure = 30 atm	POLYNRTL property method
	B5	PRESSURE CHANGER	Outlet pressure = 1 atm	Valve, Excess H_2 removal
	H2-RECOV	SEPARATOR	Temp. = 28^{o}C	
	FT401	SEPARATOR	-	Catalyst removal, included for economic purposes
	H20-BATH	SPLITTER	Pressure drop = 0	Solvent remover, included for economic purposes
	*R301	RSTOIC	Temp. = 120^{o}C, pressure = 70 bar	* Sized as a pressure vessel
	EVAP401	SEPARATOR	-	Removes moisture, included for economic purposes

Table B1-2: PE process units and conditions used in Aspen Plus ®

	Aspen Unit	Type or purpose of uni	Process conditions	Other comments
COMBUSTOR	COMP 1	PRESSURE CHANGER	25^{o}C, 1 atm	Blower
	HEATER	HEAT EXCHANGER	Temp. = 178^{o}C, pressure = 1 atm	
	COMBUST	RSTOIC	Temp, 870^{o}C, pressure =1 atm	Combustor 99% biomass conversion
	HEATER 2	HEAT EXCHANGER	Temp.= 278^{o}CPressure = 1 atm	
		HEAT EXCHANGER		
	HEATER 3	HEAT EXCHANGER	Temp. =150^{o}C, Pressure = 1 atm	
	CENTRFG	SEPARATOR	Pressure drop = 0	Centrifuge
	PUMP1	PUMP	64 bar	Boiler pump at 75% efficiency
BOILER UNIT	HEATER4	HEAT EXCHANGER	Temp. 137^{o}C, Pressure drop = 0	Boiler feed water heater
	BOILER	FLASH	Temp. = 480^{o}C, pressure = 64 bar	Boiler
CEST UNIT	CEST 1	PRESSURE CHANGER	95% mechanical efficiency,	1st extraction stage
			85% isentropic efficiency	2nd extraction stage
	CEST 2	PRESSURE CHANGER	"	3rd extraction stage
	CEST 3	PRESSURE CHANGER	"	
	CONDSR	HEAT EXCHANGER	Temp. = 90^{o}C, Pressure drop = 0	

Table B1-3: Combustion reactions during biomass combustion in excess air (Mandegari et al., 2017)

Reaction	**Reactant**	**% converted to product**
Glucan + $6O_2 \rightarrow 6CO_2 + 5H_2O$	Glucan	99%
Xylan + $5O_2 \rightarrow 5CO_2 + 4H_2O$	Xylan	99%
Arabinan + $5O_2 \rightarrow 5CO_2 + 4H_2O$	Arabinan	99%
Mannan + $6O_2 \rightarrow 6CO_2 + 5H_2O$	Mannan	99%
Lignin + $8.5O_2 \rightarrow 8CO_2 + 4H_2O$	Lignin	99%
Galactan + $6O_2 \rightarrow 6CO_2 + 5H_2O$	Galactan	99%
Glucose + $6O_2 \rightarrow 6CO_2 + 6H_2O$	Glucose	99%
Xylose + $5O_2 \rightarrow 5CO_2 + 5H_2O$	Xylose	99%
Furfural + $5O_2 \rightarrow 5CO_2 + 2H_2O$	Furfural	99%
0.5 Nitrogen + $O_2 \rightarrow NO_2$	Nitrogen	0.001 kmol/hr
ASLignin + $8.5O_2 \rightarrow 8CO_2 + 4H_2O$	Lignin	99%
$H_2SO_4 \rightarrow SO_2 + H_2O + 0.5\ O_2$	Sulphuric acid	99%
Extractant + $O_2 \rightarrow 6CO_2 + 6H_2O$	Extractant	99%
Xylo-oligomer + 5O2 $\rightarrow 5CO_2 + 5H_2O$	Xylo-oligomers	99%
Cellobiose + $O_2 \rightarrow 6CO_2 + 6H_2O$	Cellobiose	99%
Methane + $2O_2 \rightarrow CO_2 + 2H_2O$	Methane	99%
Glucan + $H_2O \rightarrow$ Acetic Acid	Glucan	99%

Table B1-4: Process conditions used to generatethe reflux ratio vs number of theoretical stages for the quech and caustic wash columns for > 99% ethylene recovery efficiency

	(a) Quench tank	**(b) Caustic wash**
Aspen block	**DSTWU**	**DSTWU**
Number of stages	20	80
Condenser type	Partial-vapour	Partial-vapour
Reboiler type	Kettle	Kettle
Reflux ratio	4.4 (mass basis)	3.5 (mole basis)
Distillate rate (kmol/h)	236.4	-
Distillate to feed ratio (mole)	-	0.91
Condenser pressure (bar)	1	17
Reboiler pressure (bar)	1	17

B-2: Mass and energy balances

Table B2-1: Ethanol to ethylene steam tables (a) and (b)

(To)	101	HT201	202	CL201	Q201	CM302	SPL301	CL202	CL302	CM303	CL303	CW301
(From)	P101	201	HT201	CM201	CL201	Q201	Q201	SPL301	CM302	CL302	CM303	CL303
	LIQUID	VAPOR	VAPOR	VAPOR	MIXED	VAPOR	LIQUID	LIQUID	VAPOR	VAPOR	VAPOR	VAPOR
Substream: MIXED												
Mass Flow kg/hr												
ETHANOL	10982.09	3.75	3.75	43.93	43.93	0.00	58.57	14.64	0.00	0.00	0.00	0.00
ETHYLENE	0.00	5658.18	5658.18	6580.55	6580.55	6572.74	10.42	2.60	6572.74	6572.74	6572.74	6572.74
DIETH-01	0.00	179.77	179.77	4.42	4.42	0.00	5.89	1.47	0.00	0.00	0.00	0.00
ACETA-01	0.00	1830.24	1830.24	21.00	21.00	0.00	28.00	7.00	0.00	0.00	0.00	0.00
ETHAN-01	0.00	0.96	0.96	14.34	14.34	0.41	18.57	4.64	0.41	0.41	0.41	0.41
METHA-01	0.00	48.83	48.83	6.88	6.88	6.88	0.00	0.00	6.88	6.88	6.88	6.88
PROPY-01	0.00	92.62	92.62	3.51	3.51	0.00	4.68	1.17	0.00	0.00	0.00	0.00
1:2-B-01	0.00	119.06	119.06	32.24	32.24	0.00	42.98	10.75	0.00	0.00	0.00	0.00
CARBO-01	0.00	230.83	230.83	14.16	14.16	0.00	18.88	4.72	0.00	0.00	0.00	0.00
CARBO-02	0.00	0.00	0.00	5.34	5.34	5.34	0.00	0.00	5.34	5.34	5.34	5.34
WATER	20.91	3725.05	3725.05	4273.58	4273.58	0.00	5831.44	1457.86	0.00	0.00	0.00	0.00
HYDRO-01	0.00	113.71	113.71	3.05	3.05	3.05	0.00	0.00	3.05	3.05	3.05	3.05
ALUMI-01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
NAOH	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
NA2CO3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
NAHCO3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
HDPE	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
ZIG-NAT	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
HYDROGEN	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
REFRIG	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Total Flow kmol/hr	239.54	521.64	521.64	476.89	476.89	236.44	328.00	82.00	236.44	236.44	236.44	236.44
Total Flow kg/hr	11003.00	12003.00	12003.00	11003.00	11003.00	6588.43	6019.43	1504.86	6588.43	6588.43	6588.43	6588.43
Temperature C	25.36	375.00	450.00	470.58	145.00	-104.22	64.85	64.85	97.90	50.00	55.18	35.00
Pressure bar	14.00	12.16	13.00	15.00	15.00	1.00	1.00	1.00	18.50	18.75	20.00	20.00
Vapor Frac	0.00	1.00	1.00	1.00	0.70	1.00	0.00	0.00	1.00	1.00	1.00	1.00
Liquid Frac	1.00	0.00	0.00	0.00	0.30	0.00	1.00	1.00	0.00	0.00	0.00	0.00
Solid Frac	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

(a)

(To)	HT301	DRY301	CL305	CRY301	Q201	CW301	B3	CM201	CL203	B3 (WWT)	B3 (WWT)	B3 (WWT)
(From)	CW301	HT301	DRY301	CL305	CL202	P301	CL203	101	SPL301	CW301	DRY301	CRY301
	VAPOR	VAPOR	VAPOR	LIQUID	LIQUID	LIQUID	LIQUID	VAPOR	LIQUID	LIQUID	VAPOR	LIQUID
Substream: MIXED												
Mass Flow kg/hr												
ETHANOL	0.00	0.00	0.00	0.00	14.64	0.00	43.93	43.93	43.93	0.00	0.00	0.00
ETHYLENE	6282.29	6282.29	6282.29	6282.29	2.60	0.00	7.81	6580.55	7.81	290.45	0.00	251.27
DIETH-01	0.00	0.00	0.00	0.00	1.47	0.00	4.42	4.42	4.42	0.00	0.00	0.00
ACETA-01	0.00	0.00	0.00	0.00	7.00	0.00	21.00	21.00	21.00	0.00	0.00	0.00
ETHAN-01	0.22	0.22	0.09	0.09	4.64	0.00	13.93	14.34	13.93	0.19	0.13	0.03
METHA-01	6.88	6.88	0.00	0.00	0.00	0.00	0.00	6.88	0.00	0.00	6.88	0.00
PROPY-01	0.00	0.00	0.00	0.00	1.17	0.00	3.51	3.51	3.51	0.00	0.00	0.00
1:2-B-01	0.00	0.00	0.00	0.00	10.75	0.00	32.24	32.24	32.24	0.00	0.00	0.00
CARBO-01	0.00	0.00	0.00	0.00	4.72	0.00	14.16	14.16	14.16	0.00	0.00	0.00
CARBO-02	5.34	5.34	0.00	0.00	0.00	0.00	0.00	5.34	0.00	0.00	5.34	0.00
WATER	0.00	0.00	0.00	0.00	1457.86	149.05	4373.58	4273.58	4373.58	149.05	0.00	0.00
HYDRO-01	3.05	3.05	0.00	0.00	0.00	0.00	0.00	3.05	0.00	0.00	3.05	0.00
ALUMI-01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
NAOH	0.00	0.00	0.00	0.00	0.00	149.05	0.00	0.00	0.00	149.05	0.00	0.00
NA2CO3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
NAHCO3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
HDPE	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
ZIG-NAT	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
HYDROGEN	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
REFRIG	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Total Flow kmol/hr	226.08	226.08	223.94	223.94	82.00	12.00	246.00	476.89	246.00	22.36	2.14	8.96
Total Flow kg/hr	6297.79	6297.79	6282.38	6282.38	1504.86	298.10	4514.57	11003.00	4514.57	588.73	15.41	251.30
Temperature C	-35.09	15.00	25.12	-37.00	25.00	24.78	35.00	450.00	64.85	-42.06	25.12	-34.66
Pressure bar	17.00	10.00	19.00	19.00	1.00	20.27	1.01	13.00	1.00	17.00	19.00	17.00
Vapor Frac	1.00	1.00	1.00	0.00	0.00	0.00	0.00	1.00	0.00	0.00	1.00	0.00
Liquid Frac	0.00	0.00	0.00	1.00	1.00	1.00	1.00	0.00	1.00	1.00	0.00	1.00
Solid Frac	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

(b)

Table B2-2: Utilities for the PE biorefinery after heat integration (excluding the bio-ethanol process unit by Mandegari et al. 2017)

Unit	Description	Utility	Duty (kW)	Usage (kWh or t/h)
P101	Pump	electricity	7.8	7.8
RXT101	Stoichiometric Reactor	High High Pressure Steam (HHPS)	8560	41
CL201	Heat exchanger (cooler)	Cooling water	-3803	656
CL203	Heat exchanger (cooler)	Cooling water	-159	27
CL202	Heat exchanger (cooler)	Cooling water	-71	20.22
Q201COND	Condenser	Cooling water	-3915	670
Q201REB	Reboiler	Low pressure steam (LPS)	1848	3.1
CM201	Compressor	Electricity	167	167
CM302	Compressor	Electricity	537	537
CL302	Heat exchanger (cooler)	Cooling water	-163	28
CL303	Heat exchanger (cooler)	Cooling water	-66	11.5
CM303	Compressor	Electricity	14.3	14.3
P301	Pump	Electricity	0.19	0.19
CRY-REB	Cryogenic reboiler	Low pressure steam (LPS)	1056	1.7
CRY-COND	Cryogenic condenser	Refrigerant	-464	1245
CW301 COND	Caustic wash condenser	Cooling water	-2513	6747
CW301REB	Caustic wash reboiler	Low pressure steam (LPS)	2248	3.7
HT301	Heat exchanger (heater)	Low pressure steam (LPS)	151	0.3
DRY301	Dryer	Electricity	0.36	0.36
CL305	Closed loop refrigerant	Refrigerant	-791	2122
CL401	Heat exchanger	Low pressure steam (LPS)	159	0.3
COMP401	Compressor	Electricity	869	869
CL402	Heat exchanger (cooler)	Cooling water	-369	79
POLYMER	Polymerisation reactor	High pressure steam (HPS)	-21700	33.8

Table B2-3: Utilities for the CHP base case after heat integration

Unit	Description	Utility	duty (kW)	Usage
CL401	Heat exchanger (cooler)	cooling water	-39204	6761 t/h
COMP1	Compressor	Electricity	567	567 kWh
PUMP4	Pump	Electricity	564	564 kWh
HEATER4	Heat exchanger (heater)	MP Steam *	13834	24 t/h
CONDNSR	Condenser	Cooling water	-102719	17714 t/h

*MP Steam is medium pressure steam at 233°C and 9.5 atm.

[a] The other process units in the boiler and CEST system are heat integrated using flue gas steam therefore not included.

B-3: Pinch analysis

Table B3-1: Polyethylene scenarios stream input variables for the calculation of the streams' heat capacity flowrates for heat integration

Stream Name	Supply Temp.	Target Temp.	dT Min Contribution	Heat Capacity Flowrate	Heat Flow	Stream Type	Supply Shift	Target Shift
	°C	°C	°C	kW/K	kW		°C	°C
CL201	471	145	10	11.7	3803.0	HOT	461.0	135.0
CW301REB	35	42	10	321.1	2248.0	COLD	45.0	52.0
CL401	-37	1	10	3.9	148.0	COLD	-27.0	11.0
HT301	-35	15	10	3.0	151.0	COLD	-25.0	25.0

A total of 1 hot and 3 cold streams were integerated. Table B3-1 shows the input and output streams and heat capacity flow rates at a ΔT_{min} of 10 min.

Table B3-2: Polyethylene problem cascade table to determine the pinch point and the hot and cold utility duties

Problem Table & Cascade

Shift Temperature	Interval	$T_{(i+1)}-T_i$	mCp_{net}	dH			Infeasible Cascade		Feasible Cascade	
°C		°C	kW/K	kW						
461						PINCH	▼	0	▼	0
	1	326	11.6656	3803.0	surplus		3803		3803	
135							▼	3803	▼	3803
	2	83	0.0	0.0	demand		0		0	
52							▼	3803	▼	3803
	3	7	-321.1429	-2248.0	demand		-2248		-2248	
45							▼	1555	▼	1555
	4	20	0.0	0.0	demand		0		0	
25							▼	1555	▼	1555
	5	14	-3.02	-42.28	demand		-42.28		-42.28	
11							▼	1512.7	▼	1512.7
	6	36	-6.9147	-248.9305	demand		-248.931		-248.9305	
-25							▼	1263.8	▼	1263.8
	7	2	-3.8947	-7.7895	demand		-7.78947		-7.789474	
-27							▼	1256	▼	1256

Hot Pinch	466 °C
Cold Pinch	456 °C

Min Hot Utility	0.0 kW
Min Cold Utility	1256.0 kW

SINGLE PINCH PROBLEM

THRESHOLD PROBLEM

Hot pinch at 466 °C and cold pinch at 456 °C

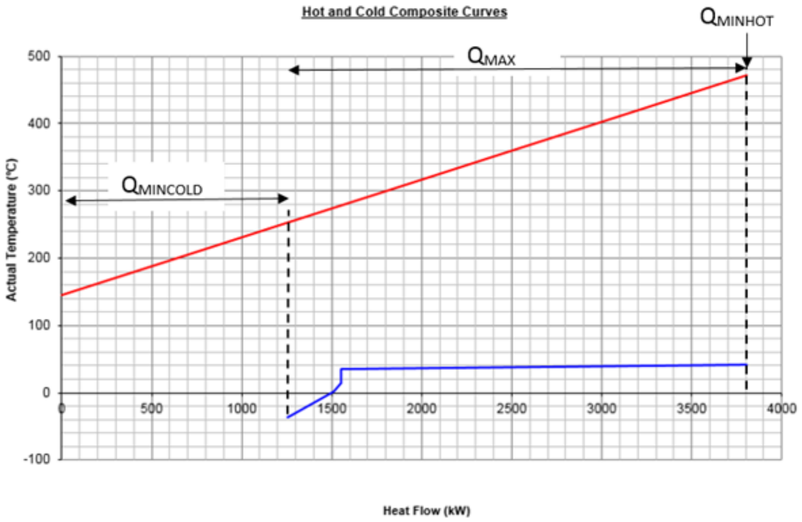


Figure 3-1: Composite curve after integrating 1 hot and 3 cold streams for the polyethylene scenario

This led to the PE scenario attaining a hot and cold utility saving of 11 % and 19% respectively.

Table B3-3: Overall pinch analysis and energy savings for all scenarios

SCENARIOS	PE	Sorbitol.$_{STEX}$	Glucaric.$_{STEX}$	Sorbitol.$_{DA}$	Glucaric.$_{DA}$	LA-F-E	LA-GVL-F-E
Hot streams	1	1	1	1	1	3	3
Cold streams	3	2	2	3	3	2	2
Hot pinch (^{o}C)	466	40	40	40	40	210	218
Cold pinch (^{o}C)	456	30	30	30	30	200	208
Min hot utility supplied to system (kW)	0	200	200	14642	14642	6202	304
Min cold utility removed (kW)	1256	0	0	0	0	3841	4267
Q_{max}(theoretical max. heat recovered) (kW)	2005	1490	1490	13500	13500	17000	12400
Total hot stream before pinch (kW)	3803	1482	1482	42573	42573	16917	13455
Total cold utility before pinch (kW)	2547	1682	1682	57215	57215	21317	9736
Total biorefinery's hot utility (kW)	36221	66430	70549	73416	88920	71500	57534
Total biorefinery's cold utility (kW)	12350	94212	98474	137490	134280	77000	130104
After pinch (hot utility) - amount used (kW)	32418	65147.54	69267	45485	60989	60785	44383
After pinch (cold utility) - amount used (kW)	9803	92530	96791	80275	77065	59524	124635
Total saving (hot utility) (%)	11.7	1.9	1.8	38	31.4	15	22.9
Total savings (cold utility) (%)	20.6	1.8	1.7	41.6	42.6	22.7	4.2

B-4: Lignocellulose components used in the Aspen Plus® models as defined in Humbird et al. (2011)

B4-1: Lignocellulose components as defined in Humbird et al. (2011) and used in the models in chapters 3, 4 and 5

Main biomass Component		**Formula**
Cellulose (Glucan)		$C_6H_{10}O_5$ - dilactic acid
Hemicellulose	Mannan	$C_6H_{10}O_5$ - dilactic acid
	Galactan	$C_6H_{10}O_5$ - dilactic acid
	Xylan	$C_5H_8O_4$ - glutaric acid
	Arabinan	$C_5H_8O_4$ - glutaric acid
Lignin		$C_8H_8O_3$ - Vanillin
Extractant		$C_6H_{12}O_6$ - dextrose
Summary of other components		
Glucose		$C_6H_{10}O_5$ - dilactic acid
Gluco - oligomer		$C_6H_{10}O_5$ - dilactic acid
Xylo – oligomer		$C_5H_8O_4$ - glutaric acid
Arabino - oligomer		$C_5H_8O_4$ - glutaric acid
Xylose		$C_5H_{10}O_6$ - xylose
Arabinose		$C_5H_{10}O_6$ - arabinose
Cellobiose		$C_{12}H_{22}O_{11}$ - cellobiose

The other components (conventional) used in the Aspen Plus ® models are present in the native Aspen Plus ® databank.

B-5: Equipment sizing

Table B5-1: Bio-based ethylene and polyethylene equipment sizing (all costs in US$)

Area 100-REACTION

No.	Equipment label	Actual equipment	description (Ref)	Material	Unit cost ($)	No. used	total cost ($)	Year of quote	scaling value	Units	scaling Exp.	Instal. Factor	Size ratio	new value	Scaled purchase price ($)	Purchase price In Proj. Year	Installed cost in Project Year
1	R 101		SINNOT * TOWLER 2M D & 11.2 LENGTH	SS	208975	2	417950	2010		kg/h	0.6	2			417950	417 950	835 900.00
2	P101	PUMP	ASPEN													32400	92600
3	EV101	VAPORISER	NREL - M-904	SS												423 124.00	761 623.20
4	HXs	NOT SHOWN			24000	3	72000									72 000.00	129 600.00
Also inculded in the above item costs are:																**869 836**	**1 674 145**

i. Sulphur burner (1)

ii. Sulphur pump (1)

AREA200-RECOVERY

No.	Equipment label	Actual equipment	description (Ref)	Material	Unit cost ($)	No. used	total cost ($)	Year of quote	scaling value	Units	scaling Exp.	Instal. Factor	Size ratio	new value	Scaled purchase price ($)	Purchase price In Proj. Year	Installed cost in Project Year
2	CL203	HX	ASPEN	304SS												10700	59400
3	CL201	HX	ASPEN													23700	120400
4	CL202	Cooler	ASPEN	SS												8500	60900
5	CM201	COMPRESSOR	ASPEN	SS												825600	841100
8	.Q201-reb															17700	97100
9	Q201-reflux pump															6900	44500
10	Q201-tower															200200	455900
																1 005 836	**995 256**

AREA300-PURIFICATION

No.	Equipment label	Actual equipment	description (Ref)	Material	Unit cost ($)	No. used	total cost ($)	Year of quote	scaling value	Units	scaling Exp.	Instal. Factor	Size ratio	new value	Scaled purchase price ($)	Purchase price In Proj. Year	Installed cost in Project Year
1	P301	PUMP	ASPEN	SS												14600	38600
2	CW301	CAUSTIC WASH	ASPEN	CS												212100	716600
3	CW301-ACC	CAUSTIC WASH	ASPEN	SS												23600	114000
4	CW301-REFLUX PUMP	Pressure filter	ASPEN	SS												6500	43900
5	CW301 TOWER	Regeneration	ASPEN	SS												1684200	2076000
6	CRY-301-COND		ASPEN	SS												54900	368000
7	CRY-301-ACC		ASPEN	SS												12000	79200
8	CRY301-REB		ASPEN	SS												303700	431700
9	CRY301-PUMP		ASPEN	SS												5000	32800
10	CRY301-TOWER		ASPEN	SS												45600	185200
11	CL302		ASPEN													10000	59500
12	CL303		ASPEN													10000	57300
13	B2		ASPEN													123500	309100
14	B4		ASPEN													2065200	2493800
15	DRY301		ASPEN													17900	89900
16	CM303	COMPRESSOR	ASPEN													678400	799100
17	CL305	HX	ASPEN													29800	129000
18	CM302	COMPRESSOR	ASPEN													1650400	1803100
19	CM303	COMPRESSOR	ASPEN													678400	799100
Also inculded in the above item costs are:																**5 002 132**	**7 197 160**
							7.65										

AREA400 POLYMERISATION

No.	Equipment label	Actual equipment	description (Ref)	Material	Unit cost ($)	No. used	total cost ($)	Year of quote	scaling value	Units	scaling Exp.	Instal. Factor	Size ratio	new value	Scaled purchase price ($)	Purchase price In Proj. Year	Installed cost in Project Year
1	FT401	FILTER				6										133200	226800
2	HT401	HX	ASPEN	SS												12900	75100
3	P401	PUMP	ASPEN	SS		1										186600	228200
4	R 401	RXTOR	TOWLER & SINNOT 30 BAR 4 HRS HIGH PRESSURE	SS	1357985	6	8147910	2010				2			8147910	8147910	16295820
5	POLYMERS.R401																
6	POLYMERS.CL401															9600	61800
7	POLYMERS.P401															186600	228200
8	POLYMERS.HT401															9900	62100
9	POLYMERS.P402					7										39200	79000
10	AGITATORS	NOT SHOWN			35000	6	210000					1.5				210000	315000
															TOTAL	**8 221 037**	**16 166 258**

Table B5-2: CHP base case equipment sizing (all costs in US$)

Boiler

No.	Equipment label	Actual equipment	description (Ref)	Material	Unit cost ($)	No. used	total cost ($)	Year of quote	scaling value	Units	scaling Exp.	Instal. Factor	Size ratio	new value	Scaled purchase price ($)	Purchase price In Proj. Year	Installed cost in Project Year
1	HEATER 4		ASPEN													68800	174700
2	CM401	compressor/air blower/fan	INCLUDED	SS	INCLUDED	1											
3	HEATER2	Heater	INCLUDED	SS	INCLUDED	1											
4	BFW HEAT RECOVERY		NREL	SS	41000	1	41000	2009	-2		0.7	2.2	1.4	-2.8	40180	41304	90869
5	HEATER1	Cooler	ASPEN	SS	1650600	1	1650600	2017		kg/h	0.7				1650600	1650600	2682100
6	HEATER3	Cooler	ASPEN	SS	390700	1	390700	2017		kg/h	0.7				390700	390800	605800
7	PUMP4		ASPEN													209600	336500
8	HEATER B2	Heater	ASPEN	SS	101500	1	101500	2017			0.7				101500	0	0
9	CL401		ASPEN													88100	196600
10	CFG401	Centrifuge/FGD BAG HOUSE	NREL	SS	INCLUDED												
11	B401	Boiler	NREL	SS	28550000	1	28550000	2010	238686	kg/h	0.6	1.8	1.32	314000	33656406	32782610	59008698
12	DEARATOR		NREL	SS	305000	1	305000	2010	235803	kg/h	0.6	3	1.331620039	314000	362182.9757	352780	1058340
																35 584 594.01	64 153 606.69

CEST

No.	Equipment label	Actual equipment	description (Ref)	Material	Unit cost ($)	No. used	total cost ($)	Year of quote	scaling value	Units	scaling Exp.	Instal. Factor	Size ratio	new value	Scaled purchase price ($)	Purchase price In Proj. Year	Installed cost in Project Year
1	CEST	Turbogenerator	NREL	SS	9500000	1	9500000	2010	230000	kg/h	0.6	1.8	1.365217391	314000	7781739.13	7579708	13643474
2	CONDENSOR	Condenser	ASPEN	SS	243700	1	243700	2017		kg/h	0.6				243700	0	0
Also inculded in the above item costs are:																7579708	13 643 474.00

B-6: Polyethylene biorefinery option 2

Table B6-1: Mass and energy balances of the PE biorefinery option 2 at 48% bypass ratio compared to a base case CHP plant scenario

		Ethanol biorefinery	**Option 2**	**CHP base case**
Parameter	Unit			
Feedstock (DM-dry mass)	t/h	65	-	65
Total feedstock (WT-wet mass)	t/h	113	-	113
By-pass to boiler	%	35	-	100
Feedstock to bio refinery (DM)	t/h	42.25	-	0
Cellulosic Ethanol[b]	t/h	8.6[b]	8.6	-
Ethylene	t/h	-	5.6	-
Ethylene/ethanol yield	kg/kg	-	0.54	-
Ethylene yield (of theoretical max.)	%	-	94.6	-
Polyethylene	t/h	-	5.4	-
Polyethylene/ethylene yield	kg/kg	-	0.95	-
Steam demand	MWh	155	32.4	7
Electricity demand	MWh	11.2	1.6	0.9
Cooling demand	MWh	50.6	11.1	110.9
Electricity produced (excess)	MWh	7.1	14	60.9

*Details from Mandegari et al. (2017).

[b] Feedstock to the BETE process.

The polyethylene (PE) scenario produced 5.4 t/h polymer (36 kt/y) by converting 8.6 t/h cellulosic ethanol from the ethanol biorefinery as shown in Table B4-1, whilst option 1 in the main body produced 6 t/h polyethylene. Details of the CHP base case and ethanol process area by Mandegari et al. 2017 have been discussed in the main text and are only provided here for context and comparison.

The total steam demand was highest in the PE scenario at 32 MWh (41 t/h steam). This additional steam demand of 32 MWh from the PE biorefinery led to the upward adjustment of the ethanol biorefinery's bypass ratio from 35% to 48% for it to be bio-energy self-sufficient. About 72% of the total cooling demand in the PE biorefinery was used to reduce the dehydration reactor outlet stream temperatures from 450 ^oC to 145 ^oC prior to the compression and quenching stages. Also, the PE biorefinery consumed 1.6 MWh electricity as shown in Table B6-1 and a surplus of 14 MWh was sold to the grid.

Table B6-2: Total capital investment, fixed and variable operating costs and total cost of production of option 2 biorefinery and CHP base case (excluding feedstock handling)

Total Capital Investment costs (US$ million)		
	Option 2	**CHP Base case**
Pretreatment	18.6	-
Enzyme Production	9.0	-
Enzymatic Hydrolysis and fermentation	9.2	-
Recovery	11.8	-
Evaporation	9.2	-
Ethanol to ethylene	1.7	-
Ethylene recovery	1.0	-
Ethylene purification	7.2	-
Ethylene to polyethylene	15.6	-
Waste water treatment	3.8	-
Boiler and CEST	56.1	73.5
Utilities	5.4	4.0
Storage	4.1	-
Total installed equipment costs	**152.7**	**77.5**
Total Direct costs	167.2	77.5
Total indirect costs	100.3	46.5
Fixed Capital Investment	267.6	123.9
Total Capital Investment	**281.0**	**130.1**
Fixed capital investment (US$ million/y)	**9.7**	**4.4**
***Variable operating cost (US$ million/y)**	**20.0**	**8.7**
Total cost of production (US$ million/y)	**29.7**	**13.1**

*The variable operating cost in option 2 was adjusted by a factor of 0.9 (with reference to 1) since the variable operating costs reduced with an increase in the by-pass ratio

Table B6-3: Option 2 and CHP base case economic viability

	Option 2	**CHP Base case**
IRR (%)	-	10.3
Hurdle rate (%)	9.7	9.7
Net Present Value (NPV) (US$ million)	-221	6.5
Minimum product selling price (NPV=0)	1745	0.077
Threshold IRR to attract investors	20	20
Price to reach threshold IRR	2865	0.12

Approaches for option 1 and 2 used to calculate the biorefinery’s profitability were acceptable. Option 1 and 2 were significantly unprofitable with NPVs of -284 and -221 US$ million respectively whilst the threshold selling price of PE (to attain an IRR of 20%) was calculated as US$ 2956/ t and US$ 2865/t respectively.

B-7: Discounted cash flow rate of return (DCFROR) spreadsheet for the polyethylene (PE) biorefinery

Table B7-1: Discounted cash flow rate of return spreadsheet (a), (b) and (c) for the PE biorefinery

	##	347		RAMP UP	0.5	0.75	1.00		
DCFROR Worksheet				2016	2017	2018	2019	2020	2021
Year			-1	0	1	2	3	4	
Fixed Capital Investment		$ 29 992 726.38	$ 179 956 358.29	$ 89 978 179.15					
Land		$ -	$ -	$ -					
Working Capital				$ 14 996 363.19					
Loan Payment					$ -	$ -	$ -	$ -	$ -
Loan Interest Payment		$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -
Loan Principal		$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -
P.E Price ($/t)				$ 886.00	$ 886.00	$ 886.00	$ 886.00	$ 886.00	$ 886.
Bio-product Sales				$ -	$ 34 464 903.84	$ 34 464 903.84	$ 34 464 903.84	$ 34 464 903.84	$ 34 464 903.
Electricty price ($/ kWh)				$ 0.080	$ 0.08	$ 0.08	$ 0.08	$ 0.08	$ 0.
Electricity Sales				$ -	$ 6 400.00	$ 6 400.00	$ 6 400.00	$ 6 400.00	$ 6 400.
Total Annual Revenue				$ -	$ 17 235 651.92	$ 25 853 477.88	$ 34 471 303.84	$ 34 471 303.84	$ 34 471 303.
Annual Manufacturing Cost									
Feedstock Price ($/ ton)									
Feedstock cost									
Other Variable Costs									
Fixed Operating Costs									
Total Product Cost				$ -	$ 15 480 762.71	$ 23 221 144.07	$ 30 961 525.43	$ 30 961 525.43	$ 30 961 525.
Annual Depreciation									
Plant Writedown				0.00%	20.00%	20.00%	20.00%	20.00%	20.0
Depreciation Charge				$ -	$ 59 985 452.76	$ 59 985 452.76	$ 59 985 452.76	$ 59 985 452.76	$ 59 985 452.
Remaining Value				$ 299 927 263.82	$ 239 941 811.05	$ 179 956 358.29	$ 119 970 905.53	$ 59 985 452.76	$ -
Net Revenue (R-COM-dk)		($29 992 726)	($179 956 358)	($104 974 542)	$ -58 230 563.56	$ -57 353 118.96	$ -56 475 674.35	$ -56 475 674.35	$ -56 475 674.
Losses Forward					$0	($58 230 564)	($115 583 683)	($172 059 357)	($228 535 0
Taxable Income					$ -58 230 563.56	$ -115 583 682.51	$ -172 059 356.87	$ -228 535 031.22	$ -285 010 705.
Income Tax					$0	$0	$0	$0	
Annual Cash Income				($314 923 627)	$1 754 889	$2 632 334	$3 509 778	$3 509 778	$3 509
Discount Factor			1.0970	1.0000	0.9116	0.8310	0.7575	0.6905	0.6
Annual Present Value (Discounted Cash Flow)				($314 923 627)	$ 1 599 716.69	$ 2 187 397.48	$ 2 658 641.72	$ 2 423 556.72	$ 2 209 258.
Cumulative Discounted Cash Flow				($314 923 627)	($313 323 910)	($311 136 513)	($308 477 871)	($306 054 314)	($303 845 0
Total Capital Investment + Interest			$ 197 412 125.04	$ 104 974 542.34					
Net Present Worth				($284 644 739)					

(a)

DCFROR Worksheet	2024	2025	2026	2027	2028	2029	2030	2031
Year	8	9	10	11	12	13	14	15
Fixed Capital Investment								
Land								
Working Capital								
Loan Payment	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -
Loan Interest Payment	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -
Loan Principal	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -
P.E Price ($/t)	$ 886.00	$ 886.00	$ 886.00	$ 886.00	$ 886.00	$ 886.00	$ 886.00	$ 886.00
Bio-product Sales	$ 34 464 903.84	$ 34 464 903.84	$ 34 464 903.84	$ 34 464 903.84	$ 34 464 903.84	$ 34 464 903.84	$ 34 464 903.84	$ 34 464 903.84
Electricty price ($/ kWh)	$ 0.08	$ 0.08	$ 0.08	$ 0.08	$ 0.08	$ 0.08	$ 0.08	$ 0.08
Electricity Sales	$ 6 400.00	$ 6 400.00	$ 6 400.00	$ 6 400.00	$ 6 400.00	$ 6 400.00	$ 6 400.00	$ 6 400.00
Total Annual Revenue	$ 34 471 303.84	$ 34 471 303.84	$ 34 471 303.84	$ 34 471 303.84	$ 34 471 303.84	$ 34 471 303.84	$ 34 471 303.84	$ 34 471 303.84
Annual Manufacturing Cost								
Feedstock Price ($/ ton)								
Feedstock cost								
Other Variable Costs								
Fixed Operating Costs								
Total Product Cost	$ 30 961 525.43	$ 30 961 525.43	$ 30 961 525.43	$ 30 961 525.43	$ 30 961 525.43	$ 30 961 525.43	$ 30 961 525.43	$ 30 961 525.43
Annual Depreciation								
Plant Writedown								
Depreciation Charge								
Remaining Value								
Net Revenue (R-COM-dk)	$ 3 509 778.41	$ 3 509 778.41	$ 3 509 778.41	$ 3 509 778.41	$ 3 509 778.41	$ 3 509 778.41	$ 3 509 778.41	$ 3 509 778.41
Losses Forward	($277 991 149)	($274 481 370)	($270 971 592)	($267 461 814)	($263 952 035)	($260 442 257)	($256 932 478)	($253 422 700)
Taxable Income	$ -274 481 370.34	$ -270 971 591.93	###########	$-263 952 035.10	$-260 442 256.69	$ -256 932 478.28	$ -253 422 699.87	$ -249 912 921.46
Income Tax	$0	$0	$0	$0	$0	$0	$0	$0
Annual Cash Income	$3 509 778	$3 509 778	$3 509 778	$3 509 778	$3 509 778	$3 509 778	$3 509 778	$3 509 778
Discount Factor	0.4768	0.4347	0.3962	0.3612	0.3292	0.3001	0.2736	0.2494
Annual Present Value (Discounted Cash Flow)	$ 1 673 503.70	$ 1 525 527.53	$ 1 390 635.85	$ 1 267 671.70	$ 1 155 580.40	$ 1 053 400.55	$ 960 255.74	$ 875 347.07
Cumulative Discounted Cash Flow	($298 321 809)	($296 796 282)	($295 405 646)	($294 137 974)	($292 982 394)	($291 928 993)	($290 968 737)	($290 093 390)
Total Capital Investment + Interest								
Net Present Worth								

(b)

DCFROR Worksheet	2032	2033	2034	2035	2036	2037	2038	2039	2040	2041
Year	16	17	18	19	20	21	22	23	24	25
Fixed Capital Investment										
Land										
Working Capital										
Loan Payment	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -
Loan Interest Payment	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -
Loan Principal	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -
P.E Price ($/t)	$ 886.00	$ 886.00	$ 886.00	$ 886.00	$ 886.00	$ 886.00	$ 886.00	$ 886.00	$ 886.00	$ 886.00
Bio-product Sales	$ 34 464 903.84	$ 34 464 903.84	$ 34 464 903.84	$ 34 464 903.84	$ 34 464 903.84	$ 34 464 903.84	$ 34 464 903.84	$ 34 464 903.84	$ 34 464 903.84	$ 34 464 903.84
Electricty price ($/ kWh)	$ 0.08	$ 0.08	$ 0.08	$ 0.08	$ 0.08	$ 0.08	$ 0.08	$ 0.08	$ 0.08	$ 0.08
Electricity Sales	$ 6 400.00	$ 6 400.00	$ 6 400.00	$ 6 400.00	$ 6 400.00	$ 6 400.00	$ 6 400.00	$ 6 400.00	$ 6 400.00	$ 6 400.00
Total Annual Revenue	$ 34 471 303.84	$ 34 471 303.84	$ 34 471 303.84	$ 34 471 303.84	$ 34 471 303.84	$ 34 471 303.84	$ 34 471 303.84	$ 34 471 303.84	$ 34 471 303.84	$ 34 471 303.84
Annual Manufacturing Cost										
Feedstock Price ($/ ton)										
Feedstock cost										
Other Variable Costs										
Fixed Operating Costs										
Total Product Cost	$ 30 961 525.43	$ 30 961 525.43	$ 30 961 525.43	$ 30 961 525.43	$ 30 961 525.43	$ 30 961 525.43	$ 30 961 525.43	$ 30 961 525.43	$ 30 961 525.43	$ 30 961 525.43
Annual Depreciation										
Plant Writedown										
Depreciation Charge										
Remaining Value										
Net Revenue (R-COM-dk)	$ 3 509 778.41	$ 3 509 778.41	$ 3 509 778.41	$ 3 509 778.41	$ 3 509 778.41	$ 3 509 778.41	$ 3 509 778.41	$ 3 509 778.41	$ 3 509 778.41	$ 3 509 778.41
Losses Forward	($249 912 921)	($246 403 143)	($242 893 365)	($239 383 586)	($235 873 808)	($232 364 029)	($228 854 251)	($225 344 473)	($221 834 694)	($218 324 916)
Taxable Income	$ -246 403 143.05	$ -242 893 364.64	$ -239 383 586.23	$ -235 873 807.82	$ -232 364 029.41	$ -228 854 251.00	$ -225 344 472.58	$ -221 834 694.17	$ -218 324 915.76	$ -214 815 137.35
Income Tax	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0
Annual Cash Income	$3 509 778	$3 509 778	$3 509 778	$3 509 778	$3 509 778	$3 509 778	$3 509 778	$3 509 778	$3 509 778	$3 509 778
Discount Factor	0.2273	0.2072	0.1889	0.1722	0.1570	0.1431	0.1305	0.1189	0.1084	0.0988
Annual Present Value (Discounted Cash Flow)	$ 797 946.28	$ 727 389.50	$ 663 071.56	$ 604 440.80	$ 550 994.35	$ 502 273.79	$ 457 861.25	$ 417 375.80	$ 380 470.19	$ 346 827.89
Cumulative Discounted Cash Flow	($289 295 444)	($288 568 054)	($287 904 983)	($287 300 542)	($286 749 548)	($286 247 274)	($285 789 413)	($285 372 037)	($284 991 567)	($284 644 739)
Total Capital Investment + Interest										
Net Present Worth										

