

Valorisation of Bio-aromatics from Pulp Mill Residues and Commercial Forest Species in South Africa

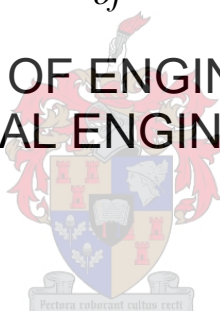
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Declaration

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Abstract

The design of industrial processes towards the production of bio-based polyethylene terephthalate (PET) gained much attention after the introduction of the PlantBottle®. This is further motivated through sustainability appeal, a continuous increase in the PET market growth as well as economic gains (most importantly revenue generation) through commercialisation of the designed process. The first component of PET, monoethylene glycol, is currently commercially produced from a bio-based source, while there is a need for a production scheme for the second component, purified terephthalic acid (TPA), which has not yet been developed. In this project, investigation of reported experimental data lead to the development of a number of novel processing schemes, which were subsequently subjected to technical and economic analyses to determine feasibilities. Multiple companies, including The Coca-Cola Company, Virent and Anellotech, have invested in this research. However technical and economic data from these sources are not publicly released, therefore alternative methods of comparison where selected.

The developed processing schemes firstly aimed to utilise second-generation feedstocks for the extraction of TPA precursors, based on feedstock availability in South Africa (scenario one). Focus was placed on terephthalic acid production from terpene precursors found in *Eucalyptus grandis* leaves and *Pinus elliottii* needles (forestry waste sources) as well as pre-hydrolysate relief gas from the pulping processes (pulp mill residue source). The industrial application of the proposed schemes was simulated in Aspen Plus®, where flow-sheet analysis revealed the production capabilities and utility demands of each scheme. Energy efficiency optimisation was performed through pinch point analysis applied through Aspen Plus®. Costing of these processes (through ASPEN Process Economic Analyser and costing formulae) as well as the calculation of the economic indicator, DCFROR, revealed that the second-generation processes are economically unviable. Contributing factors include low concentration of major terpenes (TPA precursors) within feedstocks, necessity for pure oxygen for two major section of each process, complex purifications (due to similar boiling points between major terpenes and by-products/multiple other terpenes) and small scale production that lead to a high average production cost.

The second aim (scenario two) involved determining the economic viability of first and second generation processes at a 10% PET market share (reasonable share for novel processes in the short-term). The same approach was used to derive the first generation processes as for scenario one. The discounted cash flow analyses of each process

considered a 16% hurdle rate (for nominal terms used) to determine the minimum TPA selling price:

Process	Minimum selling price	Green premium
Pine	\$5 227/tonne	647%
Eucalyptus	\$22 443/tonne	3106%
PHR	\$38 114/tonne	5345%
Starch-based	\$1953/tonne	179%
FDCA	\$2130/tonne	204%

Through the evaluation of these selling prices together with their accompanying green premiums, the second generation processes were deemed economically unviable. Through the selling price comparison of the TPA equivalent, FDCA (also from a starch-based feedstock), which was deemed worthwhile for further research and optimisation, it was concluded that the first generation process has the potential to become economically viable. Therefore, it has the potential to reach the realistic premium of 125% through fewer processing steps, more effective purification methods, optimised and less expensive catalysts and additional by-product revenue.

Ultimately, this process initialises the opportunities towards fully bio-based PET.

Samevatting

Die ontwerp van industriële prosesse wat fokus op die vervaardiging van bio-gebaseerde poliëteleen-tereftalaat (PET) het populariteit verwerf tydens die bekendstelling van die PlantBottle®. Motivering vir laasgenoemde is versterk deur die volhoubaarheids eienskappe daarvan, die groei van die PET mark asook die winste geassosieer met die kommersialisering van die ontwerpte prosesse. PET bestaan eerstens uit monoëtileenglikool (MEG), wat op hede op 'n bio-basis gekommersialiseer is. Daarenteen is 'n bio-basis proses vir die tweede komponent, gesuiwerde tereftalsuur (TPA), nog nie ontwikkel nie. In hierdie projek het die ondersoek op huidige literatuur (eksperimentele data) gelei tot die ontwikkeling van nuwe prosesskemas wat deur tegniese en ekonomiese metodes geanaliseer is, om ten einde individuele lewensvatbaarhede te bepaal. Verskeie maatskappye, insluitende The Coca-Cola Company, Virent en Anellotech, het in hierdie navorsing belê. Ongelukkig is die tegniese en ekonomiese data van hierdie prosesse nie beskikbaar aan die publiek nie en daarom was alternatiewe metodes van vergelyking van gebruik gemaak.

Die eerste doel van hierdie prosesskemas is om gebruik te maak van tweede generasie roumateriale as bronne vir die ekstraksie van TPA voorlopers (senario een). Literatuur was oorweeg met die fokus dat hierdie projek die Suid-Afrikaanse kapasiteit van die roumateriaal in ag neem. Fokus was geplaas op die vervaardiging van tereftalsuur vanuit terpeen-voorlopers wat in salignabloekom blare en basden naalde (bosbou-afval bronne) asook pre-hidrolisaat verligtingsgas (PHR) (papierfabriek afvalstroombron) gevind word. Die industriële toepassing van die ontwikkelde prosesskemas is in Aspen Plus® gesimuleer, waarna die produksiekapasiteit en energieverbruik deur 'n vloeiskema analise van elke proseskema. Energie verbruiksoptimalisering is gedoen deur gebruik te maak van energie-integrasie ("pinch-point") analise in Aspen Plus®. Die kostes geassosieer met elke proses was bereken deur gebruik te maak van ASPEN Process Economic Analyser asook koste-formules. Die berekening van die ekonomiese indikator, DCFROR, het getoon dat hierdie prosesse nie ekonomies lewensvatbaar is nie. Bydraende faktore sluit in; 'n lae konsentrasie van die hoof terpene wat in die roumateriaal voorkom, die gebruik van suiwer suurstof in twee belangrike afdelings van elke proses, suiweringsmetodes wat vermoeilik is deur ander terpene en byprodukte asook die kleinskaalse produksie wat gelei het tot 'n hoë gemiddelde produksiekoste.

Die tweede doel (senario twee) ondersoek die ekonomiese lewensvatbaarheid van eerste en tweede generasie prosesse op 'n 10% PET markskaal ('n redelike aandeel tot die mark vir

nuwe produk in die korttermyn). Dieselfde stappe, soos in senario een, was gebruik om die eerste generasie proses te ontwikkel. Die 'discounted cash flow analyses' van elke proses het 'n struikel-persentasie van 16% gebruik (omdat nominale terme gebruik was) om elke minimum TPA verkoopsprys te bepaal:

Proses	Minimum verkoopsprys	'Green premium'
Pine	\$5 227/tonne	647%
Eucalyptus	\$22 443/tonne	3106%
PHR	\$38 114/tonne	5345%
Stysel basis	\$1953/tonne	179%
FDCA	\$2130/tonne	204%

Deur die analise van elke verkoopsprys, tesame met elke ooreenkomstige 'green premium', is die tweede generasie prosesse as nie ekonomies lewensvatbaar verklaar. Deur die vergelyking met die TPA ekwivalent, FDCA (ook vervaardig vanaf styselbronne), was dit bevestig dat die eerste generasie wel die potensiaal het om ekonomies lewensvatbaar te word deur verdere navorsing en optimalisering. Dit is ook bevestig dat dit die potensiaal het om die realistiese 'green premium' van 125% te haal deur minder prosesseringstappe, meer effektiewe suiweringsmetodes, geoptimaliseerde en goedkoper kataliste asook addisionele byprodukwinste.

Uiteindelik, bied hierdie proses die begin van vele geleenthede wat poog om volledige bio-gebaseerde PET te vervaardig.

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“We shall need a substantially new way of thinking if humanity is to survive”

Albert Einstein (1954)

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Nomenclature

Chemical formulae

$\gamma\text{-Al}_2\text{O}_3$	Gamma Alumina	H_2	Hydrogen Gas
$\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$	Calcium Chloride Hexahydrate	H_2S	Hydrogen Sulphide
CaO	Calcium Oxide	H_2SO_4	Sulphuric Acid
Ca(OH)_2	Calcium Hydroxide	HNO_3	Nitric Acid
CaSO_4	Gypsum	KMnO_4	Potassium Permanganate
CeO_2	Cerium Oxide	MgO	Magnesium Oxide
CH_4	Methane Gas	$\text{Mn(CH}_3\text{COO)}_2 \cdot 4\text{H}_2\text{O}$	Manganese (II) Acetate Tetrahydrate
CH_3SH	Methyl Mercaptan	Na_2SO_4	Sodium Sulphate
$(\text{CH}_3)_2\text{S}$	Dimethyl Sulphide	Na_2O	Sodium Oxide
$(\text{CH}_3)_2\text{S}_2$	Dimethyl Disulphide	NaOH	Sodium Hydroxide
CO	Carbon Monoxide	O_2	Oxygen Gas
CO_2	Carbon Dioxide	Pd	Palladium
$\text{Co(CH}_3\text{COO)}_2 \cdot 4\text{H}_2\text{O}$	Cobalt (II) Acetate Tetrahydrate	SiO_2	Silicon Dioxide
Co(OAc)_2	Cobalt Acetate	$\text{T}(p\text{-Cl})\text{PPMnCl}$	Tetra(<i>p</i> -chlorophenylporphinato) manganese

Units of measurement and other

μm	Micrometre	km	Kilometre
$^\circ\text{C}$	Degrees Celsius	kW	Kilowatt
bar	Bar Pressure	$\text{m}_{\text{Terpene}}/\text{m}_{\text{Essential Oil}}$	Terpene Mass per Essential Oil Mass
g/hr	Gram per Hour	mg/L	Milligram per Litre
ha	Hectare	MJ/kg	Mega Joule per Kilogram
kg/hr	Kilogram per Hour	mm	Millimetre
kg/kmol	Kilogram per Kilomole	MPa	Mega Pascal
kg/m^3	Kilogram per Cubic Metre	ppm	Parts per Million

Abbreviations

4-CBA	4-Carboxybenzaldehyde
1G	First generation
2G	Second generation
ACI	Annual cash income
APEA	ASPEN Process Economic Analyser
APV	Annual present value
BCFZ	$\text{BaZr}_x\text{Co}_y\text{Fe}_z\text{O}_{3-\delta}$
CCEI	Catalysis Centre for Energy Innovation
CEPCI	Chemical engineering plant cost index
CFCI	Corrected fixed capital investment
CHP	Combined heat and power
CST	Crude sulphonated turpentine
DC	Depreciation charge
DCM	Dichloromethane
DF	Discount factor
DMF	2, 5-Dimethylfuran
DMT	Dimethyl terephthalate
DR	Discount rate
DCFROR	Discounted cash flow rate of return
EG	Ethylene glycol
FAU Y/X	Faujasite Y/X
FCI	Fixed capital investment
GDP	Gross domestic product
HMF	2-Methyl-5-hydroxymethylfuran
HQ	Hydroquinone
ICI	Inorganic chemical indices
IRR	Internal rate of return
ISBL	Inside battery limits
IT	Income tax
IUPAC	International Union of Pure and Applied Chemistry
LIP	Loan interest payment
LP	Loan payment
MC	Mid-Century Process
MEG	Monoethylene glycol
MF	Multiplying factor
MOR	Mordenite
MTSP	Minimum TPA selling price
MW	Molecular weight
NC	Non-conventional
NMP	N-Methyl pyrrolidone
NPV	Net present value

NSSC	Neutral Sulphite Semichemical
PAMSA	Paper Manufacturers Association of South Africa
PBT	Polybutylene terephthalate
PC	Purchase cost
PET	Polyethylene terephthalate
PHR	Pre-hydrolysis relief-gas
RK-Soave	Redlich-Kwong Soave
ROI	Return on investment
SAPPI	South African Pulp and Paper Industries
TAS	Total annual sales
TDC	Total direct cost
TEIC	Total equipment installed cost
THF	Tetrahydrofuran
TIC	Total installed cost
TPA	Terephthalic acid
TPC	Total production cost
UNQUAC	Universal Quasi-Chemical
WC	Working capital

1 Introduction

1.1 Background

The global reliance on plastic products has grown significantly since the early twentieth century, because of the many advantages that plastics offer, such as versatility, durability, non-corrosive nature and multiple applications. The annual global consumption has grown from 5 million tonnes of plastic during the 1950's to 280 million tonnes.

Although offering advantages to the customer, plastics have negative effects on the environment in terms of the degradation period, toxic chemicals diffusing from the plastic, harmful effect on wildlife exposed to plastic waste and use of non-sustainable sources for production (Knoblauch, 2009).

Currently, plastics are produced almost entirely from fossil fuel sources, utilising approximately 6% of the oil produced globally. Graeme Wearden (2016) predicted that the global oil consumption will rise to 20% by 2050, while the associated carbon emissions will rise from 1% to 15%. There is, however, a slow decrease in the use of fossil fuels, through the production of plastics from biomaterials, as the demand for the utilization of sustainable materials increases (British Plastics Federation, 2008).

According to Farouk (2015), there is a global movement towards the "Third Industrial Revolution", where more focus is placed on sustainability in the production of energy and consumer goods. This 'greener movement' is an effort to reduce the reliance on fossil fuels (with its detrimental impacts on the environment) and to implement solutions that look at the preservation of resources instead of the diminution thereof.

One plastic, namely polyethylene terephthalate (PET), has gained particular interest as it contributes approximately 24% to the global thermoplastic market (Figure 1) (Nowlin, 2014). Polyester fibres made from PET were first produced in the early twentieth century and a few decades later, it was discovered that it could also be used in the packaging and resin industry (Zein *et al.*, 2010). Many products used today are contained within PET packaging, such as cosmetics, consumable liquids, edible substances and pharmaceuticals (Mudgal & Lyons, 2011).

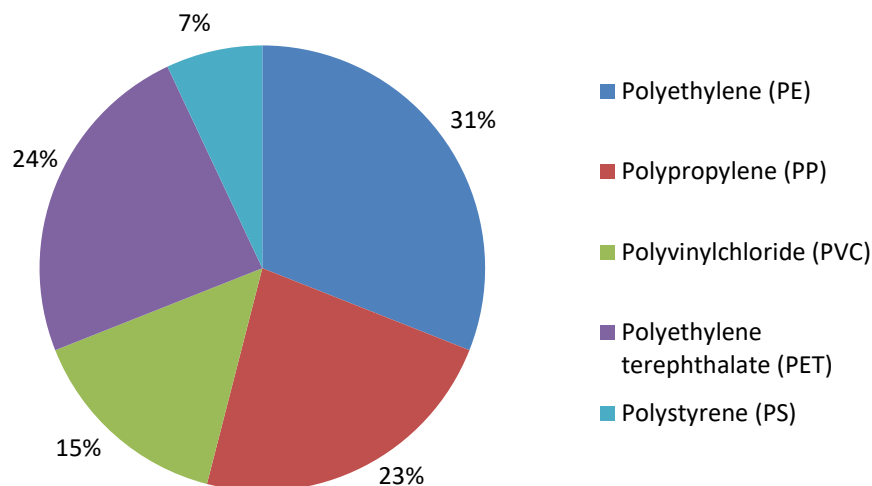


Figure 1: Global thermoplastic market share

The production of PET involves a series of esterification and poly-condensation reactions using approximately 70 wt% purified terephthalic acid (TPA) and 30 wt% monoethylene glycol (MEG), or alternatively, dimethyl terephthalate (DMT) and ethylene glycol (EG) (Banat & El-Rub, 2001). Considering the above-mentioned need for sustainability and resource preservation, there is a need to develop processes in which these PET precursors, TPA and MEG, are produced from bio-based means. These processes partially aid towards the development of fully bio-based PET.

MEG is currently produced from biomass on a commercial scale using xylitol as intermediate chemical compound. Xylitol can be produced from xylose through hydrogenation. The largest producer of commercial bio-MEG, M&G Chemicals, uses a Ni/C catalysed process to convert bagasse to MEG and PG (propylene glycol) (Bari, 2014)).

Since 2009, Coca-Cola has promoted a plastic liquid container, called PlantBottle™, as 30% “green content” due to the sugar-cane derived bio-MEG used during the production of the PET container. Coca-Cola sources bio ethanol (produced from fermenting sugar cane juice) from Brazil, where after it is converted into bio-MEG in India. The remaining 70% (terephthalic acid) has not yet been successfully produced from biomaterials on a commercial scale (Schut, 2012).

Therefore, an opportunity arises to produce bio-based terephthalic acid for polyethylene terephthalate production from sustainable biomaterials (i.e. bio-PET). This, in turn, will

gradually diminish the reliance on fossil-based sources, such as crude oil, that is currently used to produce TPA.

Table 1 shows the possible production pathways of bio-TPA. Various companies such as VTT Finland, Virent and Anellotech have invested into this research, where the first commercial scale bio-PET operation (using partially bio-based TPA) is said to commence with plant construction in 2018 with a capacity of 5 000 tonnes per annum (Johnson. 2017). Pathways for bio-TPA production from furfural or terpene pathways are still in the laboratory/research phase, while the production of TPA from isobutene obtained from sugary biomass is in the pilot plant stage. Bio-based *p*-xylene is currently being produced on a pre-industrial scale from isobutene (produced from a starch source) by Gevo. This, in turn is sold to Toray Industries for further processing (Toray, 2016). *p*-Xylene can be converted to TPA through oxidation and purified to produce a pure product with minimal by-products. Minimising by-products ensures a higher quality PET plastic in terms of colour, durability and gas and chemical permeability.

From a South African location perspective, all three options listed in Table 1 may be technically viable. Although accessible, most of the biomass sources or waste (such as rice husk and bagasse) that could serve as raw material for these monomers are utilised in other applications such as the production of cement, silica (Kaviyarasu *et al.*, 2016), biogas and electricity or used as food sources (Grain SA, 2015).

Table 1: Status of TPA production pathways

Biomass source	Intermediate Compound(s)	Processes	Production Status
Corn and rice waste (1G)	Furfural	Oxidation, dehydration, hydrolysis (Tachibana <i>et al.</i> , 2015)	Research
Forestry waste, citrus and spices (2G)	Terpenes	Dehydrogenation and oxidation (Howgego, 2014)	Research
Bagasse, palm and starches (1G)	Isobutene, <i>p</i> -xylene	Fermentation, cyclodimerization, oxidation (Toray, 2016)	Pilot Plant

On the other hand, forestry wastes (such as leaves and bark) that are lignocellulosic-based feedstocks or second-generation (2G) feedstocks have been underutilised in South African commercial forests. These feedstocks have the potential to be used to extract terpenes towards the production of bio-based TPA. Terpenes, such as α -pinene and cineole, can be converted through dehydrogenation, oxidation and purifications steps to purified bio-TPA. However, a complete process scheme has not yet been developed and no accompanying economics exist to determine whether such a process can be competitive against the current

commercial fossil-based production. This project investigates the possibility of producing bio-TPA in South Africa from these terpenes extracted from forestry waste and pulp mill residues.

A comparison will be made with first-generation (1G) feedstocks or starch-based feedstocks that can be utilised for the production of bio-TPA. It involves the processing and conversion of non-food starches such as grain sorghum and triticale that can be depolymerised through fermentation or catalytic reaction to glucose. Through additional catalytic reactions and purifications, a pure p-xylene product can be produced that can be oxidised to TPA. The use of grain sorghum and triticale is of particular interest as feedstock as its cultivation is currently being supported by the South African government through subsidies towards the production of bio-ethanol (Du Preez & Görgens, 2015). An advantage to utilising triticale as feedstock is that high levels of endogenous amylases within triticale allows up to 99.6% of the starch contained within to degrade during saccharification, an 18% higher degradation potential than other wheat sources (Eudes, 2015).

1.2 Problem statement

In order to reduce the dependence of PET production on fossil sources, the production of bio-based TPA is necessary, so that the resulting bio-PET is produced completely from sustainable sources.

Although available literature concerning the production of bio-TPA from bio-based sources containing terpenes, such as forestry waste and pulp mill residues (2G feedstocks), covers only a few facets of the terpene conversion, the development of a comprehensive process of TPA from bio-based sources is absent in literature. Thus, it is necessary to evaluate the technical and financial feasibility of a prospective industrial process.

Similarly, the conversion of 1G feedstocks to TPA can be described through literature but a complete process scheme with its accompanying economics is yet to be developed and assessed.

1.3 Aims and objectives

The aim of this study is to determine whether it is economically viable to produce terephthalic acid in South Africa using 1G or 2G feedstocks. Two scenarios were investigated to address this aim; firstly it was determined whether it is economically viable to produce TPA from 2G feedstocks on the basis of the South African biomass capacity (client's scenario). The second

scenario assumed that a realistic PET market share (10%) could be achieved. This share was used to determine the production of TPA (1G and 2G processes) scale at which the economic viability was evaluated. The detailed objectives of these scenarios are as follows:

Scenario 1	Scenario 2
Estimate the availability of biomass resources from which terpenes can be extracted from for bio-TPA production	Selection of most effective processes towards the production of TPA from 1G feedstocks
Selection of most effective processes towards the production of TPA from 2G feedstocks	Perform technical modelling of oxidation and purification of p-xylene to TPA in Aspen Plus®
Perform technical modelling on selected processes in Aspen Plus®	Determine costs associated with the construction, set-up and production of the TPA production plant (1G)
Compare 2G process modelling results	Scale-up economics from Scenario 1 to 10% PET market share scale
Determine costs associated with the construction, set-up and production of the TPA production plants (2G)	Determine economic feasibility of 1G and 2G processes through economic indicators, such as discounted cash flow rate of return and minimum TPA selling price
Determine economic feasibility of selected processes through economic indicators, such as discounted cash flow rate of return and minimum TPA selling price	Compare 1G and 2G process economics based on minimum TPA selling price

1.4 Thesis structure

Figure 2 shows the overall research structure that was followed and includes; literature review, process selection and description, technical modelling and heat integration as well as costing and economic analyses. The literature review examines all literature pertaining to feedstocks, residues as well as methods for the extraction, conversion and purification of TPA intermediates. Process selection and description involves combining the selected literature to define each process description. The modelling methodology of each process is described thereafter. Finally, costing of each plant and the comparison of each process' economics were completed.

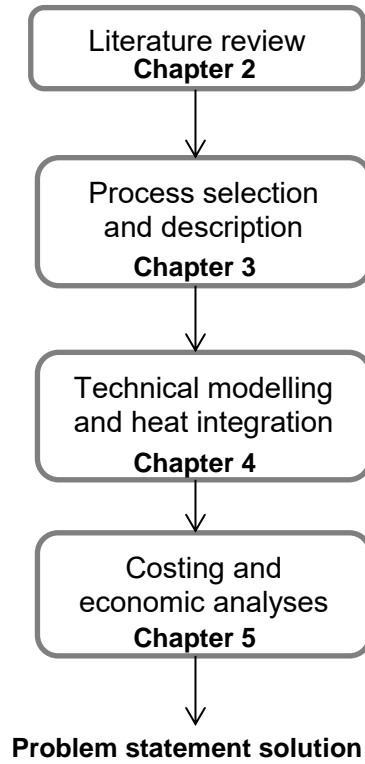


Figure 2: Overall research structure

2 Literature review

This chapter discusses the appropriate sources of 1G and 2G feedstocks within a South African context, current process technologies as well as the main intermediate compounds found in each process scheme. The selection of these sources will depend on the biomass capacity, major terpene/starch content as well as limiting the number of processing/purifying steps towards the production of bio-based terephthalic acid. The selection of the pulp mill residue will depend greatly on the type of pulping technology, which affects the content and processing of the residue to isolate the contained major terpene. From these processes, the most effective and/or data rich will be selected and outlined in Chapter 3.

2.1 Forestry sector

2.1.1. Plantation distribution and content

In 2013, the total allocated forest area for plantations in South Africa was approximated at 1.5 million hectares, and accounted for about 1.2% of the total area of South Africa. The three different genera seen within South African plantations are Pine, Eucalyptus and Wattle (Acacia) (Forestry, 2014). Table 2 depicts the names of the species of these three genera used in South African plantations.

Table 2: South African commercial forest species

Genus	Species
Pinus	<i>P. patula</i> , <i>P. elliotii</i> , <i>P. canariensis</i> , <i>P. halapensis</i> , <i>P. pinaster</i> , <i>P. pinea</i> , <i>P. radiata</i> , <i>P. roxburghii</i> and <i>P. taeda</i>
Eucalyptus	<i>E. grandis</i> , <i>E. dunnii</i> , <i>E. smithii</i> , <i>E. saligna</i> , <i>E. badjensis</i> , <i>E. nitens</i> , <i>E. dorrigoensis</i> , <i>E. fraxinoides</i> , <i>E. macarthurii</i> , <i>E. benthamii</i> , <i>E. globulus</i> and <i>E. fastigata</i>
Acacia	<i>A. mearnsii</i> , <i>A. implexa</i> , <i>A. melanoxylon</i>

2.1.1.1 Review of *Pine* species

Pinus patula has the largest planted area of *Pine* species in South African plantations (61% of the total planted *Pine* area), but has lower terpene yields and therefore, *Pinus elliotii* is a more viable choice in terms of terpene yield. It covers 29% of the total planted *Pine* area in South Africa, which is approximately 180 000 ha (Sappi, 2012).

P. elliotii, also known as slash *Pine* or pitch *Pine*, grows optimally in regions where temperatures do not regularly fall below 4°C or exceed 32°C and the annual rainfall is between 650 to 2500 mm in an acidic soil that has a high draining capacity. The natural origin of *P. elliotii* is the north-eastern part of North America and has been introduced to a few other countries including South Africa, Australia, New Zealand and Zambia. To obtain the seeds for new plantation of *Pine* trees, cones are sun-dried or oven dried at a temperature of 48°C to

remove moisture and initiate germination. After about 20 days, the seedlings are allowed to grow in a nursery usually with the aid of mycorrhizae, which is a symbiotic relationship between fungi and the roots of the seedling aiding in water, sugar and mineral intake. At a length of about 30cm and 4 to 8 months of age, the seedlings are transferred to a plantation area. Weed control is needed in the first two years after plantation to eliminate the growth inhibition of the young trees. Pine trees usually have a rotation cycle of 20 to 25 years, when used for pulping, and 45 to 55 years, when used for timber (Louppe, 2008).

Mature *P. elliottii* wood has a density range of 420 to 700 kg/m³ and a moisture content of approximately 12%. Wood fibres are on average 2 to 4mm long, while the diameter ranges from 39 to 54 µm. A typical dry-weight chemical composition of the wood is as follows: 57 to 73% holocellulose (total polysaccharide fraction), 36 to 42% alpha-cellulose and 28 to 32% lignin (structural support of wood) (Louppe, 2008).

2.1.1.2 Review of Eucalyptus species

Eucalyptus grandis is considered to be the most important hardwood in the South African forestry industry and has a planted area of just under 300 000 ha (36% of the total *Eucalyptus* planted area). It is also more favourable because of the possible additional rotation (new growth sprouting from stumps after log harvesting). Its oil also has the potential to be rich in 1, 8-cineole, which can be a precursor to the production of terephthalic acid (Sappi, 2012).

E. grandis, also referred to as rose gum, is originally found in parts of Australia, but has been utilized in Brazil and African countries. The optimal growth conditions are found in subtropical areas where temperatures do not fall below sub-zero, do not increase beyond 35°C and where the typical annual rainfall ranges from 700 to 4000 mm. Soil preferences include good drainage and sufficient natural or chemical fertilizing. Uses for this type of wood include furniture, plywood, tissue paper, flooring and most importantly paper and packaging (Louppe, 2008).

In preparation for new *Eucalyptus* plantations, the seeds are collected from the fruit of the tree one year after reaching maturity. Up to 25 seeds can be harvested per fruit and germinated within two weeks. Seedlings are placed in plastic packaging to allow growth for two to eight months. At about 30 cm tall, the young trees are transferred to the plantation where fertilizing, pruning and weed management is applied to avoid growth inhibition (Louppe, 2008). For use as pulpwood, the rotation period is usually 6 to 10 years, while the rotation period for saw log wood is 30 years.

The density range of *E. grandis* wood is 540 to 775 kg/m³ and has an average moisture content of 12%. A typical dry-weight chemical composition of the wood contains approximately 40% cellulose, 20% glucuronoxylan (a hemicellulose component) and 30% lignin. Wood fibres are on average 0.9 mm long and 20 µm in diameter. Analysis of the *E. grandis* leaf oil shows the following average range of chemical components: 30.4 to 68.9% α-pinene, 0.4 to 47% β-pinene, 16% *p*-cymene, 11% terpinen-4-ol, 5% 1, 8 –cineole and 2.4 to 5.6% limonene. The leaf oil is on average 2 to 3% of the total leaf mass (Louppe, 2008).

2.1.1.3 Review of Acacia species

The Acacia genus was not selected as possible bio-source for the production of TPA, because of the absence of terpene species, suggested as TPA precursor in literature.

2.1.2 Sustainability

Plantation sustainability is defined by the conservation of the environment, positive impact on the community and company profitability. South African legislation encourages sustainable plantation management through the National Forests Act (1998) as well as the Forestry Law Amendment Act (2005). Sustainable actions include: immediate replantation after harvesting, no harm to any indigenous species (fauna or flora), use of species not listed on the International Union for the Conservation of Nature Red List of Threatened Species, conservation of water and the limitation of emission gases regardless of photosynthesis (Mondi, 2011).

2.1.3 Estimating 2G feedstock availability in South Africa

2.1.3.1 *P. elliotii* needles

Considering the accessibility and moderate uniformity in content for feed to a production unit, the needles of *P. elliotii* could be an appropriate feedstock for the extraction of the terpene, α-pinene, which can be used as precursor towards the production of TPA. The amount of hectares potentially available to supply the needles can be estimated using the latest forestry figures (Forestry Economics Services, 2015) where a radius of 300 km of South African land was considered as origin for biomass harvest in an area that limits transportation cost and access difficulties. This area, which includes the northern and southern part of Mpumalanga as well as a section of the northern part of KwaZulu-Natal, contains the highest concentration of *P. elliotii*, without considering clones of this species.

In 2013, South Africa had just under 173 000 ha of *P. elliottii* planted area. Each region of forestry area has a different rotation age (harvest age) for the purpose of pulpwood, sawlogs and others. For softwoods, only 29% of the available biomass is used for pulpwood at its rotation age, the other 71% is harvested for sawlogs. Table 3 and Table 4 depict the available needle mass calculated for the chosen regions at the rotation age and the rotation age per region, respectively. The total biomass available at rotation age is the total amount of *P. elliottii* available within South African forests (seen in Table 3), while the biomass in prospective regions is the biomass available within the 300 km radius area. The expected leaf mass can be calculated using the following ratio: 6.3:17.5 (tonnes of needle mass: hectares of available biomass) and should account for 5% loss that could occur from spillage during transport or minor fire losses. An average of 2% of the total needle mass is expected to represent the essential oil mass. The minimum and maximum figures can then be determined with figures following the current rotation year. As the available biomass (given in hectares) following the current rotation year does not follow any pattern or growth curve, the annual feed to the plant cannot be constant (Forestry Economics Services, 2015).

Table 3: Available biomass: *P. elliottii* needles

	Unit	Minimum	Average	Maximum
Total biomass at rotation age	ha	2700	4500	6200
Biomass in Mpumalanga regions	ha	1800	2600	3500
Biomass in KwaZulu-Natal region	ha	300	400	400
Biomass in chosen regions	ha	2100	3000	3900
Expected leaf mass	ton/year	710	1030	1350
Expected essential oil mass	ton/year	14	21	27

Table 4: *P. elliottii* rotation age per region

Region	Purpose	Rotation age (years)
Northern Mpumalanga	Pulpwood	18
	Sawlogs	28
Southern Mpumalanga	Pulpwood	20
	Sawlogs	28
Northern KwaZulu-Natal	Pulpwood	20
	Sawlogs	28

2.1.3.2 *E. grandis* leaves

Considering accessibility and moderate uniformity of content for a production line feed, the leaves of *E. grandis* could be an appropriate feedstock for the extraction of the terpene 1,8-cineole. The available amount of biomass can be estimated using the latest forestry figures (Forestry Economics Services, 2015). The commercial forest area considered for biomass

harvest has a radius of 300 km of South African land and includes the northern and southern part of Mpumalanga as well as a section of the northern part of KwaZulu-Natal. These regions collectively contain the highest concentration of *E. grandis* in comparison to the rest of South Africa that contain commercial forests, which will limit the cost of transport to the plant. Clones of this species were not considered as potential feedstock because of the great variations in terpene content of each clone.

In 2013, South Africa had just under 300 000 ha of *E. grandis* planted area. Each region of forestry area has a different rotation age (harvest age) for the purpose of pulpwood, sawlogs and others. For softwoods, 73% of the available biomass is used for pulpwood at its rotation age, while 5% is harvested at the rotation age for sawlogs. Table 5 and Table 6 depict the available mass of needles calculated for the chosen regions and rotation age per region, respectively. The total biomass at rotation age depicted in Table 5 is the total amount of *E. grandis* available for harvest in South African commercial forests. The available biomass for each region in the 300km radius is then calculated by considering the amount of biomass used for pulpwood and sawlogs at each rotation age and calculating the total hectares of *E. grandis* available. The expected leaf mass can be estimated using a ratio: 1.8:3 (tonnes of expected leaf mass: hectares of biomass available), while the expected essential oil mass is assumed an average of 2% of the total leaf mass and accounts for 5% losses in the case of spillage during transport or minor fire losses. The minimum and maximum figures can then be determined with later rotation years and does not follow any correlation, therefore the annual feed to the plant cannot be constant (Forestry Economics Services, 2015).

Table 5: Available biomass: *E. grandis* leaves

	Unit	Minimum	Average	Maximum
Total biomass at rotation age	ha	23 700	24 100	24 500
Biomass in Mpumalanga regions	ha	8400	8800	9200
Biomass in KwaZulu-Natal region	ha	1900	3000	4200
Biomass in chosen regions	ha	10 300	11 800	13 400
Expected leaf mass	ton/year	5900	6800	8000
Expected essential oil mass	ton/year	120	140	160

Table 6: *E. grandis* rotation age per region

Region	Purpose	Rotation age (years)
Northern Mpumalanga	Pulpwood	9
	Sawlogs	13
Southern Mpumalanga	Pulpwood	9
	Sawlogs	21
Northern KwaZulu-Natal	Pulpwood	9
	Sawlogs	18

2.2 Paper and pulp industry

2.2.1 Plant distribution

Several pulp and paper mills exist in South Africa, of which the majority are represented by PAMSA (The Paper Manufacturers Association of South Africa). These mills mainly produce paper (for magazines, newspapers, office paper, etc.), wrapping paper, tissue paper and packaging. Table 7 shows the main paper and pulp companies in South Africa and their main products.

Table 7: South African paper and pulp companies

Company	Location	Production
Mpact	Felixton, Piet Retief, Springs	Containerboard and carton board
Sappi	Ngodwana, Stanger, Tugela, SAICCOR	Newspaper, office paper, containerboard, speciality paper
Mondi	Durban, Richard's Bay	Paper and linerboard
Kimberly-Clark	Springs	Towel and tissue products
Nampak	Isithebe, Bellville, Pietermaritzburg	Paper packaging

2.2.2 Pulping technologies

The production of pulp and paper from wood sources or other biomass (such as rice straw and bagasse) has similar steps. A simplified scheme of a pulp mill is given in Figure 3; raw material such as logs are debarked and chipped to the appropriate size for the digesting process. A cooking vessel may be used prior to digestion to prepare the pulp fibres. Either the digestion is by mechanical (fibre processing through stone or metal plate grinding) or chemical (fibre separation in an aqueous solution) means. In some cases, both digestion methods are used, for example with neutral sulphite semi-chemical pulp processing (NSSC). The chemical digestion step allows lignin and other extractives to be dissolved (partially) and releases individual fibres that are converted to the final product. Thereafter through pressing, drying and cutting within a paper machine, the product is formed, where after it can be textured, glossed or coloured depending on the product specifications (Deslauriers *et al.*, 2009).



Figure 3: Simplified pulp mill process

Table 8 shows the general types of wood pulping technologies used in pulp and paper mills. The technologies used within South African paper and pulp mills will be further discussed (Gibbons, 1989).