(c)

Table B7-2: Discounted cash flow rate of return spreadsheet (a), (b) and (c) for the CHP base case

DCFROR Worksheet			2016	2017	2018	2019	2020	2021	2022	2023
Year	-2	-1	0	1	2	3	4	5	6	7
Fixed Capital Investment	$12 084 336.26	$ 72 506 017.57	$ 36 253 008.79							
Land	$ -	$ -	$ -							
Working Capital			$ 6 042 168.13							
Loan Payment				$ -	$ -	$ -	$ -	$ -	$ -	$ -
Loan Interest Payment	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -
Loan Principal	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -
Price ($/t)			$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -
Bio-product Sales			$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -
Electricty price ($/ kWh)			$ 0.080	$ 0.080	$ 0.080	$ 0.080	$ 0.080	$ 0.080	$ 0.080	$ 0.080
Electricity Sales			$ -	$ 30 916 339.20	$ 30 916 339.20	$ 30 916 339.20	$ 30 916 339.20	$ 30 916 339.20	$ 30 916 339.20	$ 30 916 339.20
Total Annual Revenue			$ -	$ 15 458 169.60	$ 23 187 254.40	$ 30 916 339.20	$ 30 916 339.20	$ 30 916 339.20	$ 30 916 339.20	$ 30 916 339.20
Annual Manufacturing Cost										
Feedstock Price ($/ ton)										
Feedstock cost										
Other Variable Costs										
Fixed Operating Costs										
Total Product Cost			$ -	$ 6 535 277.63	$ 9 802 916.44	$ 13 070 555.26	$ 13 070 555.26	$ 13 070 555.26	$ 13 070 555.26	$ 13 070 555.26
Annual Depreciation										
Plant Writedown			0.00%	20.00%	20.00%	20.00%	20.00%	20.00%		
Depreciation Charge			$ -	$ 24 168 672.52	$ 24 168 672.52	$ 24 168 672.52	$ 24 168 672.52	$ 24 168 672.52		
Remaining Value			$ 120 843 362.62	$ 96 674 690.10	$ 72 506 017.57	$ 48 337 345.05	$ 24 168 672.52	$ -		
Net Revenue (R-COM-dk)	($12 084 336)	($72 506 018)	($42 295 177)	$ -15 245 780.55	$ -10 784 334.57	$ -6 322 888.58	$ -6 322 888.58	$ -6 322 888.58	$ 17 845 783.94	$ 17 845 783.94
Losses Forward				$0	($15 245 781)	($26 030 115)	($32 353 004)	($38 675 892)	($44 998 781)	($27 152 997)
Taxable Income				$ -15 245 780.55	$ -26 030 115.12	$ -32 353 003.71	$ -38 675 892.29	$ -44 998 780.88	$ -27 152 996.94	$ -9 307 212.99
Income Tax				$0	$0	$0	$0	$0	$0	$0
Annual Cash Income			($126 885 531)	$8 922 892	$13 384 338	$17 845 784	$17 845 784	$17 845 784	$17 845 784	$17 845 784
Discount Factor		1.0970	1.0000	0.9116	0.8310	0.7575	0.6905	0.6295	0.5738	0.5231
Annual Present Value (Discounted Cash Flow)			($126 885 531)	$ 8 133 903.35	$ 11 122 019.16	$ 13 518 102.90	$ 12 322 792.07	$ 11 233 174.17	$ 10 239 903.53	$ 9 334 460.83
Cumulative Discounted Cash Flow			($126 885 531)	($118 751 627)	($107 629 608)	($94 111 505)	($81 788 713)	($70 555 539)	($60 315 636)	($50 981 175)
Total Capital Investment + Interest		$ 79 539 101.28	$ 42 295 176.92							
Net Present Worth			$6 458 395							

(a)

DCFROR Worksheet	2024	2025	2026	2027	2028	2029	2030	2031	2032
Year	8	9	10	11	12	13	14	15	16
Fixed Capital Investment									
Land									
Working Capital									
Loan Payment	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -
Loan Interest Payment	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -
Loan Principal	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -
Price ($/t)	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -
Bio-product Sales	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -
Electricty price ($/ kWh)	$ 0.080	$ 0.080	$ 0.080	$ 0.080	$ 0.080	$ 0.080	$ 0.080	$ 0.080	$ 0.080
Electricity Sales	$ 30 916 339.20	$ 30 916 339.20	$ 30 916 339.20	$ 30 916 339.20	$ 30 916 339.20	$ 30 916 339.20	$ 30 916 339.20	$ 30 916 339.20	$ 30 916 339.20
Total Annual Revenue	$ 30 916 339.20	$ 30 916 339.20	$ 30 916 339.20	$ 30 916 339.20	$ 30 916 339.20	$ 30 916 339.20	$ 30 916 339.20	$ 30 916 339.20	$ 30 916 339.20
Annual Manufacturing Cost									
Feedstock Price ($/ ton)									
Feedstock cost									
Other Variable Costs									
Fixed Operating Costs									
Total Product Cost	$ 13 070 555.26	$ 13 070 555.26	$ 13 070 555.26	$ 13 070 555.26	$ 13 070 555.26	$ 13 070 555.26	$ 13 070 555.26	$ 13 070 555.26	$ 13 070 555.26
Annual Depreciation									
Plant Writedown									
Depreciation Charge									
Remaining Value									
Net Revenue (R-COM-dk)	$ 17 845 783.94	$ 17 845 783.94	$ 17 845 783.94	$ 17 845 783.94	$ 17 845 783.94	$ 17 845 783.94	$ 17 845 783.94	$ 17 845 783.94	$ 17 845 783.94
Losses Forward	($9 307 213)	$0	$0	$0	$0	$0	$0	$0	$0
Taxable Income	$ 8 538 570.95	$ 17 845 783.94	$ 17 845 783.94	$ 17 845 783.94	$ 17 845 783.94	$ 17 845 783.94	$ 17 845 783.94	$ 17 845 783.94	$ 17 845 783.94
Income Tax	$2 390 800	$4 996 820	$4 996 820	$4 996 820	$4 996 820	$4 996 820	$4 996 820	$4 996 820	$4 996 820
Annual Cash Income	$15 454 984	$12 848 964	$12 848 964	$12 848 964	$12 848 964	$12 848 964	$12 848 964	$12 848 964	$12 848 964
Discount Factor	0.4768	0.4347	0.3962	0.3612	0.3292	0.3001	0.2736	0.2494	0.2273
Annual Present Value (Discounted Cash Flow)	$ 7 369 118.52	$ 5 584 810.98	$ 5 090 985.40	$ 4 640 825.34	$ 4 230 469.77	$ 3 856 399.06	$ 3 515 404.80	$ 3 204 562.26	$ 2 921 205.34
Cumulative Discounted Cash Flow	($43 612 056)	($38 027 245)	($32 936 260)	($28 295 435)	($24 064 965)	($20 208 566)	($16 693 161)	($13 488 599)	($10 567 393)
Total Capital Investment + Interest									
Net Present Worth									

(b)

DCFROR Worksheet	2033	2034	2035	2036	2037	2038	2039	2040	2041
Year	17	18	19	20	21	22	23	24	25
Fixed Capital Investment									
Land									
Working Capital									
Loan Payment	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -
Loan Interest Payment	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -
Loan Principal	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -
Price ($/t)	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -
Bio-product Sales	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -
Electricty price ($/ kWh)	$ 0.080	$ 0.080	$ 0.080	$ 0.080	$ 0.080	$ 0.080	$ 0.080	$ 0.080	$ 0.080
Electricity Sales	$30 916 339.20	$ 30 916 339.20	$ 30 916 339.20	$ 30 916 339.20	$ 30 916 339.20	$ 30 916 339.20	$ 30 916 339.20	$ 30 916 339.20	$ 30 916 339.20
Total Annual Revenue	$30 916 339.20	$ 30 916 339.20	$ 30 916 339.20	$ 30 916 339.20	$ 30 916 339.20	$ 30 916 339.20	$ 30 916 339.20	$ 30 916 339.20	$ 30 916 339.20
Annual Manufacturing Cost									
Feedstock Price ($/ ton)									
Feedstock cost									
Other Variable Costs									
Fixed Operating Costs									
Total Product Cost	$13 070 555.26	$ 13 070 555.26	$ 13 070 555.26	$ 13 070 555.26	$ 13 070 555.26	$ 13 070 555.26	$ 13 070 555.26	$ 13 070 555.26	$ 13 070 555.26
Annual Depreciation									
Plant Writedown									
Depreciation Charge									
Remaining Value									
Net Revenue (R-COM-dk)	$17 845 783.94	$ 17 845 783.94	$ 17 845 783.94	$ 17 845 783.94	$ 17 845 783.94	$ 17 845 783.94	$ 17 845 783.94	$ 17 845 783.94	$ 17 845 783.94
Losses Forward	$0	$0	$0	$0	$0	$0	$0	$0	$0
Taxable Income	$17 845 783.94	$ 17 845 783.94	$ 17 845 783.94	$ 17 845 783.94	$ 17 845 783.94	$ 17 845 783.94	$ 17 845 783.94	$ 17 845 783.94	$ 17 845 783.94
Income Tax	$4 996 820	$4 996 820	$4 996 820	$4 996 820	$4 996 820	$4 996 820	$4 996 820	$4 996 820	$4 996 820
Annual Cash Income	$12 848 964	$12 848 964	$12 848 964	$12 848 964	$12 848 964	$12 848 964	$12 848 964	$12 848 964	$12 848 964
Discount Factor	0.2072	0.1889	0.1722	0.1570	0.1431	0.1305	0.1189	0.1084	0.0988
Annual Present Value (Discounted Cash Flow)	$ 2 662 903.68	$ 2 427 441.83	$ 2 212 800.21	$ 2 017 137.84	$ 1 838 776.51	$ 1 676 186.43	$ 1 527 973.04	$ 1 392 865.13	$ 1 269 703.85
Cumulative Discounted Cash Flow	($7 904 490)	($5 477 048)	($3 264 248)	($1 247 110)	$591 667	$2 267 853	$3 795 826	$5 188 691	$6 458 395
Total Capital Investment + Interest									
Net Present Worth									

(c)

APPENDIX C

C-1: Supplementary data submitted with the article in chapter 4

TECHNO-ECONOMIC ANALYSIS OF CHEMICALLY CATALYSED LIGNOCELLULOSE BIOREFINERIES AT A TYPICAL SUGAR MILL: CO-PRODUCTION OF ELECTRICITY AND SORBITOL OR GLUCARIC ACID

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Supplementary Information:	APPENDIX C 4 Tables: Tables C1, C2, C3 and C4 1 Figure: Figures C1.

Table C1-1: Feedstock composition of the sugarcane bagasse (70%) and brown leaves 30% on a dry mass basis (Mandegari et al. 2017)

Component	Bagasse* fraction (%)	Brown leaves* fraction (%)
Cellulose	41.1	29.8
Hemicellulose	26.4	28.6
Lignin	21.7	22.5
Ash	4	2.4
Extractant	6.8	6.7

*The share has been based on the average agricultural residues produced at a typical South African mill (65 t/h dry mass) assuming inefficient burning of bagasse at mills is eliminated and “green” harvesting techniques applied thus making the “brown leaf” an additional biorefinery feedstock whilst the “green tops” are left in the field for moisture and nutrient retention.

Table C1-0-1: Adjusted chemical unit and annual costs per scenario for 2016 cost year of analysis (Mandegari et al., 2017)

Material	2016 Unit Cost (US$/kg)	Annual cost per scenario (US$ million)				
		Sorbitol.**STEX**	Sorbitol.**DA**	Glucaric.**STEX**	Glucaric.**DA**	
By-pass to boiler ratio		**25%**	**29.5%**	**35%**	**37%**	**References**
Biomass feedstock	0.01	7.90	7.90	7.90	7.90	Dias et al. 2011
Sulphur	0.12	0.32	-	0.32	-	Mandegari et al. 2017
Sulphuric acid (93%)	0.09	-	0.38	-	0.37	Tao et al. 2011
Raney nickel catalyst[a]	5.14	1.44	1.53	-	-	Brown et al. 2012
Pt/C catalyst[a]	4.73	-	-	1.20	1.30	Brown et al. 2012
Hydrogen[b]	2.89	2.79	2.48	-	-	Brown et al. 2012
Pure O_2[c]	0.05	-	-	2.11	1.87	Chandler et al. 2016
Activated carbon[a]	2.69	0.09	0.04	0.08	0.04	Activated Carbon, 2018
Amberlite ion exchange resins[d]	242.5	2.24	2.23	1.96	1.40	Dow, 2018
Caustic	0.09	0.21	0.22	0.23	0.22	Humbird et al. 2011
Host Nutrients	0.76	0.20	0.19	0.20	0.23	Mandegari et al. 2017
Glucose	0.58	-	-	-	-	Humbird et al. 2011
Ammonia di-sulphate	0.46	0.27	0.26	0.26	0.22	Mandegari et al. 2017
Boiler chemicals	3.70	0.03	0.03	0.03	0.03	Mandegari et al. 2017
Cooling tower chemicals	2.20	0.01	0.01	0.01	0.02	Mandegari et al. 2017
Make-up water	0.0022	0.44	0.02	0.41	0.02	eThekwini Municipality, 2011
Total		15.95	15.30	14.70	13.64	

[a] Catalysts annual cost (Activated Carbon,2017; Riogen, 2018; Brown et al., 2012) were divided over the material effective years and this cost included a refurbishment cost of 10% of the material

[b] Price of Hydrogen from Brown et al., (2012) and [c]price of pure oxygen from Chandler et al., (2016)

[d]Amberlite resins replaced after 4 years (Dow, 2018)

Table C1-3: Mass balance (mass basis) of Aspen Plus ® flowsheet for main streams relating to glucose hydrogenation to 70 wt% sorbitol via dilute acid pretreatment

Stream	GLUCOSE	S2	S6	EVP-H20	70-SORB	TO-WWT2
Temperature C	30	120.0	80.0	101.0	101.0	30.0
Pressure bar	1.01	70.0	70.0	0.5	0.5	1.0
Mass Flow kg/hr						
WATER	9035.7	11294.7	9035.7	3326.5	1090.4	3326.5
H_2SO_4	5.4	6.7	5.4	0.0	5.4	0.0
XYLOSE	1024.6	1280.7	1024.5	0.0	717.2	0.0
GLUCOSE	9454.1	1969.6	1575.7	0.0	1103.0	0.0
5HMF	0.5	0.6	0.5	0.0	0.5	0.0
XYLOOLIG	2.4	3.0	2.4	0.0	2.4	0.0
CO	0.0	1.3	1.0	0.1	0.0	0.1
HYDROGEN	0.0	13.6	10.8	0.0	0.0	0.0
SORBITOL	0.0	9958.2	7966.6	0.0	7966.6	0.0
GLUCOLIG	0.0	793.3	634.7	0.0	444.3	0.0
Total Flow kg/hr*	20184.0	26146.2	20916.9	3326.6	11348.3	3326.6

Table C1-4: Mass balance (mass basis) of Aspen Plus® flowsheet for some streams relating to glucose oxidation to 70 wt% glucaric acid via dilute acid pretreatment

Stream	**GLUCOSE**	**S3**	**GLUCARIC**	**EVP-H20**	**70-GLU**
Temperature C	30.0	40.0	40.0	102.0	102.0
Pressure bar	1.0	1.0	1.0	0.7	0.7
Mass Flow kg/hr					
WATER	7588.6	7757.2	7707.1	6410.5	1219.5
EXTRACT	23.7	23.7	23.7	0.0	0.0
OXYGEN	0.0	275.6	14.5	0.0	0.0
NITROGEN	0.0	17.0	0.4	0.0	0.0
H_2SO_4	7.6	7.6	7.6	0.0	0.0
XYLOSE	913.5	913.5	913.5	0.0	9.1
GLUCOSE	8429.6	505.8	505.8	0.0	5.1
5HMF	0.4	0.4	0.4	0.0	0.0
XYLOOLIG	2.2	2.2	2.2	0.0	0.0
HYDROGEN	0.0	50.9	0.0	0.0	0.0
GLUCARIC	0.0	7276.1	7268.8	0.0	7188.9
GLUCOLIG	565.9	565.9	565.3	0.0	5.7
GLUCONIC	0.0	1835.7	1833.8	0.0	1832.0
Total Flow kg/hr*	17531.5	19481.5	18843.1	6410.5	10260.3

Stream	**TO-WWT1**	**TO-WWT2**	**WWT**
Temperature C	40.0	35.0	35.7
Pressure bar	1.0	1.0	1.0
Mass Flow kg/hr			
WATER	77.1	6410.5	6894.9
EXTRACT	23.7	0.0	23.7
OXYGEN	14.5	0.0	14.5
NITROGEN	0.4	0.0	0.4
H_2SO_4	7.6	0.0	7.6
XYLOSE	904.4	0.0	904.4
GLUCOSE	500.7	0.0	500.7
5HMF	0.4	0.0	0.4
XYLOOLIG	2.1	0.0	2.1
HYDROGEN	0.0	0.0	0.0
GLUCARIC	72.7	0.0	80.0
GLUCOLIG	559.7	0.0	560.2
GLUCONIC	1.8	0.0	3.7
Total Flow kg/hr*	2165.1	6410.5	8992.6

*A summation of all process streams including those not shown in the table

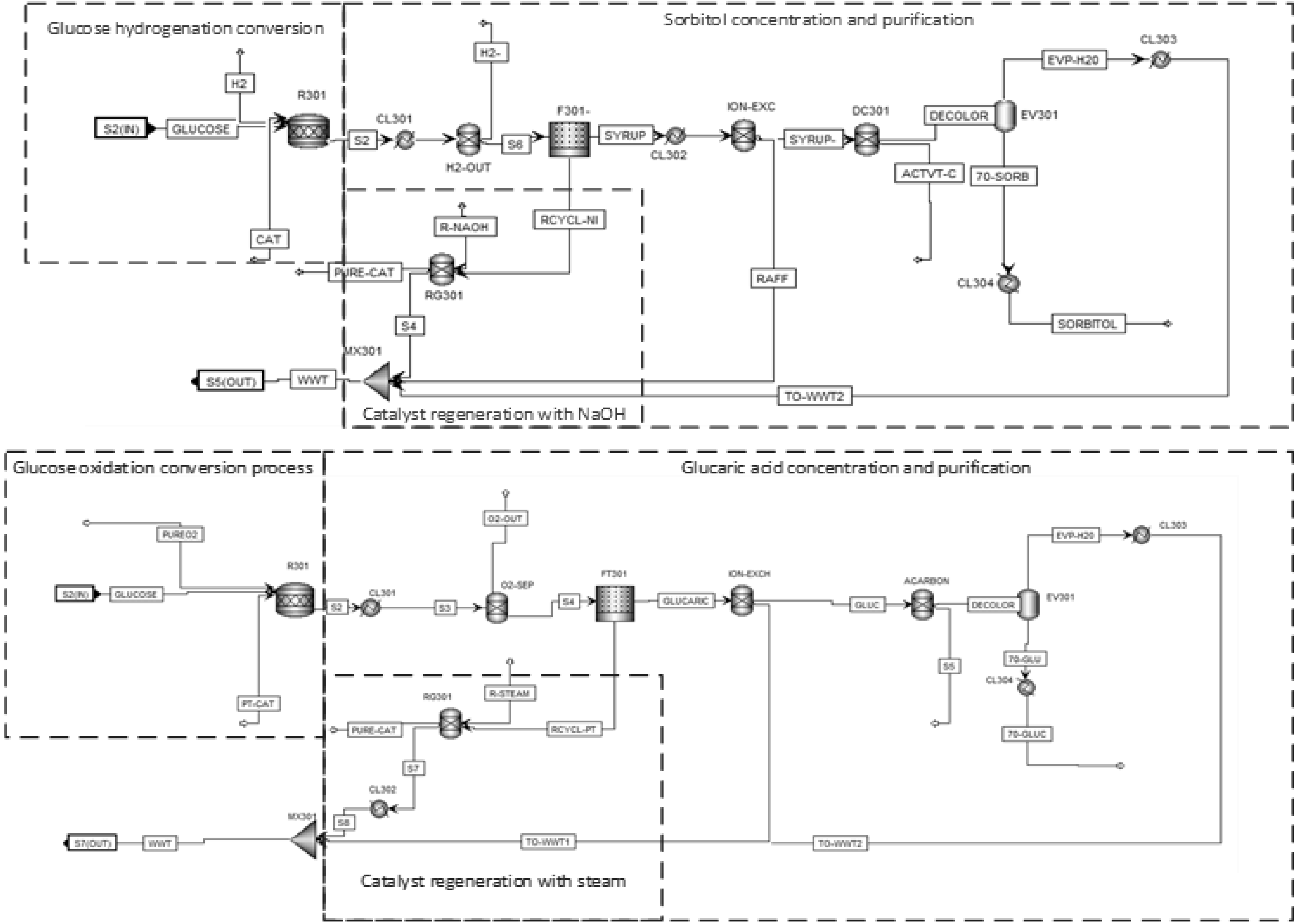

Figure C1-1: Aspen Models for a) glucose hydrogenation to sorbitol and b) glucose oxidation to glucaric acid process areas

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C-2: Aspen Plus ® models for Sorbitol.DA and Glucaric.DA and process conditions

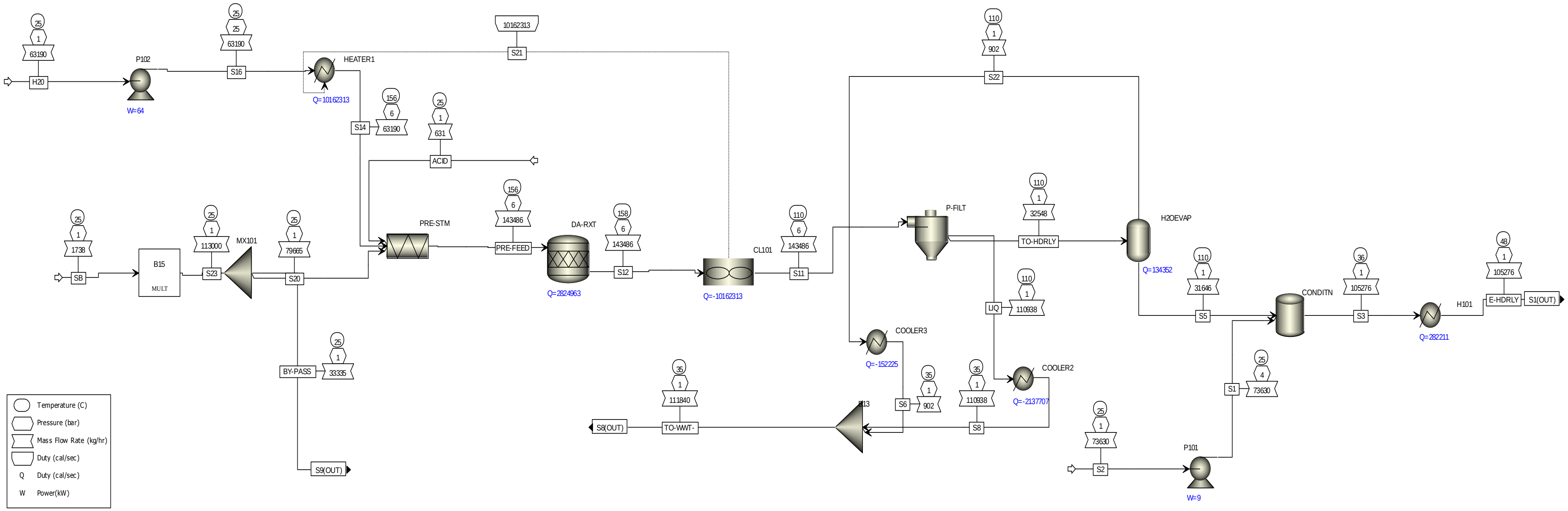

Figure C2-1: Dilute acid pretreatment configuration of the sorbitol biorefinery via dilute acid pretreatment

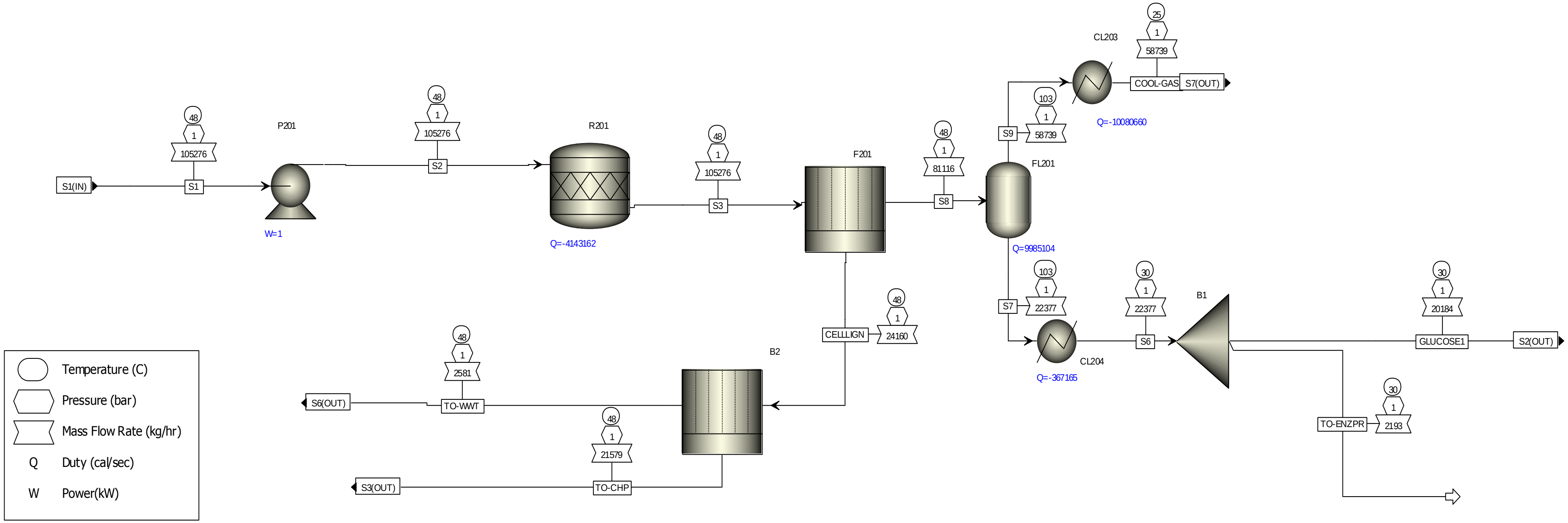

Figure C2-2: Enzymatic hydrolysis configuration of the Sorbitol.$_{DA}$ scenario

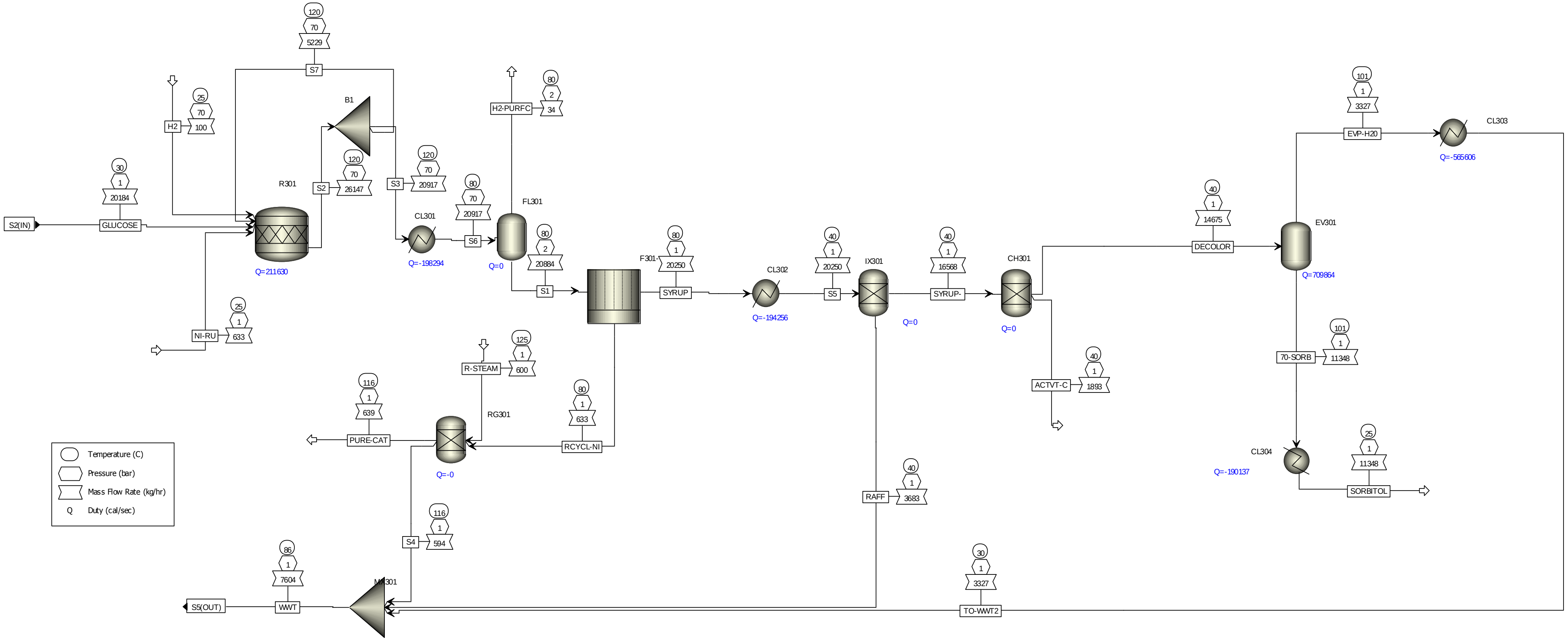

Figure C2-3: Hydrogenation process area for the Sorbitol.$_{DA}$ scenario

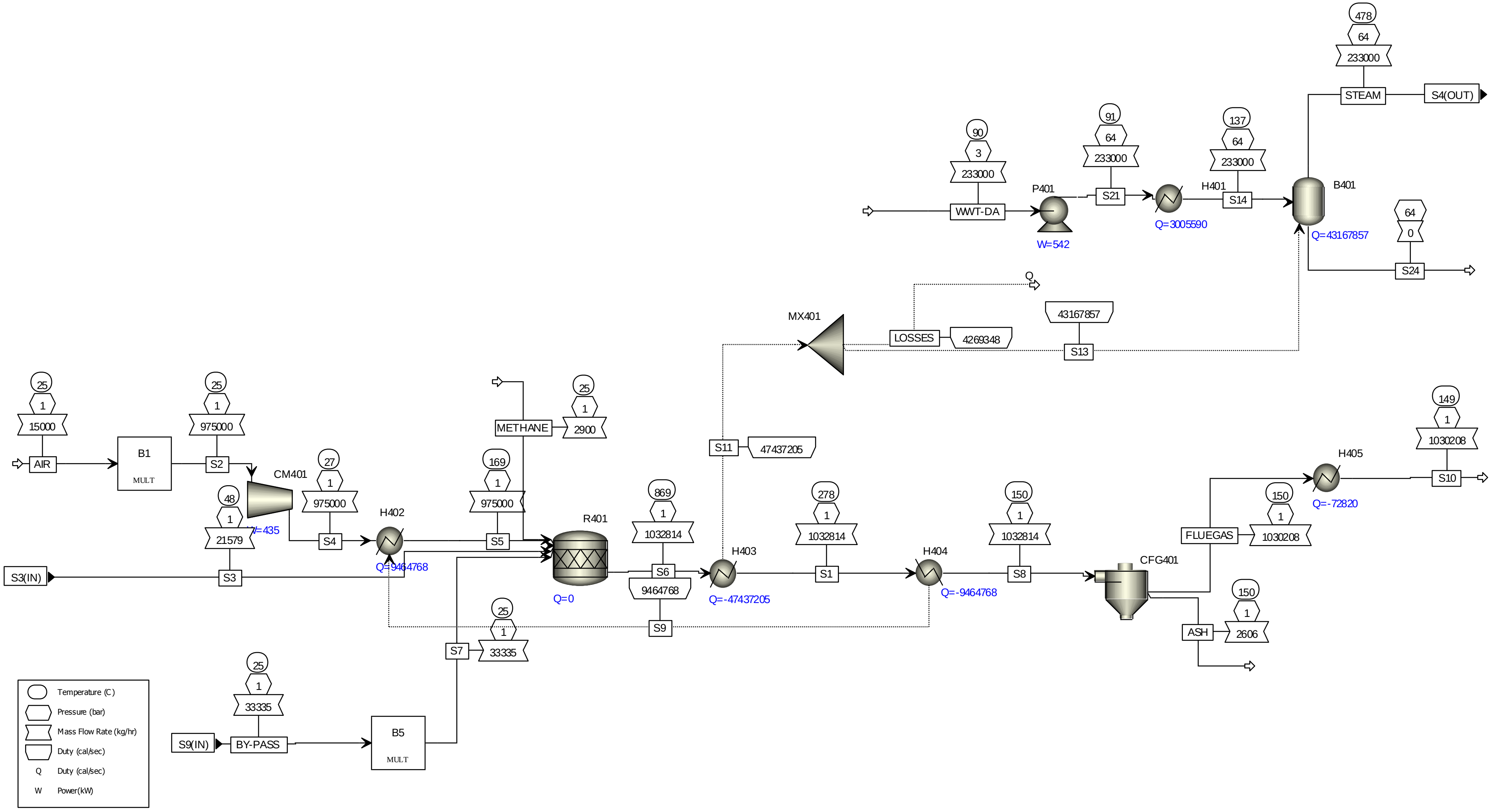

Figure C2-4: Boiler unit for the Sorbitol.$_{DA}$ biorefinery's CHP plant

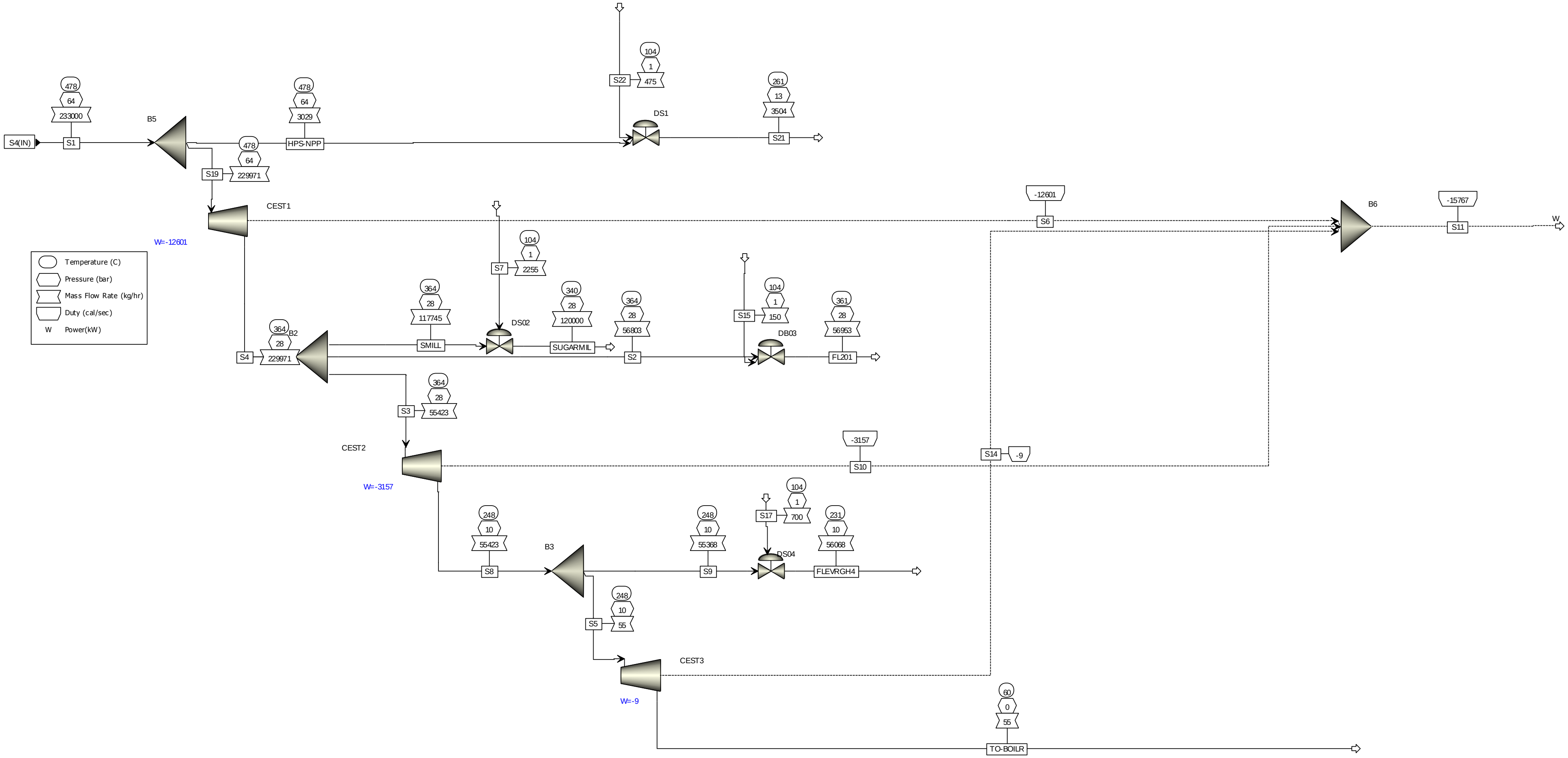

Figure C2-5: CEST unit of the Sorbitol.$_{\text{DA}}$ biorefinery's CHP plant

Note: Glucaric.$_{\text{DA}}$ has similar configurations to Sorbitol.$_{\text{DA}}$ so models not included

Table C2-1: Dilute acid pretreatment and oxidation reaction unit process conditions