Table 8: Wood-pulping technologies

Pulp grade	Wood type	Application
Chemical pulps:		
Sulphite pulp	Softwood & Hardwood	Fine and printing paper
Kraft pulp	Softwood & Hardwood	Writing paper and paperboard
Dissolving pulp	Softwood & Hardwood	Cellophane, acetate fibre and film
Semichemical pulps:		
Cold-caustic process	Softwood & Hardwood	Newsprint and groundwood paper
Neutral sulphite process	Hardwood	Newsprint and groundwood paper
Mechanical pulps:		
Stone groundwood	Softwood	Corrugating medium
Refiner mechanical	Softwood	Newsprint and groundwood paper
Thermomechanical	Softwood	Newsprint and groundwood paper

2.2.2.1 Neutral Sulphite Semi-chemical pulping process (NSSC)

The NSSC pulping process allows the use of hard- and softwood species within the digester and is a method used within Mpact's Piet Retief Mill in Mpumalanga, South Africa, in the production of containerboard liners. For this specific mill, anthraquinone is used as pulp catalyst in the continuous digester that operates above 10 bar and the pulping reagents include sodium sulphite and sodium carbonate. Debarked logs (hardwood) and sawmill chips (softwood) are introduced via a feeder after being sorted by vibrating screens and subjected to a steam vessel that extracts the air trapped within the wood particles. The cooking process allows the separation of fibres, as lignin is dissolved by chemical means and the neutral conditions prevents hemicellulose degradation. At a temperature around 179°C various volatile compounds such as sulphur oxides, nitrogen oxides, carbon monoxide and other volatile organic compounds such as terpenes are emitted from the cooking liquid and relieved through a relief-vent. Some mills have modified the digestion unit to recycle spent liquor by separating the solid particles using a mesh-type apparatus and reintroducing the spent liquor with top-up fresh liquor to reduce the waste from the pulping process.

A stronger paper can be produced by means of a chemical cooking process rather than mechanical methods that produce shorter, less flexible fibres. Semi-chemical pulping involves a combination of chemical and mechanical methods, where the mechanical aspect of the pulping follows the cooking process and combines the individual fibres. The ratio between the

dry weight of pulp to the dry weight of wood used during the semi-chemical process is between 0.7 and 0.85 (Antonides, 2000).

The pulp extracted during digestion is further processed by means of chemical separation, slurrification and water extraction (up to 96% up to the finished product). Refining the pulp defines the strength of the pulp and ultimately the strength of the linerboard. The degree of refining as well as the strength of the pulp can be observed by looking at the freeness of the pulp, as it is directly correlated. The freeness of the pulp is a measurement defined by the rate of water drainage of the pulp. The freeness of the pulp also determines the speed at which the linerboard is produced via the paper machine (Antonides, 2000). The first section of the paper machine presses the pulp between two felt rollers that gives a texture to the product and removes more water. Excess water might compromise the structure of the product line. The product line is then dried by heated cylinders where the last water part is extracted. Depending on the specifications of the end-product, imprints can be made by using rubber or metal rollers where after the product is cooled and wound up on a roller or sent for further processing to obtain colour, gloss or other finishes (The Paper Mill Store, 2015).

2.2.2.2 Soda pulping

Cold soda pulping involves the introduction of sodium hydroxide to the raw material and subjecting the mixture to mechanical digesting (El-Sakhawy, 2014). This pulping method is used at Sappi's Stanger Mill in Stanger, KwaZulu-Natal, where bagasse is used as raw material and anthraquinone is used as pulping catalyst. Matt and gloss paper for labelling and magazines, packaging and tissue paper are produced at this mill (Sappi, 2015).

2.2.2.3 Kraft pulping process

Kraft pulping is used within Sappi's Ngodwana mill in Mpumalanga, South Africa, for the production of newspaper and containerboard (shown in Figure 4). It is also utilised at Mondi's Richards bay mill in KwaZulu-Natal, South Africa. After logs are debarked and chipped, the chips are pre-steamed to remove some of the impurities before digestion. This stage is known as the pre-hydrolysate stage and utilises water approximately four times the mass of the woody biomass entering the cooking vessel. Pre-hydrolysate relief gas (CST) contains higher concentrations of terpenes (especially α -pinene when *Pine* chips are cooked) compared to other relief-gas and effluent streams in the Kraft process (SAPPI, 2016). This creates an opportunity to investigate processing the relief-gas as feed in TPA production. The majority of

the chips used in the Ngodwana mill at the time of this project have a *Pine* origin and therefore only *Pine* was considered as source for the relief-gas.

Within the digester, a white liquor of sodium hydroxide and sodium sulphide at high pressure and temperature is added to dissolve the lignin present in the wood particles. The pulp is washed after digestion to remove the black liquor (spent cooking mixture after digestion) and sent to a bleaching stage (Deslauriers *et al.*, 2009).

Chlorine dioxide and other oxygen-based chemicals are used to whiten the pulp and remove residual lignin still present after the digesting stage. Screening and press drying refines the bleached fibres according to the unique product specification and can also involve gloss addition, texture application and cutting to the desired size (Deslauriers *et al.*, 2009).

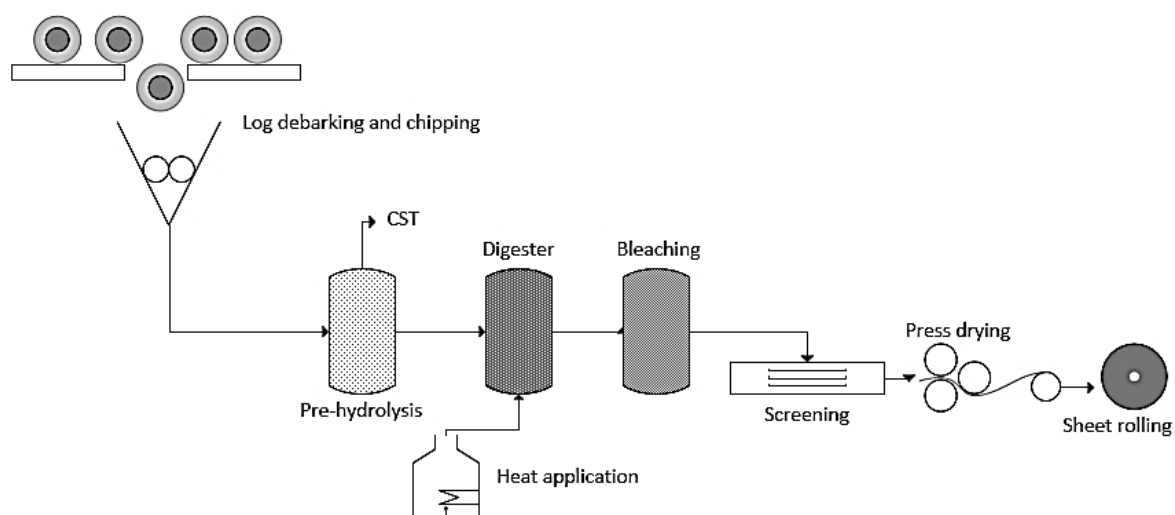


Figure 4: SAPPI Ngodwana Kraft process scheme

2.2.3 Pulp mill residue selection

The pulp mill residue for possible selection depends on the content of the residue, which will dictate possible additional processing/purification to obtain the major terpene. The location of the pulp mill can also be considered for possible integration with a similar process, where the bio-resource of this process' transport cost is a factor. Thus, SAPPI's Ngodwana mill is can be considered as the base case pulp mill and the pre-hydrolysate relief-gas as the residue described in Chapter 2.2.2.3. The majority of terpenes extracted from the wood chips are released within the pre-hydrolysate stage. Preliminary processing of the relief-gas includes

separating the water from the CST and desulphurisation of naturally occurring sulphurous compounds.

2.3 Overview of TPA production pathways from 2G feedstocks

The description and evaluation of bio-TPA production processes (from forestry waste and pulp mill residue) obtained from literature is found in Chapters 2.4 to 2.5. The evaluations of these processes were based on product concentration and yield, extraction or conversion efficiency and the practicability of industrial implementation. Figure 5 depicts a simplified scheme of the possible processes that lead to the production of bio-TPA. The major terpene (α -pinene or cineole) from each 2G feedstock should be extracted before conversion through dehydrogenation to *p*-cymene. The oxidation of *p*-cymene produces TPA that should be purified to minimise by-products. These by-products affect the quality and selling price of the final PET product.

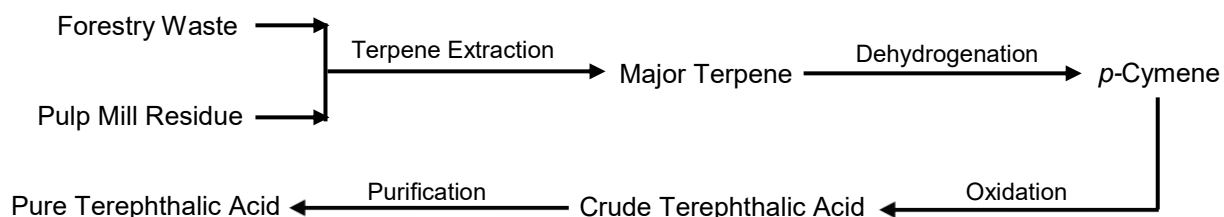


Figure 5: Simplified lignocellulosic-based process scheme

2.4 Technologies for terpene extraction and purification

2.4.1 Tapping

Traditionally, oleoresins (which include pinenes) were obtained from living trees by a method called tapping. Tapping involves etching a V-shape into the bark and collecting the resins secreted. Mature trees can be tapped several times during its lifetime, because the wounding only affects the bark of the tree. Excessive wounding of the inner flesh, however, might terminate the life of the tree (Ciesla, 1998). Associated Resins, located near St. Lucia, Kwa-Zulu Natal, extracted gum turpentine from softwood via tapping with a maximum capacity of 550 tons of resin per month. Resin usually contains 70 – 75% rosin, 15-20% turpentine and 10% unwanted compounds. The resin is distilled to produce rosin, which is used to manufacture adhesives, violin string wax and other products used during paper sizing. Due to

conservation issues in St. Lucia, the operation has been terminated (Triumph Venture Capital, 2004).

2.4.2 Steam distillation

Steam distillation can be used to distil plant material to obtain the essential oils contained within and can easily be used on a large-scale. The steam is supplied by an external boiler unit (1) and introduced at the bottom section of the contact reactor (2) as shown in Figure 6. The flask is never heated to more than 100°C to avoid thermal degradation. The components in the vapour are formed when the temperature of the flask fluid has met or exceeded the boiling point of that component. The overhead vapour line (3) condenses the vapour and carries the condensate to the collector and decanter (4) (Handa *et al.*, 2008).

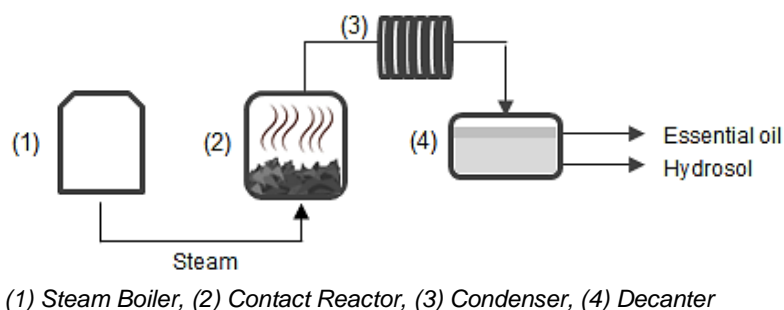


Figure 6: General Steam Distillation Setup

2.4.3 Hydro-distillation

Hydro-distillation involves boiling the feedstock (woodchips, leaves, bark, etc.) in water in a reactor to obtain the essential oils. The vapours produced flows through an overhead section that contains a condenser. The condensed liquid is collected in a decanter that separates the organic oil layer from the aqueous layer. The mechanism of this type of distillation involves hydro-diffusion, hydrolysis and decomposition. Hydro-diffusion allows the hot water to draw the essential oils through the plant cell membranes by osmosis, where it is then carried over by the formed steam. Through hydro-diffusion, the possibility of a higher essential oil yield is increased. Acids and alcohols can also be produced during the hydrolysis phase, depending on the presence of esters and the temperature of the water. However, this will decrease the yield of the essential oils when large amounts of water are used during distillation. As the temperature of the water increases, so does hydro-diffusion but also the hydrolysis of esters. Additional heat will induce the decomposition of some of the natural components (including major terpenes and their alcohols). The three mechanisms affect each other simultaneously and it is therefore essential to choose a lower temperature (preferably lower than 70° in the

presence of a vacuum) and water loading (commonly four times the weight of the fed biomass) to obtain the highest yield of essential oils (Handa *et al.*, 2008).

Potential feedstock for recovering essential oils using hydro-distillation can include shredded branches, leaves, bark, wood particles. Hydro-distillation can be used to distil macerated pieces of biomass for a few hours. The residence time of the biomass in the boiling chamber depends on the severity of the maceration, biomass and water loading, configuration in case of multiple chamber use and volatility of the contained terpenes. The extracted oil can be dried over anhydrous Na₂SO₄ or decanted, depending on the type of extracted terpenes (Salem, *et al.*, 2014).

2.4.4 Supercritical CO₂ extraction

In the case of extracting chemical components not easily released from the biomass during a distillation process or components that have a high solubility in the used solvent, another method must be used to obtain the said component. CO₂ can be used as solvent to extract terpenes at a relatively low temperature without the extraction of many other components found within the biomass. This is done through the diffusion of the liquid CO₂ within the plant cells and dissolving of terpenes into the solvent under high pressure. Cell lysis also occurs at these pressures and exposes more of the terpene oils; this increases terpene extraction efficiency. In the case of leaves or needles with a protective wax layer, the terpenes are extracted together with these waxes, which make up a small fraction of the total biomass (approximately 0.6%). These waxes can easily be condensed off because of the difference in boiling points between the terpenes and waxes. The CO₂ can also easily be separated from the liquid terpenes through distillation after the pressure is lowered (Francisco *et al.*, 2001).

2.4.5 Microwave assisted extraction

Submerging biomass in a solvent such as ethanol and hexane and introducing microwaves can lead to the extraction of terpenes. This is caused by cell lysis experienced by the microwaves. This extraction method has been successfully applied to herbs and seeds and can be modified by changing parameters, such as power, temperature, incubation period and the solvent used (Chemat *et al.*, 2005).

2.4.6 Comparison of α -Pinene extraction technologies

Tapping *Pine* trees can be a viable option because of the relatively high resin yield (1-4 kg resin per tree per year) (Ciesla, 1998). It can also create an increase in employment opportunities (etchers and resin collectors) in South Africa, though worker inexperience with tapping equipment or techniques may cause tree termination. Exposed resin is also a highly flammable substance that aggravates forest fires. It can be unfavourable in the extraction of terpenes to use the resin as a raw material in a large-scale plant due to its viscosity, as it might cause equipment problems and clogging (Lovett, 2005).

Steam distillation is preferred for large-scale operations, because of the lower possibility of hydrolysis and the control of steam supplied to the contact reactor. The risk of thermal decomposition of components is also reduced when utilizing steam distillation. There is, however, a higher capital cost when using steam-distillation and without hydro-diffusion, the yield of essential oils might be lower (Handa *et al.*, 2008). A problem that arises when using an alkaline solution to extract pinenes is that it can encourage hemicellulose extraction from polysaccharides and can therefore lead to additional separation steps when isolating the terpenes from the condensate (Bensah *et al.*, 2013).

For a process development, literature is required to describe the efficiency and parameters needed to define the process and techniques such as CO₂ and microwave assisted extraction for α -pinene from *Pine* biomass, although this is not the case. Thus, hydro-distillation is favoured as an appropriate method of extraction because of the higher concentration of α -pinene that is extracted when compared to steam distillation, and also because it is well described. There is also easy separation between the water used as solvent and α -pinene.

Table 9 shows different hydro-distillation extractions done on different species of *Pine*. The method described by Pagula *et al.* (2006) is superior to the other methods for extracting precursors from *Pine* needles, because of the high yield of the required precursor, α -pinene. The main areas in South Africa where *P. elliottii* is planted for use in paper and pulp mills, Mpumalanga and Kwa-Zulu Natal, have a similar climate and rainfall to Maputo in Mozambique and may therefore have a similar terpene composition (World Weather & Climate Information, 2016). The factors that affect the terpene content of trees include the age of the tree, the climate and rainfall of the region, the season in which the tree was harvested, the temperature and retention time at which the hydro-distillation was performed, etc. (Peñaelas & Llusà, 1997). These factors are influenced by wind or rain transporting volatile terpenes, monoterpene scavenging radicals (OH and O₃) as well as the physiological properties of the specific tree that affect the production of terpenes (Lee *et al.*, 2017).

Table 9: Needle extraction from *Pinus* species via hydro-distillation

Species	Region	Major components (m _{Terpene} /m _{Essential Oil})	Reference
<i>P. roxburghii</i>	Alexandria, Egypt	3-carene: 33.4% α -pinene: 39%	<i>Salem et al.</i> (2014)
<i>P. virginiana</i>	Huntsville, USA	β -pinene: 25.1% α -pinene: 22.8%	<i>Stewart et al.</i> (2015)
<i>P. radiata</i>	Attiki, Greece	β -pinene: 26.4% α -pinene: 16.7%	<i>Petrakis et al.</i> (2001)
<i>P. elliottii</i>	Maputo, Mozambique	β -pinene: 27% α -pinene: 43%	<i>Pagula et al.</i> (2006)

2.4.7 Comparison of cineole extraction technologies

Hydro-distillation as well as steam-distillation are viable options for the extraction of terpenes. The latter is the current industrial method for extraction of essential oils and water/oil separation is done manually. The water layer, also called floral water/hydrosol, contains a large amount of cineole and is sold separately from the oil layer. The floral water is used in many pharmaceutical and cosmetic products (Esoteric Oils, 2016). Distillation of *Eucalyptus* leaves might not be suited for the sole purpose of extracting cineole because of its large solubility in water (3500 mg/L), due to its oxygenated functional group and difficult separation with additional methods. Current literature has not yet proposed an effective method for this separation (Miller *et al.*, 2000).

Thus, supercritical fluid extraction using CO₂ as solvent might be the appropriate method of cineole extraction because it eliminates the use of water and only leafy waxes are additionally extracted (Francisco *et al.*, 2001). These waxes can range from 0.2 to 1.1% of the dry leaf mass of mature *Eucalyptus* trees, an average of 0.6% is assumed during calculations. Leafy waxes such as nonacosane, dotriacontane, pentatriacontane and hexatriacontane were considered during calculations while other waxes present in traces were ignored (Li *et al.*, 1997). Francisco *et al.* (2001) reports yields of up to 86% cineole (as per weight percentage of liquid terpenes) extracted from *E. radiata* through this method of extraction. Supercritical pressures ranges from 80 to 250 bar, while temperatures are kept relatively low between 40°C and 200°C.