	Aspen Unit	**Type or purpose of unit operation**	**Process conditions**	**other comments**
DILUTE ACID PRETREATMENT	P102	Pump	Temp =25^{o}C, Pressure = 25atm	
	HEATER	Heat exchanger (Heater)	Temp. = 156^{o}C, pressure drop = 0	
	PRE-STEM	Heat exchanger	Temp = 156^{o}C, pressure drop = 0	
	DA-RXT	RSTOIC reactor	Temp = 156^{o}C, pressure drop = 0	
	CL101	Heat exchanger (cooler)	Temp. = 110^{o}C, pressure drop = 0	
	P-FILT	Separator block (pressure filter)	Pressure drop = 0	
	COOLER 3	Heat exchanger (cooler)	Temp = 35^{o}C	
	COOLER 2	Heat exchanger (cooler)	Temp. = 35^{o}C	
	H2OEVAP	Flash tank	Temp. =110oC, pressure drop = 0	
	H101	Heat exchanger (Heater)	Temp. =48^{o}C	
	CONDITN	Mixing block		
	P101	Pump	Temp. = 25oC, Pressure = 4 atm	
OXIDATION	R 301	RSTOIC reactor	Temp. =80^{o}C, Pressure = 13 bar	Process reactions in chapter 4
	CL301	Heat exchanger (cooler)	Temp. = 40^{o}C, pressure drop = 0	
	CL302	Heat exchanger (cooler)	Temp. = 35oC, pressure drop = 0	
	FL301	Flash tank	Duty = 0	
	FT 301	Separator block, Duty = 0		
	RG301	Separator block (regeneration column)		Included for costing purposes
	IX301	Separator block (ion exchange column)		Included for costing purposes
	AC301	Separator block (activated carbon column)		Included for costing purposes
	EV301	Flash tank (Vacuum evaporator)	Temp. = 103^{o}C, Pressure = 0.8 atm	
	CL304	Heat exchanger (cooler)	Temp. = 35^{o}C, pressure drop = 0	
	CL303	Heat exchanger (cooler)	Temp. = 30^{o}C, pressure drop = 0	
	MX301	Mixing block	mixing all waste water streams to WWT plant	

Table C2-2: Steam explosion, enzymatic hydrolysis and hydrogenation unit process conditions

	Aspen Unit	Type or purpose of unit	Aspen Plus Process conditions	Other comments
SO_2 STEAM EXPLOSION PRETREATMENT	R 101	RSTOIC reactor	Temp. = 800°C, pressure = 1 atm	SO_2 production unit. Exolthermic reaction (reaches of 800oC)
	B2, MX101, MX103	Mixing of streams	Pressure drop = 0	
	CL101	Heat exchanger (cooler)	Temp. = 220°C	
	STEX 101	Flash drum	Temp. = 210°C, 9.5 atm	
	Used for STEX reactions	RSTOIC	Temp. = 195°C, pressure = 19 atm	Used to model hemicellulose hydrolysis
	FL101	Flash drum	Temp. = 123°C, pressure drop = 0	
	CL102	Heat exchanger (cooler)	Temp. = 55°C, pressure drop = 0	Cooling flue gas stream
	PRS FLT	Pressure filter (Splitter block)	Pressure drop = 0	MIXED split fraction 0.8 and CISOLID split fraction of 0
	WSH 101	Separator block	Pressure = 1 atm	Wash stage for inhibitor removal
	H101	Heat exchanger (heater)	Temp. =48°C, pressure drop = 0	
	P101	Pump	Pressure = 1 atm	Pumps hydrolysate to enzymatic hydrolysis
ENZYMATIC HYDROLYSIS	R 201	RSTOIC enzymatic hydrolysis reactor	Temp. = 48°C, pressure = 1 atm	Reactions in chapter 4
	CL202	Heat exchanger (cooler)	Temp. = 25°C	
	F201	Separator block (filter)	Pressure = 1 atm	Assume 1% of solution reported to the solids stream
	FL201	Flash drum	Temp. = 104°C, pressure = 1 atm	
	CL203	Heat exchanger (cooler)	Temp. = 25°C, pressure = 1 atm	
	CL204	Heat exchanger (cooler)	Temp. = 25°C	
HYDROGENATION	*R301	RSTOIC reactor	Temp. = 120°C, pressure = 70 bar	* Sized as a pressure vessel
	CL301	Heat exchanger	Temp. = 80°C, pressure drop = 0	
	FL301	Flash tank	Temp. = 80°C, pressure drop = 0	
	F301-	Separator block (pressure filter)		Assumed 1% of liquid reported to solids
	RG301	Separator block	Pressure drop = 0	Periodical regeneration of catalyst using steam at 125oC
	CL302	Heat exchanger (cooler)	Temp. 40°C, pressure drop = 0	
	IX301	Separator block (ion exchange column)	Pressure drop = 0	99% removal of gluconate and rutherium ions
	CH301	Separator block (activated carbon column)	Pressure drop = 0	
	EV301	Flash drum (vacuum evaporator)	Temp. = 103°C, pressure = 0.8 atm	
	CL304	Heat Exchanger (cooler)	Temp. = 25°C, pressure drop = 0	

C-3: Equipment sizing

Table C3-1: Equipment sizing and costing of the Sorbitol.$_{DA}$'s pretreatment area (all costs in US$)

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Equipment label	**Actual equipment**	**Description (Ref)**	**Material**	**Unit cost ($)**	**No. used**	**Total cost ($)**	**Yr of quote**	**Scaling value**	**Units**	**scaling Exp.**	**Instal. Factor**	**Size ratio**	**New value**	**Scaled purchase price**	**Purchase price In Proj.**	**Installed cost in Project Yr**
ACD-PRT	Depicting ACID hydrolysis	3500 cu.ft with drag chain conveyor (Humbird et al. 2011)	CS	816942	2	1633884	2009	72320	kg/h	0.85	2.5	2.1	155095	1 633 884	1 679 591	4 084 710
H2OEVAP	EVAPORATOR														14 900	103 000
P102	PUMP	ASPEN													54 400	100 600
PRE-STEAM	Solids loading mixing tank	ASPEN	SS	20500	1	20500	2017	115804		0.85	1.5	1.1	131300	22 809	22 809	34 214
Pumps	Not shown		SS	6900	5	34500	2017							34 500	34 500	94 000
Conveyors	TREAT-SB,TO-HYDRLY, S10	FROM SIMULATED sorbitol MODEL	SS	2698500	3	8095500	2017	94697	kg/h	0.6	1.7	0.9	84800	7 576 689	7 576 689	12 880 371
Agitators	For solids loading mixer &HC-RXN	NREL (used ethanol fermentor agigator price A-300)	SS	52500	2	105000	2009				1.5			105 000	107 937	161 906
H101		ASPEN													10 000	62 900
CL102	HX	ASPEN	SS	39400	1	39400	2017		kg/h				110412	39 400	39 400	121 300
COOLER3	COOLER	ASPEN													13 000	70 900
COOLER2	AIR COOLER	ASPEN													66 700	172 700
HEATER1	HEATER	ASPEN													90 500	217 100
P101	PUMP	ASPEN													8 900	51 600
CONDITN	TANK	ASPEN													14 900	103 200
CL101		ASPEN													87 200	195 400
	*Prices in US$														9 821 427	18 453 901

Table C3-2: Equipment sizing and costing of the Sorbitol.$_{DA}$'s enzymatic hydrolysis (all costs in US$)

Equipment label	Actual equipment	Description (Ref)	Material	Unit cost ($)	No. used	Total cost ($)	Yr of quote	Scaling value	Units	scaling Exp.	Instal. Factor	Size ratio	New value	Scaled purchase price	Purchase price In Proj.	Installed cost in Project Yr
P201	Pump	ASPEN	SS	6 700	2	13 400									13 400	92 800
201	SACHARIFICATION reactor	(CALCULATED 3.05mD & 7.8m H USING SORBITOL SIZING)	304SS	991 968	3	2 975 904	2009	106048	kg/h	0.8	2	0.86	90957	2632000	2 563 667	5 127 334
CL202	HX	ASPEN													19 400	84 400
FT201	Filter	ASPEN	SS	14 600	2	29 200	2017	0	kg/h					29200	29 200	58 800
PREFLT	Centrifuge/Replaced with pressure filter	ASPEN	SS	18 520	2	37 040	2017	106048	kg/h					37040	37 040	74 080
FL201	Flash tank	ASPEN	SS	32 200	2	64 400								64400	64 400	393 600
CL203	Cooler	ASPEN	SS	190 300	1	190 300	2017		kg/h						190 300	347 900
CL204	Cooler	ASPEN	SS	19 200	1	19 200	2017	14897	Kg/h						19 200	87 700
Not shown	Mixers -AHYDRO, AHFLASH	Not shown-(Used NREL ethanol fermentor agitator)	SS	52 500	2	105 000	2009				1.5			105000	107 937	161 906
															3 044 544	6 266 614

Table C3-3: Equipment sizing and costing of the Sorbitol.$_{DA}$'s enzyme production unit (all costs in US$)

Equipment label	Actual equipment	Description (Ref)	Material	Unit cost ($)	No. used	Total cost ($)	Yr of quote	Scaling value	Units	scaling Exp.	Instal. Factor	Size ratio	New value	Scaled purchase price	Purchase price In Proj.	Installed cost in Project Yr
FERMENTOR AGITATORS	nrel		SS	580000	7	4 060 000	2009	1	EACH	1	1.5	7	7	4 060 000	4 173 577	6 260 366
CELLULASE FERMENTOR AGITATORS	NREL	0.75 HP	SS	3420	3	10 260	2009	1	EACH	1	1.5	3	3	10 260	10 547	15 821
CELLULASE FERMENTOR AGITATORS	NREL	8HP	SS	63000	3	189 000	2009	1	EACH	1	1.5	3	3	189 000	194 287	291 431
CELLULASE FERMENTOR AGITATORS	NREL	80HP	SS	11000	3	33 000	2009	1	EACH	1	1.5	3	3	33 000	33 923	50 885
CELLULASE NUTRIENT MIX TANK AGITATOR	NREL	3HP	CS	4800	1	4 800	2009	174	kg/h	0.5	1.6	1	174	4 800	4 934	7 895
CELLULASE HOLDING TANK	NREL	80 000 GAL	SS	248070	1	248 070	2009	10930	kg/h	0.7	1.8	1.3	14408	300 993	309 414	556 944
CELLULOSE SEEED FERMENTOR	NREL	80 GAL SKIT	SS	46000	3	138 000	2009	1	EACH	1	1.8	3	3	414 000	425 582	766 047
CELLULASE SEED FERMENTOR	NREL	800 GAL SKIT	SS	57500	3	172 500	2009	1	EACH	1	1.8	1	1	172 500	177 326	319 186
CELLULASE FEED FERMENTOR	NREL	8000 GAL SKIT	SS	95400	3	286 200	2009	1	EACH	1	1.8	3	3	858 600	882 619	1 588 714
CELLULASE TRANSFER PUMP	NREL		SS	7357	1	7 357	2010	13399	kg/h	0.6	1.6	1.0	13182	7 285	7 096	11 354
CELLULASE FEED PUMP	NREL		SS	7493	3	22 479	2010	681	kg/h	0.8	2.3	1.7	1147	34 108	33 222	76 411
CELLULASE NUTRIENT MIX TANK	NREL	8000 GAL	SS	9000	1	9 000	2010	224	kg/h	0.7	3	1.7	378	12 989	13 352	40 056
CELLULOSE NUTRIENT TRANSFER PUMP	NREL		SS	1500	1	1 500	2009	454	kg/h	0.8	2.3	0.9	410	1 382	1 347	1 312
															5 327 142	**8 488 459**

Table C3-4: Equipment sizing and costing of the Sorbitol.$_{DA}$'s hydrogenation process area (all costs in US$)

Equipment label	Actual equipment	Description (Ref)	Material	Unit cost ($)	No. used	Total cost ($)	Yr of quote	Scaling value	Units	scaling Exp.	Instal. Factor	Size ratio	New value	Scaled purchase price	Purchase price In Proj.	Installed cost in Project Yr
R 301	Reactor(6 hr duration) Pressure vessel		SS	751 243	8	6 009 944	2010	19149	kg/h	0.85	2	0.9	17 810	5 650 808	5 504 101	11 008 201
Not shown	Hydrogen pump	277 ft2 (26 m2) surface area	CS	121 300	6	727 800	2017		kg/h	0.85	2.3		17 810	727 800	727 800	1 673 940
CL302	Cooler	ASPEN	SS	8 400	1	8 400	2017	26320	kg/h					8 400	8 400	55 200
FT301	Pressure filter	ASPEN	SS	32 000	2	64 000	2017	25522	kg/h					64 000	64 000	257 200
RG301	Regeneration	ASPEN (towler and sinnot)	SS	19 760	4	79 040	2010	670	kg/h	0.85	2.5	0.9	600	71 963	70 095	175 238
COOLER2	Cooler	ASPEN	SS	81 600	1	81 600	2017	4743	kg/h						81 600	187 900
IX301	Ion exchange	Towler & Sinnot (7m height by 1 m width)	SS	40 978	8	327 824	2010	24429	kg/h	0.85	2.5	0.6	15 601	223 924	218 110	798 280
DECLR	Activated carbon decolorisation	Towler & Sinnot (5.5m height by 1 m width)	SS	36 608	6	219 648	2010	24429	kg/h	0.85	2.5	0.5	12 781	126 645	213 870	534 675
EV301	Evaporator	Towler & Sinnot (109 m2 Surface area) -commercial continuos vacuum evaporator	SS	485 952	3	1 457 856	2010	24429	kg/h	0.85	2.5	0.5	12 315	814 449	793 304	1 983 261
CL304	Cooler	ASPEN	SS	10 603	1	10 603	2017	4743	kg/h						13 000	70 900
CL303	Cooler	ASPEN													17 000	75 300
CL301	COOLER														15 800	77 300
AC301	Heat exchanger	ASPEN													20 040	121 233
Not shown	Mixers/agitators		ss	62 193	4	248 772					1.5				248 772	373 158
															7 711 280	16 820 095

Table C3-5: Sorbitol.$_{DA}$ equipment sizing and costing of the boiler, condensing extraction steam turbine (CEST) and wastewater treatment (WWT) plant (all costs in US$)

Equipment label	Actual equipment	Description (Ref)	Material	Unit cost ($)	No. used	Total cost ($)	Yr of quote	Scaling value	Units	scaling Exp.	Instal. Factor	Size ratio	New value	Scaled purchase price	Purchase price In Proj.	Installed cost in Project Yr
COMBUSTOR		NREL		INCLUDED												
CM401	compressor/air blower/	NREL	SS	28000	1	28000	2010	83333	kg/h	0.6	1.8	9.72	810000	109 587	106 742	192 135
HEATER1	Heater	ASPEN	SS	INCLUDED	1											
BFW HEAT RECOVERY		NREL	SS	41000	1	41000	2009	-2		0.7	2	1.3	-2.6	37 310	38 354	76 707
HEATER2	Cooler	ASPEN	SS	1136500	1	1136500	2017		kg/h	0.7				1 136 500	909 200	1 468 400
HEATER3	Cooler	ASPEN	SS		1	0	2017		kg/h	0.7					728 200	1 084 700
P401		ASPEN			2										191 600	347 900
H402	Heater	ASPEN	SS		1	0	2017			0.7				-	1 317 600	2 042 700
H405															75 300	183 000
H404				INCLUDED												
H401		ASPEN		INCLUDED												
CFG401	Centrifuge/FGD BAG HO	NREL	SS	INCLUDED												
H401															69 000	172 800
B401	Boiler	NREL	SS	28550000	1	28550000	2010	238686	kg/h	0.6	1.8	0.9762	233000	28 139 961	27 409 385	49 336 893
DEARATOR		NREL	SS	305000	1	305000	2010	235803	kg/h	0.6	3	0.8736	206000	281 249	273 947	821 841
															31 119 328	**55 727 077**

Equipment label	Actual equipment	Description (Ref)	Material	Unit cost ($)	No. used	Total cost ($)	Yr of quote	Scaling value	Units	scaling Exp.	Instal. Factor	Size ratio	New value	Scaled purchase price	Purchase price In Proj.	Installed cost in Project Yr
CEST	Turbogenerator	NREL	SS	9500000	1	9500000	2010	230000	kg/h	0.6	1.8	1.0	229971	5 699 281	5 551 315	9 992 367
CONDENSOR	Condenser	ASPEN	SS	37500	1	37500	2017		kg/h	0.6			7793	37500	37500	37500
														TOTAL (BOILER AND CEST)	**36 670 643**	**65 719 444**

Equipment label	Actual equipment	Description (Ref)	Material	Unit cost ($)	No. used	Total cost ($)	Yr of quote	Scaling value	Units	scaling Exp.	Instal. Factor	Size ratio	New value	Scaled purchase price	Purchase price In Proj.	Installed cost in Project Yr
WWT		GREENFUND ESTIMATE		2600000	1	2600000	2015	95217	KG/H	0.6	1	0.03	2414	286 673	279 230	385 906
														TOTAL	**279 230**	**385 906**

Note: NREL is data from Humbird et al. (2011)
GREENFUND in WWT refers to a report by Gorgens et al. (2016)

[Gorgens, J. ., Mandegari, M. ., Farzad, S., Daful, A.. and Haigh, K. . (2016) *A Biorefinery Approach to improve the Sustainability of the South African Sugar Industry, Stellenbosch University, South Africa*.]

Table C3-6: Equipment sizing and costing of the Glucaric.$_{DA}$’s pretreatment area (all costs in US$)

Equipment label	Actual equipment	Description (Ref)	Material	Unit cost ($)	No. used	Total cost ($)	Yr of quote	Scaling value	Units	scaling Exp.	Instal. Factor	Size ratio	New value	Scaled purchase price	Purchase price In Proj.	Installed cost in Project Yr
H101		ASPEN						59 325	kg/h	0.85	1.5				10 200	63 100
ACD-PRT	Depicting ACID hydrolysis	3500 cu.ft with drag chain conveyor (NREL)	CS	803942	2	1607884	2009	72 320	kg/h	0.85	2.5	2.1	154 313	1 607 884	1 652 864	4 019 710
H2OEVAP	EVAPORATOR														14 900	103 000
P102	PUMP														7 900	48 200
PRE-STEAM	Solids loading mixing tank	ASPEN	SS	20500	1	20500	2017	115 804		0.85	1.5	1.1	131 300	22 809	22 809	34 214
Pumps	Not shown		SS	8800	5	44000	2017							44 000	44 000	88 000
Conveyors	TREAT-SB,TO-HYDRLY, S10	FROM SIMULATED sorbitol MODEL	SS	2698500	3	8095500	2017	94 697	kg/h	0.6	1.7	0.2	20 532	3 235 197	3 235 197	5 499 834
Agitators	For solids loading mixer & hydrolysis	NREL (used ethanol fermentor agigator price A-300)	SS	52500	2	105000	2009				1.5			105 000	107 937	161 906
COOLER2		ASPEN													94 600	201 500
CL102	HX	ASPEN	SS	39400	1	39400	2017		kg/h				110 412	39 400	39 400	121 300
COOLER3	COOLER														13 100	71 000
COOLER BLOW DOWN	AIR COOLER	ASPEN													1 816 400	2 827 100
HEATER1	HEATER														109 100	249 300
P101	PUMP	ASPEN													15 200	95 600
CONDITN	TANK	ASPEN													14 900	103 200
P102		ASPEN													17 600	111 400
															7 216 108	**13 798 365**

Table C3-7: Equipment sizing and costing of the Glucaric.$_{DA}$’s enzymatic hydrolysis (all costs in US$)

Equipment label	Actual equipment	Description (Ref)	Material	Unit cost ($)	No. used	Total cost ($)	Yr of quote	Scaling value	Units	scaling Exp.	Instal. Factor	Size ratio	New value	Scaled purchase price	Purchase price In Proj.	Installed cost in Project Yr
P201	Pump	ASPEN	SS	8 800	2	17 600									17600	111400
R 201	SACHARIFICATION reactor	CALCULATED 3.05mD & 7.8m H)	304SS	991 968	3	2 975 904	2009	106048	kg/h	0.8	2	0.70	74 716	2 248 784	2190401	4380801.875
CL202	HX	ASPEN													22800	87900
FT201	Filter	ASPEN	SS	17 800	2	35 600	2017	0	kg/h					35 600	35600	66800
PREFLT	Centrifuge	ASPEN	SS	18 520	2	37 040	2017	106048	kg/h					37 040	37040	74080
FL201	Flash tank	ASPEN	SS	17 800	2	35 600								35 600	35600	66800
CL203	Cooler	ASPEN	SS	276 500	1	276 500	2017		kg/h						276500	444800
CL204	Cooler	ASPEN	SS	20 400	1	20 400	2017	14897	Kg/h						20400	88900
Not shown	Mixers -AHYDRO, AHFLASH	Not shown (Used NREL ethanol fermentor agitator)	SS	52 500	2	105 000	2009				1.5			105 000	107937	161906.0165
															2 743 878	**5 321 482**

Table C3-8: Equipment sizing and costing of the Glucaric.$_{\text{DA}}$’s enzyme production unit (all costs in US$)

Equipment label	Actual equipment	Description (Ref)	Material	Unit cost ($)	No. used	Total cost ($)	Yr of quote	Scaling value	Units	scaling Exp.	Instal. Factor	Size ratio	New value	Scaled purchase price	Purchase price In Proj.	Installed cost in Project Yr
FERMENTOR AGITATORS	NREL		SS	580000	7	4060000	2009	1	EACH	1	1.5	7	7	4 060 000	4 173 577	6 260 366
CELLULASE FERMENTOR AGITATORS	NREL	0.75 HP	SS	3420	3	10260	2009	1	EACH	1	1.5	3	3	10 260	10 547	15 821
CELLULASE FERMENTOR AGITATORS	NREL	8HP	SS	63000	3	189000	2009	1	EACH	1	1.5	3	3	189 000	194 287	291 431
CELLULASE FERMENTOR AGITATORS	NREL	80HP	SS	11000	3	33000	2009	1	EACH	1	1.5	3	3	33 000	33 923	50 885
CELLULASE NUTRIENT MIX TANK AGITATOR	NREL	3HP	CS	4800	1	4800	2009	174	KG/H	0.5	1.6	1	174	4 800	4 934	7 895
CELLULASE HOLDING TANK	NREL	80 000 GAL	SS	205640	1	205640	2009	10930	kg/h	0.7	1.8	0.82891	9060	180 328	185 373	333 671
CELLULOSE SEEED FERMENTOR	NREL	80 GAL SKIT	SS	38200	3	114600	2009	1	EACH	1	1.8	3	3	343 800	353 418	636 152
CELLULASE SEED FERMENTOR	NREL	800 GAL SKIT	SS	47665	3	142995	2009	1	EACH	1	1.8	1	1	142 995	146 995	264 591
CELLULASE FEED FERMENTOR	NREL	8000 GAL SKIT	SS	79100	3	237300	2009	1	EACH	1	1.8	3	3	711 900	731 815	1 317 267
CELLULASE TRANSFER PUMP	NREL		SS	7357	1	7357	2010	13399	kg/h	0.6	1.6	0.6187	8290	5 516	5 372	8 596
CELLULASE FEED PUMP	NREL		SS	7493	3	22479	2010	681	KG/H	0.8	2.3	1.06021	722	23 555	22 944	52 771
CELLULASE NUTRIENT MIX TANK	NREL	8000 GAL	SS	7460	1	7460	2010	224	KG/H	0.7	3	1.07143	240	7 829	8 048	24 144
CELLULOSE NUTRIENT TRANSFER PUMP	NREL		SS	1500	1	1500	2009	454	KG/H	0.8	2.3	0.56828	258	954	930	2 138
															4 991 339	**7 875 868**

Table C3-9: Equipment sizing and costing of the Glucaric.$_{\text{DA}}$’s oxygenation process area (all costs in US$)

Equipment label	Actual equipment	Description (Ref)	Material	Unit cost ($)	No. used	Total cost ($)	Yr of quote	Scaling value	Units	scaling Exp.	Instal. Factor	Size ratio	New value	Scaled purchase price	Purchase price In Proj. Yr	Installed cost in Project Yr
R 301	Reactor(6 Hr duration) Pressure vessel		SS	751 243	8	6 009 944	2010	19 149	kg/h	0.85	2	1.0	18 730	5 897 981	5 744 856	11 489 712
Not shown	H2 pump	277 ft2 (26 m2) surface area	CS	121 300	6	727 800	2017		kg/h	0.85	2.3		18 730	727 800	727 800	1 673 940
CL302	Cooler	ASPEN	SS	10 700	1	10 700	2017	26 320	kg/h					10 700	10 700	66 000
FT301	Pressure filter	ASPEN	SS	15 100	2	26 320	2017	25 522	kg/h					26 320	15 600	219 000
RG301	Regeneration	ASPEN (towler and sinnot)	SS	19 760	4	79 040	2010	670	kg/h	0.85	2.5	1.4	914	102 917	100 245	250 613
COOLER2	Cooler	ASPEN	SS	81 600	1	81 600	2017	4 743	kg/h						81 600	187 900
IX301	Ion exchange	Towler & Sinnot (7m height by 1 m width)	SS	40 978	8	327 824	2010	24 429	kg/h	0.85	2.5	0.7	18 217	255 462	248 830	798 280
DECLR	Activated carbon decolorisation	Towler & Sinnot (5.5m height by 1 m width)	SS	36 608	6	219 648	2010	24 429	kg/h	0.85	2.5	0.5	12 943	128 008	213 870	534 675
EV301	Evaporator	Towler & Sinnot (109 m2 SA) continuos vacuum evaporator	SS	485 952	3	1 457 856	2010	24 429	kg/h	0.85	2.5	0.5	12 937	849 285	827 235	2 068 089
CL304	Cooler	ASPEN	SS	9 900	1	9 900	2017	4 743	kg/h						9 900	59 000
CL303	Cooler	ASPEN													40 500	125 800
CL301	COOLER														12 400	69 600
AC301	HX														20 040	121 233
Not shown	Mixers/agitators		SS	62 193	4	248 772					1.5				248 772	373 158
															8 021 136	**17 473 008**

Table C3-10: Glucaric.$_{DA}$ equipment sizing and costing of the boiler, condensing extraction steam turbine (CEST) and wastewater treatment (WWT) plant (all costs in US$)

Equipment label	Actual equipment	Description (Ref)	Material	Unit cost ($)	No. used	Total cost ($)	Yr of quote	Scaling value	Units	scaling Exp.	Instal. Factor	Size ratio	New value	Scaled purchase price	Purchase price In Proj. Yr	Installed cost in Project Yr
COMBUSTOR		NREL		INCLUDED												
CM401	compressor/air blower/fan	NREL	SS	28000	1	28 000	2010	83333	kg/h	0.6	1.8	10.8	900 000	116 738	113 708	204 674
HEATER1	Heater	ASPEN	SS	INCLUDED	1											
BFW HEAT RECOVERY		NREL	SS	41000	1	41 000	2009	-2		0.7	2	1.3	-3	37 310	38 354	76 707
HEATER2	Cooler	ASPEN	SS	1136500	1	1.14E+06	2017		kg/h	0.7				1 136 500	909 200	1 468 400
HEATER3	Cooler	ASPEN	SS		1	-	2017		kg/h	0.7					738 800	1 097 200
P401		ASPEN		INCLUDED												
B2	Heater	ASPEN	SS		1	-	2017			0.7				-	1 599 100	2 609 800
H401		ASPEN		INCLUDED												
CFG401	Centrifuge/FGD BAG HOUSE	NREL	SS	INCLUDED												
B401	Boiler	NREL	SS	28550000	1	2.86E+07	2010	238686	kg/h	0.6	1.8	1.0	233 000	28 139 961	27 409 385	49 336 893
DEARATOR		NREL	SS	305000	1	305 000	2010	235803	kg/h	0.6	3	1.0	233 000	302 819	294 958	884 873
above item costs are:															**31 103 504**	**55 678 547**

Equipment label	Actual equipment	Description (Ref)	Material	Unit cost ($)	No. used	Total cost ($)	Yr of quote	Scaling value	Units	scaling Exp.	Instal. Factor	Size ratio	New value	Scaled purchase price	Purchase price In Proj. Yr	Installed cost in Project Yr
CEST	Turbogenerator	NREL	SS	9500000	1	9500000	2010	230000	kg/h	0.6	1.8	0.9239	212496	5266205.217	5129482.751	9233068.951
CONDENSOR	Condenser	ASPEN	SS	37500	1	37500	2017		kg/h	0.6			7793	37500	0	0
														TOTAL (BOILER +CEST)	**36 232 987**	**64 911 616**

Equipment label	Actual equipment	Description (Ref)	Material	Unit cost ($)	No. used	Total cost ($)	Yr of quote	Scaling value	Units	scaling Exp.	Instal. Factor	Size ratio	New value	Scaled purchase price	Purchase price In Proj. Yr	Installed cost in Project Yr
		GREENFUND ESTIMATE		2600000	1	2600000	2015	95217	KG/H	0.6	1	1.6327	155458	3489092.612	3398507.964	4696855.439
														TOTAL	**3 398 508**	**4 696 855**

C-4: Mass and energy balances

Table C4-1: Utilities for the Sorbitol.$_{DA}$ biorefinery

Process area	Aspen unit	Description	Utility	Duty (kW)	Usage (kWh or t/h)
DILUTE ACID PRETREATMENT	DA-RXT	RSTOIC REACTOR	LP steam	11868	20
	CL101	COOLER BLOW DOWN	Cooling water	-42573	7342
	P-FILT	PRESSURE FILTER	Electricity	0	0
	H2OEVAP	WATER EVAPORATOR	HP Steam	563	0.98
	COOLER2	HEAT EXCHANGER	Cooling water	-10079	1738
	COOLER3	HEAT EXCHANGER	Cooling water	-667	115
	P101	PUMP	Electricity	64	64
	P102	PUMP	Electricity	9	9
	H101	HEAT EXCHANGER	LP steam	1176	2.1
	HEATER1	HEAT EXCHANGER	LP steam	14235	15
ENZYMATIC HYDROLYSIS	P201	PUMP	Electricity	5.2	5.2
	B2	FILTER	Electricity	0	0
	R 201	RSTOIC REACTOR	Heat (exolthermic)	-17468	0
	F201	FILTER	Electricity	0	0
	FL201	FLASH TANK	LP steam	41806	56.5
	CL204	HEAT EXCHANGER	Cooling water	-1548	267
	CL203	HEAT EXCHANGER	Cooling water	-42149	7252
HYDROGENATION PROCESS UNIT	R 301	RSTOIC HYDROGENATION REACTOR	HP Steam	1819	3.5
	CL301	HEAT EXCHANGER	Cooling water	-1315	267
	F301-	FILTER	Electricity	-0.00021	-0.00021
	IX301	IX-1		0	0
	CH301	ACTIVATED CARBON COLUMN		0	0
	CL302	HEAT EXCHANGER	Cooling water	-131	23
	EV301	EVAPORATOR (FLASH TANK)	LP steam	3222	5
	CL303	HEAT EXCHANGER	Cooling water	-2013	174
	RG301	REGENERATION COLUMN	LP steam		0.3
	CL304	HEAT EXCHANGER	Cooling water	-638	110
BOILER AND CEST UNIT	CM401	COMPRESSOR	Electricity	374	374
	P401	BOILER FEED WATER PUMP	Electricity	559	559
	H401	HEAT EXCHANGER	LP steam	12962	21.8
	H405	FLUE GAS HEAT EXCHANGER	Cooling water	-26861	4632

Table C4-2: Utilities for the Glucaric.$_{DA}$ biorefinery

Process area	Aspen unit	Description	Utility	Duty (kW)	Usage (kWh or t/h)
DILUTE ACID PRETREATMENT	PRE-STM	PRE-STEAMER	0	0	0
	ACD-PRT	RSTOIC PRETREATMENT REACTOR	MP Steam	17101	30
	C-BDOWN	COOLER BLOWDOWN (HEAT EXCHANGER)	Cooling water	-55321	39831
	P-FILT	PRESSURE FILTER	Electricity	0	0
	H2OEVAP	EVAPORATOR	HP Steam	789	1.4
	COOLER2	HEAT EXCHANGER	Cooling water	-10521	1814
	COOLER3	HEAT EXCHANGER	Cooling water	-6531	1126
	P101	PUMP	Electricity	8	8
	P102	PUMP	Electricity	15	15
	HEATER 1	HEAT EXCHANGER	LP Steam	55321	92
	H101	HEAT EXCHANGER	LP Steam	1043	1.5
ENZYMATIC HYDROLYSIS	P201	PUMP	Electricity	5	5
	PRFLT	PRESSURE FILTER	Cooling water	-1603	276
	R 201	STOIC REACTOR		-12202	0
	FT201	FILTER	Electricity	0	0
	FL201	FLASH TANK	LP Steam	37388	50
	CL204	HEAT EXCHANGER	Cooling water	-1333	230
	CL203	HEAT EXCHANGER	Cooling water	-37778	6501
OXYGENATION	R 301	OXYGENATION REACTOR	HP Steam	15069	23
	CL301	HEAT EXCHANGER	Cooling water	-447	39
	FT301	PRESSURE FILTER	Electricity	-0.00021	-0.00021
	IX301	ION EXCHANGE COLUMN	Electricity	0	0
	CL302	HEAT EXCHANGER	Cooling water	-287	25
	EV301	EVAPORATOR	LP Steam	4946	8.1
	CL303	HEAT EXCHANGER	Cooling water	-3594	310
	RG301	REGENERATION COLUMN	LP Steam		0.4
BOILER AND CEST UNIT	CL304	OXY-CLR4	Cooling water	-122	21
	CM401	COMPRESSOR/AIR BLOWER	Electricity	401	401
	P401	BOILER FEED WATER PUMP	Electricity	542	542
	H401	HEAT EXCHANGER	LP Steam	12584	22
	FGASCOOL	FUE GAS HEAT EXCHANGER	Cooling water	-26783	4619
	CONDENSR	CONDENSER	Cooling water	0	0

C-5: Pinch analysis

Table C5-1: Input data for the Sorbitol.STEX and Glucaric.STEX and heat capacity flowrate determinant

Stream Name	Supply Temperature	Target Temperature	dT Min Contrib	Heat Capacity Flowrate	Heat Flow	Stream Type	Supply Shift	Target Shift
	°C	°C	°C	kW/K	kW		°C	°C
CL101	158	110	10	886.938	42573.0	HOT	148.0	100.0
HEATER1	25	156	10	108.664	14235.0	COLD	35.0	166.0
H101	36	48	10	98.000	1176.0	COLD	46.0	58.0

Table C5-2: Problem cascade table for Sorbitol.STEX and Glucaric.STEX

Shift Temperature	Interval	$T_{(i+1)}-T_i$	mCp_{net}	dH			Infeasible Cascade	Feasible Cascade
°C		°C	kW/K	kW				
166							▼ 0	▼ 1956
	1	18	-108.6641	-1955.9542	demand		-1955.95	-1955.954
148						PINCH	▼ -1956	▼ 0
	2	48	778.2734	37357.1221	surplus		37357.12	37357.12
100							▼ 35401	▼ 37357
	3	42	-108.6641	-4563.8931	demand		-4563.89	-4563.893
58							▼ 30837	▼ 32793
	4	12	-206.6641	-2479.9695	demand		-2479.97	-2479.969
46							▼ 28357	▼ 30313
	5	11	-108.6641	-1195.3053	demand		-1195.31	-1195.305
35							▼ 27162	▼ 29118

Hot Pinch	153	°C
Cold Pinch	143	°C

Min Hot Utility	1955.95	kW
Min Cold Utility	29117.95	kW

SINGLE PINCH PROBLEM

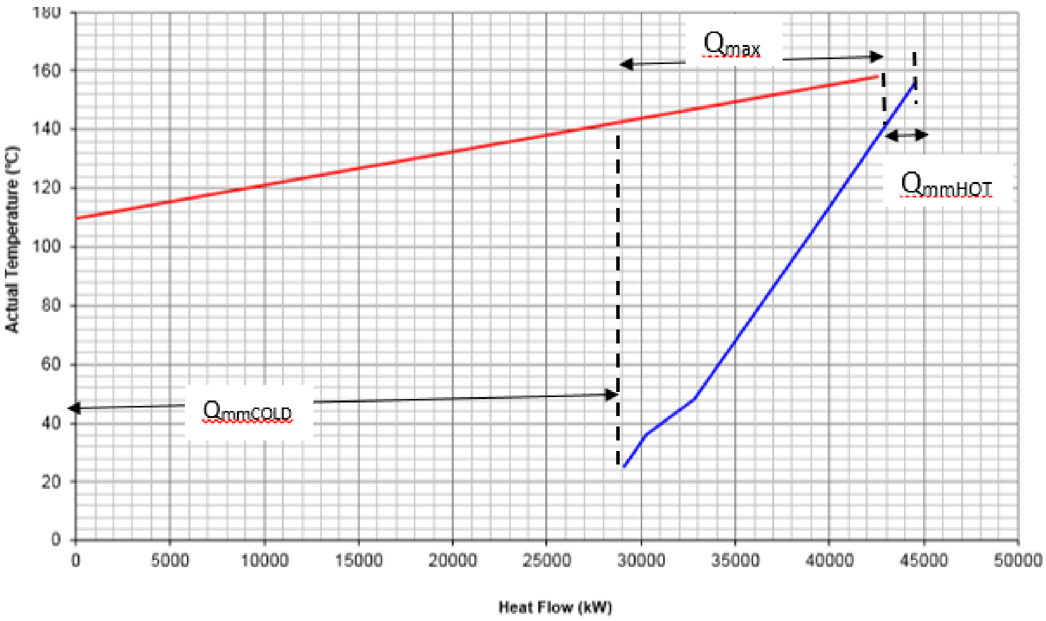

Figure C5-1: Combined composite graph for Sorbitol.STEX and Glucaric.STEX for 1 hot and 2 cold streams

Integrating 1 hot and 2 cold streams in Sorbitol.STEX and Glucaric.STEX led to a hot and cold utility saving of 1.8 – 1.9 % and 1.7 - 1.8% respectively.