2.4.7 Cineole purification

The presence of 1, 4-cineole and other monoterpenes during the dehydrogenation of 1, 8-cineole can lead to many undesired by-products that lower the quality of the final product. Mitchell (1985) suggests a purification step, where hydroquinone (HQ) (an inexpensive, common chemical used in a variety of industrial processes) is added to the terpene mixture at

a low temperature of -10°C . At this temperature the HQ forms a complex solely with 1, 8-cineole. The rest of the terpenes are flashed off under vacuum at an increased temperature of 50°C and can be sold without the need for further purification because of the insolubility of terpenes in hydroquinone. Final distillation produces 1, 8-cineole with a purity of approximately 96%, while a recovery of about 50% is accomplished. If economics allows for another extraction cycle, a recovery of about 75% can be achieved. An advantage to this type of purification step is that the HQ can be reused for each cycle with minor losses.

2.4.8 Relief-gas desulphurisation

Additional to a large amount of water, pre-hydrolysis relief-gas also contains natural sulphurous compounds such as methyl mercaptan, dimethyl sulphide, dimethyl disulphide and hydrogen sulphide. These compounds must be limited during production because they can poison the catalysts used during the production of PET, induce a foul odour in the final product, are flammable and highly toxic (Räsänen, *et al.*, 2013). Desulphurisation is therefore necessary to ensure that these compounds remain below the following odour thresholds (Rava, 2008):

Table 10: Natural sulphurous compound odour threshold

Compound	Chemical Formula	Odour Threshold (ppm)
Methyl mercaptan	CH_3SH	0.08
Dimethyl sulphide	$(\text{CH}_3)_2\text{S}$	0.65
Dimethyl disulphide	$(\text{CH}_3)_2\text{S}_2$	0.014
Hydrogen sulphide	H_2S	0.03

The desulphurisation step is applied after dehydrogenation of the relief-gas, because of the additional reactions that these sulphurous compounds undergo during the dehydrogenation of α -pinene (Figure 8).

Methods developed towards the desulphurisation of the sulphurous compounds in the relief-gas can include the use of chlorine gas, hydrogen peroxide, iron and nitrate salts or potassium permanganate. Considering toxicity, solubility, handling, corrosion and chemical cost, hydrogen peroxide is favoured as desulphurisation agent. The products formed as well as the molar ratio of hydrogen peroxide required varies according to the pH of the system (as shown in Figure 7). The second reaction equation for an alkaline environment involves the conversion of mercaptans and disulphides, where R symbolises the carbon portion of the sulphurous species (Solvay Chemicals, 2005)

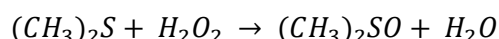
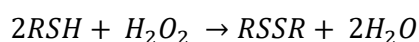
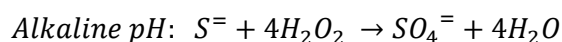
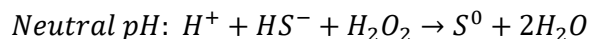
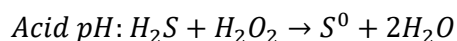
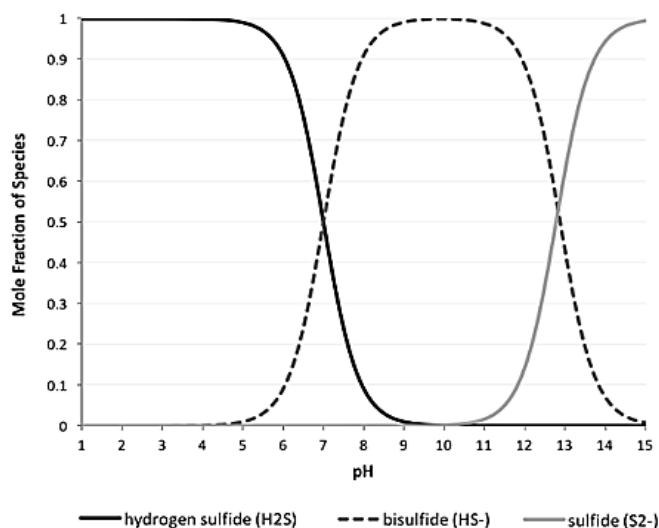


Figure 7: Variation in molar fraction of sulphurous species with pH

2.5 Terpene and p-cymene conversion technologies

2.5.1 p-Cymene production from α -pinene

The conversion of α -pinene to p-cymene via isomerisation and the desulphurisation step via dehydrogenation can occur simultaneously over a zeolite catalyst. The process takes place in a fixed bed reactor using a vapour feed, with the temperature ranging from 300°- 350° C to avoid cracking of molecules or low conversion rates (Räsänen *et al.*, 2013). The continuously fed reactor can operate at various temperatures, while the pressure is kept at around 5 bar. Faujasite Y (FAU Y), Mordenite (MOR) and Faujasite X (FAU X) are appropriate zeolite catalysts for these reactions, because of their acidity and selectivity during aromatization. Faujasite Y is the optimum choice as catalyst for this conversion reaction, because of its higher performance. It also has a much higher selectivity towards the three cymene isomers (p-, m- and o-cymene) with a cymene selectivity of 34% compared to 17% and 3.9% seen from MOR and FAU X, respectively.

At steady state, nitrogen is utilized as carrier gas because of its inert behaviour in the absence of oxygen (Batt, 2014). Linnekoski *et al.* (2014) proposed a system where the terpene feed stream is introduced to the reactor at 160°C, while the optimum cymene yield is achieved at a reactor temperature of 300°C. The mechanism for this process (shown in Figure 8) relies on a few reactions to complete the aromatization of α -pinene. Cationic intermediates usually form first and undergo further reaction to produce three cymene isomers in the product stream (para-, meta- and orto-cymene). The isomerisation has a higher conversion in the presence of

the acidic catalyst, which also catalyses the rearrangement of the terpene isomers. At a temperature above 280 °C, it is possible to achieve dehydrogenation of the monocyclic terpenes to cymenes. The selected acid catalyst aids in the formation of the cymenes. As dehydrogenation takes place, the released hydrogen molecules are accepted by other terpenes to form menthenes and menthanes. The desulphurisation of natural occurring sulphur compounds takes place as three steps (shown in Figure 8): hydrogenolysis, disproportionation and reduction by the following reactions:

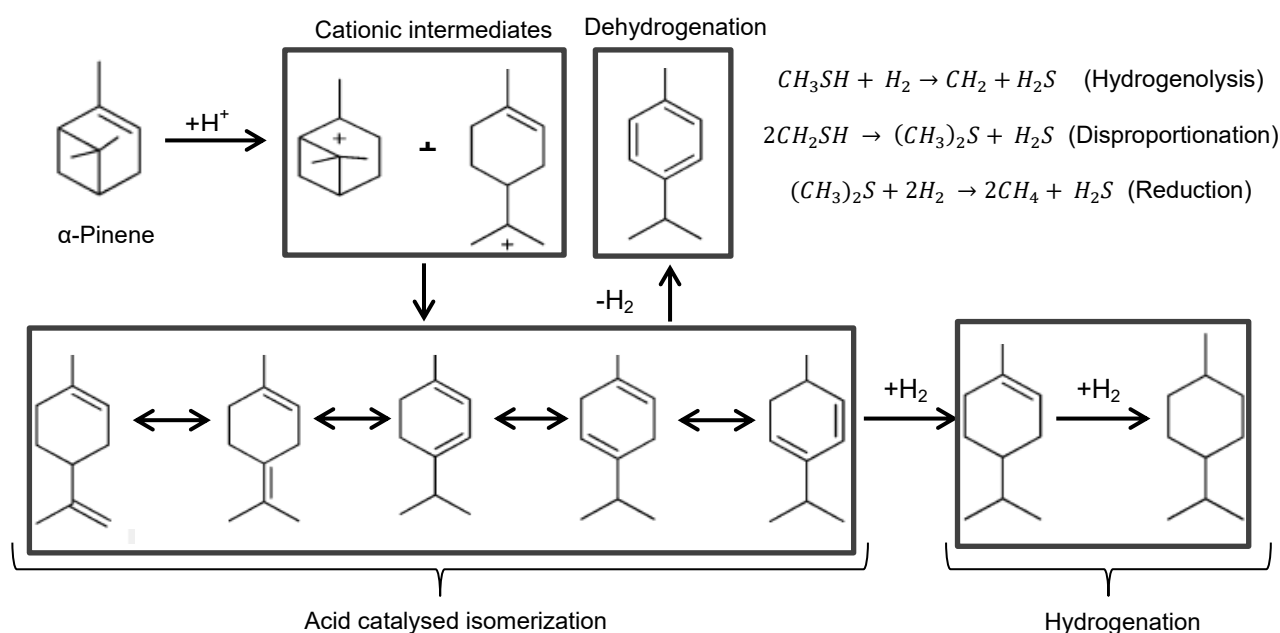


Figure 8: Reaction mechanism for α -pinene conversion

At these conditions, there is complete conversion (X) of α -pinene and the selectivity (S) of o-, m- and p-cymene is 0.31, 7.7 and 20, respectively. The selectivity of unwanted by-products, menthenes (MW = 138) and menthanes (MW = 140), are 16 and 3.8, respectively, where the selectivity and conversion is defined as:

$$S = \frac{\text{Moles product}}{\text{Moles } \alpha - \text{pinene reacted}} \times 100 \quad (1)$$

$$X = \frac{\text{Moles } \alpha - \text{pinene reacted}}{\text{Moles } \alpha - \text{pinene in feed}} \times 100 \quad (2)$$

The isomers formed during the reaction (with an overall selectivity of 11) include terpinolene, α -terpinene, γ -terpinene and menthadiene. The formation of limonene is excluded due to the absence of 3-carene in the feed (Zou *et al.*, 2012).

Due to the absence of O₂ and the medium temperature of 300°C used, coking formation is negligible, while catalyst deactivation is considered further.

2.5.2 *p*-Cymene purification

After the completion of α -pinene dehydrogenation, the *p*-cymene product can be purified prior to oxidation, to reduce the amount of oxidised by-products in the final product. Difficult distillation, such as extractive or azeotropic distillation, steps are usually needed to separate components with close boiling points, which is the case for *p*-cymene, menthenes and menthanes, with boiling points of 177°C, 174.5°C and 170.9°C, respectively. Thus, an acidic environment (1-25% w/w acid), created by sulfuric acid (98%), encourages the polymerisation of any monoterpene to form diterpenes (terpenes with twenty carbon atoms) in vacuum. This creates an opportunity to transform menthenes and menthanes, which are monoterpenes, into diterpenes. Many monoterpenes extracted during hydro-distillation can also have boiling points within 30°C of the boiling point of *p*-cymene and the formation of diterpenes (with much higher boiling points) ensures a much easier separation from *p*-cymene through downstream distillation. Typical diterpenes include isocupressic acid, cembrene-A, phytane and T-communol (Brücher *et al.*, 2013).

2.5.3 *p*-Cymene production from cineole

Various metal-doped alumina catalysts have been considered by Leita *et al.* (2009) for the conversion reaction of cineole to *p*-cymene by using an argon/oxygen mix as carrier gas (shown in Figure 9). Metals such as molybdenum, cobalt, iron, chromium and palladium have been evaluated for this specific reaction. Pd γ -Al₂O₃ is the superior catalyst option for obtaining a higher yield and selectivity towards cineole. Leita *et al.* (2011) suggested a method for conversion within a tubular reactor that utilises the optimal catalyst at a reactor temperature of 280° C. Cineole in vapour form is introduced into the reactor via the carrier gas, argon (together with oxygen to utilize some of the hydrogen produced). It is reported that a maximum yield of nearly 99% can be obtained within one hour, whilst producing hydrogen in large amounts (which can be purified and sold as additional product). The catalyst remains stable throughout the process with an almost negligible rate of deactivation. This route can be

promising because of the conditions at which the reaction takes place and the high yields of *p*-cymene observed. The reaction mechanism starts with the dehydration of the cineole molecule producing several isomers including α - and γ -terpinene, dipentene, iso-terpinolene and menthadienes. This first step is encouraged due to the weak oxygen-carbon bond and occurs much faster than the following step, which is dehydrogenation. The isomers experience dehydrogenation and rearrangement to produce *p*-cymene, and as a result expel hydrogen gas. An advantage to using specifically Pd γ -Al₂O₃ is that dehydration products (isomers) are absent due to rapid dehydrogenation.

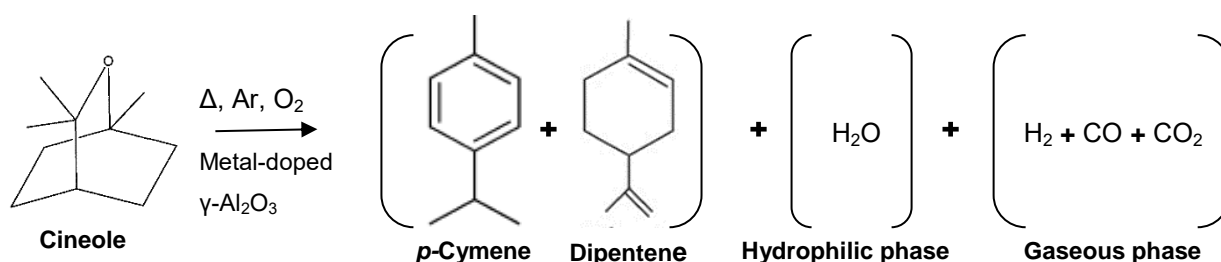


Figure 9: Cineole conversion reaction scheme

2.5.4 Terephthalic acid production from *p*-cymene

A method for the conversion of *p*-cymene to TPA is a two-step oxidation process suggested by Berti et al. (2015). *p*-Cymene is firstly acidified with a mineral acid, such as HNO₃ (65%), within a mixture of the crude *p*-cymene and water. This mixture is left to react at 80°C for 24 hours in an isolated vessel and then cooled to 25°C for dichloromethane (DCM) extraction. The extracted organic layer is washed with water and concentrated to remove any remaining acid and reduce the amount of by-products, such as *p*-toluic acid, present in this layer.

Water and NaOH is introduced to the solids obtained to convert the formed *p*-toluic acid from the first oxidation step to TPA. The second step adds a transition metal oxidant, such as potassium permanganate into the reactor. The reaction medium is allowed to proceed within an isolated vessel for 16 hours at 100°C. A celite pad is used to filter the slurry after the reaction, while water is gradually added to remove additional solvent. To ensure a maximum precipitation of TPA, H₂SO₄ (98%) is added to the aqueous layer. The solids obtained by filtration after precipitation is washed with DCM and water. The product obtained is a white solid, which is approximately 85% bio-based terephthalic acid. This research proposed by Berti et al. (2015) is still in the patent phase with little information regarding tested runs of the reaction, therefore this method can be excluded further.

An alternative method described by Neatu *et al.* (2016), the direct oxidation of *p*-cymene might be a viable process to produce TPA and Figure 10 shows the reaction scheme. The possible intermediates produced is as follows: (a) tertiary cymene hydroperoxide, (b) *p*, α -dimethylstyrene, (c) *p*-cymenol, (d) *p*-methylacetophenone, (e) *p*-tolualdehyde, (f) *p*-toluic acid, (g) cuminaldehyde, (h) *p*-isopropyl benzoic acid. At a reactor temperature of 140°C and pressure of 20 bar, full conversion of *p*-cymene is observed together with a higher selectivity of *p*-toluic acid and TPA (56 and 38, respectively). Another intermediate formed at these parameters is *p*-isopropyl benzoic acid with a selectivity of 5. The selectivity (S) and conversion (X) is calculated by the following equations:

$$S = \frac{\text{Moles product}}{\text{Moles } p - \text{cymene reacted}} \times 100 \quad (3)$$

$$X = \frac{\text{Moles } p - \text{cymene reacted}}{\text{Moles } p - \text{cymene in feed}} \times 100 \quad (4)$$

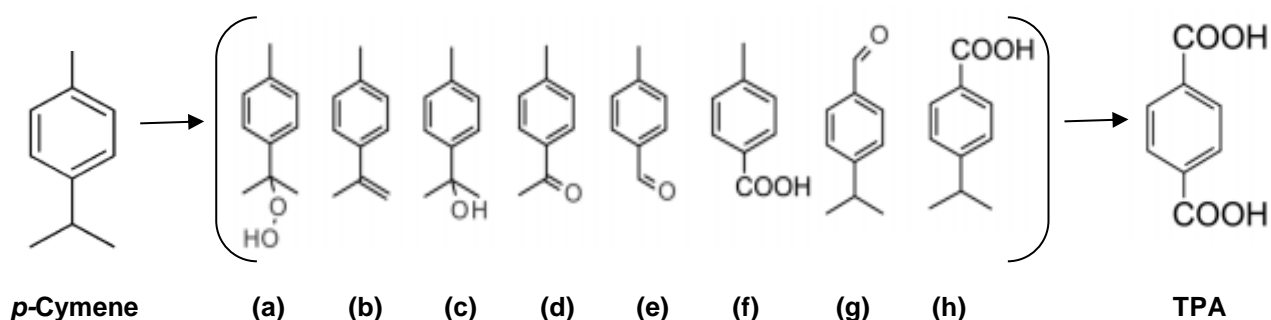


Figure 10: TPA formation reaction scheme

As demonstrated, the catalyst and oxidising compounds are introduced into the reactor, Mn/Fe/O, and accelerates the reaction by the introduction of a free-radical chain mechanism. The activation of one C-H bond is initiated by removing a hydrogen atom (shown in Figure 11). This reaction consumes surrounding energy and takes place at a slow rate to form tertiary cymene hydroperoxide, which in turn can form the rest of the intermediates (shown as (b)-(h) in Figure 10) and eventually TPA through a second oxygen diatom addition.

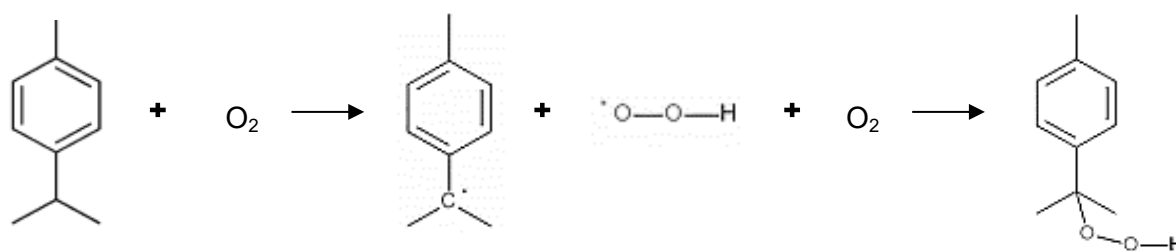


Figure 11: Free-radical chain mechanism

The oxidation of unconverted α -pinene present in the feed to the reactor is also included in the study by Neuenschwander *et al.* (2010). In the presence of oxygen, various products can form including verbenyl-hydroperoxide, pinenol, pinocarveol, α -pinene oxide, verbenol, pinocarvone and myrtenol. At the reactor conditions only α -pinene oxide, verbenol and verbenyl-hydroperoxide were considered the main formed products.

The direct oxidation of *p*-cymene produces TPA and *p*-toluic acid with selectivities of 38 and 56, respectively. Thus, an additional oxidation stage is therefore necessary to convert *p*-toluic acid to TPA. This process involves a high pressure environment (approximately 1.2 MPa) in which air is introduced to the system together with acetic acid and a low concentration of T(*p*-Cl)PPMnCl and $\text{Co}(\text{OAc})_2$ as catalysts. These catalysts fall under the category of metalloporphyrins. Depending on the concentration of *p*-toluic acid, the selectivity of TPA can be up to 97.6% with a 56.4% conversion of *p*-toluic acid. 4-carboxybenzaldehyde (4-CBA), an undesired product, forms together with TPA with a much lower selectivity than TPA. Figure 12 shows the scheme for this reaction where a formation of peroxides, due to the specific combination of catalysts, induce the oxidation reaction by the formation of free radicals. With the formation of peroxides, Co^{3+} is formed which in turn increases the number of free radicals (Xiao *et al.* 2010).

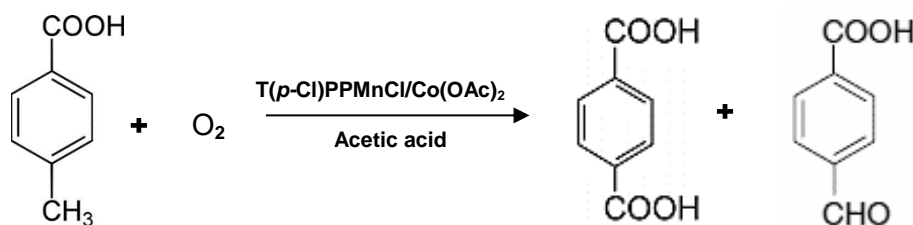


Figure 12: Oxidation of *p*-toluic acid reaction scheme

2.5.5 Terephthalic acid purification

The filter cake produced through the two-step oxidation of p-cymene (Chapter 2.5.4) consists of a few products and by-product solids formed during these steps. Two of the undesired products (by-products), namely *p*-toluic acid and 4-CBA, lower the quality and selling price of TPA significantly (and in turn, the quality and selling price of PET). According to Azarpour *et al.* (2015), selective crystallization using a solvent can be used to purify TPA in the formed cake. The solvent is chosen by comparing the solubility of the undesired products in the solvent or by choosing a solvent in which more or less only TPA is soluble. Previous studies conducted by Arai *et al.* (1969) concluded that solvents, such as dimethyl formide and pyridine can be used to purify TPA but lack stability in air and can form additional unwanted products. Therefore, an industrial available solvent that is stable, non-corrosive and will not react with TPA, N-methyl-pyrrolidone (NMP), is favoured. In order to determine the degree to which purification should take place, the specifications for purified terephthalic acid should be taken into consideration (listed in Table 11).

Table 11: Purified terephthalic acid specifications

Parameter	Specification
4-CBA concentration	< 25 ppm
p-Toluic acid concentration	< 150 ppm
Moisture content	< 0.2%
Metal content	< 8 ppm

2.6 Estimating 1G feedstock availability

As mentioned in Chapter 1.1, sorghum and triticale can be promising first-generation feedstocks for the production of bio-TPA in South Africa. It is estimated that by 2020 the total sorghum area in South Africa will amount to 234 000 hectares from 81 000 hectares in 2011. This increase is because the cultivation of this grain is more favoured above white and yellow maize because of a higher grain yield and ability to grow in more severe conditions (Lemmer, 2011). Triticale is favoured above other small grains, as it can be cultivated in more inhospitable land areas not suitable for common food-source grains (Du Preez & Görgens, 2015). This in turn evades a different version of the food versus fuel debate as land area not suitable for food-crops can be utilized for the cultivation of these starch sources for the production of bio-based TPA.

2.7 Overview of TPA production pathways from 1G feedstocks

As mentioned in Chapter 1.1, Gevo has developed a process where *p*-xylene is produced from a starch source. *p*-Xylene is currently being produced on a pilot-plant scale and can be used to produce TPA. Little information is known of the process itself, but intermediate chemical compounds have been derived. A similar process has been developed that also utilises starch sources, namely the Catalysis Centre of Energy Innovation (CCEI) process. Table 12 shows the intermediate chemical compounds for both the Gevo and CCEI processes.

Table 12: Gevo & CCEI process intermediates

Process	Intermediate Chemical Compounds
Gevo	Starch → glucose → isobutanol → isobutene → isooctane → <i>p</i> -xylene
CCEI	Starch → glucose → fructose → HMF → DMF → <i>p</i> -xylene

The CCEI process can be integrated into the starch-based production of bio-TPA as shown in Figure 13. Oxidation of the pure *p*-xylene product obtained from the CCEI process produces crude terephthalic acid that can be purified to produce a pure TPA product with the appropriate specifications for PET production.

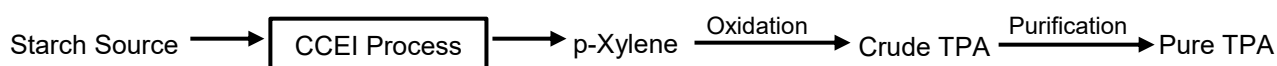


Figure 13: Simplified starch-based process scheme

2.9 Technologies for terephthalic acid production from 1G feedstocks

2.9.1 Starch-based feedstock conversion to *p*-xylene

The CCEI process involves a starch source that is depolymerised to glucose in the presence of water and hydrogen chloride in a biphasic reactor. Tetrahydrofuran (THF) is then added as solvent together with sodium chloride to convert the formed sugars into 5-hydroxymethylfuran (HMF). A Sn-beta zeolite is used as catalyst during this reaction. Products formed (present in the aqueous phase) include fructose, glucose, HMF as well as levulinic and formic acid, while humic compounds are formed in the solid phase. After this reaction, the liquid phase is flashed to recycle the THF solvent, while the rest of the organic-rich phase is sent to a

fluidised bed reactor. Hydrogen at 6.9 bar together with a copper-ruthenium-carbon catalyst is used to produce 2, 5-dimethylfuran (DMF) from HMF. Purification of DMF and recycling of THF and water is done within a distillation column, where separation is initiated by the difference in boiling points between chemical compounds. The final reaction takes place within a continuous flow stirred-tank reactor where the addition of ethylene and removal of water produces *p*-xylene with a purity of 99.5 wt%. The water removed during this step is separated from the product by decanting (Lin *et al.*, 2014).

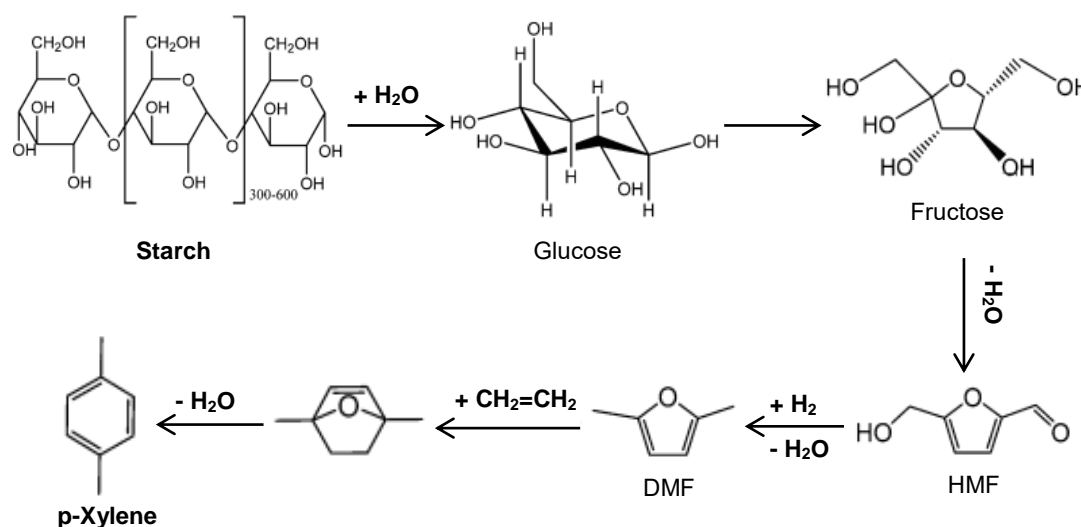


Figure 14: Starch-based *p*-xylene production reaction scheme

2.9.2 *p*-Xylene conversion to terephthalic acid

Terephthalic acid can be produced from *p*-xylene through oxidation using oxygen; where after the solid powder is subjected to a purification stage(s) to obtain a product at the required product specifications (specified in Table 11). The oxidation includes the use of a μ_3 -oxo-bridged cobalt/manganese cluster complex as solid catalyst. Zeolite Y serves as solid matrix for the catalyst, which not only encourages the selective oxidation of *p*-xylene to TPA but limits the formation of the impurity 4-CBA. It is suggested that the increased catalytic activity is promoted by the redox behaviour of $CoMn_2O$. At 550 psig and 200°C complete conversion of *p*-xylene can be achieved with 99.6% selectivity towards TPA. A selectivity of 0.01% and 0.03% is achieved for the by-products, benzoic acid and 4-CBA, respectively (Figure 15). The rest of the product is comprised of *p*-toluic acid (Chavan *et al.*, 2001).

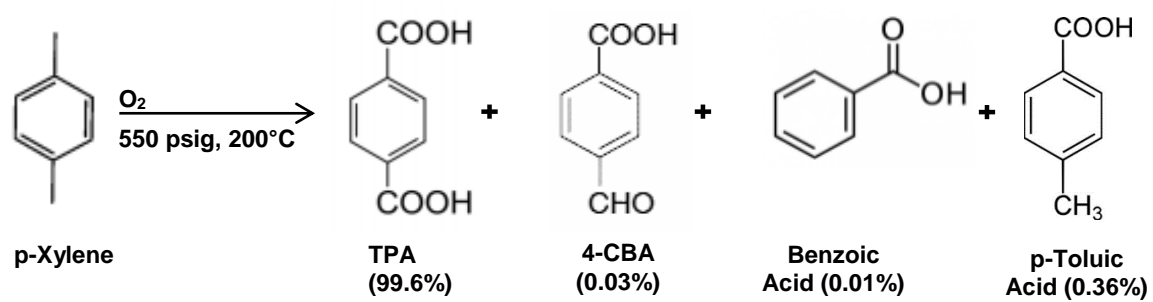


Figure 15: Starch-based p-xylene oxidation reaction to TPA

3 Research design methodology

3.1 General methodology and envisagement

Aspen Plus® provides a platform for process simulation based on experimental data extracted from appropriate literature sources. From these simulations, mass and energy balances reveal technical performance indicator such as production rates, energy generation and utility demands that form the basis of the technical modelling results analysis. From the mass and energy balances generated, the cost of acquiring and operating the prospective plant are included in the cash-flowsheet to determine economic indicators, such as the internal rate of return (IRR) and minimum selling price of TPA. From these indicators, a decision can be made on the attractiveness investing in the prospective plant compared to other investment opportunities including financial institutions and investors.

It is envisaged that technical modelling results analysis considering pinch point heat integration as well as economic (cash flow) analysis would reveal certain outcomes that would be comparable to each developed process. From these analyses, the status of economic viability of these processes and/or integrations/combinations thereof can be deducted.

3.2 Overview of processes developed for techno-economic investigation

Based on the literature review of the various feedstocks and processing steps that are involved in the conversion of bio-based materials to TPA, the overall process descriptions presented in this chapter presents the flowsheets that have been derived. These processes flowsheets form the basis of the mass and energy balances, and the economic evaluations that will be carried out.

3.2.1 Process description for TPA production from *Pine* needles

Figure 16 depicts the main processes selected for the *Pine* needle bio-resource processing towards purified TPA. The bio-resource is first subjected to size reduction and hydro-distillation to extract the major terpene, α -pinene (Chapter 2.4.3).

To obtain a more continuous extraction of biomass, a semi-batch configuration of vessel will be modelled, while slurry pumps will be used to transport biomass from one vessel to the other. Control over the mass flow of water within the system as well as the heat duty applied

to the vessels will ensure maximum extraction efficiency and prevent biomass flow restrictions. Lastly, the extracted terpenes and water vapour is condensed and separated via decanter to produce an essential oil product stream.

The major terpene, α -pinene, is then converted through dehydrogenation to *p*-cymene in the presence of a catalyst, FAU Y, since it is the favoured catalyst in terms of yield and selectivity (Chapter 2.5.1). This catalyst requires preparation within a fired heater to remove any moisture contained in the matrix. This ensures optimal efficiency of the catalyst. It is then loaded into the reactor and reactivated after a period when poisoning and possible active site compromise has occurred up to the point where a noticeable change in yield is detected. Complete conversion of the major terpene is achieved under the described conditions (5 bar and 300°C), while *p*-cymene is the main product formed. The majority of the menthenes and menthanes formed are represented by *p*-menth-3-ene and *p*-menthane, respectively. Terpene isomers include terpinolene (30.5%), α -terpinene (45.4%), γ -terpinene (15.7%) and menthadiene (8.4%) (Linnekoski *et al.*, 2014).

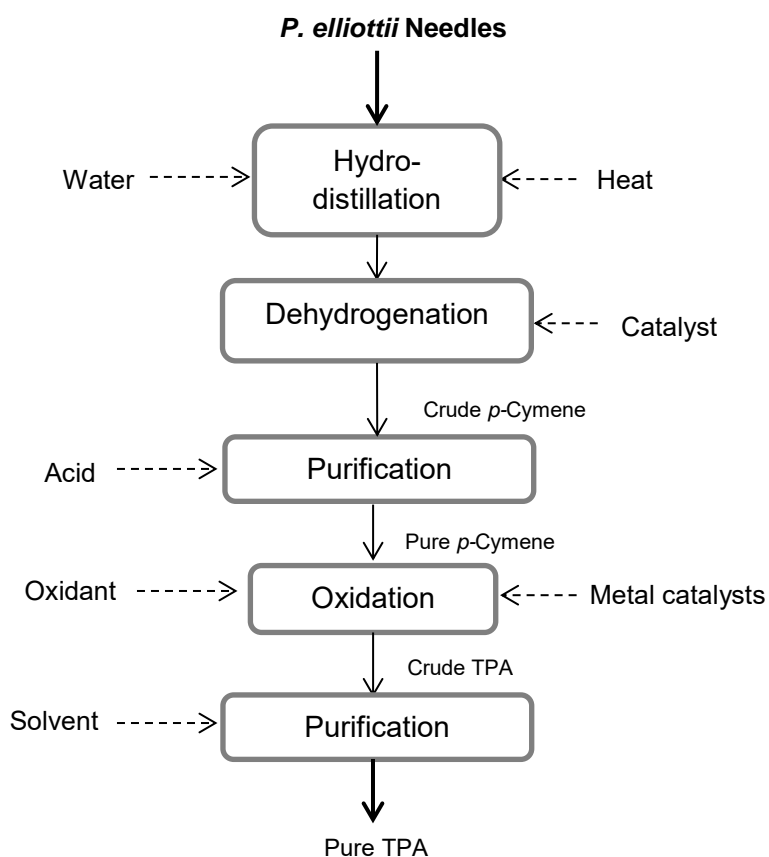


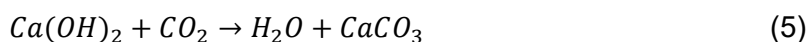
Figure 16: Pine process flow diagram

In order to purify crude *p*-cymene (Chapter 2.5.2), sulphuric acid is firstly used to catalyse the conversion of monoterpenes in the feed stream to diterpenes, such as cembrene A, isocupressic acid and elliotinol. The formed diterpenes can easily be separated from *p*-cymene in a distillation column due to the difference in boiling points.

Oxidation of the pure *p*-cymene occurs in two steps, where the product from the first step consists mostly of *p*-toluic acid and a small amount of TPA (Chapter 2.5.4). The products formed at these parameters are *p*-toluic acid, *p*-isopropyl benzoic acid (cumic acid) and terephthalic acid, with complete conversion of *p*-cymene. Together with oxygen, Fe and Mn (at an atomic ratio of 3:1) form the appropriate catalyst for this reaction.

The intermediate product (*p*-toluic acid) is mainly converted to TPA in the second oxidation step, while 4-CBA and benzoic acid form as by-products. The catalyst added for the second oxidation step is tetra(*p*-chlorophenylporphinato)manganese/cobalt acetate (T(*p*-Cl)PPMnCl/Co(OAc)₂) and is required in small doses depending on the amount of *p*-toluic acid present within the reactor.

Gas expelled during both oxidation steps need to be treated to recycle excess oxygen. The main gas formed is carbon dioxide and can be extracted from the oxygen by passing it through calcium hydroxide to form calcium carbonate in the following reaction:



Purification of TPA is necessary to bring the product up to the required specifications (Chapter 2.5.5) by limiting the amount of by-products formed during oxidation. A wash-filter unit is used where the powder will be in contact with a solvent, NMP, in which TPA has a much higher solubility than the by-products. Multiple contact sessions are necessary to bring the product up to standard, but is also limited by the increase in capital cost. The product stream is then introduced to a mixing vessel, where acetone is added to break any NMP-TPA complex salts formed and to remove a fraction of additional by-products. The amount of acetone added to each mixing vessel is determined by the amount of TPA present within the vessel. The solid product powder is dried (removing added solvents) within a drier, where approximately 80% of the flue gas is recycled to be used as fluidising agent. The final step is cooling the pure product powder in a screw cooler for safer handling.

3.2.2 Process description for TPA production from *Eucalyptus* leaves

Figure 17 depicts a simplified process flow of the selected processes towards the production of TPA from *Eucalyptus* leaves. The *Eucalyptus* leaves are decreased in size before entering the extraction section through milling. Supercritical fluid extraction using carbon dioxide will be used for the extraction of cineole from the biomass source (Chapter 2.4.4). This will result in a higher capital cost than utilising steam- or hydro-distillation technology, but ensures maximum extraction of the major terpene, without the need for additional water-cineole separation steps (of which no literature exists for this specific separation) (Handa *et al.*, 2008).