Table C5-3: Input data for the Sorbitol.DA and Glucaric.DA and heat capacity flowrate determinant

Stream Name	Supply Temp.	Target Temp.	dT Min Contribution	Heat Capacity Flowrate		Heat Flow	Stream Type	Supply Shift	Targe Shift
	°C	°C	°C	kW/K		kW		°C	°C
CL101	158	110	10	886.9		42573.0	HOT	148.0	100.0
HEATER1	25	156	10	108.7		14235.0	COLD	35.0	166.0
H101	36	48	10	98.0		1176.0	COLD	46.0	58.0
FL201	48	103	10	760.1		41804.0	COLD	58.0	113.0

Table C5-4: Problem cascade table for Sorbitol.DA and Glucaric.DA

Problem Table & Cascade

Shift Temperature	Interval	$T_{(i+1)}-T_i$	mCp_{net}	dH			Infeasible Cascade		Feasible Cascade	
°C		°C	kW/K	kW						
166							▼	0	▼	14642
	1	18	-108.6641	-1955.9542	demand		-1955.95		-1955.954	
148							▼	-1956	▼	12686
	2	35	778.2734	27239.5682	surplus		27239.57		27239.57	
113							▼	25284	▼	39926
	3	13	18.2007	236.6085	surplus		236.6085		236.6085	
100							▼	25520	▼	40162
	4	42	-868.7368	##########	demand		-36486.9		-36486.95	
58							▼	-10967	▼	3675.3
	5	12	-206.6641	-2479.9695	demand		-2479.97		-2479.969	
46							▼	-13447	▼	1195.3
	6	11	-108.6641	-1195.3053	demand		-1195.31		-1195.305	
35						**PINCH**	▼	-14642	▼	0

Hot Pinch	40 °C
Cold Pinch	30 °C

Min Hot Utility	14642.0 kW
Min Cold Utility	0.0 kW

SINGLE PINCH PROBLEM

THRESHOLD PROBLEM

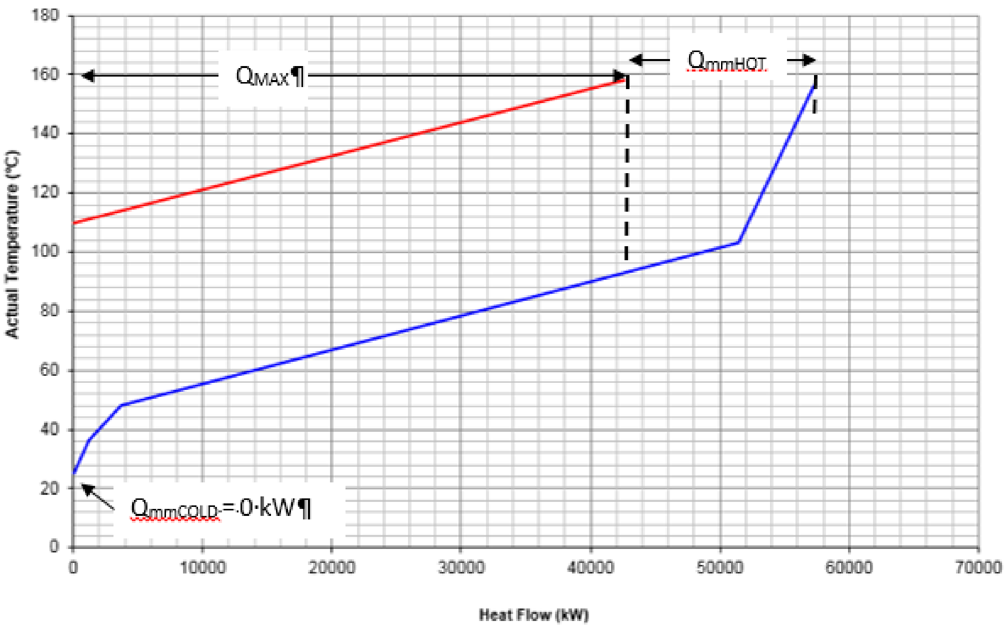

Figure C5-2: Combined composite graph for Sorbitol.DA and Glucaric.DA for 1 hot and 2 cold streams

Integrating 1 hot and 2 cold streams in Sorbitol.DA and Glucaric.DA led to a hot and cold utility saving of 31 – 38 % and 42 - 43% respectively.

C-6: Discounted cash flow rate of return spreadsheet

Table C6-1: Discounted cash flow rate of return spreadsheet for Sorbitol.$_{\text{DA}}$ (a), (b) and (c)

DCFROR Worksheet			2016	2017	2018	2019	2020	2021	2022	2023
Year	-2	-1	0	1	2	3	4	5	6	7
Fixed Capital Investment	$ 21 663 374.83	$ 129 980 248.95	$ 64 990 124.48							
Land	$ -	$ -	$ -							
Working Capital			$ 10 831 687.41							
Loan Payment				$ -	$ -	$ -	$ -	$ -	$ -	$ -
Loan Interest Payment	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -
Loan Principal	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -
Glucaric acid Price ($/t)			$ 654.55	$ 654.55	$ 654.55	$ 654.55	$ 654.55	$ 654.55	$ 654.55	$ 654.55
Bio-product Sales			$ -	$ 48 132 360.43	$ 48 132 360.43	$ 48 132 360.43	$ 48 132 360.43	$ 48 132 360.43	$ 48 132 360.43	$ 48 132 360.43
Electricty price ($/ kWh)			$ 0.080	$ 0.08	$ 0.08	$ 0.08	$ 0.08	$ 0.08	$ 0.08	$ 0.08
Electricity Sales			$ -	$ 7 182 950.40	$ 7 182 950.40	$ 7 182 950.40	$ 7 182 950.40	$ 7 182 950.40	$ 7 182 950.40	$ 7 182 950.40
Total Annual Revenue			$ -	$ 27 657 655.42	$ 41 486 483.12	$ 55 315 310.83	$ 55 315 310.83	$ 55 315 310.83	$ 55 315 310.83	$ 55 315 310.83
Annual Manufacturing Cost										
Feedstock Price ($/ ton)										
Feedstock cost										
Other Variable Costs										
Fixed Operating Costs										
Total Product Cost			$ -	$ 11 231 963.71	$ 16 847 945.56	$ 22 463 927.42	$ 22 463 927.42	$ 22 463 927.42	$ 22 463 927.42	$ 22 463 927.42
Annual Depreciation										
Plant Writedown			0.00%	20.00%	20.00%	20.00%	20.00%	20.00%		
Depreciation Charge			$ -	$ 43 326 749.65	$ 43 326 749.65	$ 43 326 749.65	$ 43 326 749.65	$ 43 326 749.65		
Remaining Value			$ 216 633 748.26	$ 173 306 998.60	$ 129 980 248.95	$ 86 653 499.30	$ 43 326 749.65	$ -		
Net Revenue (R-COM-dk)	($21 663 375)	($129 980 249)	($75 821 812)	$ -26 901 057.94	$ -18 688 212.09	$ -10 475 366.24	$ -10 475 366.24	$ -10 475 366.24	$ 32 851 383.41	$ 32 851 383.41
Losses Forward				$0	($26 901 058)	($45 589 270)	($56 064 636)	($66 540 003)	($77 015 369)	($44 163 985)
Taxable Income				$ -26 901 057.94	$ -45 589 270.03	$ -56 064 636.27	$ -66 540 002.51	$ -77 015 368.74	$ -44 163 985.33	$ -11 312 601.91
Income Tax				$0	$0	$0	$0	$0	$0	$0
Annual Cash Income			($227 465 436)	$16 425 692	$24 638 538	$32 851 383	$32 851 383	$32 851 383	$32 851 383	$32 851 383
Discount Factor		1.0970	1.0000	0.9116	0.8310	0.7575	0.6905	0.6295	0.5738	0.5231
Annual Present Value (Discounted Cash Flow)			($227 465 436)	$ 14 973 283.23	$ 20 473 951.55	$ 24 884 778.55	$ 22 684 392.48	$ 20 678 571.08	$ 18 850 110.38	$ 17 183 327.60
Cumulative Discounted Cash Flow			($227 465 436)	($212 492 152)	($192 018 201)	($167 133 422)	($144 449 030)	($123 770 459)	($104 920 348)	($87 737 021)
Total Capital Investment + Interest		$ 142 588 333.10	$ 75 821 811.89							
Net Present Worth			$17 223 434							

(a)

DCFROR Worksheet	2024	2025	2026	2027	2028	2029	2030	2031	2032
Year	8	9	10	11	12	13	14	15	16
Fixed Capital Investment									
Land									
Working Capital									
Loan Payment	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -
Loan Interest Payment	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -
Loan Principal	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -
Glucaric acid Price ($/t)	$ 654.55	$ 654.55	$ 654.55	$ 654.55	$ 654.55	$ 654.55	$ 654.55	$ 654.55	$ 654.55
Bio-product Sales	$ 48 132 360.43	$ 48 132 360.43	$ 48 132 360.43	$ 48 132 360.43	$ 48 132 360.43	$ 48 132 360.43	$ 48 132 360.43	$ 48 132 360.43	$ 48 132 360.43
Electricty price ($/ kWh)	$ 0.08	$ 0.08	$ 0.08	$ 0.08	$ 0.08	$ 0.08	$ 0.08	$ 0.08	$ 0.08
Electricity Sales	$ 7 182 950.40	$ 7 182 950.40	$ 7 182 950.40	$ 7 182 950.40	$ 7 182 950.40	$ 7 182 950.40	$ 7 182 950.40	$ 7 182 950.40	$ 7 182 950.40
Total Annual Revenue	$ 55 315 310.83	$ 55 315 310.83	$ 55 315 310.83	$ 55 315 310.83	$ 55 315 310.83	$ 55 315 310.83	$ 55 315 310.83	$ 55 315 310.83	$ 55 315 310.83
Annual Manufacturing Cost									
Feedstock Price ($/ ton)									
Feedstock cost									
Other Variable Costs									
Fixed Operating Costs									
Total Product Cost	$ 22 463 927.42	$ 22 463 927.42	$ 22 463 927.42	$ 22 463 927.42	$ 22 463 927.42	$ 22 463 927.42	$ 22 463 927.42	$ 22 463 927.42	$ 22 463 927.42
Annual Depreciation									
Plant Writedown									
Depreciation Charge									
Remaining Value									
Net Revenue (R-COM-dk)	$ 32 851 383.41	$ 32 851 383.41	$ 32 851 383.41	$ 32 851 383.41	$ 32 851 383.41	$ 32 851 383.41	$ 32 851 383.41	$ 32 851 383.41	$ 32 851 383.41
Losses Forward	($11 312 602)	$0	$0	$0	$0	$0	$0	$0	$0
Taxable Income	$ 21 538 781.50	$ 32 851 383.41	$ 32 851 383.41	$ 32 851 383.41	$ 32 851 383.41	$ 32 851 383.41	$ 32 851 383.41	$ 32 851 383.41	$ 32 851 383.41
Income Tax	$6 030 859	$9 198 387	$9 198 387	$9 198 387	$9 198 387	$9 198 387	$9 198 387	$9 198 387	$9 198 387
Annual Cash Income	$26 820 525	$23 652 996	$23 652 996	$23 652 996	$23 652 996	$23 652 996	$23 652 996	$23 652 996	$23 652 996
Discount Factor	0.4768	0.4347	0.3962	0.3612	0.3292	0.3001	0.2736	0.2494	0.2273
Annual Present Value (Discounted Cash Flow)	$ 12 788 342.16	$ 10 280 790.55	$ 9 371 732.49	$ 8 543 056.06	$ 7 787 653.65	$ 7 099 046.17	$ 6 471 327.41	$ 5 899 113.41	$ 5 377 496.28
Cumulative Discounted Cash Flow	($74 948 679)	($64 667 888)	($55 296 156)	($46 753 100)	($38 965 446)	($31 866 400)	($25 395 072)	($19 495 959)	($14 118 463)
Total Capital Investment + Interest									
Net Present Worth									

(b)

DCFROR Worksheet	2033	2034	2035	2036	2037	2038	2039	2040	2041
Year	17	18	19	20	21	22	23	24	25
Fixed Capital Investment									
Land									
Working Capital									
Loan Payment	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -
Loan Interest Payment	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -
Loan Principal	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -
Glucaric acid Price ($/t)	$ 654.55	$ 654.55	$ 654.55	$ 654.55	$ 654.55	$ 654.55	$ 654.55	$ 654.55	$ 654.55
Bio-product Sales	$ 48 132 360.43	$ 48 132 360.43	$ 48 132 360.43	$ 48 132 360.43	$ 48 132 360.43	$ 48 132 360.43	$ 48 132 360.43	$ 48 132 360.43	$ 48 132 360.43
Electricty price ($/ kWh)	$ 0.08	$ 0.08	$ 0.08	$ 0.08	$ 0.08	$ 0.08	$ 0.08	$ 0.08	$ 0.08
Electricity Sales	$ 7 182 950.40	$ 7 182 950.40	$ 7 182 950.40	$ 7 182 950.40	$ 7 182 950.40	$ 7 182 950.40	$ 7 182 950.40	$ 7 182 950.40	$ 7 182 950.40
Total Annual Revenue	$ 55 315 310.83	$ 55 315 310.83	$ 55 315 310.83	$ 55 315 310.83	$ 55 315 310.83	$ 55 315 310.83	$ 55 315 310.83	$ 55 315 310.83	$ 55 315 310.83
Annual Manufacturing Cost									
Feedstock Price ($/ ton)									
Feedstock cost									
Other Variable Costs									
Fixed Operating Costs									
Total Product Cost	$ 22 463 927.42	$ 22 463 927.42	$ 22 463 927.42	$ 22 463 927.42	$ 22 463 927.42	$ 22 463 927.42	$ 22 463 927.42	$ 22 463 927.42	$ 22 463 927.42
Annual Depreciation									
Plant Writedown									
Depreciation Charge									
Remaining Value									
Net Revenue (R-COM-dk)	$ 32 851 383.41	$ 32 851 383.41	$ 32 851 383.41	$ 32 851 383.41	$ 32 851 383.41	$ 32 851 383.41	$ 32 851 383.41	$ 32 851 383.41	$ 32 851 383.41
Losses Forward	$0	$0	$0	$0	$0	$0	$0	$0	$0
Taxable Income	$ 32 851 383.41	$ 32 851 383.41	$ 32 851 383.41	$ 32 851 383.41	$ 32 851 383.41	$ 32 851 383.41	$ 32 851 383.41	$ 32 851 383.41	$ 32 851 383.41
Income Tax	$9 198 387	$9 198 387	$9 198 387	$9 198 387	$9 198 387	$9 198 387	$9 198 387	$9 198 387	$9 198 387
Annual Cash Income	$23 652 996	$23 652 996	$23 652 996	$23 652 996	$23 652 996	$23 652 996	$23 652 996	$23 652 996	$23 652 996
Discount Factor	0.2072	0.1889	0.1722	0.1570	0.1431	0.1305	0.1189	0.1084	0.0988
Annual Present Value (Discounted Cash Flow)	$ 4 902 002.07	$ 4 468 552.48	$ 4 073 429.79	$ 3 713 245.03	$ 3 384 908.87	$ 3 085 605.16	$ 2 812 766.79	$ 2 564 053.59	$ 2 337 332.35
Cumulative Discounted Cash Flow	($9 216 461)	($4 747 908)	($674 478)	$3 038 767	$6 423 676	$9 509 281	$12 322 048	$14 886 101	$17 223 434
Total Capital Investment + Interest									
Net Present Worth									

(c)

Table C6-2: Discounted cash flow rate of return spreadsheet for Glucaric.$_{DA}$ scenario (a), (b) and (c)

DCFROR Worksheet			2016	2017	2018	2019	2020	2021	2022	2023
Year	-2	-1	0	1	2	3	4	5	6	7
Fixed Capital Investment	$ 20 315 699.79	$ 121 894 198.72	$ 60 947 099.36							
Land	$ -	$ -	$ -							
Working Capital			$ 10 157 849.89							
Loan Payment				$ -	$ -	$ -	$ -	$ -	$ -	$ -
Loan Interest Payment	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -
Loan Principal	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -
Glucaric acid Price ($/t)			$ 654.55	$ 654.55	$ 654.55	$ 654.55	$ 654.55	$ 654.55	$ 654.55	$ 654.55
Bio-product Sales			$ -	$ 43 517 625.84	$ 43 517 625.84	$ 43 517 625.84	$ 43 517 625.84	$ 43 517 625.84	$ 43 517 625.84	$ 43 517 625.84
Electricty price ($/ kWh)			$ 0.080	$ 0.08	$ 0.08	$ 0.08	$ 0.08	$ 0.08	$ 0.08	$ 0.08
Electricity Sales			$ -	$ 7 357 651.20	$ 7 357 651.20	$ 7 357 651.20	$ 7 357 651.20	$ 7 357 651.20	$ 7 357 651.20	$ 7 357 651.20
Total Annual Revenue			$ -	$ 25 437 638.52	$ 38 156 457.78	$ 50 875 277.04	$ 50 875 277.04	$ 50 875 277.04	$ 50 875 277.04	$ 50 875 277.04
Annual Manufacturing Cost										
Feedstock Price ($/ ton)										
Feedstock cost										
Other Variable Costs										
Fixed Operating Costs										
Total Product Cost			$ -	$ 10 044 290.85	$ 15 066 436.28	$ 20 088 581.70	$ 20 088 581.70	$ 20 088 581.70	$ 20 088 581.70	$ 20 088 581.70
Annual Depreciation										
Plant Writedown			0.00%	20.00%	20.00%	20.00%	20.00%	20.00%		
Depreciation Charge			$ -	$ 40 631 399.57	$ 40 631 399.57	$ 40 631 399.57	$ 40 631 399.57	$ 40 631 399.57		
Remaining Value			$ 203 156 997.87	$ 162 525 598.30	$ 121 894 198.72	$ 81 262 799.15	$ 40 631 399.57	$ -		
Net Revenue (R-COM-dk)	($20 315 700)	($121 894 199)	($71 104 949)	$ -25 238 051.91	$ -17 541 378.07	$ -9 844 704.24	$ -9 844 704.24	$ -9 844 704.24	$ 30 786 695.34	$ 30 786 695.34
Losses Forward				$0	($25 238 052)	($42 779 430)	($52 624 134)	($62 468 838)	($72 313 543)	($41 526 847)
Taxable Income				$ -25 238 051.91	$ -42 779 429.98	$ -52 624 134.22	$ -62 468 838.46	$ -72 313 542.70	$ -41 526 847.36	$ -10 740 152.03
Income Tax				$0	$0	$0	$0	$0	$0	$0
Annual Cash Income			($213 314 848)	$15 393 348	$23 090 022	$30 786 695	$30 786 695	$30 786 695	$30 786 695	$30 786 695
Discount Factor		1.0970	1.0000	0.9116	0.8310	0.7575	0.6905	0.6295	0.5738	0.5231
Annual Present Value (Discounted Cash Flow)			($213 314 848)	$ 14 032 222.12	$ 19 187 177.01	$ 23 320 786.40	$ 21 258 693.17	$ 19 378 936.34	$ 17 665 393.20	$ 16 103 366.64
Cumulative Discounted Cash Flow			($213 314 848)	($199 282 626)	($180 095 449)	($156 774 662)	($135 515 969)	($116 137 033)	($98 471 640)	($82 368 273)
Total Capital Investment + Interest		$ 133 717 936.00	$ 71 104 949.26							
Net Present Worth			$16 013 981							

(a)

DCFROR Worksheet	2024	2025	2026	2027	2028	2029	2030	2031	2032
Year	8	9	10	11	12	13	14	15	16
Fixed Capital Investment									
Land									
Working Capital									
Loan Payment	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -
Loan Interest Payment	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -
Loan Principal	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -
Glucaric acid Price ($/t)	$ 654.55	$ 654.55	$ 654.55	$ 654.55	$ 654.55	$ 654.55	$ 654.55	$ 654.55	$ 654.55
Bio-product Sales	$ 43 517 625.84	$ 43 517 625.84	$ 43 517 625.84	$ 43 517 625.84	$ 43 517 625.84	$ 43 517 625.84	$ 43 517 625.84	$ 43 517 625.84	$ 43 517 625.84
Electricty price ($/ kWh)	$ 0.08	$ 0.08	$ 0.08	$ 0.08	$ 0.08	$ 0.08	$ 0.08	$ 0.08	$ 0.08
Electricity Sales	$ 7 357 651.20	$ 7 357 651.20	$ 7 357 651.20	$ 7 357 651.20	$ 7 357 651.20	$ 7 357 651.20	$ 7 357 651.20	$ 7 357 651.20	$ 7 357 651.20
Total Annual Revenue	$ 50 875 277.04	$ 50 875 277.04	$ 50 875 277.04	$ 50 875 277.04	$ 50 875 277.04	$ 50 875 277.04	$ 50 875 277.04	$ 50 875 277.04	$ 50 875 277.04
Annual Manufacturing Cost									
Feedstock Price ($/ ton)									
Feedstock cost									
Other Variable Costs									
Fixed Operating Costs									
Total Product Cost	$ 20 088 581.70	$ 20 088 581.70	$ 20 088 581.70	$ 20 088 581.70	$ 20 088 581.70	$ 20 088 581.70	$ 20 088 581.70	$ 20 088 581.70	$ 20 088 581.70
Annual Depreciation									
Plant Writedown									
Depreciation Charge									
Remaining Value									
Net Revenue (R-COM-dk)	$ 30 786 695.34	$ 30 786 695.34	$ 30 786 695.34	$ 30 786 695.34	$ 30 786 695.34	$ 30 786 695.34	$ 30 786 695.34	$ 30 786 695.34	$ 30 786 695.34
Losses Forward	($10 740 152)	$0	$0	$0	$0	$0	$0	$0	$0
Taxable Income	$ 20 046 543.31	$ 30 786 695.34	$ 30 786 695.34	$ 30 786 695.34	$ 30 786 695.34	$ 30 786 695.34	$ 30 786 695.34	$ 30 786 695.34	$ 30 786 695.34
Income Tax	$5 613 032	$8 620 275	$8 620 275	$8 620 275	$8 620 275	$8 620 275	$8 620 275	$8 620 275	$8 620 275
Annual Cash Income	$25 173 663	$22 166 421	$22 166 421	$22 166 421	$22 166 421	$22 166 421	$22 166 421	$22 166 421	$22 166 421
Discount Factor	0.4768	0.4347	0.3962	0.3612	0.3292	0.3001	0.2736	0.2494	0.2273
Annual Present Value (Discounted Cash Flow)	$ 12 003 099.25	$ 9 634 649.55	$ 8 782 725.20	$ 8 006 130.54	$ 7 298 204.69	$ 6 652 875.74	$ 6 064 608.70	$ 5 528 357.97	$ 5 039 524.13
Cumulative Discounted Cash Flow	($70 365 174)	($60 730 524)	($51 947 799)	($43 941 668)	($36 643 464)	($29 990 588)	($23 925 979)	($18 397 621)	($13 358 097)
Total Capital Investment + Interest									
Net Present Worth									

(b)

DCFROR Worksheet	2033	2034	2035	2036	2037	2038	2039	2040	2041
Year	17	18	19	20	21	22	23	24	25
Fixed Capital Investment									
Land									
Working Capital									
Loan Payment	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -
Loan Interest Payment	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -
Loan Principal	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -
Glucaric acid Price ($/t)	$ 654.55	$ 654.55	$ 654.55	$ 654.55	$ 654.55	$ 654.55	$ 654.55	$ 654.55	$ 654.55
Bio-product Sales	$ 43 517 625.84	$ 43 517 625.84	$ 43 517 625.84	$ 43 517 625.84	$ 43 517 625.84	$ 43 517 625.84	$ 43 517 625.84	$ 43 517 625.84	$ 43 517 625.84
Electricty price ($/ kWh)	$ 0.08	$ 0.08	$ 0.08	$ 0.08	$ 0.08	$ 0.08	$ 0.08	$ 0.08	$ 0.08
Electricity Sales	$ 7 357 651.20	$ 7 357 651.20	$ 7 357 651.20	$ 7 357 651.20	$ 7 357 651.20	$ 7 357 651.20	$ 7 357 651.20	$ 7 357 651.20	$ 7 357 651.20
Total Annual Revenue	$ 50 875 277.04	$ 50 875 277.04	$ 50 875 277.04	$ 50 875 277.04	$ 50 875 277.04	$ 50 875 277.04	$ 50 875 277.04	$ 50 875 277.04	$ 50 875 277.04
Annual Manufacturing Cost									
Feedstock Price ($/ ton)									
Feedstock cost									
Other Variable Costs									
Fixed Operating Costs									
Total Product Cost	$ 20 088 581.70	$ 20 088 581.70	$ 20 088 581.70	$ 20 088 581.70	$ 20 088 581.70	$ 20 088 581.70	$ 20 088 581.70	$ 20 088 581.70	$ 20 088 581.70
Annual Depreciation									
Plant Writedown									
Depreciation Charge									
Remaining Value									
Net Revenue (R-COM-dk)	$ 30 786 695.34	$ 30 786 695.34	$ 30 786 695.34	$ 30 786 695.34	$ 30 786 695.34	$ 30 786 695.34	$ 30 786 695.34	$ 30 786 695.34	$ 30 786 695.34
Losses Forward	$0	$0	$0	$0	$0	$0	$0	$0	$0
Taxable Income	$ 30 786 695.34	$ 30 786 695.34	$ 30 786 695.34	$ 30 786 695.34	$ 30 786 695.34	$ 30 786 695.34	$ 30 786 695.34	$ 30 786 695.34	$ 30 786 695.34
Income Tax	$8 620 275	$8 620 275	$8 620 275	$8 620 275	$8 620 275	$8 620 275	$8 620 275	$8 620 275	$8 620 275
Annual Cash Income	$22 166 421	$22 166 421	$22 166 421	$22 166 421	$22 166 421	$22 166 421	$22 166 421	$22 166 421	$22 166 421
Discount Factor	0.2072	0.1889	0.1722	0.1570	0.1431	0.1305	0.1189	0.1084	0.0988
Annual Present Value (Discounted Cash Flow)	$ 4 593 914.43	$ 4 187 706.87	$ 3 817 417.38	$ 3 479 869.99	$ 3 172 169.55	$ 2 891 676.89	$ 2 635 986.22	$ 2 402 904.49	$ 2 190 432.53
Cumulative Discounted Cash Flow	($8 764 183)	($4 576 476)	($759 058)	$2 720 812	$5 892 981	$8 784 658	$11 420 644	$13 823 549	$16 013 981
Total Capital Investment + Interest									
Net Present Worth									

(c)

APPENDIX D

D-1: Supplementary data submitted with the article in chapter 5

TECHNO-ECONOMICS OF LIGNOCELLULOSE BIOREFINERIES AT SOUTH AFRICAN SUGAR MILLS USING THE BIOFINE PROCESS TO CO-PRODUCE LEVULINIC ACID, FURFURAL AND ELECTRICITY ALONG GAMMA VALERACTONE

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Supplementary Information:	2 Tables: Tables D1-1 and D1-2 2 Figures: Figure D1-1 and D1-2

Table D1-1: Average bagasse and trash composition (Farzad et al., 2017)

Material	**Percentage**	**$t.h^{-1}$**
Sugarcane		300
Wet bagasse	30% of sugarcane	90
Dry bagasse (extractant included)	50% of wet bagassee	45
Total harvesting residues (trash + green tops)	15% of sugarcane	45
Trash available to biorefinery	50% of total harvesting residues	22.5
Dry trash	15% of wet	20
Total dry feedstock		65

Table D1-2: Scenario A, B1 and B2-Distillation column conditions

Parameters	**Vacuum distillation**	**Steam Stripping**
Stages	23	6
Condenser	Total	Total
Reboiler	Kettle	Kettle
Reflux ratio (mass)	9.8	9.8
Distillate to Feed ratio (mass)	0.51	0.58
Column pressure (atm)	0.1	1

Table D1-3: Scenario C-separating and purifying process conditions for the gamma valerolactone production process area

	Column 1 (GVL-DIST1)	**Column 2 (GVL-DIST2)**
Parameters	Solvent removal and purification	GVL product purification
Stages	23	23
Condenser	Partial Vapour	Total
Reboiler	Kettle	Kettle
Reflux ratio	0.26 (mol)	0.88 (mass)
Distillate to Feed ratio	0.892 (mol)	0.25 (mass)
Column pressure (atm)	1.2	1.0

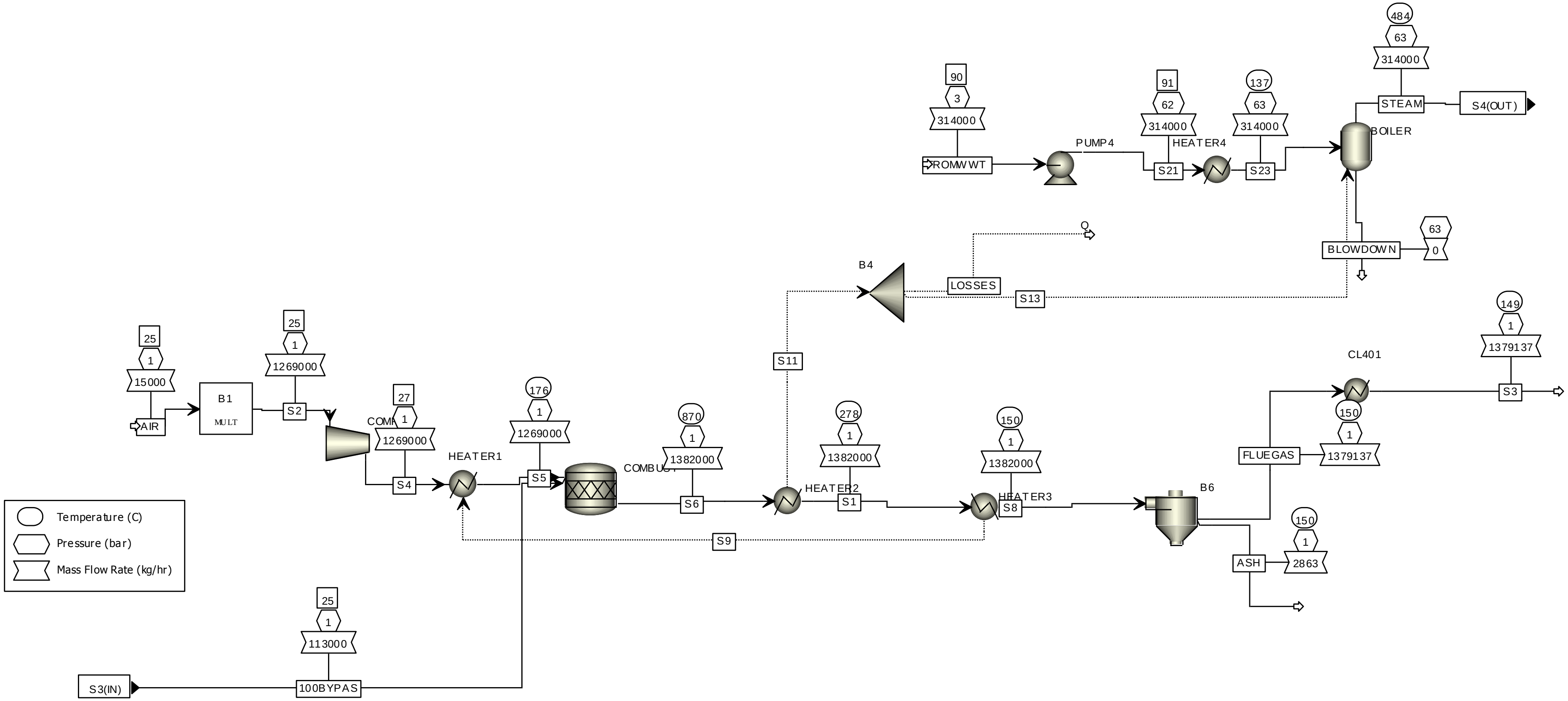


Figure D1-1: Boiler unit of the base case combined heat and power plant

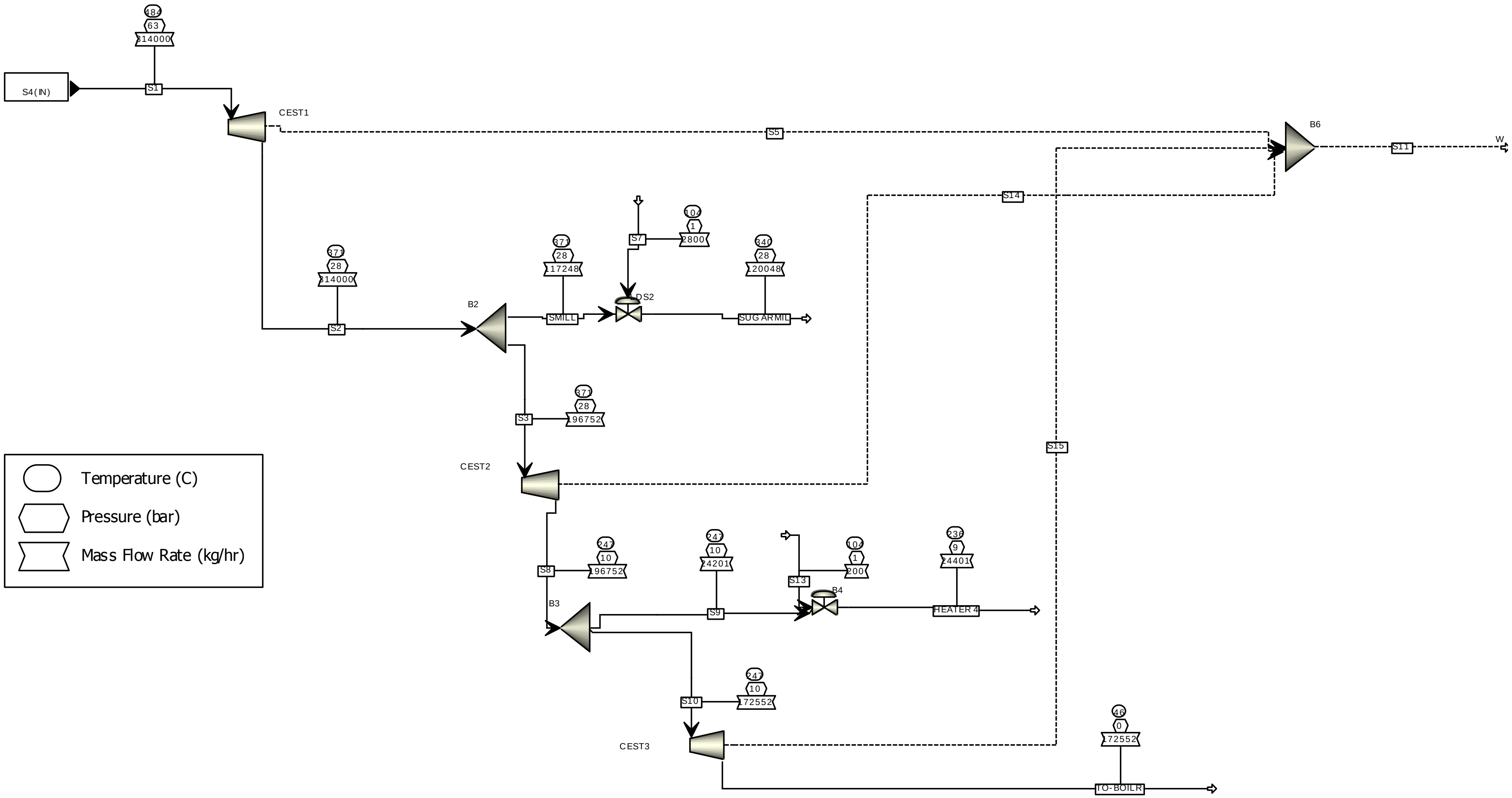


Figure D1-2: Condensing extraction steam turbine (CEST) unit of the base case combined heat and power plant

Table D1-4: Mass balance around the CHP plant for all scenarios

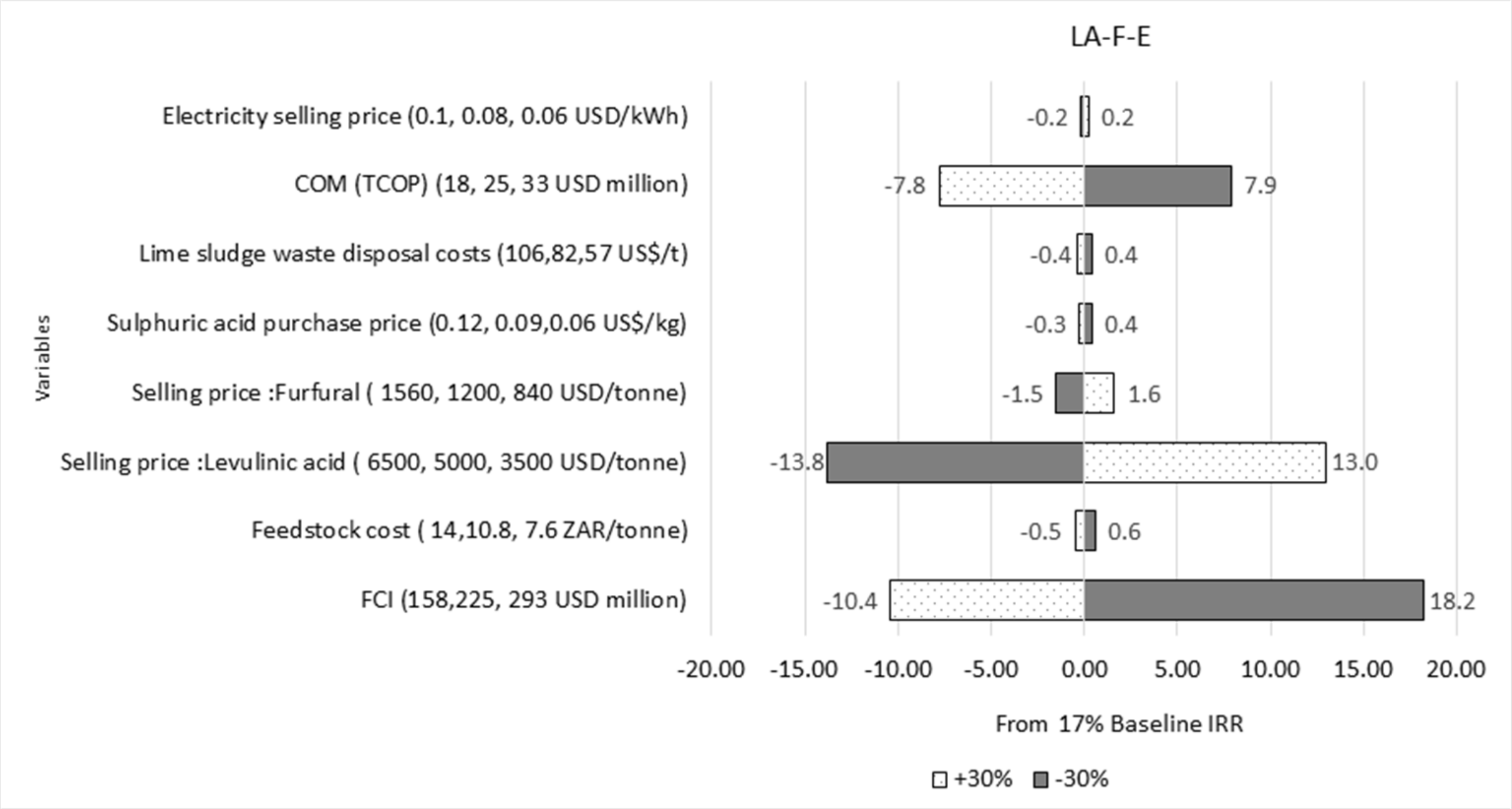
	A	B1	B2	C	CHP base case
BOILER UNIT					
Compressed air (t/h)	976	1319	605	998	1269
Flue gas (t/h)	1057	1430	654	1077	1379
Methane (t/h)	2	2	2	2	0
Cellulignin (t/h)	33.2	0.7	0.8	37	0
Ash (t/h)	3.3	2.9	1.3	3.3	2.9
CEST UNIT					
Boiler feed water (t/h)	242	326	149	243	314

D-2: Sensitivity analysis of the LA-F-E and LA-GVL-F-E scenarios

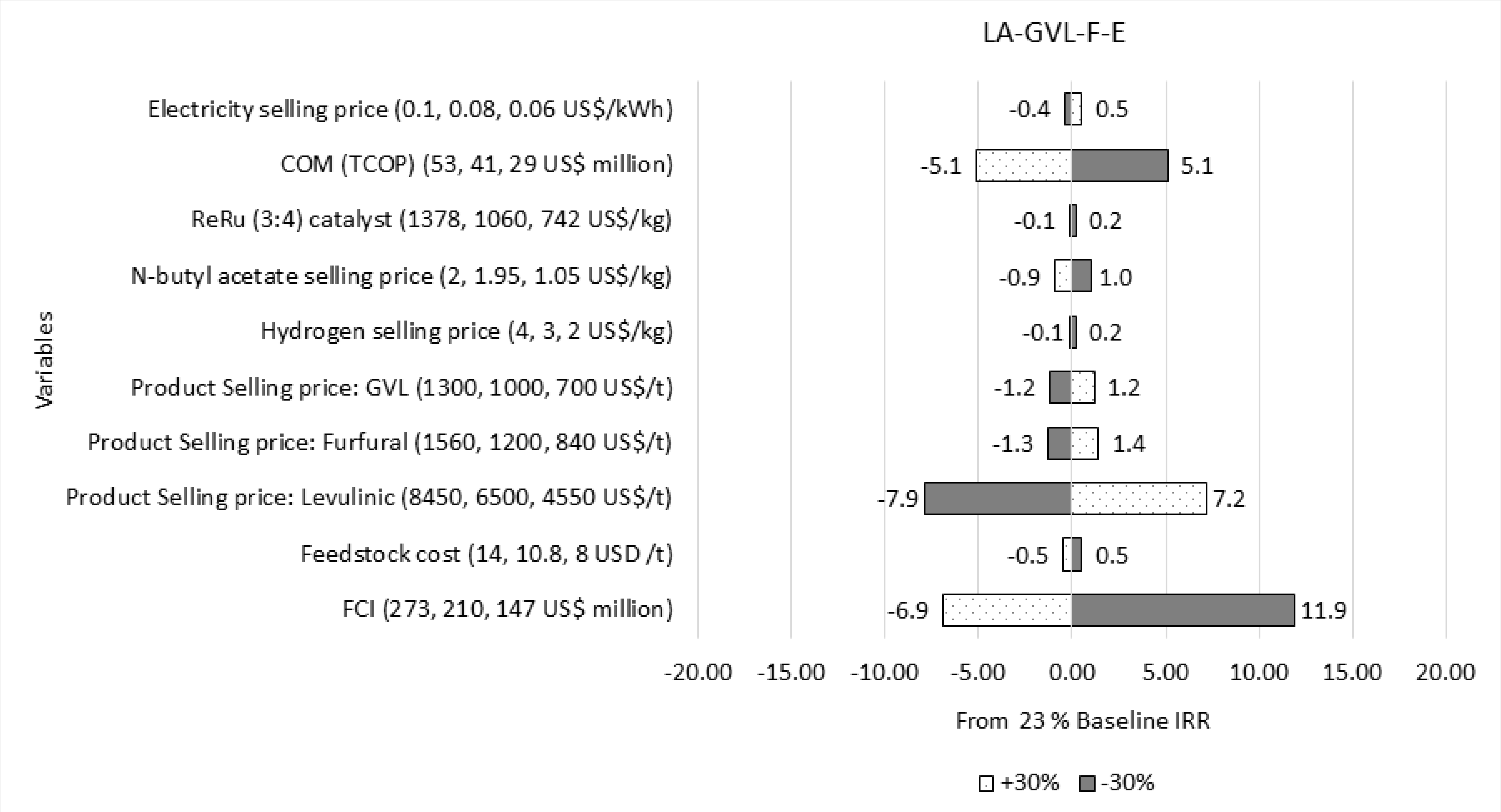
A market report has predicted that the levulinic acid selling price will plunge to US$ 920/t if manufacturers are to reach mass markets (IAR 2015a). At this selling price, scenarios with multiple products LA-F-E and LA-GVL-F-E have an economic advantage. Scenario LA-GVL-F-E, with the highest sellable products was more profitable because producing several products improved profit margins (although not the most significant contributor).