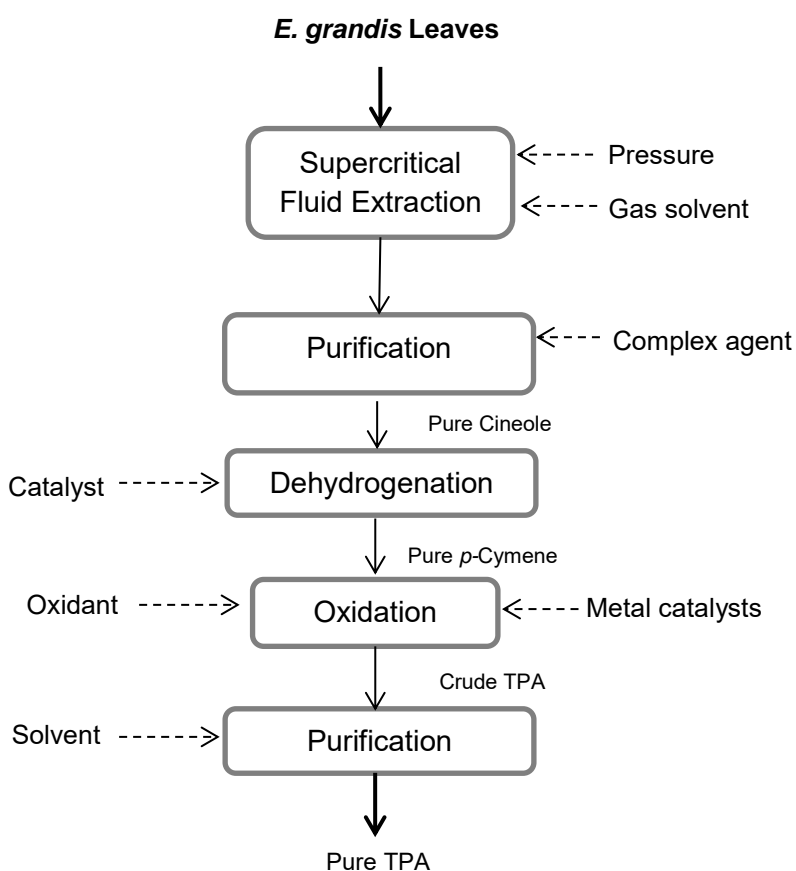


Figure 17: *Eucalyptus* process flow diagram

Purification of the major terpene, 1, 8-cineole, was chosen, rather than the purification of *p*-cymene after dehydrogenation, because of the use of a reusable and cheap complex forming solvent (as discussed in Chapter 2.4.7). Hydroquinone forms a complex with cineole at a low temperature, while the residual terpenes remain unaffected. Separation of the complex and residual terpenes is done by distillation column in vacuum at 50°C. The energy intensive part of this purification step is supplying the low temperature of -10°C prior to separation.

Conversion of cineole to *p*-cymene is governed by yields calculated through the selectivities given in literature (as discussed in Chapter 2.5.3). 99% conversion of cineole is achieved under the specified conditions (1 bar and 280°C). In order to allow for continuous catalyst replacement or regeneration, the reactor configuration is that of a moving bed reactor with a palladium doped γ -Al₂O₃ catalyst consisting of 0.38 wt % palladium. A carrier gas, consisting of argon (92.7 wt %) and oxygen (7.3% wt %), is used to deliver the purified major terpene to the reactor.

The pure *p*-cymene produced during dehydrogenation is structurally identical to the *p*-cymene produced during the *Pine* process, it is therefore appropriate to apply the same oxidation steps towards the production of TPA as described in Chapter 2.5.4. The purification method also remains the same, with the only difference being the concentration of by-products formed.

3.2.3 Process description for TPA production from PHR

At the time of this study, the majority of biomass processed within Ngodwana's pulp mill was *Pine*; therefore, the major terpene for this process is α -pinene. The pre-hydrolysate or pre-cooking stage releases the naturally occurring terpenes and sulphurous compounds from the wood chips together with a large amount of water (approximately 40% of the wood chip mass present in the pre-cooking vessel). Separation of the oil and water layer occurs in a decanter. Ideally, the next step would consist of desulphurisation, but as shown in Figure 8, the conversion of α -pinene produces hydrogen sulphide from naturally occurring sulphurous compounds. Therefore, even a fraction of these compounds would result in the formation of hydrogen sulphide, which is most important to limit during this process.

Dehydrogenation of the major terpene follows decanting and produces a crude *p*-cymene product (Chapter 2.5.1). The product stream is treated with hydrogen peroxide, which reacts with the sulphurous compounds and especially with hydrogen sulphide to form elemental sulphur and dimethyl sulfoxide (Chapter 2.4.8). The modelling of this specific reactor will make use of stoichiometry and conversions to define the desulphurisation. The formed compounds can be discarded in a more environmentally friendly way and pose a decreased risk to the processing plant employees.

The crude, desulphurised *p*-cymene product is then purified in a vessel with an acidic pH produced by sulphuric acid to encourage the formation of diterpenes from each monoterpene species present in the vessel (Chapter 2.5.2). A large difference between the boiling points of the *p*-cymene and diterpenes allows easy separation within a distillation column.

A two-step oxidation is used where *p*-toluic acid is the major intermediate product formed during the first oxidation, while the second step produces mainly TPA. Oxygen at an excess of 20% is used as oxidising agent for both stages (Chapter 2.5.4).

Lastly, the crude TPA product is subjected to washing and drying steps to produce a product at the required specifications (Chapter 2.5.5).

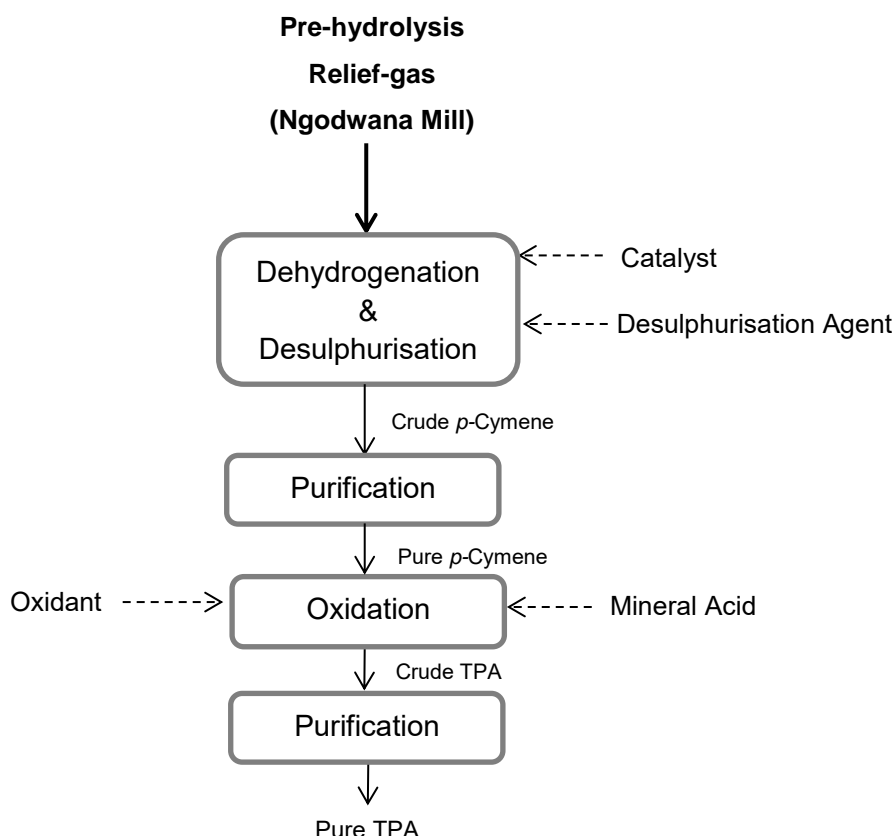


Figure 18: Pre-hydrolysis relief-gas process flow diagram

3.2.4 Process description for TPA production from 1G feedstocks

Figure 19 depicts a simplified process flow of the selected processes towards the production of TPA from starch-based feedstocks. The CCEI process represents the processing and conversion of the starch-based feedstocks to *p*-xylene. Depolymerisation of the starch source in the presence of a dehydration catalyst, HCl, produces solely glucose with a conversion rate of 75% (based on mass of reactant fed). Reactor conditions for this process are at 1.9 MPa and 180°C. Within the next reactor, NaCl and THF is added together with the zeolite Sn-Beta catalyst in order to fully isomerise the sugar content (glucose and/or fructose) within the reactor to produce HMF (with a selectivity of 69%). Salt is added to encourage the HMF

product into the extracting phase without the need for a solvent. It also increases the product yield and suppresses by-product formation. By-products of this reaction such as levulinic acid and formic acid leave the reactor together with HMF and unreacted sugars. Humins are separated from the product stream via filter. Excess THF is recovered and recycled within a flash column and separated from levulinic and formic acid within a distillation column.

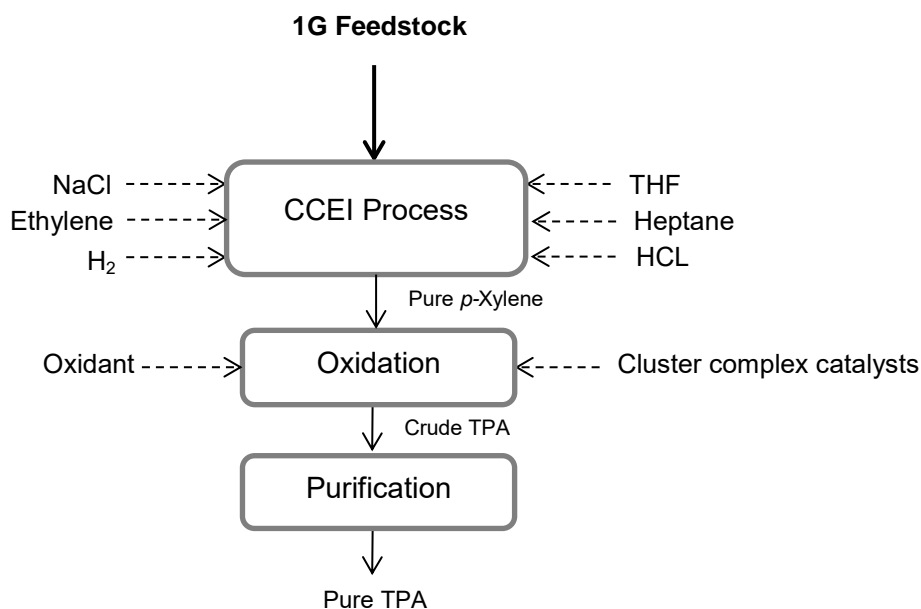


Figure 19: Starch-based process flow diagram

At 220 °C and 0.69 MPa HMF is fully converted to DMF (with a selectivity of 78%) in the presence of a Cu-Ru/C catalyst and with the addition of hydrogen. The distillation of the product stream separates water and other unreacted or by-products such as 2, 5-dihydroxymethyltetrahydrofuran from DMF. The next conversion step takes place within a reactor at 300°C and 5.7 MPa and involves the addition of n-heptane and ethylene to produce p-xylene from purified DMF. 95% conversion is achieved during this reaction with a selectivity of 75.5% towards p-xylene. Unreacted ethylene is recycled in a flash downstream from the p-xylene reactor, while water is removed from the product stream via decanter. The final purification involves distillation of the inorganic layer retrieved from the decanter. By-products such as n-tridecane are removed through distillation to produce a product stream containing 99.5% pure p-xylene.

The oxidation of the pure p-xylene involves the utilisation of pure oxygen and an equimolar mixture of $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ and $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ salts (Chapter 2.9.2). At 200°C and

550 psig p-xylene is fully converted within the reactor to terephthalic acid (99.6%), p-toluic acid (0.36%), 4-CBA (0.03%) and benzoic acid (0.01%).

A similar approach as described in Chapter 2.5.5 will be used to describe the purification of TPA. The final product should have the specifications listed in Table 11 in order to be sold as purified TPA powder.

4 Technical modelling and analysis

This chapter describes the modelling routes taken to utilise the chosen literature for the development of industrial scale simulations. The simulations as well as the heat integration thereof were completed using Aspen Plus® together with the integrated Aspen Energy Analyser. Finally, a comparison is drawn between the 2G models (*Pine*, *Eucalyptus* and PHR) in terms of TPA production rates, overall yields, power generation and utility usage. A technical comparison with the starch-based model is not done due to incomplete technical information of the CCEI process.

4.1 Plant model layout

For each of the models, a set of codes have been assigned to each section, stream and equipment. Each section is chosen based on the main processes and other surrounding processes. For example, the hydro-distillation process (main process) together with the condensation and decanting of oils (other processes) is regarded as one section. Each section is coded with an 'S' and numbered accordingly. Streams are named according to section and number, for example S1-02, which is the second stream in the first section. Equipment is coded using a symbol to describe the type of equipment and numbered first showing the section number and then the number of the equipment. The equipment codes are shown in Table 13. E-210, for example, represents the tenth heat exchanger in section 2. Any equipment or stream coded with an 'X' is placed in the section for simulation purposes and does not necessarily represent actual equipment in the plant.

Table 13: Equipment code description

Equipment code	Description
C	Compressor/Turbine
E	Heat Exchanger
H	Fired Heater
P	Pump
R	Reactor
T	Tower
V	Vessel
D	Decanter
M	Mixing Tank
F	Filter
Y	Solids Dryer/Crusher

4.2 Property methods and assumptions

The following property methods and assumptions were applied during modelling:

- The base method chosen for all three models is the UNIQUAC (Universal Quasi-Chemical) method, an appropriate method in a system with liquid mixtures at relatively low pressures (lower than 10 bar). Certain sections were modelled with other methods depending on the phase and types of components as well as the operating parameters. For example, the super critical fluid extraction of the Eucalyptus biomass required the property method RK-Soave because of the use of super critical CO₂ with a pressure above 80 bar (AspenTech Inc., 2001).
 - For most of the simulated equipment, such as heat exchangers, the pressure drop was neglected.
 - Some equipment, such as decanters and extraction vessels it is assumed to be well insulated; therefore the heat lost to the environment is zero.
 - To simplify calculations, some of the reactors were broken down into sections, where a simulated heat exchanger at the end of the section represents the heat duty of the actual reactor.
 - Medium pressure steam was added as utility to provide endothermic energy to reactors, while cooling water was added as utility where an exothermic reaction took place within a reactor with a COP of 7 (Bergstein, 2009).
 - It was assumed that an 80% recirculation of flue gas obtained from solids driers would be sufficient for fluidisation (Driscoll, 2014).
 - 20% excess oxygen was assumed sufficient during combustion of biomass and oxidation.
 - A number of minor chemical components were not available in the Aspen Plus® databanks and were added manually through the 'user defined' option. Each compound's chemical structure was uploaded in a mol file format, where after the 'calculate bonds' button was selected. Additional information such as boiling point, molecular weight, formation and Gibbs energy was inserted to more accurately define each unknown compound.
 - Pump inputs in Aspen were specified as the discharge pressure, where the efficiencies that Aspen calculates were lower than expected in reality. Mechanical and electrical efficiencies were specified between 80% and 85%.
 - Compressors were specified as isentropic together with a discharge pressure. The overall efficiency was averaged at 78%.

4.3 Lignocellulosic-based (2G) Feedstock

The *Pine* needle and *Eucalyptus* leaves biomass was defined by their proximate and ultimate compositions (shown in Table 14). It represents the solid portion and water moisture of the *Pine* and *Eucalyptus* biomass given by Janajreh *et al.* (2012) and Mishra *et al.* (2010), respectively. This represents approximately 98% of the total biomass mass and placed in the NC (non-conventional) Solid section of the biomass feed stream. The terpene oil contained within each biomass type make up approximately 2% of the total biomass and was set as mixed input in the same biomass feed stream. The average terpene content for each biomass type is given in Table 15. In addition to the liquid portion of the *Eucalyptus* biomass, natural waxes are also included and make up approximately 0.6% of the total biomass.

Ngodwana Mill produces pulp at a rate of 410 tonnes/year of a combination of hardwood and softwood, while the capacity for crude sulphonated turpentine (CST) from softwood is approximately 180 tonnes/year. Table 15 shows the average terpene content of CST expelled as a relief-gas in the pre-hydrolysate cooking stage (described in Figure 4) (Triumph Venture Capital, 2004).

Table 14: Proximate and ultimate composition: *P. elliottii* needles and *E. grandis* leaves

	Pine needles	Eucalyptus leaves
Proximate composition:		
Moisture	9%	4.4%
Volatile matter	49%	57%
Fixed carbon	46.5%	34.5%
Ash	4.5%	4.1%
Ultimate Composition:		
C	46.4%	51.1%
H	6%	8.8%
N	1.4%	40.1%
S	0%	0%
O	41.7%	0%

Table 15: Average biomass oil composition

Chemical compound	Pine needle oil	Eucalyptus leaf oil	PHR CST
α -Pinene	43%	2.2%	51.3%
β -Pinene	27.1%	1.3%	24.7%
β -Phellandrene	6.1%	-	11.6%
Myrcene	2.9%	-	3.6%
Camphene	1.9%	-	2.6%
Limonene	2.9%	1.9%	2.6%
δ -Terpineol	-	1.6%	3.6%
α -Terpineol	9.6%	7.7%	-
α -Terpinene	0.1%	1.3%	-
1,8 Cineole	-	81.4%	-
Terpin-4-ol	0.1%	2.6%	-
α -Thujene	0.3%	-	-
Tricyclene	2%	-	-
α -Fenchol	0.5%	-	-
Fenchene	1.1%	-	-
β -Caryophyllene	0.6%	-	-
Terpinen-4-yl Acetate	0.2%	-	-
γ -Cadinene	0.3%	-	-
Methyl Salicylate	0.1%	-	-
Methyl Eugenol	0.1%	-	-
γ -Terpinene	0.1%	-	-
<i>p</i> -Cymene	0.2%	-	-
Linalool	0.8%	-	-

4.4 Model scenarios studied

Each model scenario simulated was divided in sections to represent each processing section. Some section elements are shared between scenarios (as shown in Figure 20), where minor differences, such as stream composition, product and by-product concentrations as well as by-product treatment will be discussed.

Figure 20 (a) shows the *Pine* biomass model section layout. Each section contains the following:

S1: Hydro-distillation of biomass in vessels arranged in series to extract terpenes contained within the biomass.