A sensitivity analysis of LA-F-E and LA-GVL-F-E scenarios with several sellable bio-based products revealed that the IRR for LA-F-E was highly impacted by the fixed capital investment and levulinic acid selling price. On the other hand, LA-GVL-F-E was largely affected by the fixed capital investment, followed by levulinic acid selling price and manufacturing cost (COM) to a lesser extent as shown in Figure D2-1(a) and (b). A 30% increase in FCI led to a 10% and 7% reduction in the IRR for LA-F-E and LA-GVL-F-E respectively, whilst a 30% increase in the LA selling of LA-F-E and LA-GVL-F-E resulted in a 13% and 7% increase respectively in the IRR. The manufacturing cost (COM) in LA- F-E and LA-GVL-F-E impacted on the IRR by an ± 8% and 5% change respectively.

It was observed that reagents, catalysts, sludge disposal costs and electricity selling price had a minimal impact on the IRR for the scenarios but the electricity selling price had the largest impact on CHP Baseline (not shown) since it is the process' only sellable product. Unfortunately, even though CHP Baseline produced 7-12 times more the amount of electricity than the other scenarios, the electricity selling price is low (US$ 0.08/kWh) leading to a small return on profit. Therefore, at current prevailing economic conditions, a biorefinery‘s profitability lies in its sale of more chemicals than electricity. It is hence vital that the new integrated processes are designed to produce just enough electricity for internal consumption, with little for sale to the grid.


LA-F-E
Variables
Electricity selling price (0.1, 0.08, 0.06 USD/kWh)
COM (TCOP) (18, 25, 33 USD million)
Lime sludge waste disposal costs (106,82,57 US$/t)
Sulphuric acid purchase price (0.12, 0.09,0.06 US$/kg)
Selling price :Furfural (1560, 1200, 840 USD/tonne)
Selling price :Levulinic acid (6500, 5000, 3500 USD/tonne)
Feedstock cost (14,10.8, 7.6 ZAR/tonne)
FCI (158,225, 293 USD million)
-0.2
0.2
-7.8
7.9
-0.4
0.4
-0.3
0.4
-1.5
1.6
-13.8
13.0
-0.5
0.6
-10.4
18.2
-20.00
-15.00
-10.00
-5.00
0.00
5.00
10.00
15.00
20.00
From 17% Baseline IRR
☐ +30%
■ -30%

(a)



(b)

Figure D2-1: Sensitivity analysis of the baseline IRRs for LA-F-E and LA-GVL-F-E using several economic variables

D-3: Aspen Plus® models and process conditions for the profitable levulinic acid scenarios

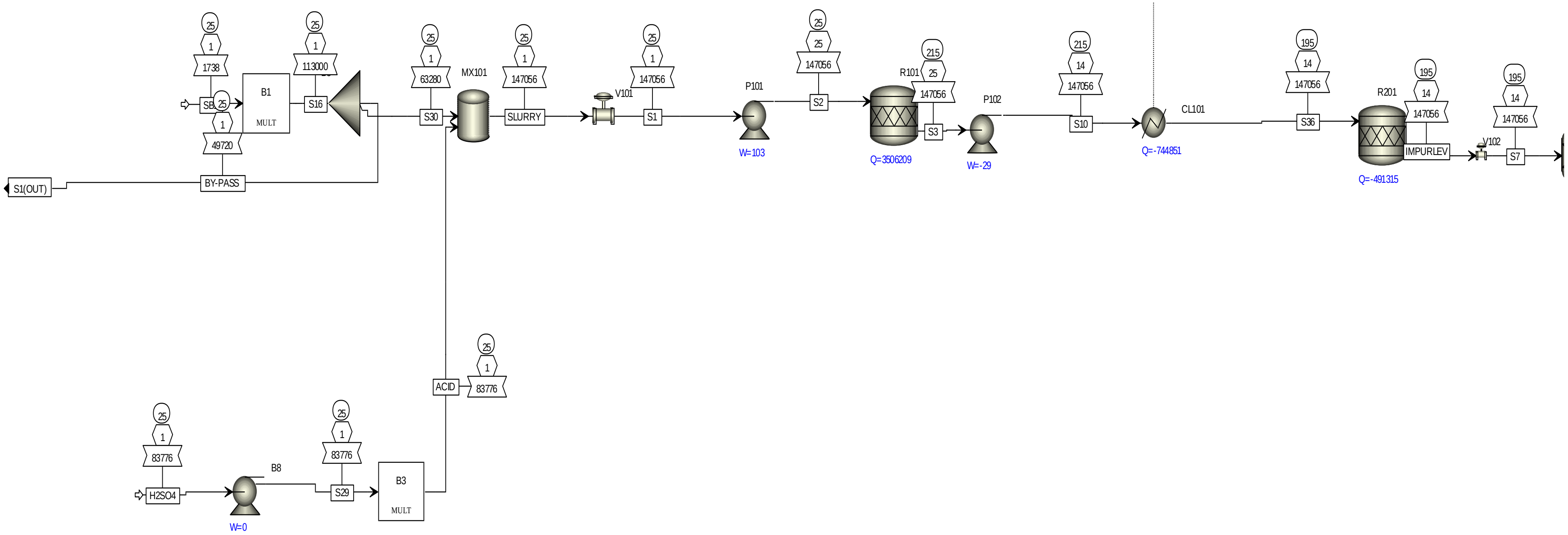


Figure D3-1: The 1st and 2nd reactor stages of the levulinic acid scenarios

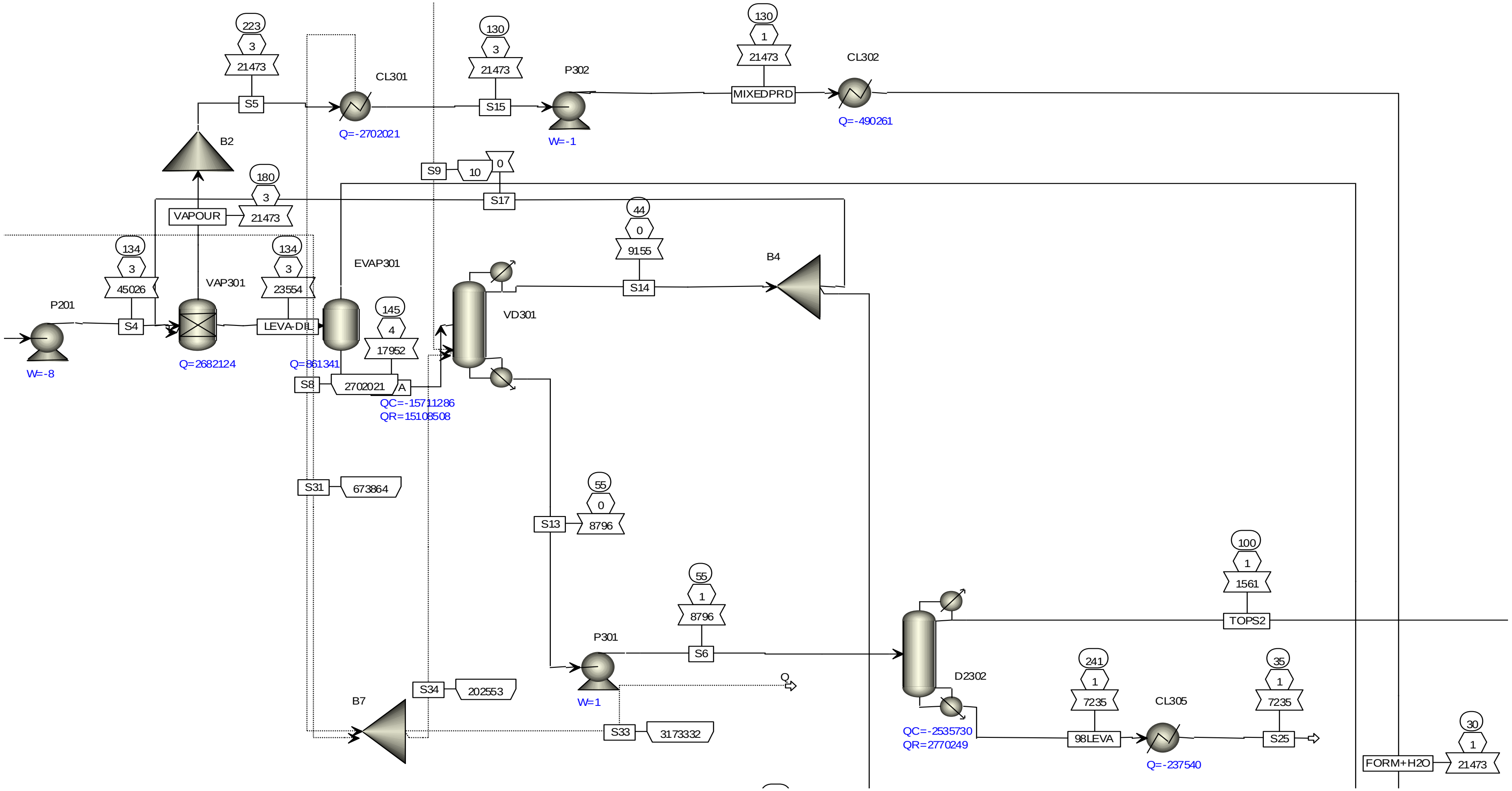


Figure D3-2: The purification stages of the levulinic acid production process

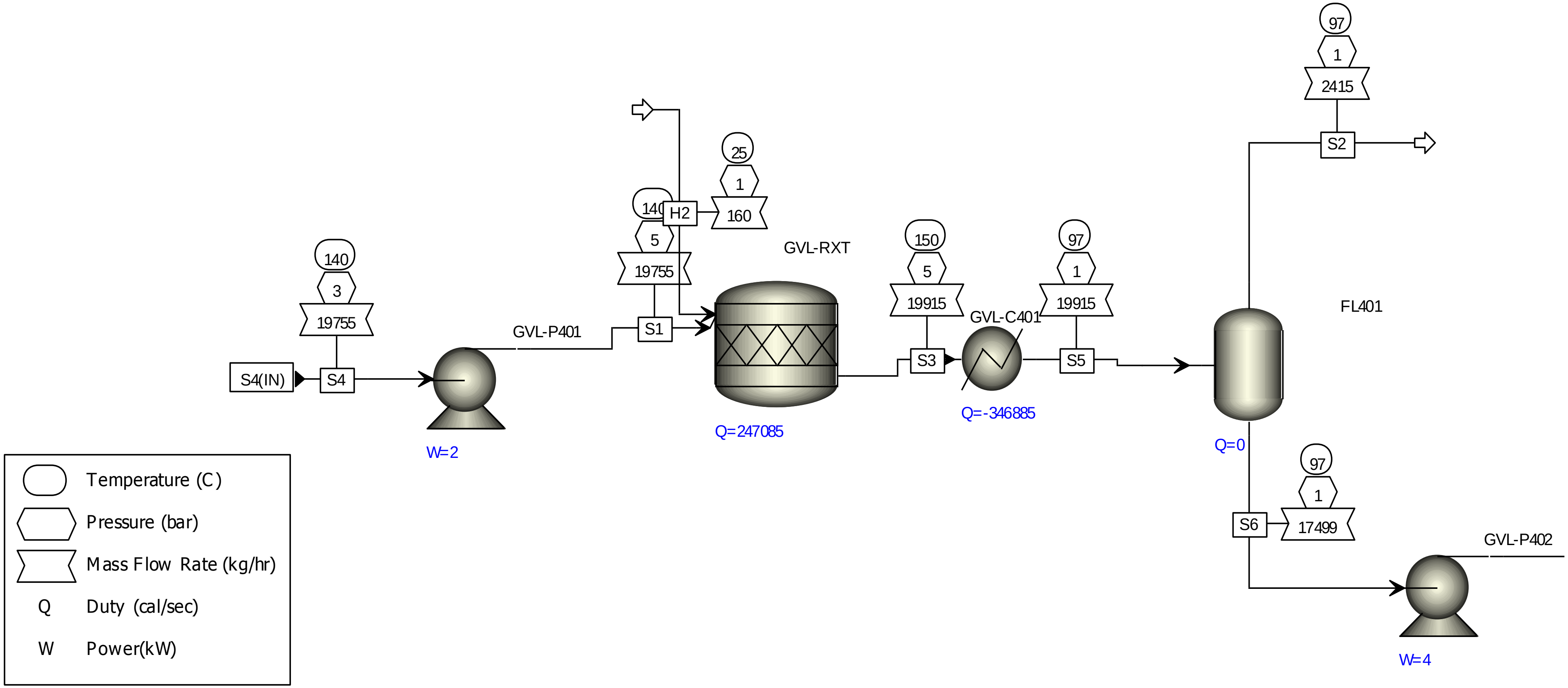


Figure D3-3: Levulinic acid hydrogenation to gamma valerolactone process area flowsheet

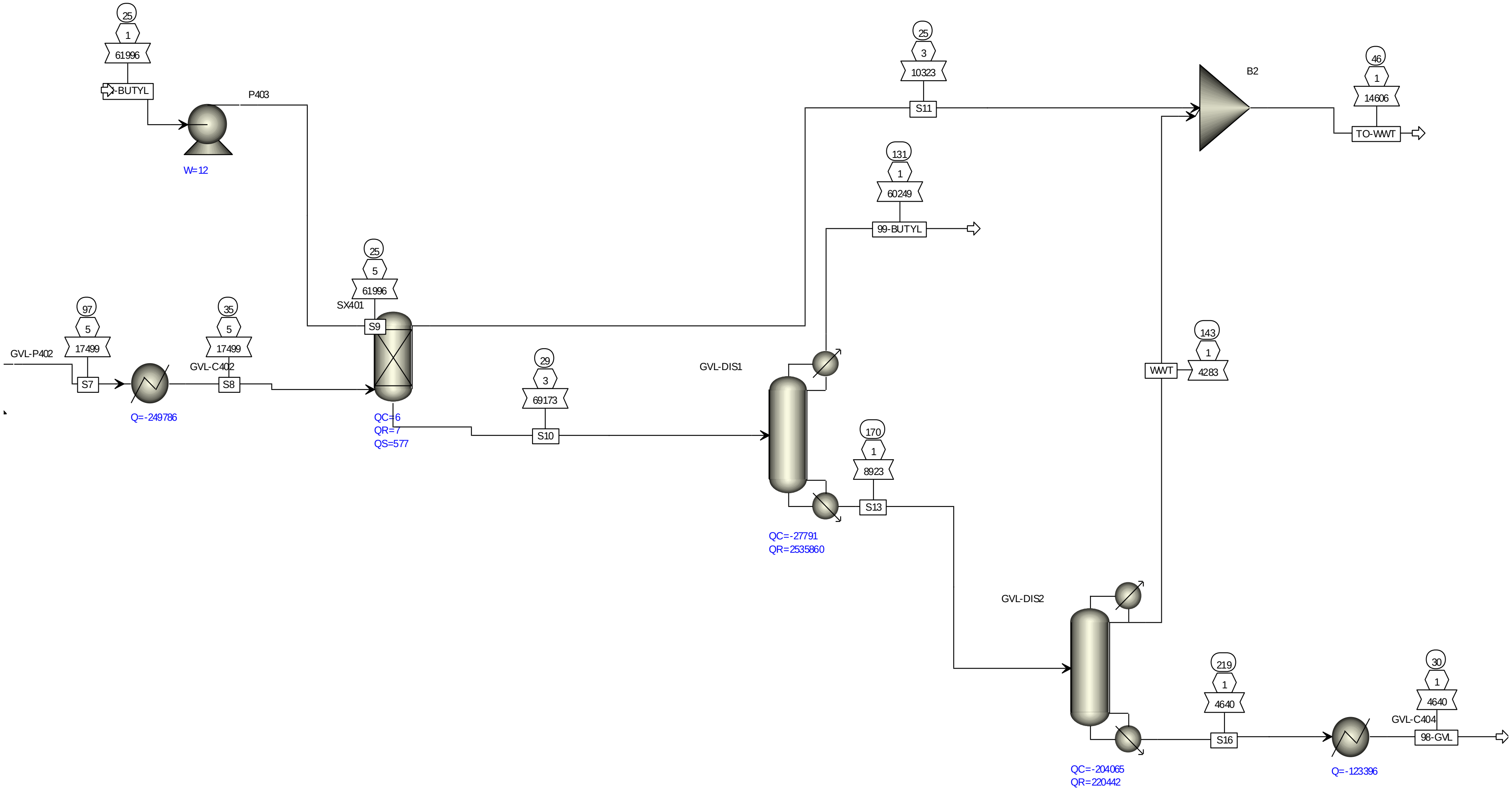


Figure D3-4: GVL purification stages via solvent extraction and distillation

Table D3-1: LA-F-E process conditions for the conversion and purification stages

	Aspen Unit	**Type or purpose of unit operatior**	**Process conditions**
1st REACTOR	MX101	Feedstock conditioning	Temp. = 25°C, Pressure = 1 atm
	B8	Dilute acid pump	1 atm
	P101	Pump	pressure = 25 atm
	R 101	1st reactor	Temp 215°C, 25 atm
2ND REACTOR	P102	Pump	Pressure = 13.9 atm
	CL101	Cooler	195°C
	R 201	2nd reactor	Temp. = 195°C, Pressure = 13.9 atm
	FT201	Filter	Pressure drop = 0
PURIFICATION	CL-FURF	Cooler	Temp. = 30°C
	CL201	Cooler	Temp. = 134°C
	P201	Pump	Pressure = 3 atm
	P302	Pump	Pressure 1 atm
	EVAP301	Flash tank	Temp. = 145°C, Pressure = 4 atm
	VD301	Vacuum distillation column	Pressure = 0 bar, NRTL property method, conditions in chapter 3
	D2302	Distillation column	Pressure = 1 bar, NRTL property method
	CL305	Cooler	Temp. = 35°C, Pressure = 1 atm
	CL306	Cooler	Temp. = 35°C, Pressure = 1 atm
	NZ201	Neutralizing mixing tank	Pressure drop = 0

Table D3-2: Additional process conditions applicable to the LA-GVL-F-E scenario

	Aspen Unit	Type or purpose of unit operation	Process conditions	Other comments
GVL PRODUCTION	GVL-P401	Pump	5 atm	
	GVL-RXT	GVL production reactor	Temp. = 150^oC, pressure = 4 atm	
	GVL-C401	Cooler	Temp, 98^oC, pressure drop =0	
	GVL-P402	Pump	Pressure = 5 bar	
	FL401	Flash tank	Pressure=1 atm, Temp = 97^oC	
	P403	N-butyl acetate solvent pump	Pressure =1 atm	
	SX401	Solvent extraction columns	Temp = 25^oC, pressure =5 atm	
	GVL-DIS1	Distillation column	Reflux ratio =0.26 mol, distillate to feed 0.892 (mole) 23 stages, Pressure=1.2 atm	Solvent recovery to 99 wt% purity, NRTL property method
	GVL-DIS2	Distillation column	Reflux ratio=0.88 mass, distillate to feed ratio =0.25 (mass), 23 stages, pressure =1 atm	GVL recovery, NRTL property method
	GVL-C404	Cooler	Temp. = 30^oC	

D-4: Equipment sizing

Table D4-1: Equipment sizing and costing of the LA-F-E biorefinery's 1st and 2nd reaction and purification stages (all costs in US$)

Equipment label	Actual equipment	description (Ref)	Material	Unit cost ($)	No. used	total cost ($)	Year of quote	scaling value	Units	scaling Exp.	Instal. Factor	Size ratio	new value	Scaled purchase price ($)	Purchase price In Proj. Year	Installed cost in Project Year
MX101	MIXING TANK	INCLUDED	SS													
CL102	HX	ASPEN	SS												67 400	186 900
P301		ASPEN													9 000	66 200
SEP101	FLASH	ASPEN	SS												-	-
CL306	HX	ASPEN	6920												8 400	57 300
CL307?	HX	ASPEN	CS												9 300	48 500
P301	PUMP	ASPEN	SS												9 000	68 400
VAP301	VAPORISER	ASPEN	SS												18 700	131 800
LEVA.VD301-cond	DISTIL. COLUMNS	ASPEN	SS												917 100	1 485 000
LEVA.VD301-cond acc	DISTIL. COLUMNS	ASPEN	SS												81 300	456 600
LEVA.VD301-overhead split	DISTIL. COLUMNS	ASPEN	SS												-	-
LEVA.VD301-reb	DISTIL. COLUMNS	ASPEN													198 300	597 300
LEVA.VD301-reflux pump	DISTIL. COLUMNS	ASPEN	SS												19200	102000
LEVA.VD301-tower	DISTIL. COLUMNS	ASPEN	SS												8868000	18078600
LEVA.CL305	HX	ASPEN	SS												11000	70300
LEVA.CL303	HX		SS												0	0
LEVA.CL304	HX		SS												0	0
LEVA.CL301	HX	ASPEN	SS												23 700	94 400
LEVA.CL201	HX	ASPEN	SS												11200	61400
LEVA.FT201	FLASH	ASPEN	SS												95100	459300
P102	PUMP	ASPEN	SS												27 200	139 400
LEVA.P302	PUMP	ASPEN	SS												11 200	69 400
LEVA.CL201	HX	ASPEN	SS												13 300	72 600
LEVA.P201	PUMP	ASPEN	SS												12 800	82 800
LEVA.EVAP301	EVAP	ASPEN	SS												18 200	115 800
LEVA.D2302-cond	DISTIL. COLUMNS	ASPEN	SS												71 100	278 700
LEVA.D2302-cond acc	DISTIL. COLUMNS	ASPEN	SS												35 700	262 800
LEVA.D2302-reb	DISTIL. COLUMNS	ASPEN	SS												113 700	271 800
LEVA.D2302-reflux pump	DISTIL. COLUMNS	ASPEN	SS												11 000	68 800
LEVA.D2302-tower	DISTIL. COLUMNS	ASPEN	SS												399 300	1 294 500
LEVA.P302			SS												11 400	78 000
LEVA.P101		ASPEN	SS												155 400	271 400
LEVA.FT101	FILTER	ASPEN	SS												59 700	345 300
LEVA.CL302			SS												-	-
CL101	HX	ASPEN	SS												11 200	61 400
B9(PUMP to rxt 2)		ASPEN	SS												17 600	99 000
CL-FURF		ASPEN	SS												9 600	59 300
B8(PUMP to rxt1)		ASPEN	SS												19 800	102 200
REACTORS R101(53400LBS)	SINNOT & TOWLER	(15 seconds)	SS(213000,389000)	529185	2	1058370	2010			0.85	2.5			60 058	1 058 370	4 233 480
REACTOR R201(29800LBS)	SINNOT & TOWLER	30 MINUTES	(189400,354400)	328934	3	986802	2010			0.85	2.5			7 713 404	986 802	3 947 208
															18 881 446	**43 153 224**

Table D4-2: Equipment sizing and costing of the LA-F-E biorefinery's (a) boiler (b) CEST unit and (c) wastewater treatment plant (all costs in US$)

7.65

Equipment label	Actual equipment	description (Ref)	Material	Unit cost ($)	No. used	total cost ($)	Year of quote	scaling value	Units	scaling Exp.	Instal. Factor	Size ratio	new value	Scaled purchase price ($)	Purchase price In Proj. Year	Installed cost in Project Year
HEATER4	HX	ASPEN													47 400.00	170 100.00
AIR BLOWER	compressor/air blower/fan	MANUALLY	SS	INCLUDED	1											
HEATER 1	HX	ASPEN	SS	INCLUDED	1										1146200	1742600
															1554200	2467700
HEATER3	HX	ASPEN													2466100	4102000
CHP.PUMP1	PUMP	ASPEN	SS												408800	662400
CL401	HX AT BAG HOUSE	ASPEN													12800	71200
CFG401	Centrifuge/FGD BAG HOUSE	NREL	SS	INCLUDED												
CHP.BOILER	Boiler (FLASH VESSEL)	NREL	SS	28550000	1	2.9E+07	2010	238686	kg/h	0.6	1.8	1.03274	246500	29107177.81	28 351 490	51 032 682.66
DEARATOR		NREL	SS	305000	1	305000	2010	235803	kg/h	0.6	3	1.04536	246500	313227.8705	305 096	915 287
															34 244 686	**60 993 870**

(a)

Equipment label	Actual equipment	description (Ref)	Material	Unit cost ($)	No. used	total cost ($)	Year of quote	scaling value	Units	scaling Exp.	Instal. Factor	Size ratio	new value	Scaled purchase price ($)	Purchase price In Proj. Year	Installed cost in Project Year
CEST	Turbogenerator	NREL	SS	9500000	1	9500000	2010	230000	kg/h	0.6	1.8	0.83381	191777	4752734.348	4 629 343	8 332 817
CONDENSOR (B8)	Condenser	ASPEN	SS	35500	1	35500	2017		kg/h					0	12400	70300
conveyor	Cellu-lignin and by-pass conveyc	not shown (based on the bigger mass on conveyoı	CS	2698500	2	5397000	2009	94697	kg/h	0.6	1.7	0.82289	77925	4801277.108	6026308.915	10244725.16
													TOTAL		**44 912 738**	**79 641 712**

(b)

Equipment label	Actual equipment	description (Ref)	Material	Unit cost ($)	No. used	total cost ($)	Year of quote	scaling value	Units	scaling Exp.	Instal. Factor	Size ratio	new value	Scaled purchase price ($)	Purchase price In Proj. Year	Installed cost in Project Year
		GREENFUND ESTIMATE		2600000	1	2600000	2015	95217	kg/h	0.6	1	1.9	184674	3 868 905	3 768 460	5 208 142
													TOTAL		**3 768 460**	**5 208 142**

Note: NREL is data from Humbird et al. (2011)
GREENFUND in WWT refers to Gorgens et al. (2016)

(c)

Table D4-3: Equipment sizing and costing of the LA-GVL-F-E biorefinery’s 1st and 2nd reaction stages and purification stages (all costs in US$)

Equipment label	Actual equipment	description (Ref)	Material	Unit cost ($)	No. used	total cost ($)	Year of quote	scaling value	Units	scaling Exp.	Instal. Factor	Size ratio	new value	Scaled purchase price ($)	Purchase price In Proj. Year	Installed cost in Project Year
MX101	MIXING TANK	INCLUDED	SS													
CL102	HX	ASPEN													88100	199200
P301		ASPEN													7 600	62 400
SEP101	FLASH	ASPEN													22 000	135 400
CL306	HX	ASPEN													8 200	58 200
CL103	HX	ASPEN	CS												9 300	48 500
P301	PUMP	ASPEN	SS												9 000	68 400
VAP301	VAPORISER	ASPEN	SS												22 000	137 400
LEVA.VD301-cond	DISTIL. COLUMNS	ASPEN	SS												68 700	264 000
LEVA.VD301-cond acc	DISTIL. COLUMNS	ASPEN	SS												45 300	296 700
LEVA.VD301-overhead split	DISTIL. COLUMNS	ASPEN	SS												-	-
LEVA.VD301-reb	DISTIL. COLUMNS	ASPEN													44 400	243 900
LEVA.VD301-reflux pump	DISTIL. COLUMNS	ASPEN	SS												8600	63400
LEVA.VD301-tower	DISTIL. COLUMNS	ASPEN	SS												427200	1305900
LEVA.CL305	HX	ASPEN	SS												7600	44900
LEVA.CL303	HX		SS												0	0
LEVA.CL304	HX		SS												0	0
LEVA.CL301	HX	ASPEN	SS												27800	114600
LEVA.CL308	HX	ASPEN	SS												10200	60700
LEVA.CL201	HX	ASPEN	SS												13200	72500
LEVA.FT201	FLASH	ASPEN	SS												37500	160800
P102	PUMP	ASPEN	SS												26800	139000
LEVA.P303	PUMP	ASPEN	SS												9000	66200
LEVA.P302	PUMP	ASPEN													11 400	78 000
LEVA.CL201	HX	ASPEN	SS												13 100	72 400
LEVA.P201	PUMP	ASPEN	SS												14200	96200
LEVA.EVAP301	EVAP	ASPEN	SS												63300	398700
LEVA.D2302-cond	DISTIL. COLUMNS	ASPEN	SS												30 600	179 700
LEVA.D2302-cond acc	DISTIL. COLUMNS	ASPEN	SS												32 700	224 100
LEVA.D2302-reb	DISTIL. COLUMNS	ASPEN	SS												81 900	266 400
LEVA.D2302-reflux pump	DISTIL. COLUMNS	ASPEN	SS												10 400	69 000
LEVA.D2302-tower	DISTIL. COLUMNS	ASPEN	SS												341 100	916 500
LEVA.P302			SS												12 200	81 400
LEVA.P101		ASPEN	SS												155400	271400
LEVA.FT101	FILTER	ASPEN	SS												59700	345300
LEVA.CL302															-	-
CL101	HX	ASPEN	SS												12 800	72 800
B9(PUMP to rxt 2)		ASPEN	SS												20 800	121 200
CL-FURF		ASPEN	SS												9 800	59 500
B8(PUMP to rxt1)															19800	102200
LEVA.B7		ASPEN														
REACTORS R101(53400LBS)	SINNOT & TOWLER	(15 seconds)	SS(213000,389000)	528185	2	1056370	2010			0.85	2.5			60058	1 056 370	4 231 480
REACTOR R201(29800LBS)	SINNOT & TOWLER	30 MINUTES	(189400,354400)	328934	3	986802	2010			0.85	2.5			7713404	986 802	3 947 208
														TOTAL	**8 861 591**	**23 638 011**

Table D4-4: Equipment sizing and costing of the LA-GVL-F-E biorefinery's GVL production and purification unit (all costs in US$)

Equipment label	Actual equipment	description (Ref)	Material	Unit cost ($)	No. used	total cost ($)	Year of quote	scaling value	Units	scaling Exp.	Instal. Factor	Size ratio	new value	Scaled purchase price ($)	Purchase price In Proj. Year	Installed cost in Project Year
GVL.GVL-DIST-cond acc	DISTIL.. COLUMN	ASPEN													59100	363600
GVL.GVL-DIST-cond															24300	135000
GVL.GVL-DIST-reb	DISTIL.. COLUMN	ASPEN													227700	559500
GVL.GVL-DIST-reflux pump	PUMP	ASPEN													8600	57200
GVL.GVL-DIST-tower	DISTIL.. COLUMN	ASPEN													1011900	2091300
GVL.CL404	COOLER	ASPEN													10800	60900
GVL.GVL-C402	COOLER	ASPEN													10900	60100
GVL.GVL-RXT (10700LBS)	REACROR	(93900,239200)													9900	59600
GVL.GVL-DIS2-cond	DISTIL.. COLUMN	ASPEN													22800	133200
GVL.GVL-DIS2-cond acc	DISTIL.. COLUMN	ASPEN													37200	308400
GVL.GVL-DIS2-overhead split	DISTIL.. COLUMN	ASPEN													80700	265200
GVL.GVL-DIS2-reb	DISTIL.. COLUMN	ASPEN													34200	181200
GVL.GVL-DIS2-reflux pump	DISTIL.. COLUMN PUMP	ASPEN													8600	54400
GVL.GVL-DIS2-tower	DISTIL.. COLUMN TOWER	ASPEN													67200	474000
GVL.GVL-P401	PUMP														9600	76600
GVL.GVL-C401	COOLER														12800	71200
GVL.P403	PUMP														15600	96200
GVL.P402	PUMP														10400	76000
GVL.FL402-flash vessel		ASPEN													17700	120500
GVL LIQ-LIQ EXTRACTORS	SINNOT & TOWLER		3 hrs mixing												1333910	3334760
GVL HIGH PRESSURE REACTOR	SINNOT & TOWLER	ASSUME 2 HR REACTION TIME (6 TANKS)													2234472	8937894
GVL-C402															14200	72300
															5 262 582.00	17 589 054.00
															22 985 764	**64 865 075**

Table D4-5: LA-GVL-F-E equipment sizing and costing of the boiler, condensing extraction steam turbine (CEST) and wastewater treatment (WWT) plant (all costs in US$)

Equipment label	Actual equipment	description (Ref)	Material	Unit cost ($)	No. used	total cost ($)	Year of quote	scaling value	Units	scaling Exp.	Instal. Factor	Size ratio	new value	Scaled purchase price	Purchase price In Proj.	Installed cost in Project Year
HEATER4	HX	ASPEN													47 400.00	170 100.00
AIR BLOWER	compressor/air blower/fan	MANUALLY	SS	INCLUDED	1											
HEATER 1	HX	ASPEN	SS	INCLUDED	1										1177900	1774900
															1554200	2467700
HEATER3	HX	ASPEN													2481300	4120200
CHP.PUMP1	PUMP	ASPEN	SS												204400	331200
CL401	HX AT BAG HOUSE	ASPEN													12700	71100
CFG401	Centrifuge/FGD BAG HOUSE	NREL	SS	INCLUDED												
CHP.BOILER	Boiler (FLASH VESSEL)	NREL	SS	28550000	1	28550000	2010	238686	kg/h	0.6	1.8	1.014	242000	28787182.71	28 039 803	50 471 645.51
DEARATOR		NREL	SS	305000	1	305000	2010	235803	kg/h	0.6	3	0.1	23500	76455.89227	74 471	223 413
					(a)										**33 544 774**	**59 460 158**

Equipment label	Actual equipment	description (Ref)	Material	Unit cost ($)	No. used	total cost ($)	Year of quote	scaling value	Units	scaling Exp.	Instal. Factor	Size ratio	new value	Scaled purchase price	Purchase price In Proj.	Installed cost in Project Year
CEST	Turbogenerator	NREL	SS	9500000	1	9500000	2010	230000	kg/h	0.6	1.8	0.657	151000	3742174	3645019	6561034
CONDENSOR (B8)	Condenser	ASPEN	SS	35500	1	35500	2017		kg/h					0	8100	45000
conveyor	Cellu-lignin and by-pass conveyor	not shown (based on a bigger conveyor)	CS	2698500	2	5397000	2009	94697	kg/h	0.6	1.7	0.638	60448	4122682	5174572	8796773
					(b)									TOTAL	**42 372 465**	**74 862 965**

Equipment label	Actual equipment	description (Ref)	Material	Unit cost ($)	No. used	total cost ($)	Year of quote	scaling value	Units	scaling Exp.	Instal. Factor	Size ratio	new value	Scaled purchase price	Purchase price In Proj.	Installed cost in Project Year
WWT UNIT		GREENFUND ESTIMATE		2600000	1	2600000	2015	95217	KG/H	0.6	1	1.8	170797	3 691 754	3 595 908	4 969 669
					(C)									TOTAL	3 595 908	4 969 669

D-5: Mass and energy balances

Table D5-1: Utilities for the LA-F-E biorefinery

Process area	Aspen unit	Description	Utility	Duty (kW)	Usage (kWh of t/h)
1ST REACTOR STAGE	P101	PUMP	Electricity	103	103
	R 101	RSTOIC REACTOR	HP Steam	16645	33
	P102	PUMP	Electricity	30	30
	CL101	HEAT EXCHANGER	Cooling water	-3113	3113
	CL-FURF	HEAT EXCHANGER	Cooling water	-520	90
	FT101	PRESSURE FILTER	Electricity		
2ND REACTOR STAGE	R 201	RSTOIC REACTOR	Heat	-1763	1763
	P201	PUMP	Electricity	8	8
	CL201	HEAT EXCHANGER	Cooling water	-2735	262
	FT201	PRESSURE FILTER	Electricity	116	116
PURIFICATION AND PRODUCT CONCENTRATION	P302	PUMP	Electricity	1	1
	CL301	HEAT EXCHANGER	Cooling water	-11069	1909
	CL302	HEAT EXCHANGER	Cooling water	-1355	234
	VAP301	FLASH TANK	HP Steam	10987	14
	EVAP301	FLASH TANK	HP Steam	2037	3.6
	VD-REB	DISTILLATION REBOILER	HP Steam	27355	46
	VD-COND	DISTILLATION CONDENSOR	Cooling water	-50833	8766
	P301	PUMP	Electricity	1	1
	D2-REB	DISTILLATION REBOILER	HP Steam	116	0.2
	D2-COND	DISTILLATION CONDENSOR	Cooling water	-8291	1430
	CL305	HEAT EXCHANGER	Cooling water	-759	131
	CL306	HEAT EXCHANGER	Cooling water	-91	16
BOILER AND CEST UNIT	COMP1	FAN/BLOWER/COMPRESSOR	Electricity	805	805
	PUMP1	PUMP	Electricity	562	562
	HEATER4	HEAT EXCHANGER	HP Steam	12961	23
	CL401	HEAT EXCHANGER	Cooling water	-316	55
	CONDNSR	CONDENSOR	Cooling water	-28	5

Table D5-2: Utilities for the LA-GVL-F-E biorefinery

Process area	Aspen unit	Description	Utility	Duty (kW)	Usage (kWh or t/h)
1st REACTOR STAGE	P101	PUMP	Electricity	103	103
	R 101	RSTOIC REACTOR	HP Steam	17101	34
	P102	PUMP	Electricity	29	29
	CL101	HEAT EXCHANGER	Cooling water	-3111	385
	CL102	HEAT EXCHANGER	Cooling water	-22194	3827
	CL-FURF	HEAT EXCHANGER	Cooling water	-417	72
	FT101	PRESSURE FILTER	Electricity	-4410	-4410
2nd REACTOR STAGE	R 201	RSTOIC REACTOR	HEAT (Exolthermic)	-10	10
	P201	PUMP	Electricity	6	6
	CL201	HEAT EXCHANGER	Cooling water	-2117	203
	FT201	PRESSURE FILTER	Electricity	0	0
PURIFICATION AND PRODUCT CONCENTRATION	P302	PUMP	Electricity	1	1
	CL301	HEAT EXCHANGER	Cooling water	-8225	1418
	CL302	HEAT EXCHANGER	Cooling water	-1476	255
	CL304F	HEAT EXCHANGER	Cooling water	-772	133
	EVAP301	FLASH TANK	HP Steam	245	0.4
	VAP301	FLASH TANK	HP Steam	8165	14
	CL308	HEAT EXCHANGER	Cooling water	-408	70
	P301	PUMP	Electricity	0.14	0.14
	CL304	HEAT EXCHANGER	Cooling water	-747	129
	CL305F	HEAT EXCHANGER	Cooling water	-772	133
	VD-REB	DISTILLATION REBOILER	HP Steam	11432	20.3
	VD-COND	DISTILLATION CONDENSOR	Cooling water	-42659	7357
	D2-REB	DISTILLATION REBOILER	HP Steam	1329	2.9
	D2-COND	DISTILLATION CONDENSOR	Cooling water	-996	172
	CL306	HEAT EXCHANGER	Cooling water	-1027	177
BOILER AND CEST UNIT	COMP1	FAN/BLOWER	Electricity	788	788
	PUMP1	PUMP	Electricity	562	562
	HEATER4	HEAT EXCHANGER	HP Steam	12690	23
	CL401	HEAT EXCHANGER	Cooling water	-28488	4912
	CONDNSR	CONDENSOR	Cooling water	-8278	1428
GAMMA VALEROLACTONE PRODUCTION AND PURIFICATION	GVL-P401	PUMP	Electricity	1.1	1.1
	GVL-RXT	HYDROGENATION REACTOR	HP Steam	669	1.1
	GVL-C401	HEAT EXCHANGER	Cooling water	-699	120
	FL401	FLASH TANK	LP Steam	318	0.6
	GVL-P402	PUMP	Electricity	2	2
	GVL-C402	HEAT EXCHANGER	Cooling water	-465	80
	SX401	SOLVENT EXTRACTION	-	-	-
	GVL-DIS1REB	DISTILLATIN REBOILER	HP Steam	3924	8.7
	GVL-DISCOND	DISTILLATION CONDENSOR	Cooling water	-22	3.9
	P403	PUMP	Electricity	9	9
	GVL-DIS2RED	DISTILLATION REBOILER	HP Steam	162	0.3
	GVL-DIS2COND	DISTILLATION CONDENSOR	Cooling water	-137	24
	GVL-C404	HEAT EXCHANGER	Cooling water	-268	46

Table D5-3 : Mass balance for the LA-F-E biorefinery

	H2OSPLIT	CL-FURF	CL102	V102	VD301	EVAP301	CL201	CL302	MX	R 101	P102	VAP301	FT101	P201	P301	P302	MIXER2	H2OSPLIT	MX103	MX103	CL306	HEATER3	HEATER1	COMBUST	HEATER2	CENTRFG	HEATER4	BOILER
	CL302	FT101	FT101	R 201	EVAP301	VAP301	FT201	P302	FT101	P101	R 101	P201	P102	CL201	VD301	CL301	EVAP301	CL306	P-FILT	CL102	D2302	HEATER2	COMP1	HEATER1	COMBUST	HEATER3	PUMP1	HEATER4
Substream: MIXED																												
Mass Flow kg/hr																												
LIGNIN	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
AINSLIG	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
ASL	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
GLUCAN	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
GALACTAN	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
MANNAN	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
XYLAN	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
ARABINAN	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
WATER	11360	11	102225	75731	8277	11360	22719	11360	5381	107724	107616	22719	107616	22719	1218	11360	3083	1206	43008	102225	1206	66583	10077	10077	66583	66583	246500	246500
EXTRACT	0	0	2464	0	0	0	0	0	0	2464	2464	0	2464	0	0	0	0	0	0	2464	0	39	0	0	39	39	0	0
ASH	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
OXYGEN	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	159434	221703	221703	159434	159434	0	0
SULPHUR	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
NITROGEN	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	775961	775961	775961	775961	775961	0	0
CO2	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	81951	0	0	81951	81951	0	0
NO2	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
SO2	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	352	0	0	352	352	0	0
SO3	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
METHANE	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	10	0	0	10	10	0	0
H2SO4	0	0	2785	2698	0	0	0	0	147	2932	2932	0	2932	0	0	0	0	0	2158	2785	0	0	0	0	0	0	0	0
XYLOSE	0	1	6171	325	32	32	32	0	325	0	6496	32	6496	32	32	0	0	0	234	6171	0	1	0	0	1	1	0	0
GLUCOSE	0	0	0	16	2	2	2	0	0	0	0	2	0	2	2	0	0	0	12	0	0	0	0	0	0	0	0	0
MANOLIG	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
GALAOLIG	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
ACETATE	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
A.ACID	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
FURFURAL	0	2150	0	0	0	0	0	0	0	0	2150	0	2150	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
LEVA	0	0	0	5511	5495	5506	5506	0	0	0	0	5506	0	5506	5495	0	11	8	5	0	8	0	0	0	0	0	0	0
5HMF	0	0	0	12	1	1	1	0	0	0	0	1	0	1	1	0	0	0	8	0	0	0	0	0	0	0	0	0
FORMIC	2161	0	0	2185	17	22	2182	2161	0	0	0	2182	0	2182	0	2161	5	0	68	0	0	0	0	0	0	0	0	0
XYLOOLIG	0	0	1064	56	50	50	50	0	56	0	1120	50	1120	50	50	0	0	0	4	1064	0	0	0	0	0	0	0	0
ALKYLP	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
CO	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
HYDROGEN	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
CARBO-01	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Total Flow kmol/hr	677	23	5765	4329	508	679	1357	677	303	6023	6090	1357	6090	1357	115	677	171	67	2413	5765	67	38246	35187	35187	38246	38246	13683	13683
Total Flow kg/hr	13520	2162	114708	86534	13875	16973	30493	13520	5908	113120	122779	30493	122779	30493	6799	13520	3098	1214	45497	114708	1214	1084330	1007740	1007740	1084330	1084330	246500	246500
Temperature C	30	165	195	195	145	134	195	130	195	25	215	134	215	134	55	130	145	35	100	25	100	278	28	175	871	150	91	137
Pressure bar	1	2	14	14	4	3	14	1	14	25	25	3	14	14	0	3	4	1	1	1	1	1	1	1	1	1	64	64
Vapor Frac	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	1	1	1	1	1	0	0
Liquid Frac	1	0	1	1	1	1	1	1	1	1	1	1	1	1	1	1	0	1	1	1	1	0	0	0	0	0	1	1
Solid Frac	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0

Table D5-4: Mass balance for the LA-GVL-F-E biorefinery

	CL401	HEATER3	COMP1	HEATER1	COMBUST	HEATER2	CENTRFG	CEST1	HEATER4	BOILER	CONDSR	B13	CL404	GVL-C401	GVL-RXT	FL402	P402	B3	GVL-DIS2	SX401	GVL-C402	B10	GVL-DIST	SX401	H2OSPLIT	CL-FURF	CL102	V102	CL201	CL302
	CENTRFG	HEATER2	B1	COMP1	HEATER1	COMBUST	HEATER3	B5	PUMP1	HEATER4	CEST3	CEST2	GVL-DIS2	GVL-RXT	GVL-P401	GVL-C401	FL402	SX401	GVL-DIST	P403	P402	GVL-C402	SX401	B10	CL302	FT101	FT101	R 201	FT201	P302
Substream: MIXED																														
Mass Flow kg/hr																														
LIGNIN	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
AINSLIG	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
ASL	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
GLUCAN	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
GALACTAN	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
MANNAN	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
XYLAN	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
ARABINAN	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
WATER	63818	63818	9797	9797	9797	63818	63818	176714	238900	238900	57	56902	0	6543	6078	6543	5218	4456	0	0	5218	5218	762	5218	12374	12	111352	82494	24748	12374
EXTRACT	34	34	0	0	0	34	34	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	2684	0	0	0
ASH	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
OXYGEN	155376	155376	215525	215525	215525	155376	155376	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
SULPHUR	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
NITROGEN	754338	754338	754338	754338	754338	754338	754338	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
CO2	79052	79052	0	0	0	79052	79052	0	0	0	0	0	0	11	0	11	1	0	0	0	1	1	1	1	0	0	0	0	0	0
NO2	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
SO2	396	396	0	0	0	396	396	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
SO3	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
METHANE	10	10	0	0	0	10	10	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
H2SO4	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	2	1	3	0	0	1	0	0	0	3034	3028	0	0
XYLOSE	1	1	0	0	0	1	1	0	0	0	0	0	18	18	18	18	18	0	18	0	18	18	18	18	0	1	6721	354	35	0
GLUCOSE	0	0	0	0	0	0	0	0	0	0	0	0	1	1	1	1	1	0	1	0	1	1	1	1	0	0	0	18	2	0
MANOLIG	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
GALAOLIG	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
ACETATE	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
A.ACID	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
FURFURAL	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	2342	0	0	0	0
LEVA	0	0	0	0	0	0	0	0	0	0	0	0	0	0	2998	0	0	0	0	0	0	0	0	0	0	0	0	6004	5997	0
5HMF	0	0	0	0	0	0	0	0	0	0	0	0	1	1	1	1	1	0	1	0	1	1	1	1	0	0	0	13	1	0
FORMIC	0	0	0	0	0	0	0	0	0	0	0	0	0	0	12	0	0	0	0	0	0	0	0	0	2353	0	0	2380	2377	2353
XYLOOLIG	0	0	0	0	0	0	0	0	0	0	0	0	27	27	27	27	27	0	27	0	27	27	27	27	0	0	1159	61	55	0
ALKYLP	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
CO	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
HYDROGEN	0	0	0	0	0	0	0	0	0	0	0	0	0	28	0	28	0	0	0	0	0	0	0	0	0	0	0	0	0	0
CARBO-01	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
GAMMA-01	0	0	0	0	0	0	0	0	0	0	0	0	2250	2585	0	2585	2564	0	2448	0	2564	2564	2564	2564	0	0	0	0	0	0
N-BUTYL	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	23	1923	31997	0	0	31973	0	0	0	0	0	0	0
Total Flow kmol/hr	37129	37129	34207	34207	34207	37129	37129	9809	13261	13261	3	3159	23	404	364	404	316	248	41	275	316	316	343	316	738	25	6279	4716	1478	738
Total Flow kg/hr	1053020	1053020	979659	979659	979659	1053020	1053020	176714	238900	238900	57	56902	2298	9215	9135	9215	7829	4482	4418	32000	7829	7829	35348	7829	14728	2355	124950	94351	33216	14728
Temperature C	150	278	25	28	175	871	150	483	91	137	109	243	219	150	140	97	97	25	167	25	97	35	28	35	30	165	195	195	195	130
Pressure bar	1	1	1	1	1	1	1	64	64	64	1	10	1	5	5	1	1	3	1	5	5	5	3	5	1	2	14	14	14	1
Vapor Frac	1	1	1	1	1	1	1	1	0	0	1	1	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0
Liquid Frac	0	0	0	0	0	0	0	0	1	1	0	0	1	1	1	1	1	1	1	1	1	1	1	1	1	0	1	1	1	1
Solid Frac	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0

D-6: Pinch analysis

3 hot and 2 cold streams let to a hot and cold utility saving of 15% and 23% respectively

Table D6-1: Input data for the LA-F-E scenario and heat capacity flowrate determination

Stream Name	Supply Temp.	Target Temp.	dT Min Contribution	Heat Capacity Flowrate		Heat Flow	Stream Type	Supply Shift	Target Shift
	°C	°C	°C	kW/K		kW		°C	°C
CL101	215	195	10	155.7		3113	HOT	205.0	185.0
CL201	195	134	10	44.8		2735	HOT	185.0	124.0
CL301	223	130	10	119.0		11069	HOT	213.0	120.0
D2-302	55	100	10	184.2		8291	COLD	65.0	110.0
VAP301	180	223	10	255.5		10987	COLD	190.0	233.0

Table C6-2: Problem cascade table for LA-F-E scenario

Problem Table & Cascade

Shift Temperature	Interval	$T_{(i+1)}-T_i$	mCp_{net}	dH			Infeasible Cascade		Feasible Cascade	
°C		°C	kW/K	kW						
233							▼	0	▼	6202.2
	1	20	-255.5116	-5110.2326	demand		-5110.23		-5110.233	
213							▼	-5110.2	▼	1091.9
	2	8	-136.4901	-1091.921	demand		-1091.92		-1091.921	
205						PINCH	▼	-6202.2	▼	0
	3	15	19.1599	287.3982	surplus		287.3982		287.3982	
190							▼	-5914.8	▼	287.4
	4	5	274.6715	1373.3575	surplus		1373.358		1373.358	
185							▼	-4541.4	▼	1660.8
	5	61	163.8576	9995.3118	surplus		9995.312		9995.312	
124							▼	5453.9	▼	11656
	6	4	119.0215	476.086	surplus		476.086		476.086	
120							▼	5930	▼	12132
	7	10	0.0	0.0	demand		0		0	
110							▼	5930	▼	12132
	8	45	-184.2444	-8291.0	demand		-8291		-8291	
65							▼	-2361	▼	3841.2

Hot Pinch	210 °C
Cold Pinch	200 °C

Min Hot Utility	6202.15 kW
Min Cold Utility	3841.15 kW

SINGLE PINCH PROBLEM

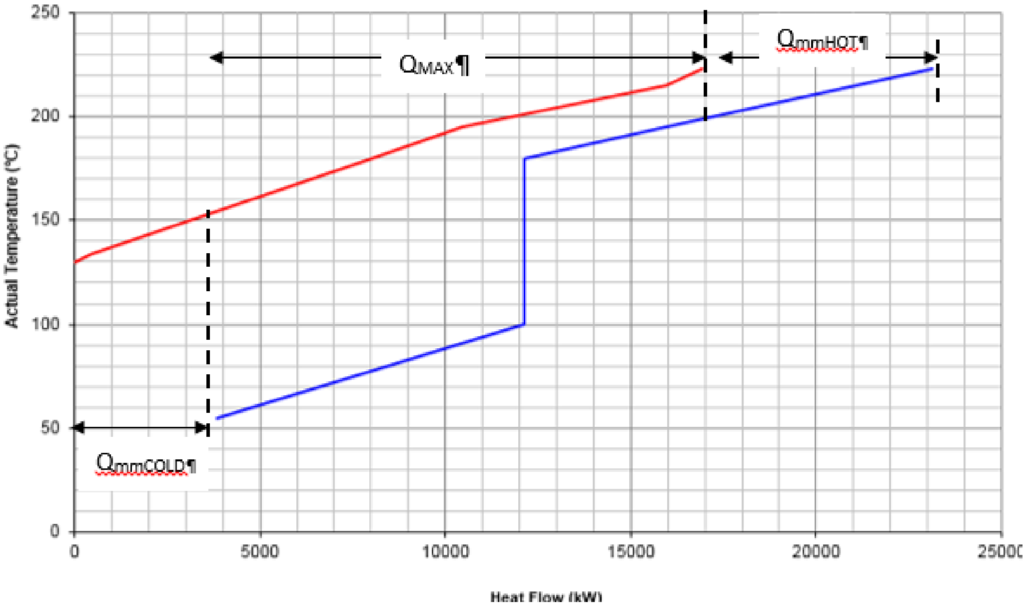


Figure C6-1: Combined composite graph for LA-F-E scenario

Integrating 3 hot streams and 2 cold streams led to a hot and cold utility saving of 15% and 23% respectively.

Table C6-3: Input data and heat capacity flowrate determination for LA-GVL-F_E

Stream Name	Supply Temp.	Target Temp.	dT Min Contribution	Heat Capacity Flowrate		Heat Flow	Stream Type	Supply Shift	Target Shift
	°C	°C	°C	kW/K		kW		°C	°C
CL101	215	195	10	155.7		3113.0	HOT	205.0	185.0
CL201	195	134	10	34.7		2117.0	HOT	185.0	124.0
CL301	223	130	10	88.4		8225.0	HOT	213.0	120.0
VAP301	134	180	10	177.5		8165.0	COLD	144.0	190.0
D2-302	75	241	10	8.0		1326.0	COLD	85.0	251.0

Table C6-4: Problem cascade table for LA-GVL-F-E

Problem Table & Cascade

Shift Temperature	Interval	$T_{(i+1)}-T_i$	mCp_{net}	dH			Infeasible Cascade	Feasible Cascade
°C		°C	kW/K	kW				
251							▼ 0	▼ 303.54
	1	38	-7.988	-303.5422	demand		-303.542	-303.5422
213						PINCH	▼ -303.54	▼ 0
	2	8	80.4529	643.6233	surplus		643.6233	643.6233
205							▼ 340.08	▼ 643.62
	3	15	236.1029	3541.5436	surplus		3541.544	3541.544
190							▼ 3881.6	▼ 4185.2
	4	5	58.6029	293.0145	surplus		293.0145	293.0145
185							▼ 4174.6	▼ 4478.2
	5	41	-62.3422	-2556.0291	demand		-2556.03	-2556.029
144							▼ 1618.6	▼ 1922.2
	6	20	115.1578	2303.1565	surplus		2303.157	2303.157
124							▼ 3921.8	▼ 4225.3
	7	4	80.4529	321.8116	surplus		321.8116	321.8116
120							▼ 4243.6	▼ 4547.1
	8	35	-7.988	-279.5783	demand		-279.578	-279.5783
85							▼ 3964	▼ 4267.5

Hot Pinch	218	°C
Cold Pinch	208	°C

Min Hot Utility	303.54	kW
Min Cold Utility	4267.54	kW

SINGLE PINCH PROBLEM

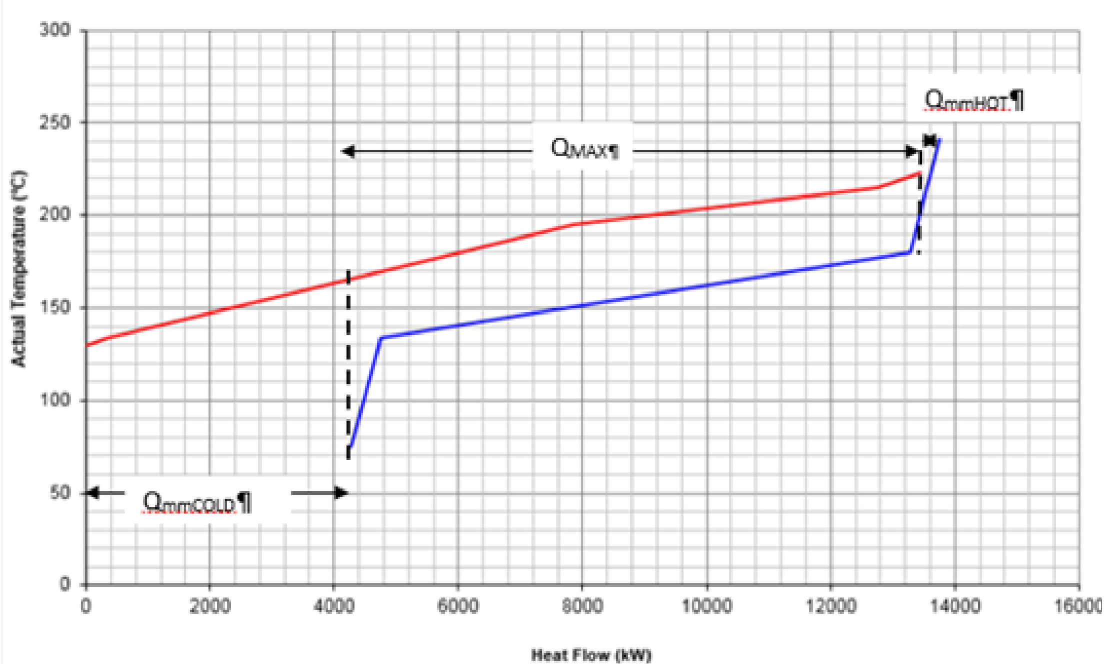


Figure C6-2: Combined composite graph for LA-GVL-F-E scenario

The integration of 3 hot streams and 2 cold streams led to an overall hot and cold utility saving of 23% and 4% respectively.

D-7: Discounted cash flow rate of return spreadsheet

Table D7-1: Discounted cash flow rate of return spreadsheet for LA-F-E (a), (b) and (c)

			RAMP	0.5	0.75	1.00			
DCFROR Worksheet			2016	2017	2018	2019	2020	2021	2022
Year	-2	-1	0	1	2	3	4	5	6
Fixed Capital Investment	$ 20 843 646.11	$ 125 061 876.69	$ 62 530 938.34						
Land	$ -	$ -	$ -						
Working Capital			$ 10 421 823.06						
Loan Payment				$ -	$ -	$ -	$ -	$ -	$ -
Loan Interest Payment	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -
Loan Principal	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -
Levulinic acid Price ($/t)			$ 905.00	$ 905.00	$ 905.00	$ 905.00	$ 905.00	$ 905.00	$ 905.00
Bio-product Sales			$ -	$ 42 428 934.00	$ 42 428 934.00	$ 42 428 934.00	$ 42 428 934.00	$ 42 428 934.00	$ 42 428 934.00
Electricty price ($/ kWh)			$ 0.080	$ 0.08	$ 0.08	$ 0.08	$ 0.08	$ 0.08	$ 0.08
Electricity Sales			$ -	$ 6 340 550.40	$ 6 340 550.40	$ 6 340 550.40	$ 6 340 550.40	$ 6 340 550.40	$ 6 340 550.40
Furfural & Formic mixture Price ($/t)			$ 1 207.00	$ 1 207.00	$ 1 207.00	$ 1 207.00	$ 1 207.00	$ 1 207.00	$ 1 207.00
Furfural & Formic mixture sales			$ -	$ 26 678 658.96	$ 26 678 658.96	$ 26 678 658.96	$ 26 678 658.96	$ 26 678 658.96	$ 26 678 658.96
			$ -	$ -	$ -	$ -	$ -	$ -	$ -
			$ -	$ -	$ -	$ -	$ -	$ -	$ -
Total Annual Revenue			$ -	$ 37 724 071.68	$ 56 586 107.52	$ 75 448 143.36	$ 75 448 143.36	$ 75 448 143.36	$ 75 448 143.36
Annual Manufacturing Cost									
Feedstock Price ($/ ton)									
Feedstock cost									
Other Variable Costs									
Fixed Operating Costs									
Total Product Cost			$ -	$ 12 438 046.50	$ 18 657 069.76	$ 24 876 093.01	$ 24 876 093.01	$ 24 876 093.01	$ 24 876 093.01
Annual Depreciation									
Plant Writedown			0.00%	20.00%	20.00%	20.00%	20.00%	20.00%	
Depreciation Charge			$ -	$ 41 687 292.23	$ 41 687 292.23	$ 41 687 292.23	$ 41 687 292.23	$ 41 687 292.23	
Remaining Value			$ 208 436 461.15	$ 166 749 168.92	$ 125 061 876.69	$ 83 374 584.46	$ 41 687 292.23	$ -	
Net Revenue (R-COM-dk)	($20 843 646)	($125 061 877)	($72 952 761)	$ -16 401 267.05	$ -3 758 254.47	$ 8 884 758.12	$ 8 884 758.12	$ 8 884 758.12	$ 50 572 050.35
Losses Forward				$0	($16 401 267)	($20 159 522)	($11 274 763)	($2 390 005)	$0
Taxable Income				$ -16 401 267.05	$ -20 159 521.52	$ -11 274 763.40	$ -2 390 005.28	$ 6 494 752.84	$ 50 572 050.35
Income Tax				$0	$0	$0	$0	$1 818 531	$14 160 174
Annual Cash Income			($218 858 284)	$25 286 025	$37 929 038	$50 572 050	$50 572 050	$48 753 520	$36 411 876
Discount Factor		1.0970	1.0000	0.9116	0.8310	0.7575	0.6905	0.6295	0.5738
Annual Present Value (Discounted Cash Flow)			($218 858 284)	$ 23 050 159.69	$ 31 517 994.10	$ 38 308 105.87	$ 34 920 789.30	$ 30 688 300.30	$ 20 893 119.71
Cumulative Discounted Cash Flow			($218 858 284)	($195 808 125)	($164 290 130)	($125 982 025)	($91 061 235)	($60 372 935)	($39 479 815)
Total Capital Investment + Interest		$ 137 192 878.73	$ 72 952 761.40						
Net Present Worth			$138 819 003						

(a)

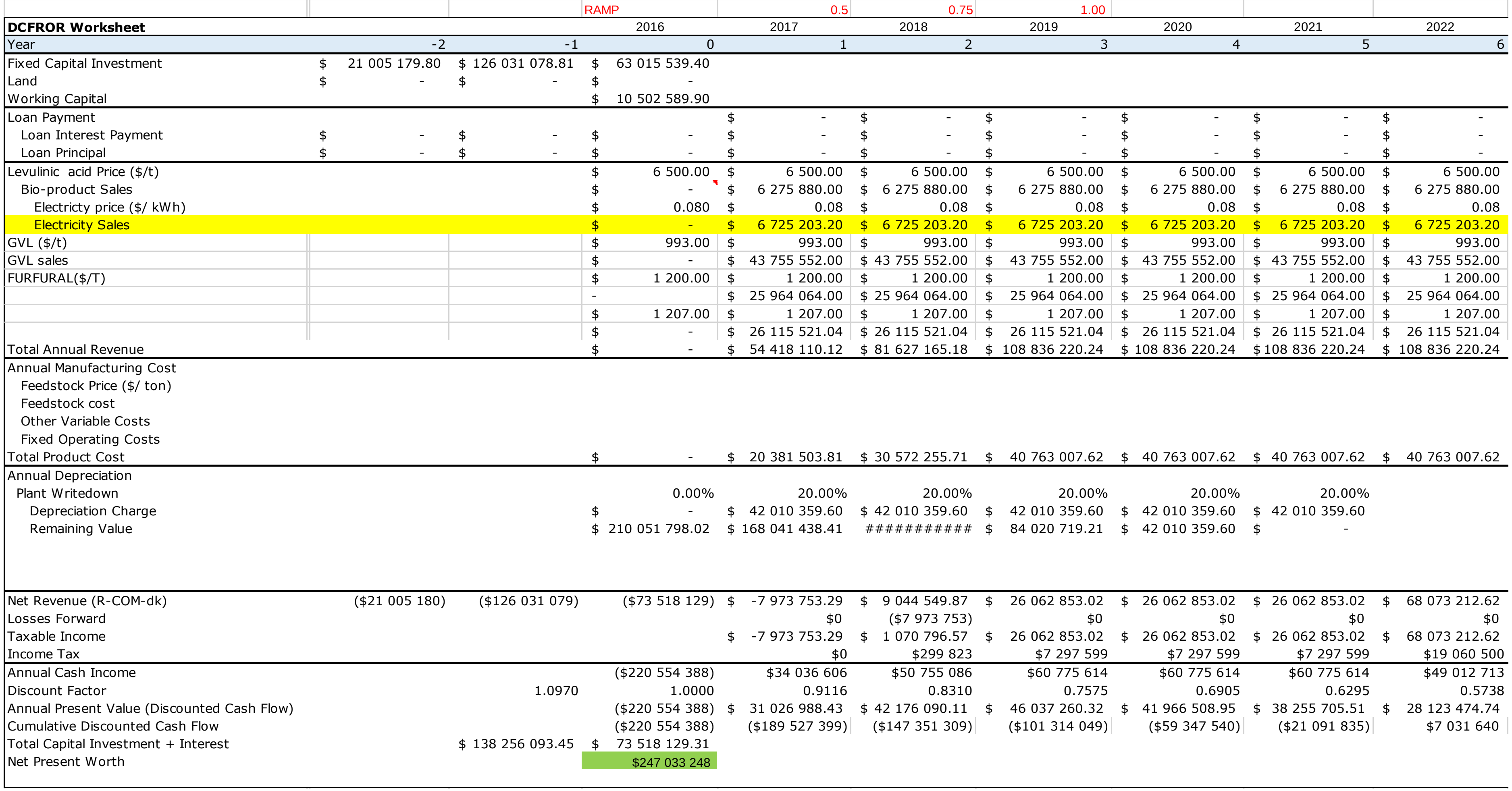
DCFROR Worksheet	2023	2024	2025	2026	2027	2028	2029	2030	2031	2032
Year	7	8	9	10	11	12	13	14	15	16
Fixed Capital Investment										
Land										
Working Capital										
Loan Payment	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -
Loan Interest Payment	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -
Loan Principal	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -
Levulinic acid Price ($/t)	$ 905.00	$ 905.00	$ 905.00	$ 905.00	$ 905.00	$ 905.00	$ 905.00	$ 905.00	$ 905.00	$ 905.00
Bio-product Sales	$ 42 428 934.00	$ 42 428 934.00	$ 42 428 934.00	$ 42 428 934.00	$ 42 428 934.00	$ 42 428 934.00	$ 42 428 934.00	$ 42 428 934.00	$ 42 428 934.00	$ 42 428 934.00
Electricty price ($/ kWh)	$ 0.08	$ 0.08	$ 0.08	$ 0.08	$ 0.08	$ 0.08	$ 0.08	$ 0.08	$ 0.08	$ 0.08
Electricity Sales	$ 6 340 550.40	$ 6 340 550.40	$ 6 340 550.40	$ 6 340 550.40	$ 6 340 550.40	$ 6 340 550.40	$ 6 340 550.40	$ 6 340 550.40	$ 6 340 550.40	$ 6 340 550.40
Furfural & Formic mixture Price ($/t)	$ 1 207.00	$ 1 207.00	$ 1 207.00	$ 1 207.00	$ 1 207.00	$ 1 207.00	$ 1 207.00	$ 1 207.00	$ 1 207.00	$ 1 207.00
Furfural & Formic mixture sales	$ 26 678 658.96	$ 26 678 658.96	$ 26 678 658.96	$ 26 678 658.96	$ 26 678 658.96	$ 26 678 658.96	$ 26 678 658.96	$ 26 678 658.96	$ 26 678 658.96	$ 26 678 658.96
	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -
	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -
Total Annual Revenue	$ 75 448 143.36	$ 75 448 143.36	$ 75 448 143.36	$ 75 448 143.36	$ 75 448 143.36	$ 75 448 143.36	$ 75 448 143.36	$ 75 448 143.36	$ 75 448 143.36	$ 75 448 143.36
Annual Manufacturing Cost										
Feedstock Price ($/ ton)										
Feedstock cost										
Other Variable Costs										
Fixed Operating Costs										
Total Product Cost	$ 24 876 093.01	$ 24 876 093.01	$ 24 876 093.01	$ 24 876 093.01	$ 24 876 093.01	$ 24 876 093.01	$ 24 876 093.01	$ 24 876 093.01	$ 24 876 093.01	$ 24 876 093.01
Annual Depreciation										
Plant Writedown										
Depreciation Charge										
Remaining Value										
Net Revenue (R-COM-dk)	$ 50 572 050.35	$ 50 572 050.35	$ 50 572 050.35	$ 50 572 050.35	$ 50 572 050.35	$ 50 572 050.35	$ 50 572 050.35	$ 50 572 050.35	$ 50 572 050.35	$ 50 572 050.35
Losses Forward	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0
Taxable Income	$ 50 572 050.35	$ 50 572 050.35	$ 50 572 050.35	$ 50 572 050.35	$ 50 572 050.35	$ 50 572 050.35	$ 50 572 050.35	$ 50 572 050.35	$ 50 572 050.35	$ 50 572 050.35
Income Tax	$14 160 174	$14 160 174	$14 160 174	$14 160 174	$14 160 174	$14 160 174	$14 160 174	$14 160 174	$14 160 174	$14 160 174
Annual Cash Income	$36 411 876	$36 411 876	$36 411 876	$36 411 876	$36 411 876	$36 411 876	$36 411 876	$36 411 876	$36 411 876	$36 411 876
Discount Factor	0.5231	0.4768	0.4347	0.3962	0.3612	0.3292	0.3001	0.2736	0.2494	0.2273
Annual Present Value (Discounted Cash Flow)	$ 19 045 687.98	$ 17 361 611.65	$ 15 826 446.35	$ 14 427 024.93	$ 13 151 344.51	$ 11 988 463.55	$ 10 928 407.98	$ 9 962 085.67	$ 9 081 208.45	$ 8 278 221.01
Cumulative Discounted Cash Flow	($20 434 127)	($3 072 516)	$12 753 931	$27 180 956	$40 332 300	$52 320 764	$63 249 172	$73 211 257	$82 292 466	$90 570 687
Total Capital Investment + Interest										
Net Present Worth										

(b)

CFROR Worksheet	2034	2035	2036	2037	2038	2039	2040	2041
ear	18	19	20	21	22	23	24	25
ixed Capital Investment								
and								
Vorking Capital								
oan Payment	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -
Loan Interest Payment	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -
Loan Principal	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -
evulinic acid Price ($/t)	$ 905.00	$ 905.00	$ 905.00	$ 905.00	$ 905.00	$ 905.00	$ 905.00	$ 905.00
Bio-product Sales	$ 42 428 934.00	$ 42 428 934.00	$ 42 428 934.00	$ 42 428 934.00	$ 42 428 934.00	$ 42 428 934.00	$ 42 428 934.00	$ 42 428 934.00
Electricty price ($/ kWh)	$ 0.08	$ 0.08	$ 0.08	$ 0.08	$ 0.08	$ 0.08	$ 0.08	$ 0.08
Electricity Sales	$ 6 340 550.40	$ 6 340 550.40	$ 6 340 550.40	$ 6 340 550.40	$ 6 340 550.40	$ 6 340 550.40	$ 6 340 550.40	$ 6 340 550.40
urfural & Formic mixture Price ($/t)	$ 1 207.00	$ 1 207.00	$ 1 207.00	$ 1 207.00	$ 1 207.00	$ 1 207.00	$ 1 207.00	$ 1 207.00
urfural & Formic mixture sales	$ 26 678 658.96	$ 26 678 658.96	$ 26 678 658.96	$ 26 678 658.96	$ 26 678 658.96	$ 26 678 658.96	$ 26 678 658.96	$ 26 678 658.96
	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -
	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -
otal Annual Revenue	$ 75 448 143.36	$ 75 448 143.36	$ 75 448 143.36	$ 75 448 143.36	$ 75 448 143.36	$ 75 448 143.36	$ 75 448 143.36	$ 75 448 143.36
nnual Manufacturing Cost								
Feedstock Price ($/ ton)								
Feedstock cost								
Other Variable Costs								
Fixed Operating Costs								
otal Product Cost	$ 24 876 093.01	$ 24 876 093.01	$ 24 876 093.01	$ 24 876 093.01	$ 24 876 093.01	$ 24 876 093.01	$ 24 876 093.01	$ 24 876 093.01
nnual Depreciation								
Plant Writedown								
Depreciation Charge								
Remaining Value								
et Revenue (R-COM-dk)	$ 50 572 050.35	$ 50 572 050.35	$ 50 572 050.35	$ 50 572 050.35	$ 50 572 050.35	$ 50 572 050.35	$ 50 572 050.35	$ 50 572 050.35
osses Forward	$0	$0	$0	$0	$0	$0	$0	$0
axable Income	$ 50 572 050.35	$ 50 572 050.35	$ 50 572 050.35	$ 50 572 050.35	$ 50 572 050.35	$ 50 572 050.35	$ 50 572 050.35	$ 50 572 050.35
ncome Tax	$14 160 174	$14 160 174	$14 160 174	$14 160 174	$14 160 174	$14 160 174	$14 160 174	$14 160 174
nnual Cash Income	$36 411 876	$36 411 876	$36 411 876	$36 411 876	$36 411 876	$36 411 876	$36 411 876	$36 411 876
iscount Factor	0.1889	0.1722	0.1570	0.1431	0.1305	0.1189	0.1084	0.0988
nnual Present Value (Discounted Cash Flow)	$ 6 878 975.49	$ 6 270 716.03	$ 5 716 240.68	$ 5 210 793.70	$ 4 750 039.83	$ 4 330 027.19	$ 3 947 153.32	$ 3 598 134.30
umulative Discounted Cash Flow	$104 995 898	$111 266 614	$116 982 855	$122 193 649	$126 943 689	$131 273 716	$135 220 869	$138 819 003
otal Capital Investment + Interest								
et Present Worth								

(c)

Table D7-2: Discounted cash flow rate of return spreadsheet for LA-GVL-F-E (a), (b) and (c)