S2: Dehydrogenation of major terpene, α -pinene, to *p*-cymene via a fixed bed reactor.

S3: Acid catalysed purification of *p*-cymene through diterpene formation.

S4: *p*-Cymene oxidation through oxygen to TPA and oxidation of *p*-toluic acid to TPA.

S5: TPA purification to minimise by-products.

S6: Biomass combustion and steam cycle power generation.

S7: Purified TPA drying and cooling section (contained within S5).

Figure 20 (b) shows the *Eucalyptus* biomass model section layout. Each section contains the following:

- S1: Supercritical fluid extraction of *Eucalyptus* biomass towards the extraction of terpenes.
- S2: Purification of terpene cineole via complex formation with hydroquinone.
- S3: Dehydrogenation of major terpene to *p*-cymene.
- S4: Two-stage oxidation of *p*-cymene to *p*-toluic acid, TPA and 4-CBA.
- S5: TPA purification to minimise 4-CBA and *p*-toluic acid.
- S6: Biomass combustion and steam cycle power generation.
- S7: Purified TPA drying and cooling (contained within S5).

Figure 20 (c) shows the pre-hydrolysate relief-gas (PHR) model section layout. Each section contains the following:

- S1: Dehydrogenation of terpene α -pinene to *p*-cymene and desulphurisation of natural sulphurous compounds
- S2: Purification of *p*-cymene via diterpene formation using an acid catalysed environment.
- S3: Two-stage oxidation of *p*-cymene to *p*-toluic acid, TPA and 4-CBA.
- S4: TPA purification to minimise 4-CBA and *p*-toluic acid.
- S5: Purified TPA drying and cooling (contained within S4).

Figure 20 (d) shows the starch-based model section layout. Each section contains the following:

- S1-1: Single stage oxidation to TPA, 4-CBA, *p*-toluic acid and benzoic acid.
- S1-2: Purification of TPA solid to minimise by-products.

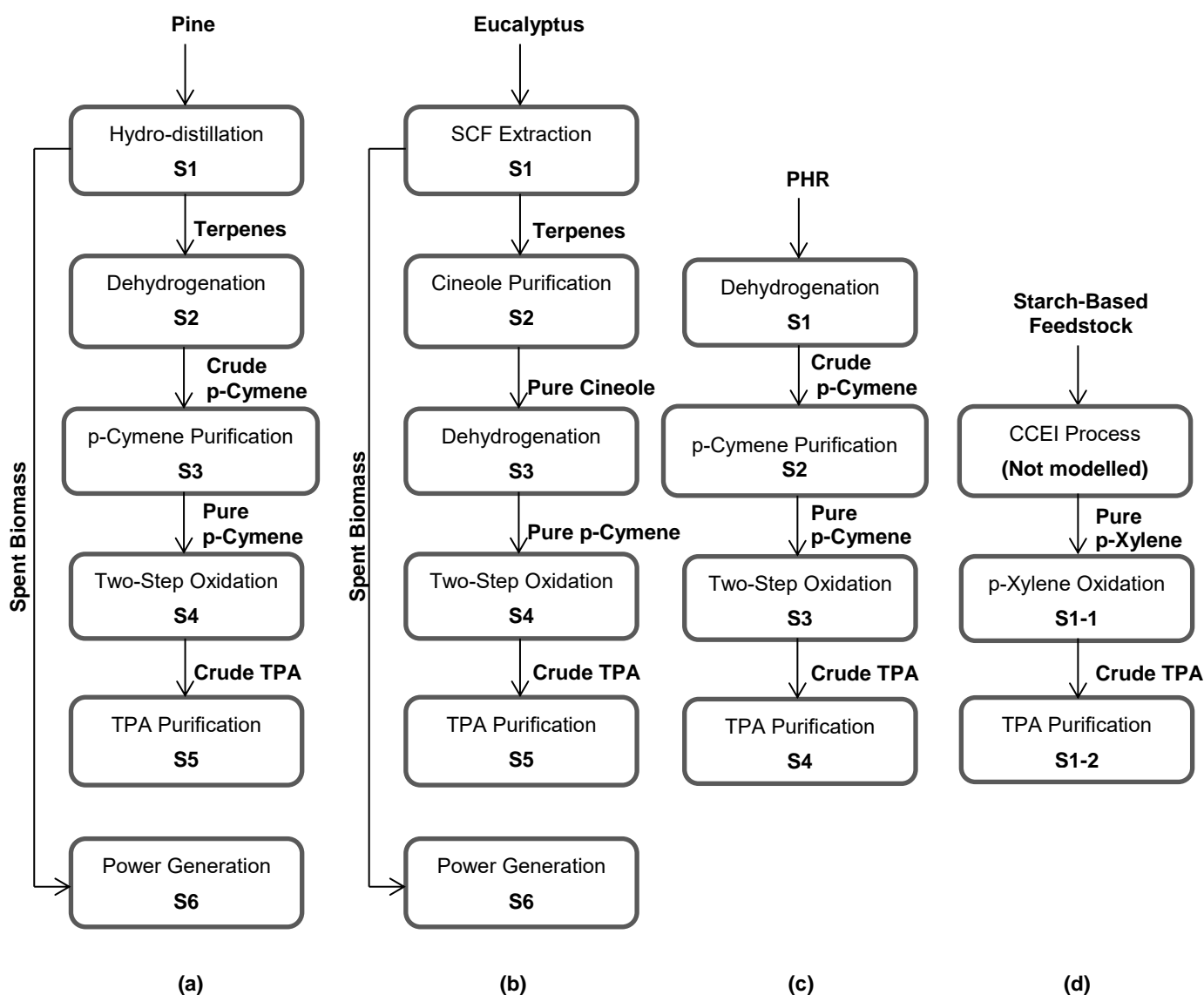


Figure 20: Technical modelling process sections

4.4.1 Size reduction

In order to determine which size reduction block to simulate, the feed size, product size and capacity for each 2G feedstock was compared in Table 16 (Anwar, 2011). In terms of the *Pine* biomass, the typical average needle size is 150mm x 3mm, which suggests that either a cone crusher, impact breaker or rod mill can be used. Considering the product size, particle diameters should range from 0.5 mm to 2 mm, where these smaller particle sizes expose more terpene oils and create an opportunity for further lysis of the underlying cells (Kim *et al.*, 2013). Therefore, impact breakers, rod mills can be used. Lastly, considering the capacity of this unit, the equipment should be able to handle the *Pine* capacity range of 80 kg/hr to 150 kg/hr. Hammer and jet mills are able to handle this capacity, but the reduction of the particle

are too severe and might cause some of the particles to escape the hydro-distillation area together with formed vapours. Rod mills are therefore chosen to simulate the size reduction of the *Pine* biomass.

Table 16: ASPEN Plus size reduction blocks

Equipment	Size of feed (mm)	Size of product (mm)	Reduction ratio	Capacity (tons/hr)	Power consumption (kW)
Gyratory crusher	200-2000	25-250	8	100-500	100-700
Jaw crusher	100-1000	25-100	8	10-1000	5-200
Cone crusher	50-300	5-50	8	10-1000	20-250
Impact breakers	50-300	1-10	40	10-1000	100-2000
Rod mills	5-20	0.5-2	10	20-500	100-4000
Ball mills	1-10	0.01-0.1	100	10-300	50-5000
Hammer mills	5-30	0.01-0.1	400	0.1-5	1-100
Jet mills	1-10	0.003-0.05	300	0.1-2	2-100

Using the same deduction method for the *Eucalyptus* biomass and considering its capacity range of 660 kg/hr to 900 kg/hr and leaves with diameters less than 200 mm. To prepare the biomass for supercritical fluid extraction a cone crusher can provide the correct size range.

The bond work index is essential for size reduction calculations and depends on the type of biomass and is the work required to reduce 80% thereof to a size of at least 100 mm per ton of the fed biomass. The range of this index for agricultural waste is 7 to 15.8 kW/ton. For the *Pine* and *Eucalyptus* biomass an index of 8 and 15.8 kW/ton is used, respectively that correlate with each fed particle size (Serna, 2015).

4.4.2 Terpene Extraction

4.4.2.1 α -Pinene Extraction from *Pine* Biomass

Size reduction equipment will not be modelled but costed according to the necessary capacity, which will contribute to the total estimated installation cost of equipment. The extraction of terpenes through hydro-distillation is simulated by vessels operated in semi-batch (Figure 21). The macerated biomass (*Pine* needles) (S1-01) are fed to three vessels (V-101, V-102 and V-103). The mass flow rate of the biomass feed is determined by amount of biomass available calculated in Table 3.

Water (S1-02) is fed to the same vessels at a mass flow rate four times greater than the biomass flow rate (calculated in CALC1), to ensure full submersion of the biomass and to avoid clumping and clogging in the vessels and pipes. The biomass slurry is fed to each

vessel using slurry pumps (P-101 A/B and P-102 A/B). A/B denotes a backup pump for major pipelines (these symbols are omitted further but included during the costing of the plant). Pump P-103 A/B transports the slurry to section 6 (power generation). A heat stream is connected to V-103, where the heat duty is varied in CALC2 to extract the maximum amount of terpene oil to S1-11.

Vapour from V-103 and V-102 is recycled through S1-09 and S1-10 to increase the rate of terpene extraction and transport the vapours to V-101 to be sent through a condenser (E-101 via S1-11). The vapours, which contain a large amount of steam, are condensed in E-101 up to the point of a zero vapour fraction (approximately 51°C). The liquid is then decanted (D-101) to separate the water fraction from the essential oils, where complete separation can be assumed, due to the negligible solubility of the oils in water. S1-14 carries the terpene layer to section 2, while the water layer (floral water) is carried through S1-13 to be recycled back to S1-02.

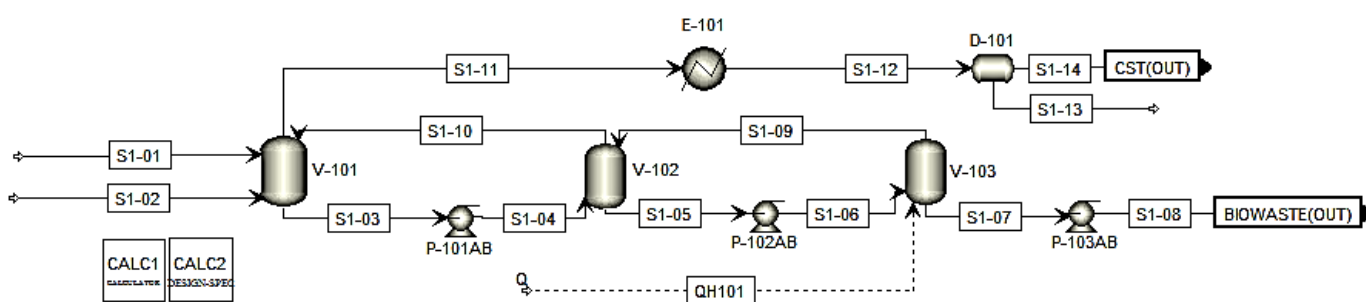


Figure 21: Pine Model Terpene Extraction

4.4.2.2 Cineole Extraction from Eucalyptus Biomass and Purification

The *Eucalyptus* biomass was defined as a solid, terpene liquid and wax fraction, where the wax fraction was calculated in CALC1 as 0.6% of the total mass containing the solid and terpene fractions (shown in Figure 22). The solid and terpene fractions (X101) and the wax fraction (X102) is combined in X103 to form the biomass feed stream (S1-01) to the supercritical fluid extraction tower (T-101). The size decreasing equipment will not be modelled but added to the total installed equipment cost. The volumetric flowrate of CO₂ needed for this extraction is calculated in CALC2 and is a ratio of the mass flow of terpenes in stream S1-01. T-101 is operated at 80°C and 163 bar to ensure the complete extraction of the terpenes from the biomass, which also include the natural waxes (Francisco *et al.*, 2001). A slurry pump is added to the equipment costs to bring the biomass up to 163 bar. After

extraction, the spent solid biomass is sent to section 6 after extraction through S1-05, while the terpene-wax mixture is removed by the solvent through stream S1-06. The mixture is heated further to 160°C to remove the solvent in T-102 and then cooled to 80°C (in E-104) to further remove terpenes in T-104. The CO₂ solvent in S1-17 is recycled back to S1-02.

The terpene-wax mixture from tower T-102 is sent through stream S1-08 to a hydraulic turbine to lower the pressure of the system back to 1 bar. The mixture is then heated to 180°C to separate the terpene liquid from the natural waxes in tower T-103. The wax leaves the section through stream S1-11 and is discarded (production rates of these waxes are too small to contribute economically through sales but could be added to section 6 together with S1-05). The terpenes obtained from towers T-103 and T-104 through streams S1-12 and S1-14 are combined in vessel M-101 to be sent to section 2 through stream S1-13.

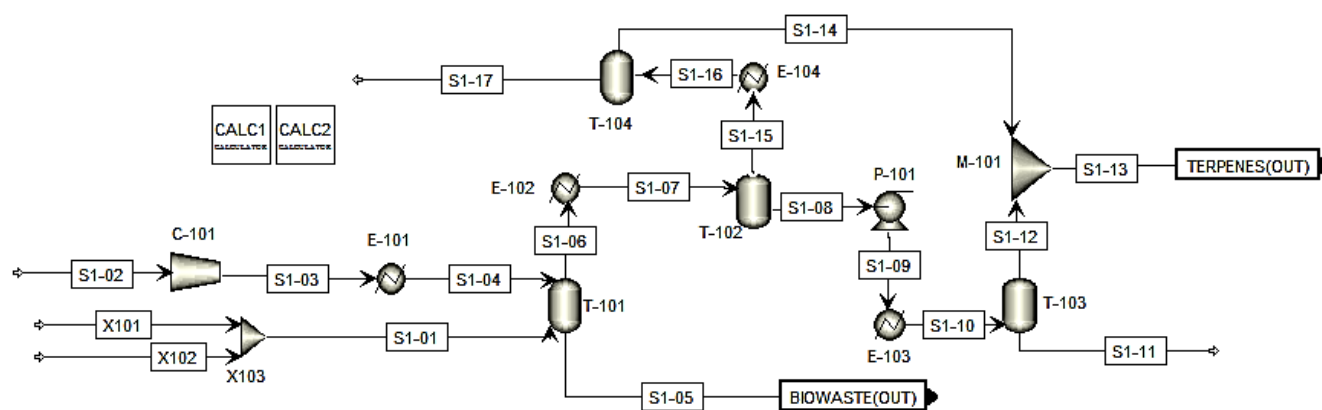


Figure 22: Eucalyptus Model SCF Terpene Extraction

Terpenes extracted in section 1 enters section 2 through stream S2-01 and is added to an amount of HQ in vessel M-201, calculated in CALC1 as a mass ratio of the amount of cineole entering M-201 (shown in Figure 23). The mixture is then cooled to -5°C to initiate the formation of a cineole-hydroquinone complex in tower T-201. The complex is removed and heated through E-202 to 50°C to break the complex in tower T-202 under vacuum.

Purified cineole leaves the tower through S2-06, while the solvent (S2-07) is cooled to -5°C and reused to extract residual cineole retrieved from tower T-201 through S2-09. The HQ and terpenes are mixed in M-202 and sent to the second extraction tower (T-203) through S2-10. The unreacted terpenes (with a lower boiling point than the complex) leave the tower through S2-11, while the complex is sent to tower T-204 through S2-12. The complex is heated to 40°C in E-204 and separated in tower T-204. Purified cineole from S2-14 and S2-06 is mixed

in vessel M-203 before entering the conversion section. X202 to X204 is used to remove any traces of HQ that might interfere with further calculations. The final purified mixture of cineole with a purity of 96 wt % leaves the section through S2-16.

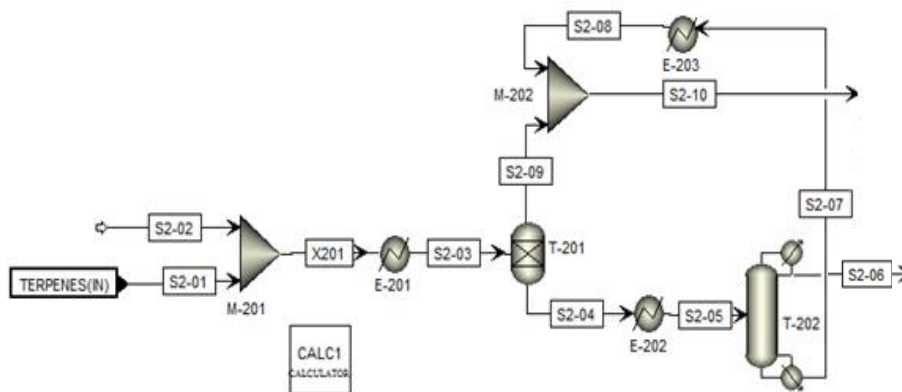


Figure 23: Eucalyptus Model Cineole Purification: Section One

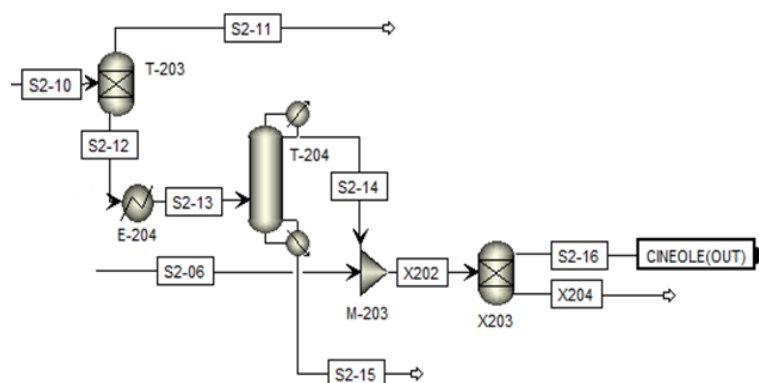


Figure 24: Eucalyptus Model Cineole Purification: Section Two

4.4.3 p-Cymene Production

4.4.3.1 Crude α -Pinene Conversion

Due to the absence of kinetic data on this conversion, it was necessary to create mass balances that utilise the given selectivities to calculate the yield of the product stream (shown in Table 17). Therefore, a yield reactor will be used to simulate the dehydrogenation (shown in Figure 25) due to the nature of data found in literature (selectivities and conversion given in Table 17). To simplify calculations, the reactor was broken down into the reaction section where the terpenes are converted, a section where the carrier gas, nitrogen, is pressurised and heated and lastly a section where the catalyst and carrier gas is added to the system. In reality, the terpenes could be introduced to the carrier gas through an atomizer. QY201

represents the overall heat duty resulting from the reaction as well as mixing of all components.