			RAMP	0.5	0.75	1.00			
DCFROR Worksheet			2016	2017	2018	2019	2020	2021	2022
Year	-2	-1	0	1	2	3	4	5	6
Fixed Capital Investment	$ 21 005 179.80	$ 126 031 078.81	$ 63 015 539.40						
Land	$ -	$ -	$ -						
Working Capital			$ 10 502 589.90						
Loan Payment				$ -	$ -	$ -	$ -	$ -	$ -
Loan Interest Payment	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -
Loan Principal	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -
Levulinic acid Price ($/t)			$ 6 500.00	$ 6 500.00	$ 6 500.00	$ 6 500.00	$ 6 500.00	$ 6 500.00	$ 6 500.00
Bio-product Sales			$ -	$ 6 275 880.00	$ 6 275 880.00	$ 6 275 880.00	$ 6 275 880.00	$ 6 275 880.00	$ 6 275 880.00
Electricty price ($/ kWh)			$ 0.080	$ 0.08	$ 0.08	$ 0.08	$ 0.08	$ 0.08	$ 0.08
Electricity Sales			$ -	$ 6 725 203.20	$ 6 725 203.20	$ 6 725 203.20	$ 6 725 203.20	$ 6 725 203.20	$ 6 725 203.20
GVL ($/t)			$ 993.00	$ 993.00	$ 993.00	$ 993.00	$ 993.00	$ 993.00	$ 993.00
GVL sales			$ -	$ 43 755 552.00	$ 43 755 552.00	$ 43 755 552.00	$ 43 755 552.00	$ 43 755 552.00	$ 43 755 552.00
FURFURAL($/T)			$ 1 200.00	$ 1 200.00	$ 1 200.00	$ 1 200.00	$ 1 200.00	$ 1 200.00	$ 1 200.00
			-	$ 25 964 064.00	$ 25 964 064.00	$ 25 964 064.00	$ 25 964 064.00	$ 25 964 064.00	$ 25 964 064.00
			$ 1 207.00	$ 1 207.00	$ 1 207.00	$ 1 207.00	$ 1 207.00	$ 1 207.00	$ 1 207.00
			$ -	$ 26 115 521.04	$ 26 115 521.04	$ 26 115 521.04	$ 26 115 521.04	$ 26 115 521.04	$ 26 115 521.04
Total Annual Revenue			$ -	$ 54 418 110.12	$ 81 627 165.18	$ 108 836 220.24	$ 108 836 220.24	$ 108 836 220.24	$ 108 836 220.24
Annual Manufacturing Cost									
Feedstock Price ($/ ton)									
Feedstock cost									
Other Variable Costs									
Fixed Operating Costs									
Total Product Cost			$ -	$ 20 381 503.81	$ 30 572 255.71	$ 40 763 007.62	$ 40 763 007.62	$ 40 763 007.62	$ 40 763 007.62
Annual Depreciation									
Plant Writedown			0.00%	20.00%	20.00%	20.00%	20.00%	20.00%	
Depreciation Charge			$ -	$ 42 010 359.60	$ 42 010 359.60	$ 42 010 359.60	$ 42 010 359.60	$ 42 010 359.60	
Remaining Value			$ 210 051 798.02	$ 168 041 438.41	###########	$ 84 020 719.21	$ 42 010 359.60	$ -	
Net Revenue (R-COM-dk)	($21 005 180)	($126 031 079)	($73 518 129)	$ -7 973 753.29	$ 9 044 549.87	$ 26 062 853.02	$ 26 062 853.02	$ 26 062 853.02	$ 68 073 212.62
Losses Forward				$0	($7 973 753)	$0	$0	$0	$0
Taxable Income				$ -7 973 753.29	$ 1 070 796.57	$ 26 062 853.02	$ 26 062 853.02	$ 26 062 853.02	$ 68 073 212.62
Income Tax				$0	$299 823	$7 297 599	$7 297 599	$7 297 599	$19 060 500
Annual Cash Income			($220 554 388)	$34 036 606	$50 755 086	$60 775 614	$60 775 614	$60 775 614	$49 012 713
Discount Factor		1.0970	1.0000	0.9116	0.8310	0.7575	0.6905	0.6295	0.5738
Annual Present Value (Discounted Cash Flow)			($220 554 388)	$ 31 026 988.43	$ 42 176 090.11	$ 46 037 260.32	$ 41 966 508.95	$ 38 255 705.51	$ 28 123 474.74
Cumulative Discounted Cash Flow			($220 554 388)	($189 527 399)	($147 351 309)	($101 314 049)	($59 347 540)	($21 091 835)	$7 031 640
Total Capital Investment + Interest		$ 138 256 093.45	$ 73 518 129.31						
Net Present Worth			$247 033 248						

(a)

(c)

DCFROR Worksheet	2023	2024	2025	2026	2027	2028	2029	2030	2031	2032
Year	7	8	9	10	11	12	13	14	15	16
Fixed Capital Investment										
Land										
Working Capital										
Loan Payment	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -
Loan Interest Payment	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -
Loan Principal	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -
Levulinic acid Price ($/t)	$ 6 500.00	$ 6 500.00	$ 6 500.00	$ 6 500.00	$ 6 500.00	$ 6 500.00	$ 6 500.00	$ 6 500.00	$ 6 500.00	$ 6 500.00
Bio-product Sales	$ 6 275 880.00	$ 6 275 880.00	$ 6 275 880.00	$ 6 275 880.00	$ 6 275 880.00	$ 6 275 880.00	$ 6 275 880.00	$ 6 275 880.00	$ 6 275 880.00	$ 6 275 880.00
Electricty price ($/ kWh)	$ 0.08	$ 0.08	$ 0.08	$ 0.08	$ 0.08	$ 0.08	$ 0.08	$ 0.08	$ 0.08	$ 0.08
Electricity Sales	$ 6 725 203.20	$ 6 725 203.20	$ 6 725 203.20	$ 6 725 203.20	$ 6 725 203.20	$ 6 725 203.20	$ 6 725 203.20	$ 6 725 203.20	$ 6 725 203.20	$ 6 725 203.20
GVL ($/t)	$ 993.00	$ 993.00	$ 993.00	$ 993.00	$ 993.00	$ 993.00	$ 993.00	$ 993.00	$ 993.00	$ 993.00
GVL sales	$ 43 755 552.00	$ 43 755 552.00	$ 43 755 552.00	$ 43 755 552.00	$ 43 755 552.00	$ 43 755 552.00	$ 43 755 552.00	$ 43 755 552.00	$ 43 755 552.00	$ 43 755 552.00
FURFURAL($/T)	$ 1 200.00	$ 1 200.00	$ 1 200.00	$ 1 200.00	$ 1 200.00	$ 1 200.00	$ 1 200.00	$ 1 200.00	$ 1 200.00	$ 1 200.00
	$ 25 964 064.00	$ 25 964 064.00	$ 25 964 064.00	$ 25 964 064.00	$ 25 964 064.00	$ 25 964 064.00	$ 25 964 064.00	$ 25 964 064.00	$ 25 964 064.00	$ 25 964 064.00
	$ 1 207.00	$ 1 207.00	$ 1 207.00	$ 1 207.00	$ 1 207.00	$ 1 207.00	$ 1 207.00	$ 1 207.00	$ 1 207.00	$ 1 207.00
	$ 26 115 521.04	$ 26 115 521.04	$ 26 115 521.04	$ 26 115 521.04	$ 26 115 521.04	$ 26 115 521.04	$ 26 115 521.04	$ 26 115 521.04	$ 26 115 521.04	$ 26 115 521.04
Total Annual Revenue	$ 108 836 220.24	$ 108 836 220.24	$ 108 836 220.24	$ 108 836 220.24	$ 108 836 220.24	$ 108 836 220.24	$ 108 836 220.24	$ 108 836 220.24	$ 108 836 220.24	$ 108 836 220.24
Annual Manufacturing Cost										
Feedstock Price ($/ ton)										
Feedstock cost										
Other Variable Costs										
Fixed Operating Costs										
Total Product Cost	$ 40 763 007.62	$ 40 763 007.62	$ 40 763 007.62	$ 40 763 007.62	$ 40 763 007.62	$ 40 763 007.62	$ 40 763 007.62	$ 40 763 007.62	$ 40 763 007.62	$ 40 763 007.62
Annual Depreciation										
Plant Writedown										
Depreciation Charge										
Remaining Value										
Net Revenue (R-COM-dk)	$ 68 073 212.62	$ 68 073 212.62	$ 68 073 212.62	$ 68 073 212.62	$ 68 073 212.62	$ 68 073 212.62	$ 68 073 212.62	$ 68 073 212.62	$ 68 073 212.62	$ 68 073 212.62
Losses Forward	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0
Taxable Income	$ 68 073 212.62	$ 68 073 212.62	$ 68 073 212.62	$ 68 073 212.62	$ 68 073 212.62	$ 68 073 212.62	$ 68 073 212.62	$ 68 073 212.62	$ 68 073 212.62	$ 68 073 212.62
Income Tax	$19 060 500	$19 060 500	$19 060 500	$19 060 500	$19 060 500	$19 060 500	$19 060 500	$19 060 500	$19 060 500	$19 060 500
Annual Cash Income	$49 012 713	$49 012 713	$49 012 713	$49 012 713	$49 012 713	$49 012 713	$49 012 713	$49 012 713	$49 012 713	$49 012 713
Discount Factor	0.5231	0.4768	0.4347	0.3962	0.3612	0.3292	0.3001	0.2736	0.2494	0.2273
Annual Present Value (Discounted Cash Flow)	$ 25 636 713.53	$ 23 369 839.13	$ 21 303 408.51	$ 19 419 697.82	$ 17 702 550.43	$ 16 137 238.31	$ 14 710 335.74	$ 13 409 604.14	$ 12 223 887.09	$ 11 143 014.67
Cumulative Discounted Cash Flow	$32 668 354	$56 038 193	$77 341 601	$96 761 299	$114 463 850	$130 601 088	$145 311 424	$158 721 028	$170 944 915	$182 087 930
Total Capital Investment + Interest										
Net Present Worth										

(b)

	2033	2034	2035	2036	2037	2038	2039	2040	2041
Year	17	18	19	20	21	22	23	24	25
Fixed Capital Investment									
Land									
Working Capital									
Loan Payment	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -
Loan Interest Payment	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -
Loan Principal	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -
Levulinic acid Price ($/t)	$ 6 500.00	$ 6 500.00	$ 6 500.00	$ 6 500.00	$ 6 500.00	$ 6 500.00	$ 6 500.00	$ 6 500.00	$ 6 500.00
Bio-product Sales	$ 6 275 880.00	$ 6 275 880.00	$ 6 275 880.00	$ 6 275 880.00	$ 6 275 880.00	$ 6 275 880.00	$ 6 275 880.00	$ 6 275 880.00	$ 6 275 880.00
Electricty price ($/ kWh)	$ 0.08	$ 0.08	$ 0.08	$ 0.08	$ 0.08	$ 0.08	$ 0.08	$ 0.08	$ 0.08
Electricity Sales	$ 6 725 203.20	$ 6 725 203.20	$ 6 725 203.20	$ 6 725 203.20	$ 6 725 203.20	$ 6 725 203.20	$ 6 725 203.20	$ 6 725 203.20	$ 6 725 203.20
GVL ($/t)	$ 993.00	$ 993.00	$ 993.00	$ 993.00	$ 993.00	$ 993.00	$ 993.00	$ 993.00	$ 993.00
GVL sales	$ 43 755 552.00	$ 43 755 552.00	$ 43 755 552.00	$ 43 755 552.00	$ 43 755 552.00	$ 43 755 552.00	$ 43 755 552.00	$ 43 755 552.00	$ 43 755 552.00
FURFURAL($/T)	$ 1 200.00	$ 1 200.00	$ 1 200.00	$ 1 200.00	$ 1 200.00	$ 1 200.00	$ 1 200.00	$ 1 200.00	$ 1 200.00
	$ 25 964 064.00	$ 25 964 064.00	$ 25 964 064.00	$ 25 964 064.00	$ 25 964 064.00	$ 25 964 064.00	$ 25 964 064.00	$ 25 964 064.00	$ 25 964 064.00
	$ 1 207.00	$ 1 207.00	$ 1 207.00	$ 1 207.00	$ 1 207.00	$ 1 207.00	$ 1 207.00	$ 1 207.00	$ 1 207.00
	$ 26 115 521.04	$ 26 115 521.04	$ 26 115 521.04	$ 26 115 521.04	$ 26 115 521.04	$ 26 115 521.04	$ 26 115 521.04	$ 26 115 521.04	$ 26 115 521.04
Total Annual Revenue	$ 108 836 220.24	$ 108 836 220.24	$ 108 836 220.24	$ 108 836 220.24	$ 108 836 220.24	$ 108 836 220.24	$ 108 836 220.24	$ 108 836 220.24	$ 108 836 220.24
Annual Manufacturing Cost									
Feedstock Price ($/ ton)									
Feedstock cost									
Other Variable Costs									
Fixed Operating Costs									
Total Product Cost	$ 40 763 007.62	$ 40 763 007.62	$ 40 763 007.62	$ 40 763 007.62	$ 40 763 007.62	$ 40 763 007.62	$ 40 763 007.62	$ 40 763 007.62	$ 40 763 007.62
Annual Depreciation									
Plant Writedown									
Depreciation Charge									
Remaining Value									
Net Revenue (R-COM-dk)	$ 68 073 212.62	$ 68 073 212.62	$ 68 073 212.62	$ 68 073 212.62	$ 68 073 212.62	$ 68 073 212.62	$ 68 073 212.62	$ 68 073 212.62	$ 68 073 212.62
Losses Forward	$0	$0	$0	$0	$0	$0	$0	$0	$0
Taxable Income	$ 68 073 212.62	$ 68 073 212.62	$ 68 073 212.62	$ 68 073 212.62	$ 68 073 212.62	$ 68 073 212.62	$ 68 073 212.62	$ 68 073 212.62	$ 68 073 212.62
Income Tax	$19 060 500	$19 060 500	$19 060 500	$19 060 500	$19 060 500	$19 060 500	$19 060 500	$19 060 500	$19 060 500
Annual Cash Income	$49 012 713	$49 012 713	$49 012 713	$49 012 713	$49 012 713	$49 012 713	$49 012 713	$49 012 713	$49 012 713
Discount Factor	0.2072	0.1889	0.1722	0.1570	0.1431	0.1305	0.1189	0.1084	0.0988
Annual Present Value (Discounted Cash Flow)	$ 10 157 716.20	$ 9 259 540.75	$ 8 440 784.64	$ 7 694 425.38	$ 7 014 061.42	$ 6 393 857.26	$ 5 828 493.40	$ 5 313 120.70	$ 4 843 318.77
Cumulative Discounted Cash Flow	$192 245 646	$201 505 186	$209 945 971	$217 640 396	$224 654 458	$231 048 315	$236 876 809	$242 189 929	$247 033 248
Total Capital Investment + Interest									
Net Present Worth									

(c)

APPENDIX E

E-1: Supplementary data for the article

Life Cycle and Sustainability Assessments of Biorefineries Producing Glucaric Acid, Sorbitol or Levulinic acid Annexed to a Sugar Mill

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Supplementary Information: 14 Tables: E1-1(a-b), E1-2, E1-3, E1-4, E1-5, E1-6, E1-7, E1-8, E1-9, E1-10, E1-11, E1-12, E1-13, E1-14 (a-f) and E10
2 Figures: Figure E1-1 and Figure E1-2

Table E1-1(a): Summary of the mass and energy balances, techno-economic and social assessments of the levulinic acid scenarios (Kapanji, 2020)

	Scenario	Units	LA-F-E	LA-GVL-F-E
Feedstock to boiler	**Biomass (WM)**	**t/h**	49.7	44.1
	Bypass Ratio	**%**	44	39
Biorefinery Feedstock	**Biomass (WM)***	**t/h**	63.3	68.9
Material inputs	**3.5wt% dil. H_2SO_4**	**t/h**	156.7	171.2
	Hydrogen	**t/h**	-	0.08
	n-butyl acetate	**t/h**	-	32
	Boiler feed water	**t/h**	247	239
	Methane	**t/h**	2.0	2.0
Energy inputs	**Steam (MWh)**		58.4	70.1
	Cooling water (MWh)		86.2	76
	Electricity (MWh)		1.6	1.6
Products	**Levulinic acid**	**t/h**	7.2	0.15
	Furfural	**t/h**	2.2	2.4
	Gamma valerolactone (GVL)	**t/h**	-	6.8
	Electricity	**MWh**	13.7	14.6
wastes	**Wastewater**	**t/h**	185	206
	Flue gas	**t/h**	1084	1050
	Ash	**t/h**	3.3	3.3
Techno-economic and social assessments				
	Total Cap. Investment	**US$ million**	219	221
	Hurdle rate	**%**	9.7	9.7
	IRR	**%**	17	23
	NPV	**US$ million**	139	253
	Extra jobs created	**unit**	52	60

*MW is wet mass basis, feedstock with 50% inherent bagasse moisture and 15% trash moisture in a 70:30 bagasse and trash mixture.

Table E1-1(b): Summary of the mass and energy balances, techno-economic and social assessments of the sorbitol and glucaric acid biorefineries using steam explosion (STEX) and dilute acid (DA) pretreatments (Kapanji et al., 2019).

	Sorbitol.$_{\text{STEX}}$	**Sorbitol.$_{\text{DA}}$**	**Glucaric.$_{\text{STEX}}$**	**Glucaric.$_{\text{DA}}$**
NPV (US$ Million)	-12.8	17.2	-12.3	16.0
IRR (%)	-	10.7	-	10.7
MPSP (US$/t)	679	619	681	618
Market Selling Price (US$/t)*	655	655	655	655
Payback period (yr)	-	19	-	19
Extra jobs created	48	49	48	49
Feedstock to boiler (WM*) t/h	28	33	39	42
Bypass ratio (%)	25	29.5	35	37
Feedstock to biorefinery (WM) t/h	85	80	74	71
Materials input				
Boiler feed water (t/h)	221	233	232	247
Energy inputs				
Steam (MWh/y)	65.1	74.3	70.6	88.9
Cooling demand (MWh/y)	94.2	133.5	96.5	134.3
Electricity demand (MWh/y)	2	1.9	1.9	1.9
Products				
Glucaric acid (t/h)	-	-	11.1	10.3
Sorbitol (t/h)	12.2	11.3	-	-
Electricity (MWh/y)	13.1	15.8	14.8	16.1
Wastes				
Wastewater (t/h)	141	122	188	145
Flue gas (t/h)	998	1030	1015	1066
Ash (t/h)	0.92	2.6	1.9	2.6

*WM is wet mass

Table E1-2: A quantitative breakdown (A-H) of the energy process inputs for a bio(energy) self-sufficient biorefinery.

	A=E Steam demand	B=F Electricity	Cooling duty Cooling demand	C Excess electricity	D Feedstock to CHP	D Bypass ratio	G Boiler feed water	H Cellulignin and methane
Unit	MWh/y	MWh/y	MWh/y	MWh/y	t/h	(%)	t/h	t/h
S1	65.1	2	94.2	13.1	28	25	221	23
S2	74.3	1.9	133.5	15.8	33	29.5	233	25
S3	70.6	1.9	96.5	14.8	40	35	232	19
S4	88.9	1.9	134.3	16.1	42	37	247	22
S5	58.4	1.6	70.1	14.6	44	39	243	39
S6	70.1	1.5	76	13.7	50	44	242	35

Table E1-3: Input data for the sugar cultivation, harvesting and processing adjusted for a typical sugar mill processing 113 t/h (wet mass) of bagasse and brown leaves (Mashoko et al. 2010; Mashoko et al. 2013; Farzad et al. 2017)

SUGAR CULTIVATION			**Adjusted value**
Cane harvested area[a]	400 000	Ha	400000
Avg cane harvested/Ha[b]	60	t/Ha	
Irrigation water required/Ha	8000	m^3	8000
Elec. consumption for irrigation/Ha	108	kWh	108
N_2O emissions from soil	1.25	% of Nitrogen input	7.5
NO_x emissions from soil	0.5	% of Nitrogen input	3kg
Fertiliser application/Ha	120	kg Nitrogen	600
	30	kg P_2O_5	150
	125	kg K_2O	625
Herbicides used (for weed control)	26.9	g/MT of sugarcane	8.07
Herbicides loss to water bodies	0.2	%	0.016 kg
Nitrogen loss to water bodies	10	%	60 kg
Phosphorus loss in surface runoff/Ha	1	kg/Ha	5
Pesticide use (GLOBAL)	2.21	g/Mt of sugar cane	0.66
INORGANIC FERTILISERS AND HERBICIDES			
Energy needed for herbicide production/kg	120	MJ/kg	968
Fuel input to produce herbicide/kg	15	% diesel	1 kg
	70	% coal	6 kg
	15	% electricity	1 kWh
Energy needed to produce N fertiliser /kg	48	MJ	28800
Energy needed to produce P_2O_5 /kg	14	MJ	2100
Energy needed to produce K_2O_5/kg	8	MJ	5000
Pesticides & herbicides transport distance (1 way)		km	166
CANE TRANSPORTATION			
Transportation by road (average distance)	90	km	25
Transportation by rail (average distance)	50	km	50
Diesel consumption litres/t km	0.075	l diesel	1 L rail, 21 L road
Fertilisers & Herbicides transport distance	60	km	60
SUGAR PROCESSING AND ELECTRICITY GENERATION			
Sugar produced/Ha under cultivation	6	t	30
Bagasse produced	27.8	% of cane	45 t
Molasses produced/Ha	4.1	% of cane	12.3t
Filter cake produced/Ha (used as fertiliser)	6.8	% of cane	20.4t
Electricity exported to the grid from sugar mill	0	MWh	0
Steam consumed/t of cane	520	kg	120
Electricity consumed/ t of cane	35	kWh	10500
Coal consumption/ t of cane	8.4	kg	2520
Water used for cane processing/ t cane	0.6	m^3	18

Pollutant loading of COD/t of cane	3320	kg	996
Pollutant loading of BOD/t of cane	1590	kg	447

[a] 300 t/h cane is harvested

[b] 30 t/h of sugar is harvested (10% of cane harvested) and so process requirements adjusted to suit this mill.

Table E1-4: A summary of the economic values and allocations used for the main biorefinery system input and output streams

		% ECONOMIC ALLOCATION			
Product	**Quantity (kg)**	**Amount ($/t)**	**Proceeds**	**% allocation**	**Reference**
Harvested cane	300000	0.31	93000	98	Mashoko et al. (2010)
Brown leaves*	20000	0.11	2200	2	Kapanji et al., (2019)
TOTAL		-	**95200**	**100**	
Sugar	30000	0.61	18300	88.0	Statistica, (2020)
Molasses	12300	0.20	2460	11.8	Statistica, (2020)
Filter Cake	20400	0.0014	28.6	0.2	Madiri, (2010)
Bagasse*	45000	0	0	0	Kapanji et al., (2019)
TOTAL			**20788.6**	**100**	**-**

* Price of bagasse assumed 0 (Farzad et al., 2017).The lignocellulose cost used (US$ 10.79/t) was allocated to the brown leaves only and based on the collection and transportation costs from the fields to the biorefinery, in exchange for 120 t/h steam to the mill.

Table E1-5: LCIA results for scenario 1 (Sorbitol.$_{STEX}$) based on 1 kg of product

Impact category	Unit	Pretreatment	Enzymatic hydrolysis	Conversion and purification	WWT	CHP combustion unit	Cultivation and milling
Abiotic depletion (ADP)	**kg Sb eq.**	5.30E-07	4.85E-06	3.60E-06	8.99E-07	7.77E-07	1.21E-05
Abiotic depletion (fossil fuels)	**MJ**	9.98E-04	1.24E+00	3.03E+00	4.33E-01	2.17E-01	9.81E+01
Global warming potential (GWP$_{100a}$)	**kg CO$_2$ eq.**	7.16E-05	1.22E-01	2.36E-01	6.83E-02	5.90E-02	6.23E+00
Ozone layer depletion (ODP)	**kg CFC - 11 eq.**	1.19E-11	7.96E-09	1.97E-08	4.34E-09	1.83E-09	1.16E-06
Human toxicity	**kg 1,4 - DB eq.**	5.05E-04	7.60E-02	7.67E-02	1.37E-02	1.61E-02	2.64E+00
Fresh water aquatic ecotoxocity	**kg 1,4 - DB eq.**	7.28E-06	5.44E-02	5.24E-02	7.05E-03	9.15E-03	7.43E-01
Marine aquatic ecotoxicity	**kg 1,4 - DB eq.**	2.41E-02	1.44E+02	1.60E+02	2.12E+01	2.48E+01	2.53E+03
Terrestrial ecotoxicity	**kg 1,4 - DB eq.**	1.17E-07	8.35E-04	7.30E-04	1.05E-04	1.38E-04	9.83E-03
Photochemical oxidation (POCP)	**kg C$_2$H$_4$ eq.**	2.39E-04	1.92E-03	1.42E-03	3.87E-04	1.90E-03	1.03E-03
Acidification (AP)	**kg SO$_2$ eq.**	5.98E-03	4.81E-02	3.55E-02	9.48E-03	4.74E-02	1.80E-02
Eutrophication (EP)	**kg PO$^{3-}_4$ eq.**	1.76E-02	1.47E-01	1.08E-01	2.81E-02	2.54E-01	7.64E-02

Table E1-6: LCIA results for scenario 2 (Sorbitol.$_{DA}$) based on 1 kg of product

Impact category	Unit	Pretreatment	Enzymatic hydrolysis	Conversion and purification	WWT	CHP combustion unit	Cultivation and milling
Abiotic depletion (ADP)	**kg Sb eq.**	2.21E-10	8.06E-07	7.19E-07	1.07E-07	1.14E-07	1.21E-05
Abiotic depletion (fossil fuels)	**MJ**	2.15E-02	1.28E+00	3.88E+00	5.68E-01	1.87E-01	9.81E+01
Global warming potential (GWP$_{100a}$)	**kg CO$_2$ eq.**	2.95E-03	4.67E-01	5.89E-01	1.27E-01	5.21E+00	6.23E+00
Ozone layer depletion (ODP)	**kg CFC - 11 eq.**	2.28E-11	7.24E-09	2.50E-08	5.35E-09	1.44E-09	1.16E-06
Human toxicity	**kg 1,4 - DB eq.**	5.29E-05	6.50E-02	8.13E-02	1.52E-02	9.38E-03	2.64E+00
Fresh water aquatic ecotoxocity	**kg 1,4 - DB eq.**	9.56E-06	4.88E-02	5.66E-02	8.08E-03	6.93E-03	7.48E-01
Marine aquatic ecotoxicity	**kg 1,4 - DB eq.**	5.82E-02	1.29E+02	1.80E+02	2.47E+01	1.88E+01	2.53E+03
Terrestrial ecotoxicity	**kg 1,4 - DB eq.**	3.41E-07	7.51E-04	7.53E-04	1.20E-04	1.04E-04	9.83E-03
Photochemical oxidation (POCP)	**kg C$_2$H$_4$ eq.**	7.08E-07	9.81E-05	1.16E-04	2.65E-05	1.12E-03	1.03E-03
Acidification (AP)	**kg SO$_2$ eq.**	2.34E-06	7.17E-04	1.25E-03	1.99E-04	1.12E-04	1.18E-02
Eutrophication (EP)	**kg PO$^{3-}_4$ eq.**	9.86E-06	1.98E-03	1.72E-03	2.57E-04	2.00E-02	7.64E-02

Table E1-7: LCIA results for scenario 3 (Glucaric.$_{STEX}$) based on 1 kg of product

Impact category	Unit	Pretreatment	Enzymatic hydrolysis	Conversion and purification	WWT	CHP combustion unit	Cultivation and milling
Abiotic depletion (ADP)	**kg Sb eq.**	5.93E-07	4.80E-06	3.91E-06	1.05E-06	6.76E-07	1.21E-05
Abiotic depletion (fossil fuels)	**MJ**	9.50E-04	1.11E+00	1.30E+01	6.78E-01	1.75E-01	9.81E+01
Global warming potential (GWP$_{100a}$)	**kg CO$_2$ eq.**	1.11E-03	4.92E-01	1.38E+00	1.36E-01	5.74E+00	6.23E+00
Ozone layer depletion (ODP)	**kg CFC - 11 eq.**	1.14E-11	7.08E-09	9.41E-08	6.39E-09	1.54E-09	1.16E-06
Human toxicity	**kg 1,4 - DB eq.**	5.59E-04	6.78E-02	1.98E-01	1.74E-02	1.03E-02	2.64E+00
Fresh water aquatic ecotoxocity	**kg 1,4 - DB eq.**	6.52E-06	4.83E-02	1.26E-01	8.95E-03	7.25E-03	7.43E-01
Marine aquatic ecotoxicity	**kg 1,4 - DB eq.**	2.19E-02	1.28E+02	4.69E+02	2.87E+01	1.97E+01	2.53E+03
Terrestrial ecotoxicity	**kg 1,4 - DB eq.**	1.05E-07	7.42E-04	1.23E-03	1.22E-04	1.09E-04	9.83E-03
Photochemical oxidation (POCP)	**kg C$_2$H$_4$ eq.**	2.67E-04	1.90E-03	1.68E-03	4.52E-04	1.48E-03	1.03E-03
Acidification (AP)	**kg SO$_2$ eq.**	6.67E-03	4.57E-02	3.95E-02	1.08E-02	6.36E-03	1.80E-02
Eutrophication (EP)	**kg PO$^{3-}_4$ eq.**	1.95E-02	1.46E-01	1.17E-01	3.26E-02	2.27E-01	7.64E-02

Table E1-8: LCIA results for scenario 4 (Glucaric.$_{DA}$) based on 1 kg of product

Impact category	Unit	Pretreatment	Enzymatic hydrolysis	Conversion and purification	WWT	CHP combustion unit	Cultivation and milling
Abiotic depletion (ADP)	**kg Sb eq.**	2.21E-10	8.28E-07	7.17E-07	9.64E-08	1.06E-07	1.21E-05
Abiotic depletion (fossil fuels)	**MJ**	3.37E-02	1.40E+00	1.10E+01	6.72E-01	1.83E-01	9.81E+01
Global warming potential (GWP$_{100a}$)	**kg CO$_2$ eq.**	1.55E-03	5.04E-01	1.18E+00	1.29E-01	5.27E+00	6.23E+00
Ozone layer depletion (ODP)	**kg CFC - 11 eq.**	2.93E-11	7.48E-09	7.84E-08	6.01E-09	1.43E-09	1.16E-06
Human toxicity	**kg 1,4 - DB eq.**	6.56E-05	6.68E-02	1.70E-01	1.56E-02	8.67E-03	2.64E+00
Fresh water aquatic ecotoxocity	**kg 1,4 - DB eq.**	8.07E-06	5.00E-02	1.10E-01	8.27E-03	6.36E-03	7.48E-01
Marine aquatic ecotoxicity	**kg 1,4 - DB eq.**	7.11E-02	1.33E+02	4.04E+02	2.65E+01	1.75E+01	2.53E+03
Terrestrial ecotoxicity	**kg 1,4 - DB eq.**	4.33E-07	7.68E-04	1.13E-03	1.15E-04	9.47E-05	9.83E-03
Photochemical oxidation (POCP)	**kg C$_2$H$_4$ eq.**	4.53E-07	1.07E-04	2.15E-04	2.66E-05	1.13E-03	1.03E-03
Acidification (AP)	**kg SO$_2$ eq.**	3.59E-06	7.49E-04	3.14E-04	2.20E-04	1.10E-04	1.80E-02
Eutrophication (EP)	**kg PO$^{3-}_4$ eq.**	3.70E-06	2.12E-03	2.06E-03	2.37E-04	2.02E-02	7.64E-02

Table E1-9: LCIA results for scenario 5 (LA-F-E) based on 1 kg of product

Impact category	Unit	1st reaction stage	2nd reaction stage	Conversion and purification	WWT	CHP combustion unit	Cultivation and milling
Abiotic depletion (ADP)	**kg Sb eq.**	4.82E-09	4.76E-09	2.34E-07	3.73E-08	3.62E-08	1.21E-05
Abiotic depletion (fossil fuels)	**MJ**	3.68E-01	6.17E-01	3.14E+01	1.51E+00	3.13E-01	9.81E+01
Global warming potential (GWP$_{100a}$)	**kg CO$_2$ eq.**	9.15E-03	1.31E-02	2.35E+00	1.72E-01	3.05E-02	6.23E+00
Ozone layer depletion (ODP)	**kg CFC - 11 eq.**	4.63E-10	5.49E-10	2.10E-07	1.17E-08	2.51E-09	1.16E-06
Human toxicity	**kg 1,4 - DB eq.**	1.10E-03	1.28E-03	3.47E-01	2.00E-02	6.26E-03	2.64E+00
Fresh water aquatic ecotoxocity	**kg 1,4 - DB eq.**	2.58E-04	2.23E-04	2.09E-01	7.53E-03	2.29E-03	7.43E-01
Marine aquatic ecotoxicity	**kg 1,4 - DB eq.**	1.43E+00	1.63E+00	8.77E+02	3.03E+01	8.82E+00	2.53E+03
Terrestrial ecotoxicity	**kg 1,4 - DB eq.**	6.17E-06	8.21E-06	1.47E-03	8.99E-05	2.57E-05	9.83E-03
Photochemical oxidation (POCP)	**kg C$_2$H$_4$ eq.**	1.19E-04	9.61E-05	7.97E-04	1.26E-04	1.19E-03	1.03E-03
Acidification (AP)	**kg SO$_2$ eq.**	2.93E-03	2.34E-03	1.75E-02	2.59E-03	2.97E-02	1.80E-02
Eutrophication (EP)	**kg PO$^{3-}_4$ eq.**	2.22E-02	1.75E-02	7.78E-02	2.28E-02	2.28E-01	7.64E-02

Table E1-10: LCIA results for scenario 6 (LA-GVL-F-E) based on 1 kg of product

Impact category	Unit	1st reaction stage	2nd reaction stage	LeVa conversion and purification	GVL conversion and purification	WWT	CHP combustion unit	Cultivation and milling
Abiotic depletion (ADP)	**kg Sb eq.**	1.59E-09	4.05E-09	2.06E-07	1.37E-04	3.00E-08	4.11E-08	1.21E-05
Abiotic depletion (fossil fuels)	**MJ**	3.40E-01	1.08E+00	3.04E+01	8.36E+02	1.24E+00	3.72E-01	9.81E+01
Global warming potential (GWP$_{100a}$)	**kg CO$_2$ eq.**	6.37E-03	1.98E-02	2.10E+00	3.95E+01	1.39E-01	3.43E-02	6.23E+00
Ozone layer depletion (ODP)	**kg CFC - 11 eq.**	2.46E-10	6.88E-10	1.85E-07	4.55E-06	8.81E-09	2.87E-09	1.16E-06
Human toxicity	**kg 1,4 - DB eq.**	5.51E-04	1.55E-03	3.07E-01	1.55E+01	1.55E-02	7.39E-03	2.64E+00
Fresh water aquatic ecotoxocity	**kg 1,4 - DB eq.**	5.05E-05	1.10E-04	1.83E-01	9.94E+00	5.36E-03	2.60E-03	7.43E-01
Marine aquatic ecotoxicity	**kg 1,4 - DB eq.**	6.25E-01	1.82E+00	7.72E+02	3.74E+04	2.15E+01	1.01E+01	2.53E+03
Terrestrial ecotoxicity	**kg 1,4 - DB eq.**	3.89E-06	1.17E-05	1.32E-03	5.01E-02	7.09E-05	2.95E-05	9.83E-03
Photochemical oxidation (POCP)	**kg C$_2$H$_4$ eq.**	6.09E-06	1.36E-05	3.97E-04	3.48E-02	3.32E-05	1.48E-03	1.03E-03
Acidification (AP)	**kg SO$_2$ eq.**	1.23E-04	2.47E-04	7.60E-03	1.83E-01	3.50E-04	3.69E-02	1.80E-02
Eutrophication (EP)	**kg PO$^{3-}_4$ eq.**	5.82E-04	9.00E-04	5.44E-03	5.24E-02	5.56E-04	2.46E-01	7.64E-02

Table E1-11(a) and (b): Life cycle inventories for the scenarios given in (a) and (b)

No	Parameter	Sorbitol.STEX	Sorbitol.DA	Glucaric.STEX	Glucaric.DA	LA-F-E	LA-GVL-F-E	CHP base case
1	CHP_AIR	948000	975000	958500	247000	1007741	979660	1269000
2	CHP_ASH	918	2606	1890	2624	3335	3318	2863
3	CHP_BOILER_CHEM	1.8	1.8	1.9	3	3.5	3.3	1.5
4	CHP_CWU	4912000	4632000	4654000	4619000	60000	6430000	24475
5	CHP_ELECU	920	933	940	943	1400	1400	1131
6	CHP_FEED_BL	6060	7150.8	8484	8968.8	10665.6	7999.2	20000
7	CHP_FEED_SB	9090	10726.2	12726	13453.2	15998.4	11998.8	45000
8	CHP_FLUE_CH4	17.85	14.79	15.3	15.24	10.2	10.2	0.00001
9	CHP_FLUE_CO2	73181.56	74814.67	75643.8	79091.03	81951.33	79051.8	110738
10	CHP_FLUE_H2O	43684.51	47853.46	49249	53123.21	66583.06	63818.2	94045.7
11	CHP_FLUE_N2	720480	741000	728460	763800	775961	754338	977130
12	CHP_FLUE_NO2	0.046055	0.0460055	0.0460055	0.0460055	0.0460055	0.0460055	0.0460055
13	CHP_FLUE_O2	161080	166482	162037	170223	159434	155376	197179
14	CHP_FLUE_ORGANICS	12.041379	16.7	16.31	19.6	39.54816	35.2199984	44
15	CHP_FLUE_SO2	434.4266	0.0822618	0.00001	0.1167223	352.4769	395.607	0.00001
16	CHP_HYDRAZ	1	1	1.1	1.11	5.3	5.5	1.5
17	ELEC_GENERATED	13090	15767	14826	16064	14733	12902	60514
18	HHP_STEAM	15200	3500	13000	23000	63177	72000	0.00001
19	HPU	0.00001	0.00001	0.00001	0.00001	0.00001	0.00001	0.00001
20	HPU_CEST	21000	21800	21000	22000	23000	23000	24000
21	LIMESTONE_WASTE	490.04	500	490	498	5981	6790	0.00001
22	LPU	0.00001	0.00001	0.00001	0.00001	0.00001	0.00001	0.00001
23	LPU_CEST	0.00001	0.00001	0.00001	0.00001	0.00001	0.00001	0.00001
24	PA_100_200_GLUCAN	102040.8	105270	91793.44	93614.7	29964.36	32640	0.00001
25	PA_100_400_HYDROL_TOWWT	133416.7	111782.3	176803.5	133550	0.00001	0.00001	0.00001
26	PA_100_AIR	8030	0.00001	8035	0.00001	0.00001	0.00001	0.00001
27	PA_100_BL	18180	17089.2	15756	15271.2	13574.4	25312	0.00001
28	PA_100_CWU	2558000	9203000	3204000	42779000	62340000	3899000	0.00001
29	PA_100_ELECU	30	73	24	23	4175	110	0.00001
30	PA_100_FURFURAL_BYPRDT	0.00001	0.00001	0.00001	0.00001	2162	2355	0.00001
31	PA_100_H2SO4	0.00001	631	0.00001	896	2932.16	3193.96	0.000001
32	PA_100_HPU	0.00001	0.00001	0.00001	0.00001	63000	72000	0.0001
33	PA_100_LPU	103200	38000	19500	125000	0.00001	0.00001	0.00001
34	PA_100_PW	84000	136820	198800	154930	80843.84	88062.04	0.00001
35	PA_100_SB	27270	25633.8	23634	22906.8	20361.6	37968	0.00001
36	PA_100_SULPHUR	400	0.00001	403	0.00001	0.00001	0.00001	0.00001
37	PA_100_VENT_CO	0.00001	0.00001	0.00001	0.00001	0.00001	0.00001	0.000001
38	PA_100_VENT_CO2	0.00001	0.00001	0.00001	0.00001	0.00001	0.00001	0.00001
39	PA_100_VENT_H2	0.00001	0.00001	0.00001	0.00001	0.00001	0.00001	0.00001
40	PA_100_VENT_N	6082.207	0.00001	6082.683	0.00001	0.00001	0.00001	0.00001
41	PA_100_VENT_O2	1430.1	0.00001	1430.339	0.00001	0.00001	0.00001	0.00001
42	PA_100_VENT_S	0.00001	0.00001	0.00001	0.00001	0.00001	0.00001	0.00001
43	PA_100_VENT_SO2	725.6815	0.00001	729.03	0.00001	0.00001	0.00001	0.00001
44	PA_100_VENT_VAP	21923.9	0.00001	19422	0.00001	0.00001	0.00001	0.00001
45	PA_100_VENT_VOC	1145.91	0.00001	1018.61	0.00001	0.00001	0.00001	0.00001
46	PA_200_300_TOPURIF	11041.56	11148.28	10989.31	9942.962	30493	18269.35	0.00001
47	PA_200_400_HYDROL_TOWWT	49.79519	2561.666	209.1922	2452.931	160426	174732	0.000001
48	PA_200_CHP_CELIGNIN	19534.69	21564.06	16261.63	19114.02	28204.88	30613.23	0.00001
49	PA_200_CWU	8029000	7764000	7166000	7007000	186000	203000	0.00001
50	PA_200_ELEC	902	905.2	909	905	6	6	0.00001

(a)

No	Parameter	Sorbitol.$_{STEX}$	Sorbitol.$_{DA}$	Glucaric.$_{STEX}$	Glucaric.$_{DA}$	LA-F-E	LA-GVL-F-E	CHP base case
51	PA_200_ENZY_DIAMMON	44.5	45.3	43.3	38.4	0.00001	0.00001	0.00001
52	PA_200_ENZY_GLUCOSE	1132.48	1027.17	1002.2	936	0.00001	0.00001	0.00001
53	PA_200_ENZY_H2O	1021.52	1165.76	1157.08	1011.95	0.00001	0.00001	0.00001
54	PA_200_ENZY_NUT1	10.2	9.7	9.9	11.85	0.00001	0.00001	0.00001
55	PA_200_ENZY_NUT2	10.2	9.7	9.9	11.85	0.00001	0.00001	0.00001
56	PA_200_ENZYM	0.00001	0.00001	0.00001	0.00001	0.00001	0.00001	0.00001
57	PA_200_H2SO4	0.00001	0.00001	0.00001	0.00001	2551.5	2782.5	0.00001
58	PA_200_HPU	63000	56500	52000	50000	23000	14000	0.00001
59	PA_200_PW	0.00001	0.00001	0.00001	0.00001	70348.5	76717.5	0.00001
60	PA_200_VENT_AMMONIA	0.00001	0.00001	0.00001	0.00001	0.00001	0.00001	0.00001
61	PA_200_VENT_CO	0.00001	0.00001	0.00001	0.00001	0.00001	0.00001	0.00001
62	PA_200_VENT_CO2	0.00001	0.000001	0.00001	0.00001	0.00001	0.00001	0.00001
63	PA_200_VENT_H2	0.00001	0.00001	0.00001	0.00001	0.00001	0.00001	0.00001
64	PA_200_VENT_N	0.00001	0.00001	0.00001	0.00001	0.00001	0.00001	0.00001
65	PA_200_VENT_O2	0.00001	0.00001	0.00001	0.00001	0.00001	0.00001	0.00001
66	PA_200_VENT_S	0.00001	0.00001	0.00001	0.00001	0.00001	0.00001	0.00001
67	PA_200_VENT_SO2	0.00001	0.00001	0.00001	0.00001	0.00001	0.00001	0.00001
68	PA_200_VENT_VAP	0.00001	0.00001	0.00001	0.00001	0.00001	0.00001	0.00001
69	PA_200_VENT_VOC	0.00001	0.00001	0.00001	0.00001	0.00001	0.00001	0.00001
70	PA_300_400_HYDROL_TOWWT	6487.404	7321.537	10183.67151	8908.5214	24908.541	14947.094	0.00001
71	PA_300_600_FEED	0.00001	0.00001	0.00001	0.00001	0.00001	9134.663	0.00001
72	PA_300_ACTC_CAT	2.09	1.9	1.9	1.9	0.00001	0.00001	0.00001
73	PA_300_CWU	568000	3100	504000	370000	12000	9844000	0.00001
74	PA_300_ELEC	38.5	44	48	1	2	1.14	0.00001
75	PA_300_FURF_SOLVENT	0.00001	0.00001	0.00001	0.00001	0.00001	0.00001	0.00001
76	PA_300_H2	102	100	0.00001	0.00001	0.00001	0.00001	0.000001
77	PA_300_HPU	6700	8800	41500	31500	50000	24000	0.00001
78	PA_300_NAOH	186	189.9	200	190	0.00001	0.00001	0.00001
79	PA_300_NI_CAT	14	14	0.00001	0.00001	0.00001	0.00001	0.00001
80	PA_300_O2	0.00001	0.00001	2000	1700	0.00001	0.00001	0.00001
81	PA_300_PRDT1	12171.21	11342.38	11051.49	10260.28	5584.719	3053.261	0.00001
82	PA_300_PT_CAT	0.00001	0.00001	13	14	0.00001	0.00001	0.00001
83	PA_300_RESINS	1.5	1.4	1.9	1.3	0.00001	0.00001	0.00001
84	PA_400_500_CH4	3500	2900	3000	2990	2000	2000	0.0001
85	PA_400_CHP_BFW	221	233	232	247	246500	238900	0.00001
86	PA_400_LIME	490.04	500	500	501	670	593.8636	0.00001
87	PA_400_MAKEUPH2O	37870	2124	34874	2124	32152.2	31397	0.00001
88	PA_400_PW	216089	180699	187344	155458	184674	201802	0.00001
89	PA_600_400TOWWT	0.00001	0.00001	0.00001	0.00001	0.00001	6602.556	0.00001
90	PA_600_CWU	0.00001	0.00001	0.00001	0.00001	0.00001	9844000	0.00001
91	PA_600_ELECU	0.00001	0.00001	0.00001	0.00001	0.00001	1.14	0.000001
92	PA_600_GVL	0.00001	0.00001	0.00001	0.00001	0.00001	2297.59	0.00001
93	PA_600_H2	0.00001	0.00001	0.00001	0.00001	0.00001	80	0.00001
94	PA_600_HPU	0.00001	0.00001	0.00001	0.00001	0.00001	24000	0.000001
95	PA_600_N_BUTYL_A	0.00001	0.00001	0.00001	0.00001	0.00001	32000	0.00001
96	PA_600_VENT_H2	0.00001	0.00001	0.00001	0.00001	0.00001	28.45688	0.00001
97	PA_600_VENT_O2	0.00001	0.00001	0.00001	0.00001	0.00001	0.00001	0.00001
98	SAT_STEAM_CEST	0.00001	0.00001	0.00001	0.00001	0.00001	0.00001	0.00001
99	SUGAR_MILL_STEAM	120000	120000	120000	120000	120000	120000	120000
100	PA_600_VENT_ORGANICS	0.00001	0.00001	0.00001	0.00001	0.00001	21.24	0.00001
101	PA_600_VENT_H2SO4	0.00001	0.00001	0.00001	0.00001	0.00001	0.00001	0.00001
102	PA_600_VENT_H2O	0.00001	0.00001	0.00001	0.00001	0.00001	1325.261	0.00001
103	PA_600_VENT_CO2	0.00001	0.00001	0.00001	0.00001	0.00001	10.49262	0.00001
104	PA_400_WWT_EMISSION_COD	1.64	1.57	1.58	1.49	1254	1.29	0.00001

Note: Data on moisture has been included in Table S11 (a) and (b) as process water (PW). This also includes the inherent feedstock moisture content of 50% (based on a wet mass basis).

(b)

KEY

KEY

PA–PROCESS AREA
WWT–WASTEWATER TREATMENT
PRDT–PRODUCT
BL–BROWN LEAVES
H_2SO_4 –SULPHURIC ACID
ELECU–ELECTRICITY UTILITY
CHP–COMBINED HEAT AND POWER
HYDRA –HYDRAZINE
BFW–BOILER FEED WATER
N-BUTYL–N-BUTYL ACETATE
PT/C–PLATINUM CARBON
RESINS_AMBERLITE–AMBERLITE RESINS
ELEC-ELECTRICITY
NI-CAT-NICKEL CATALYST
ENZY_NUT1-ENZYME NUTRIENT1

HYDROL–HYDROLYSATE
PW–PROCESS WATER
SB–SUGARCANE BAGASSE
CWU–COOLING WATER UTILITY
HPU–HIGH PRESSURE UTILITY
BOIL.CHEM–BOILER CHEMICALS
C.TOWERCHEM–COOLING TOWER CHEMICALS
MAKEUPH2O–MAKE UP WATER
GVL–GAMMA VALEROLACTONE
VAP–VAPOUR
ACTC_CAT–ACTIVATED CARBON CATALYST
FURF-SOLVENT-FURFURAL SOLVENT
VOC-VOLATILE ORGANIC COMPOUNDS
ENZYM-ENZYMES

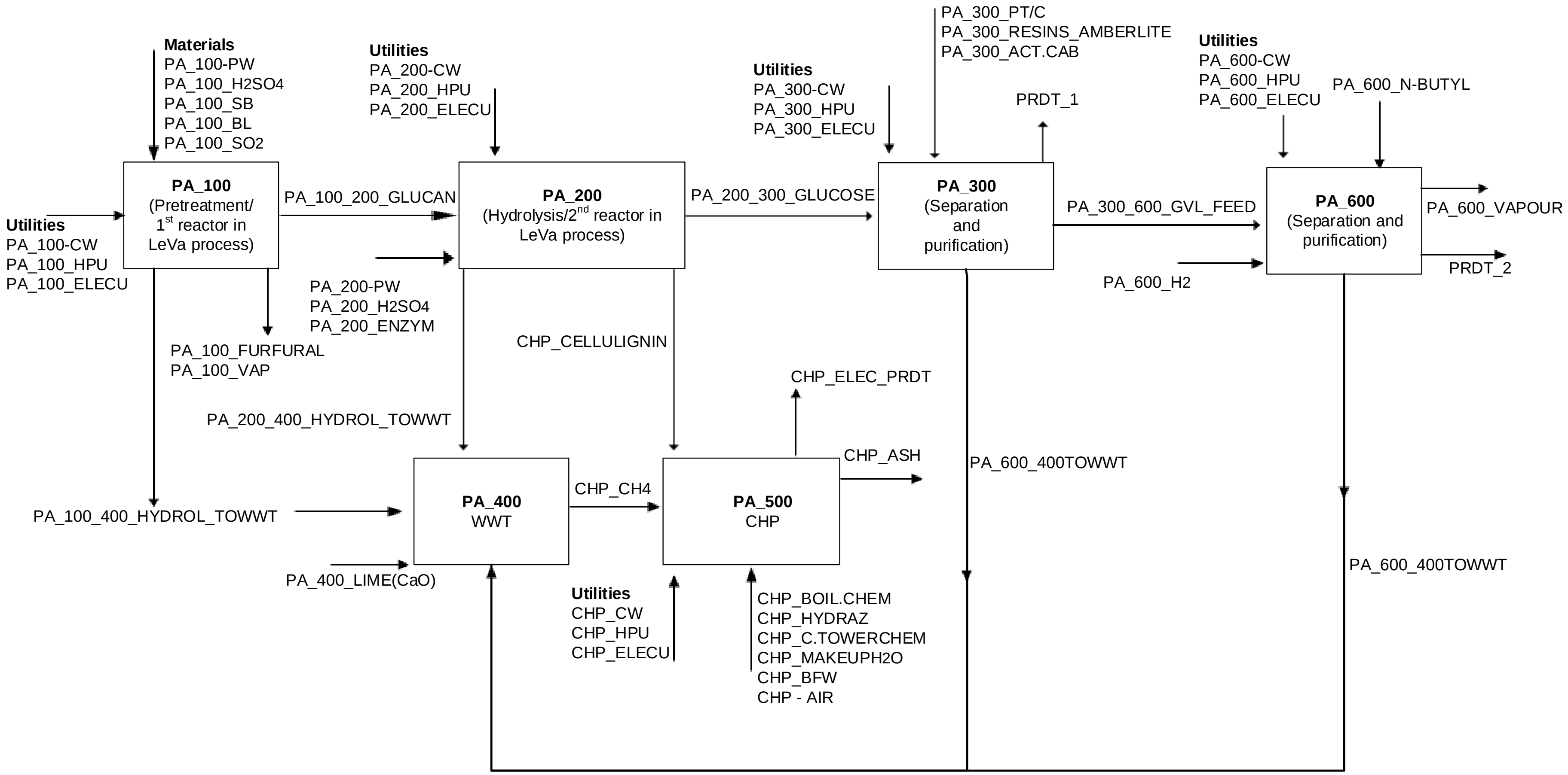

Figure E1-1: Product stages used in the life cycle inventory

Sensitivity analysis

Introducction

A sensitivity analysis has been conducted on two LCA methods commonly used in the environmental impact studies. Also, a brief discussion has been included on the effects of process water on the overall energy demand of a biorefinery.

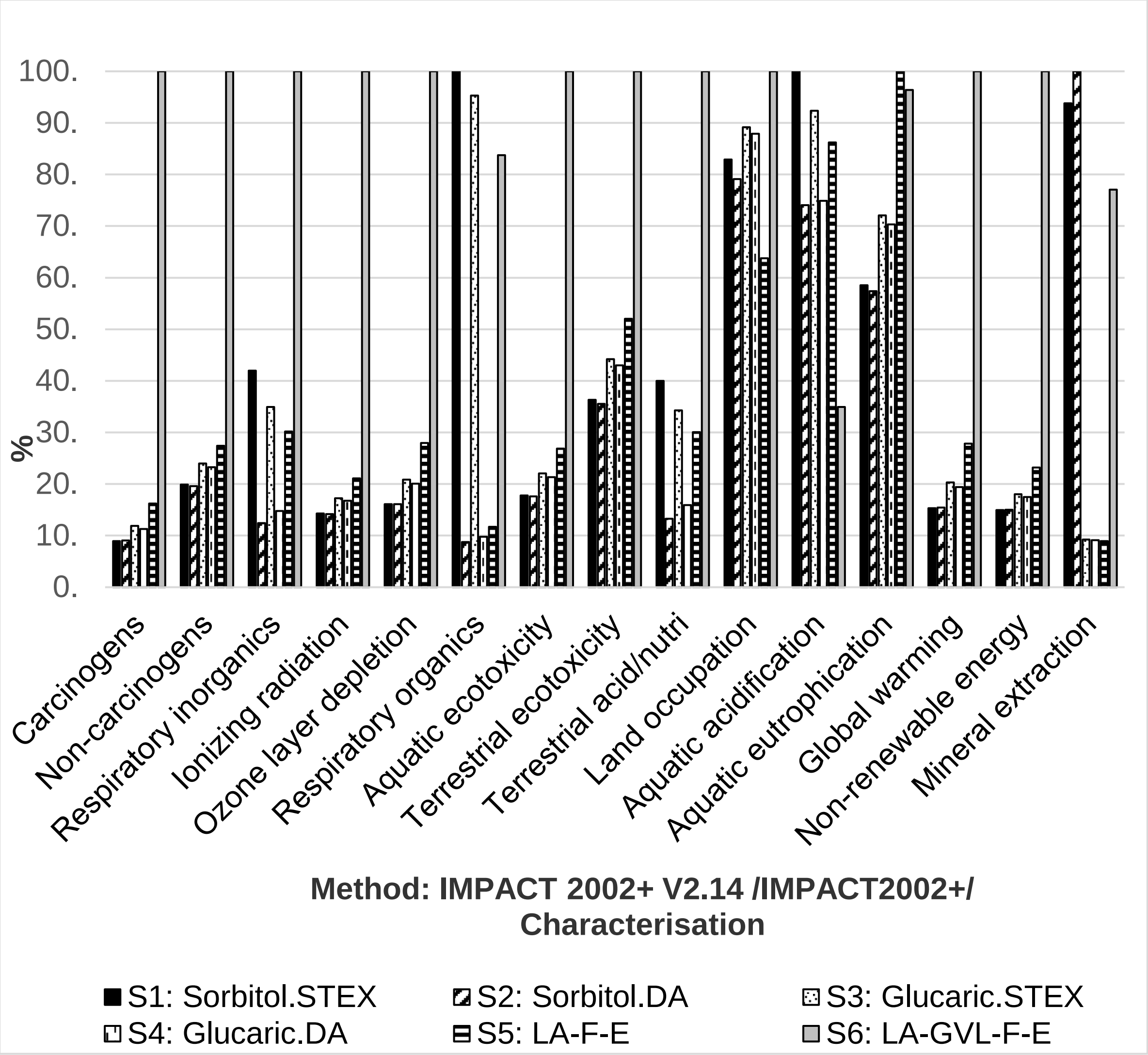

Figure E1-2: Sensitivity analysis using IMPACT 2002+ methodology.

As an alternative method to CML-IA (CML) baseline method used in this current study was compared to the IMPACT 2002+ method for the sensitivity analysis and the IMPACT 2002+ results are demonstrated in Figure 6-6. A comparison of the methods (Figures 6-6 in the manuscript and E1-2) showed similar trends and magnitudes and no major shifts in the ordering of scenarios in most of the similar and equivalent categories.

It was assumed that a 10% or more difference in the environmental loads or a shift in the ordering of most scenarios per category with the application of a different method signified the threshold point for a significant sensitivity change of an impact (Farzad et al. 2017). The two methods have some variations in their impact categories but most of the categories are similar as discussed herein. Whilst the CML-IA baseline (CML method) has three ecotoxicity sub-categories (fresh water, marine and terrestrial), IMPACT 2002+ has two (aquatic and terrestrial). Common impacts to the two methods are eutrophication (EP), acidification (AP), global warming (GWP_{100a}) and ozone layer depletion (ODP) whilst others are equivalents, such as photochemical oxygen demand (POCP) in the CML method (summer smog), which corresponds to the respiratory organics category in IMPACT 2002+. The respiratory organics impact considers the respiratory effects as a result of being exposed to organic compounds in summer smog (Goedkoop and Oele, 2004). Additionally, abiotic depletion (fossil fuels) in the CML method that encompasses aggregated mineral fossil resources is equivalent to the non-renewable energy category in IMPACT 2002+. Impact categories stated in IMPACT 2002+ and not available in the CML method include carcinogens, non-carcinogens, ionising radiation, terrestrial acid/nutrition, land occupancy and mineral extraction and so are not discussed.

Results and discussion

For the similar categories (based on Figures 6 in the manuscript and S2 from the supplementary data) namely terrestrial and (fresh water) aquatic ecotoxicities, no shifts in the ordering of scenarios occurred. However, a significant change of 18-29% was observed in S1-S5 for terrestial ecotoxicity whilst a minimal change in the fresh water/aquatic ecotoxicity of less than 9% was observed in S1-S6 except for S5 with a 12% difference, denoting a substantial sensitivity change of an impact category.

The AP, GWP_{100a} and ODP were comparable in the two methods with a 0–4% change in impacts in all scenarios and no shift in their ordering occurred. The GWP_{100a} has been used as the main impact category in most LCAs including sorbitol (Akmalina et al., 2019), glucaric acid (Thaore et al., 2019) and levulinic acid (Hafyan et al., 2020; Isoni et al., 2018). As for the common category EP, a shift in the ordering of S1, S2 and S6 was noted and differences of 16–52% were observed for S1 and S6. In conclusion, it was generally observed that the two methods had similar trends and agreed in most of the impacts common to them, except in EP that was sensitive to a change in methodology mainly for S1 and S6.

For the equivalent categories, a significant change and reordering of S1 and S3 was seen between photochemical oxidation and respiratory organics. A 69-71% significant difference between photochemical oxidation (in CML) and the respiratory organics (in IMPACT 2002+) was also noted for S1 and S3. Additionally, S5 and S6, the levulinic acid scenarios had 16-17% variances between photochemical oxidation and the respiratory category in the two methods. The difference in S2 and S3 between the two methods for POCP and the respiratory category was insignificant (0.7-1%) therefore, did not reach the sensitivity threshold values.

The non-renewable energy category in IMPACT 2002+ and its equivalent abiotic depletion (fossil fuels) in CML had similar trends and magnitudes of the impacts per scenario and there was no shift in the ordering of the scenarios.

Conclusion

Generally, the results of the IMPACT 2002+ method broadly agreed with CML for the sorbitol, glucaric acid and levulinic acid biorefineries in terrestrial ecotoxicity, GWP_{100}, POCP and abiotic depletion (fossil fuels) except in EP and POCP with its respiratory organics equivalent.

Effect of process water on energy demand

Concerning the effects of process water on the energy demands of a bioenergy self-sufficient biorefinery, it has been established that increased process water increases the biorefinery's energy demand because this water has to be removed during product purification (chapter 4). Reducing process water can be achieved by increasing the feedstock solids loading and it was observed that this improves glucose yields (chapter 4) to an extent. As detailed inchapter 4, a 5% increase in the solids loading (to 35%) led to an 8% reduction in the process steam demand of the $\text{Sorbitol.}_{\text{DA}}$ scenario (S4), which therefore can lead to a reduction in the bypass ratio and subsequently increase the biorefinery capacity. However, optimum solid loadings and the effects of slurries on the pumping capability of pumps should be determined experimentally per feedstock as increasing solids loading on the other hand also affects sugar yields and enzyme performance (Modenbach and Nokes, 2013, 2012). Also, the reduction in the bypass ratio with an increase in solids loading reduces emissions from the CHP combustion unit but consequently leads to an increase in biorefinery emissions due to a higher process throughput. Therefore, future studies can focus on trade-offs between process water and emissions reduction.

Table E1-12: Sources of input parameter uncertainty from literature guidelines*

SO_2 PRODUCTION UNIT	Uncertainty	Comment	Reference
Sulphur	± 0.01 kg	Industrial digital scale with reading to 2 d.p	www.chemistry.stackexchange.com
Air	± 0.01 kg		
Reaction to SO2(conversion)	± 0.005%		
STEX			
Steam explosion tank +reaction	± 0.005%		
Temperature	± 1 deg C		
Pressure	± 0.00031 bar		(Schiering & Schnelle-Werner, 2019)
Flash tank	± 1 deg C	works best at 55 - 77deg C	(Stewartjr, 2014)
PW to 30% solids loading	± 0.01		
heater to get 48°C for enz. Hydrolysis	Q=U A LMTD	U= ± 10%, A= ± 0.01 m and Temp is '± 1 de	(U = 2000W/m$^{2.\circ}$C so absolute uncertainity is ± 200)
DA			
Reaction	± 0.005%		
Air blower temp	± 1 deg C		
Evaporator temp	± 1 deg C		
Evaporator pressure conditions	± 0.00031 bar		
ENZYMATIC HYDROLYSIS			
Reaction	± 0.005%		
Flash tank temp to 50 wt% glucose	± 1 deg C		
Flash tank pressure	± 0.00031 bar		Schiering & Schnelle-Werner, 2019
HYDROGENATION & OXIDATION			
Reaction (temp)	± 1 deg C		
Reaction pressure	± 0.00031 bar		Schiering & Schnelle-Werner, 2019
Heat exchanger to 80OC for flash tank	± 1 deg C		
Flash tank removes water	±1 deg C		
Evaporator	± 1 deg C		
Duty (0 KW) Q=U A LMTD		U= ± 10%, A= ± 0.01 m and Temp is ± 1 deg. C	
OXIDATION			
Reaction (temp)	± 1 deg C		
Reaction pressure	± 0.00031 bar		Schiering & Schnelle-Werner, 2019
Conversion of main prdt	± 0.005%		
Heat exchanger to 80OC for flash tank	± 1 deg C		
Flash tank removes water	± 1 deg C		
Evaporator	±1 deg C		
1st REACTION			
Pressure	± 0.00031 bar		Schiering & Schnelle-Werner, 2019
Temp	± 1 deg C		
Conversion of main prdt	± 0.005%		
2nd REACTION			
Pressure	± 0.00031 bar		Schiering & Schnelle-Werner, 2019
Temp	± 1 deg C		
Conversion of main prdt	± 0.005%		

*The parameter uncertainties obtained from literature guidelines are added to the model variables to generate a worst and best case scenario from the baseline (initial values used) as tabulated in Tables S13-S14.

Table E1-13 (a): Propagated bio-based chemical uncertainty

Scenario	Best (kg/h)	Base (kg/h)	Worst (kg/h)	Mean (μ) (kg/h)	Absolute uncertainty (± kg)	Relative uncertainty (%)
S1	12173	12171	11866	12070	154	1.3
S2	11046	11052	11335	11144	145	1.3
S3	11149	11051	10353	10851	398	3.6
S4	10390	10118	10053	10187	169	1.7
S5	7304	7236	7217	7252	44	0.6
S6 - LA	157	150	143	150	7	4.7
-GVL	6485	6481	6426	6464	30	0.5

Table E1-13(b): Propagated bio-electricity uncertainty

Scenario	Best (kg/h)	Best (kWh)	Worst (kg/h)	Mean (μ) (kg/h)	Absolute uncertainty* (± kWh)	Relative uncertainty* (%)
S1	13.18	13.10	12.79	13.02	0.20	
S2	15.77	15.77	11.05	14.20	2.36	14.98
S3	22.24	22.11	19.60	21.32	1.32	5.97
S4	22.28	22.19	20.83	21.77	0.73	3.27
S5	14.28	14.12	13.09	13.83	0.60	4.21
S6	14.00	13.90	13.77	13.89	0.12	0.83

*The absolute uncertainty obtained by the formula (Maximum value obtained– Minimum value obtained)/2 and the relative uncertainty by the formula (Absolute uncertainty/ baseline value)*100%).

Table E1-14 (a-f): Uncertainty per category for S1-S6 using scenario analysis

Scenario 1	Unit	Max (unit)	Base (unit)	Min (unit)	Mean (µ) (unit)	Absolute uncertainty (± Unit)	Relative uncertainty (%)
Abiotic depletion (ADP)	kg Sb eq.	2.34E-05	2.28E-05	2.30E-05	2.31E-05	2.00E-07	8.79E-01
Abiotic depletion (fossil fuels)	MJ	103.90	103.02	104.10	103.67	0.10	0.10
Global warming potential (GWP)	kg CO2 eq.	7.51	6.72	6.60	6.94	0.46	6.78
Ozone layer depletion (ODP)	kg CFC - 11 eq.	1.30E-06	1.19E-06	1.90E-06	1.46E-06	3.00E-07	25.13
Human toxicity	kg 1,4 - DB eq.	3.15	2.82	2.69	2.89	0.23	8.15
Fresh water aquatic ecotoxocity	kg 1,4 - DB eq.	0.77	0.87	0.93	0.86	0.08	9.24
Marine aquatic ecotoxicity	kg 1,4 - DB eq.	2885.00	2880.02	2826.00	2863.67	29.50	1.02
Terrestrial ecotoxicity	kg 1,4 - DB eq.	0.01	0.01	0.01	0.01	0.001	9.24
Photochemical oxidation (POCP)	kg C2H4 eq.	0.01	0.01	0.01	0.01	0.00	5.08
Acidification (AP)	kg SO2 eq.	0.20	0.16	0.15	0.17	0.03	15.20
Eutrophication (EP)	kg PO3-4 eq.	0.57	0.63	0.68	0.63	0.06	8.71

(a)

Scenario 2	Unit	Max (unit)	Base (unit)	Min (unit)	Mean (µ) (unit)	Absolute uncertainty (± Unit)	Relative uncertainty (%)
Abiotic depletion (ADP)	kg Sb eq.	0.00002	1.38E-05	2.30E-05	2.01E-05	2.00E-07	1.44E+00
Abiotic depletion (fossil fuels)	MJ	104.90	104.04	104.01	104.32	0.45	0.43
Global warming potential (GWP)	kg CO2 eq.	12.78	12.63	12.48	12.63	0.15	1.19
Ozone layer depletion (ODP)	kg CFC - 11 eq.	1.30E-06	1.20E-06	1.50E-06	1.33E-06	1.00E-07	8.34
Human toxicity	kg 1,4 - DB eq.	3.15	2.81	2.69	2.88	0.23	8.18
Fresh water aquatic ecotoxocity	kg 1,4 - DB eq.	0.87	0.87	0.93	0.89	0.03	3.45
Marine aquatic ecotoxicity	kg 1,4 - DB eq.	2885.00	2882.56	2876.00	2881.19	4.50	0.16
Terrestrial ecotoxicity	kg 1,4 - DB eq.	0.01	0.01	0.01	0.01	0.002	13.63
Photochemical oxidation (POCP)	kg C2H4 eq.	0.003	0.002	0.002	0.002	0.000	10.45
Acidification (AP)	kg SO2 eq.	0.01	0.01	0.01	0.01	0.002	10.65
Eutrophication (EP)	kg PO3-4 eq.	0.17	0.10	0.18	0.15	0.005	4.98

(b)

Scenario 3	Unit	Max (unit)	Base (unit)	Min (kg/h)	Mean (µ) (unit)	Absolute uncertainty (± Unit)	Relative uncertainty (%)
Abiotic depletion (ADP)	kg Sb eq.	0.00002	2.31E-05	2.30E-05	2.32E-05	2.00E-07	8.65E-01
Abiotic depletion (fossil fuels)	MJ	114.09	113.06	113.01	113.39	0.54	0.48
Global warming potential (GWP100a)	kg CO2 eq.	12.68	13.98	14.20	13.62	0.76	5.44
Ozone layer depletion (ODP)	kg CFC - 11 eq.	1.30E-06	1.27E-06	1.19E-06	1.25E-06	5.50E-08	4.33
Human toxicity	kg 1,4 - DB eq.	3.05	2.93	2.79	2.92	0.13	4.43
Fresh water aquatic ecotoxocity	kg 1,4 - DB eq.	0.90	0.93	0.94	0.92	0.02	2.14
Marine aquatic ecotoxicity	kg 1,4 - DB eq.	2885.00	3175.42	2876.00	2978.81	4.50	0.14
Terrestrial ecotoxicity	kg 1,4 - DB eq.	0.013	0.012	0.011	0.01	0.001	8.93
Photochemical oxidation (POCP)	kg C2H4 eq.	0.002	0.007	0.001	0.003	0.001	8.08
Acidification (AP)	kg SO2 eq.	0.01	0.13	0.01	0.05	0.002	1.18
Eutrophication (EP)	kg PO3-4 eq.	0.67	0.62	0.58	0.62	0.045	7.28

(c)

Scenario 4	Unit	Max (unit)	Base (unit)	Min (kg/h)	Mean (µ) (unit)	Absolute uncertainty (± Unit)	Relative uncertainty (%)
Abiotic depletion (ADP)	kg Sb eq.	0.00001	1.38E-05	2.30E-05	1.67E-05	4.80E-06	3.47E+01
Abiotic depletion (fossil fuels)	MJ	112.70	111.39	111.01	111.70	0.84	0.76
Global warming potential (GWP)	kg CO2 eq.	12.68	13.31	13.50	13.16	0.41	3.08
Ozone layer depletion (ODP)	kg CFC - 11 eq.	1.30E-06	1.25E-06	1.19E-06	1.25E-06	5.50E-08	4.39
Human toxicity	kg 1,4 - DB eq.	3.05	2.90	2.79	2.91	0.13	4.48
Fresh water aquatic ecotoxocity	kg 1,4 - DB eq.	0.90	0.92	0.94	0.92	0.02	2.17
Marine aquatic ecotoxicity	kg 1,4 - DB eq.	3185.00	3111.07	3106.00	3134.02	39.50	1.27
Terrestrial ecotoxicity	kg 1,4 - DB eq.	0.013	0.012	0.009	0.01	0.002	18.85
Photochemical oxidation (POCP)	kg C2H4 eq.	0.003	0.003	0.003	0.003	0.000	5.98
Acidification (AP)	kg SO2 eq.	0.01	0.02	0.01	0.01	0.002	7.73
Eutrophication (EP)	kg PO3-4 eq.	0.17	0.10	0.18	0.15	0.005	4.95

(d)

Scenario 5	Unit	Max (unit)	Base (unit)	Min (kg/h)	Mean (µ) (unit)	Absolute uncertainty (± Unit)	Relative uncertainty (%)
Abiotic depletion (ADP)	kg Sb eq.	0.00001	1.24E-05	1.29E-05	1.27E-05	6.50E-08	5.23E-01
Abiotic depletion (fossil fuels)	MJ	132.70	132.31	131.01	132.01	0.84	0.64
Global warming potential (GWP100a)	kg CO2 eq.	8.93	8.80	9.62	9.12	0.35	3.92
Ozone layer depletion (ODP)	kg CFC - 11 eq.	1.30E-06	1.39E-06	1.39E-06	1.36E-06	4.50E-08	3.25
Human toxicity	kg 1,4 - DB eq.	3.08	3.02	2.99	3.03	0.04	1.49
Fresh water aquatic ecotoxocity	kg 1,4 - DB eq.	0.97	0.96	0.98	0.97	0.003	0.26
Marine aquatic ecotoxicity	kg 1,4 - DB eq.	3485.00	3449.18	3406.00	3446.73	39.50	1.15
Terrestrial ecotoxicity	kg 1,4 - DB eq.	0.013	0.011	0.011	0.01	0.001	10.94
Photochemical oxidation (POCP)	kg C2H4 eq.	0.004	0.003	0.003	0.003	0.000	10.42
Acidification (AP)	kg SO2 eq.	0.07	0.07	0.07	0.07	0.002	2.05
Eutrophication (EP)	kg PO3-4 eq.	0.49	0.44	0.49	0.47	0.001	0.11

(e)

Scenario 6	Unit	Max (unit)	Base (unit)	Min (kg/h)	Mean (µ) (unit)	Absolute uncertainty (± Unit)	Relative uncertainty (%)
Abiotic depletion (ADP)	kg Sb eq.	0.00016	1.49E-04	1.59E-04	1.56E-04	6.50E-07	4.35E-01
Abiotic depletion (fossil fuels)	MJ	969.70	967.53	966.01	967.75	1.85	0.19
Global warming potential (GWP100a)	kg CO2 eq.	48.63	48.03	50.41	49.02	0.89	1.85
Ozone layer depletion (ODP)	kg CFC - 11 eq.	5.93E-06	5.91E-06	5.94E-06	5.93E-06	4.50E-09	0.08
Human toxicity	kg 1,4 - DB eq.	18.78	18.47	18.19	18.48	0.30	1.60
Fresh water aquatic ecotoxocity	kg 1,4 - DB eq.	10.77	10.87	10.98	10.87	0.10	0.94
Marine aquatic ecotoxicity	kg 1,4 - DB eq.	40805.00	40736.05	40654.00	40731.68	75.50	0.19
Terrestrial ecotoxicity	kg 1,4 - DB eq.	0.063	0.061	0.061	0.06	0.001	2.04
Photochemical oxidation (POCP)	kg C2H4 eq.	0.039	0.038	0.029	0.035	0.005	12.58
Acidification (AP)	kg SO2 eq.	0.25	0.25	0.24	0.25	0.005	2.08
Eutrophication (EP)	kg PO3-4 eq.	0.49	0.39	0.38	0.42	0.054	13.90

(f)

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E-2: Environmental loads for all scenarios including the CHP Base case

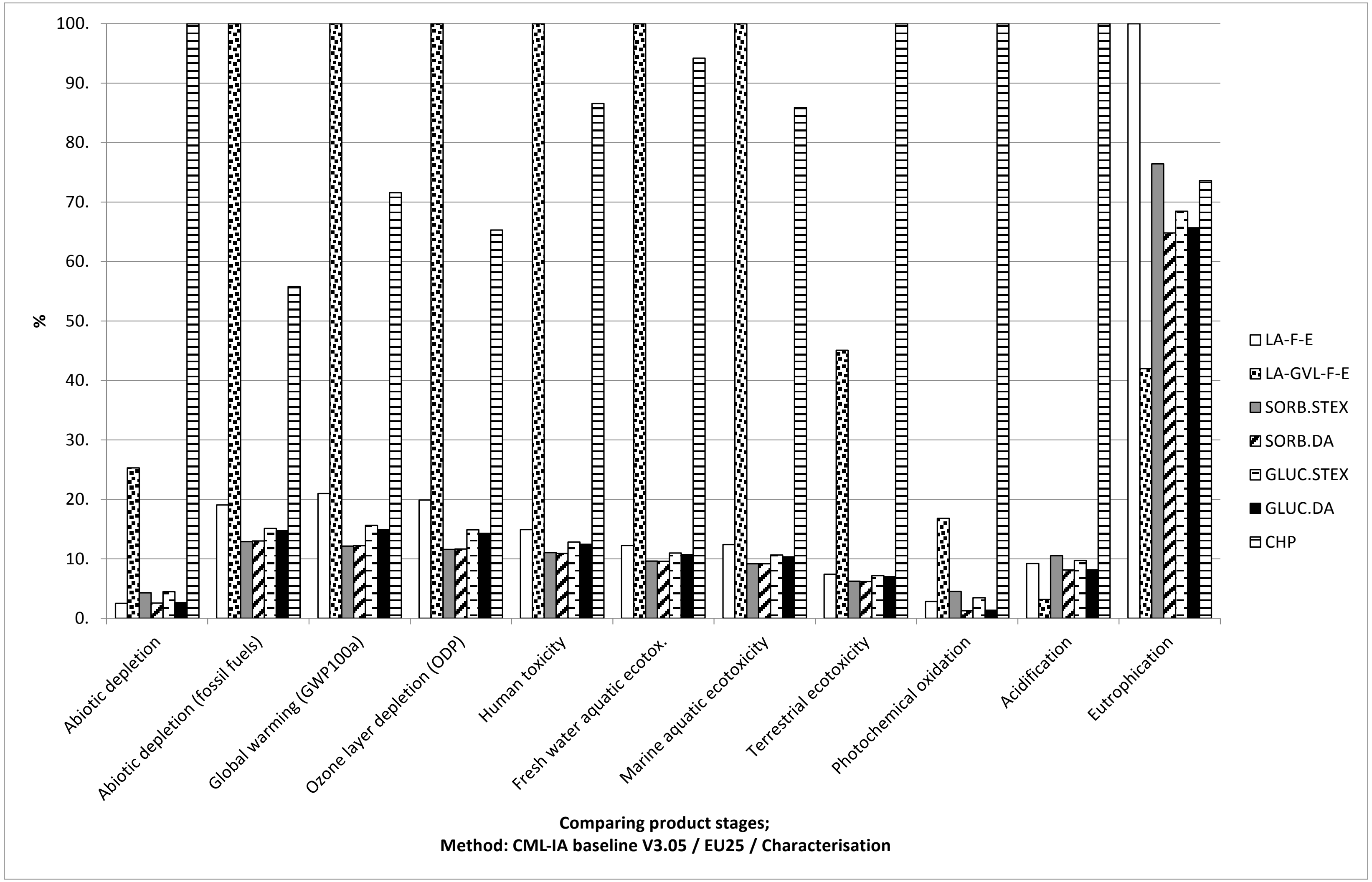

Figure E2-1: Environmental loads for the CHP base case and scenarios (actual values in Table F1-1 Appendix F-1)

APPENDIX F

F-1*:* Economic, environmental and social indicators and values used in the MCDA

Table F1-1: MCDAs input data

Label	**LA-F-E**	**LA-GVL-F-E**	**SORB.DA**	**GLUC.DA**	**CHP**
Environmental indicators					
Abiotic depletion	2.5	25.3	2.6	2.6	100.
Abiotic depletion (fossil fuels)	19.	100.	13.	14.7	55.8
Global warming (GWP_{100a})	21.	100.	12.2	14.9	71.6
Ozone layer depletion (ODP)	19.9	100.	11.7	14.3	65.3
Human toxicity	14.9	100.	10.9	12.5	86.6
Fresh water aquatic ecotox.	12.3	100.	9.6	10.7	94.2
Marine aquatic ecotoxicity	12.4	100.	9.2	10.4	85.9
Terrestrial ecotoxicity	7.4	45.1	6.2	7.	100.
Photochemical oxidation	2.8	16.8	1.3	1.4	100.
Acidification	9.2	3.1	8.1	8.2	100.
Eutrophication	100.	42.	64.8	65.7	73.6
Social indicator					
Jobs	52	60	49	49	18
Techno-economics					
NPV(US$ million)	139	253	17.2	16	6.5
IRR (%)	17	23	10.7	10.7	10.3