The terpene liquid extracted in section 2 is introduced (from S2-01, S2-03 to S2-05A) to the reactor (R-201) after being pressurised to 5 bar by P-201A and heated to 160°C via heat exchanger (E-201A), according to specifications given in the discussed literature (Section 2.5.1). The carrier gas is compressed (C-201B) and heated (E-201B) and added to the mixing block of the reactor model. The catalyst loading (S2-06) was calculated in CALC1 using a ratio of the terpene feed (mass flow rate of terpenes to catalyst mass over an active catalyst period). Moisture is removed within a fired heater (H-201) at 500°C.

Together with the *p*-cymene product (X201), carrier gas (S2-05B) and catalyst (X206), the heat of reaction (QR201) from R-201 was added to X204 to determine the total heat of the reactor system (QY201). X210 simulates the separation of the solid catalyst from the vapour product and carrier gas. The vapour stream is then de-pressurised in a turbine (C-202) and cooled (E-202) to 60°C to separate the gaseous nitrogen from the liquid products in a flash column (T-201). The liquid products (S2-13) from the column are then sent to section 3. Complete recycling of the nitrogen is achieved (so that S2-12 is joined at S2-02) because of the absence of sulphurous compounds in the *Pine* needles that cause the formation of H₂S, CH₄ and (CH₃)₂S under these conditions.

It would then be necessary to simulate the catalyst as a continuous stream, where the activated period is divided by the mass of the catalyst to determine the mass flow rate. The composition of the catalyst will be defined by the chemical compounds that it comprises of, where the distribution of these components is given in Table 18.

Table 17: *α*-Pinene Dehydrogenation Conversion and Selectivities

	<i>α</i> -Pinene	<i>p</i> -Cymene	<i>o</i> -Cymene	<i>m</i> -Cymene	Terpene Isomers	Menthenes	Menthanes
Conversion	100%						
Selectivity		20%	0.31%	7.7%	11%	16%	3.8%

Table 18: Faujasite Y Composition

Component	Mass Percentage (%)
H ₂ O	27.30
Na ₂ O	0.20
CaO	2.70
MgO	0.60
Al ₂ O ₃	16.92
SiO ₂	52.28

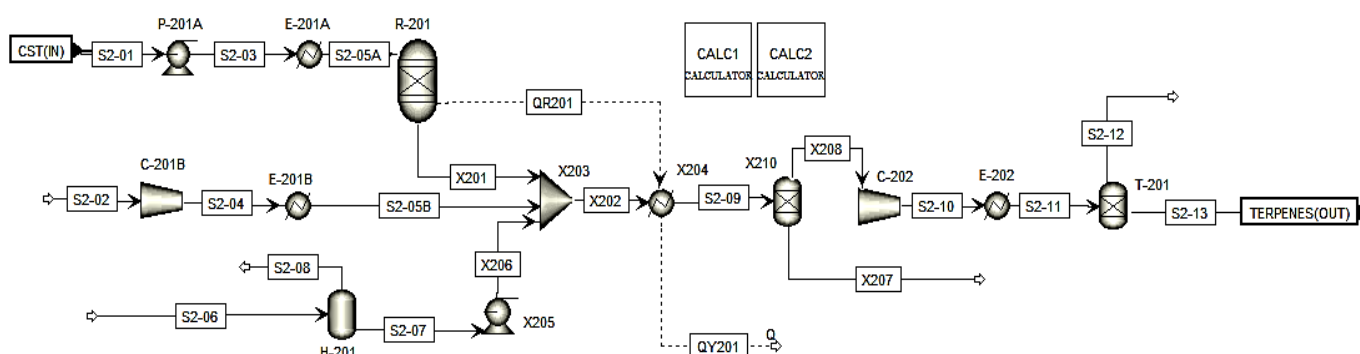


Figure 25: Pine Model Alpha-Pinene Conversion

The conversion of α -pinene in the PHR model shares similarities to that of the *Pine* model. Section 1 of the PHR model (described in Figure 20 (c)) receives CST from the pre-hydrolysate cooking stage (entering stream S1-01 shown in Figure 26) at a rate of 180 tonnes/year. The terpene portion of the CST enters in X114, while the steam enters in X115. The mass flow of steam is approximately four times the mass of the original biomass in the pre-cooking stage and is calculated in CALC3. The CST is cooled to 30°C to allow easy separation of the oil layer (containing terpenes) from the water in D-101. The oil layer leaves the decanter through S1-04 and is heated to 300°C before entering reactor R-101. The dehydrogenation steps are approached the same as for the *Pine* model, where conversion of the major terpene takes place in yield reactor R-101. The carrier gas is introduced through S1-06, while the catalyst (characterised in Table 18) is introduced through S1-09. X106 represents the total heat duty from reaction and mixing.

The product stream is brought back to atmospheric pressure from 5 bar through C-102 and cooled to 25°C in E-103 before desulphurisation. Hydrogen peroxide (S1-14) is added according to the stoichiometric ratios for each natural sulphurous species described in Section 2.4.8. Desulphurisation takes place within R-102 (shown in Figure 27) and relies on stoichiometric equations to determine the product composition exiting the reactor (S1-15).

(in reality the catalyst would not exit the reactor as a product). The product stream is then sent to tower T-301 to remove any gases through S3-09. The final *p*-cymene product (with a purity of approximately 98 wt %) is then sent to section 4 for oxidation through stream S3-08 (shown in Figure 28). To simplify the calculations surrounding the reactor, the modelling will be broken down into three different sections: a reacting section dependent on product yields, pressurising and heating of the carrier gas as well as the introduction of the catalyst.

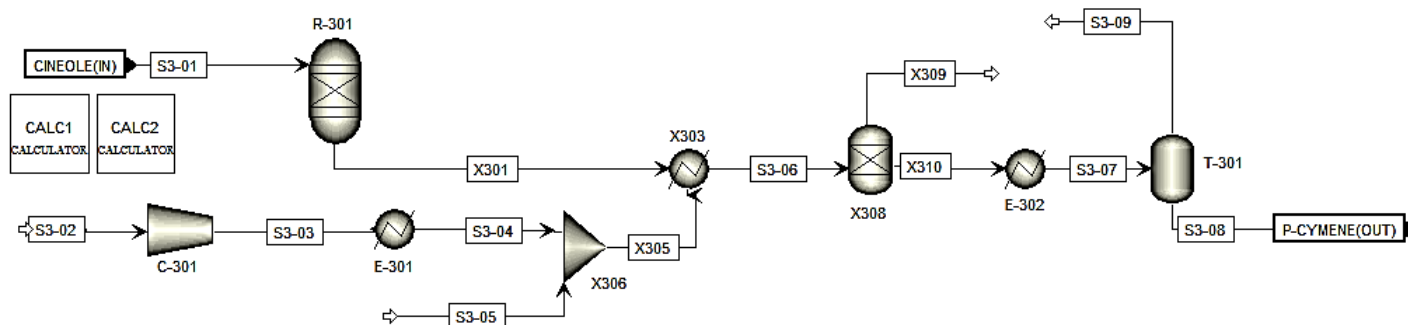


Figure 28: Eucalyptus Model Cineole Conversion

4.4.4 *p*-Cymene Purification

The terpene liquid product (stream S3-01 shown in Figure 29) obtained in section 3 is added to 95 w/w% sulfuric acid (S3-02) and heated to 75°C (the temperature at which the acidic environment promotes the production of diterpenes from the monoterpenes present in the feed). CALC 1 calculates the amount of sulphuric acid needed, which is 25% of the terpene mass flow in stream S3-01. R-301 simulates the formation of diterpenes by using the yields of the products determined through mass balances (Brücher *et al.*, 2013). The reactor product is cooled to 70°C by E-302 to be distilled in tower T-301. The higher boiling point diterpenes and sulfuric acid are easily separated in the tower and leaves through stream S3-07, while the purified *p*-cymene (98% w/w) leaves at the top of the tower through S3-06 to section 4. X304 is used to remove excess traces of sulphuric acid.

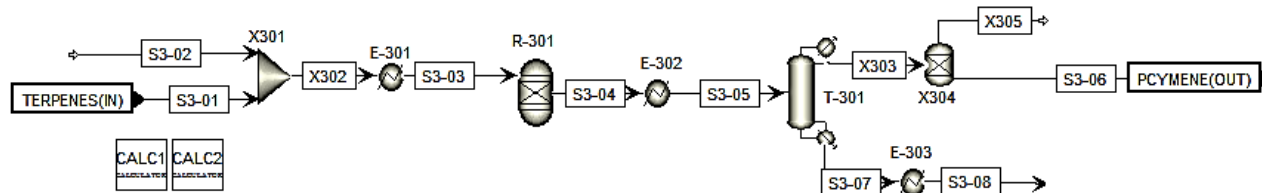


Figure 29: Pine Model *p*-Cymene Purification

The PHR model *p*-cymene purification (shown in Figure 30) was modelled in the same manner as for the *Pine* model, with minor differences resulting from section 1.

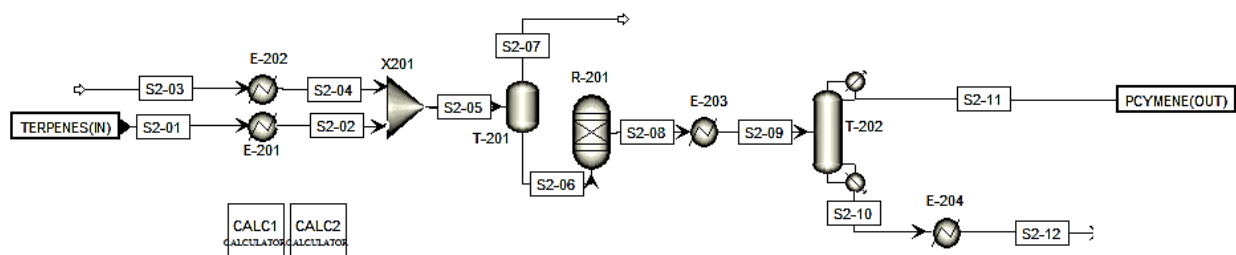


Figure 30: PHR Model *p*-Cymene Purification

4.4.5 Crude Terephthalic Acid Production

Purified *p*-cymene obtained from section 3 is introduced to yield reactor R-401 through stream S4-01 (shown in Figure 31). Selectivities given in literature were used to determine the product composition through mass balances in Excel (given in Table 19) (Neatu *et al.*, 2016). CALC 1 calculates the mole flow of oxygen (entering in stream S4-02) needed for the oxidation of *p*-cymene, which is six times the mole flow of *p*-cymene present in the feed stream to R-401. 20% excess oxygen is added to the calculated mole flow. Before oxidation, the oxygen is pressurised to 20 bar in C-401 and heated to 140°C in E-401 before entering the reactor. The product stream exiting the reactor (S4-05) enters a vessel (V-401) that serves as a blow-off for build-up gasses and separates any excess oxygen from the product.

Table 19: Two-Step Oxidation Conversions and Selectivities

	<i>p</i> -Cymene	TPA	<i>p</i> -Toluic Acid	Cumic Acid	4-CBA
1st Conversion	100%				
1st Selectivity		38%	56%	5%	
2nd Conversion			62.9%		
2nd Selectivity		96.8%			3.4%

p-Toluic acid is the intermediate product to the production of terephthalic acid and is the major product from R-401. The second oxidation step's conversion and selectivities are given in Table 19 and was used to determine the product composition (Xiao *et al.* 2010). To increase the amount of the desired product (TPA), another oxidation step is added, which requires different conditions (190°C and 1.2 MPa) to convert *p*-toluic acid to TPA (in R-402). The required mass flow of oxygen is calculated in CALC2 and is determined by a ratio defined by literature as equal to approximately 2.28 times the mass flow of *p*-toluic acid present within the reactor. The oxygen is pressurised (C-402) and heated (E-402) before entering the reactor. The product stream is sent to a vessel (V-402) where excess gas is expelled to stream S4-13. Medium utility steam at 12 bar was specified to provide the endothermic energy required during the oxidation reactions.

The gases expelled from both reactors are treated within R-403 using CaOH to remove any carbon dioxide formed during oxidation (due to the contact of oxygen with the reacting carbon-based species). The mole flow of calcium hydroxide necessary in R-403 is calculated in CALC3 and is equal to the mole flow of carbon dioxide in S4-06 and S4-13. The calcium hydroxide is suspended in an aqueous solution, where the amount of water entering in S4-17 is also calculated in CALC3 as a fraction of the mole flow of calcium hydroxide (Han *et al.*, 2011).

The crude TPA solid is dried (in Y-401) before purification to increase the efficiency of the purification steps that follow oxidation. To provide fluidisation in the drier, 80% of the flue gas leaving the drier (through S-14) is recycled to S4-21. The dried product powder exits the drier through S4-15 for purification.

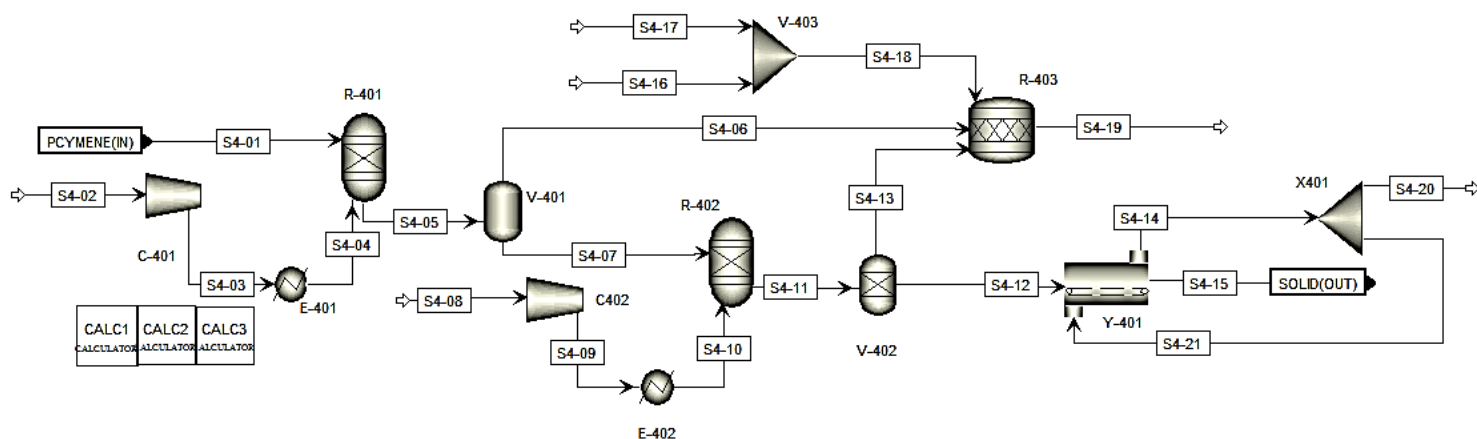


Figure 31: Pine and Eucalyptus Model *p*-Cymene Conversion

The *p*-cymene conversion sections for the Eucalyptus and PHR models (section 4 and section 3, respectively) were modelled in the same manner as the *Pine* model and is represented by Figure 31 and Figure 32, respectively. Differences in the feed composition (S4-01 and S3-01) causes differences in the product streams compositions from each oxidation step, while the reactions within both reactors (R-401, R-402 and R-301, R-302, respectively) are dictated by the conversions and selectivities in Table 19.

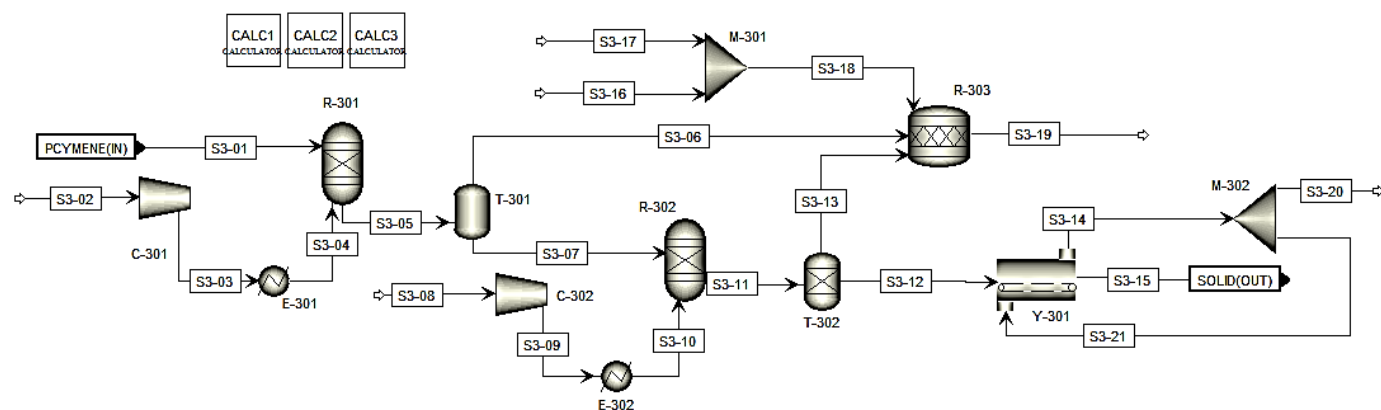


Figure 32: PHR Model *p*-Cymene Conversion

4.4.6 Crude Terephthalic Acid Purification

The TPA purification section (section 5 shown in Figure 33) involves two extraction stages, where the purity of the TPA product is dependent on the initial TPA weight fraction of the feed stream as well as the amount of NMP added to the system (Lee *et al.*, 1999). These stages

aid in removing a portion of 4-CBA (that poisons the product) and ensures that the TPA product is of adequate purity for either medium or high-quality terephthalic acid. The amount of solvent introduced to each filter as well as the product stream yields are determined by the concentration range of the TPA and by-products. Due to the high solubility of TPA in NMP, the NMP is added to the filter vessel, where contact with the solid cake allows the TPA to dissolve into the liquid. The liquid then passes through a static filter (Guo *et al.*, 2008)

The solid product from section 4 enters in stream S5-01 and is mixed with NMP (entering stream S5-02) at a mass flow rate three times the amount of TPA entering stream S5-01 (calculated by CALC1). The mixture is then heated to 160°C (in E-501) to allow the TPA to dissolve into the solvent in reactor R-501. The NMP-rich fraction is then cooled down to 45°C (in E-502) to allow crystallisation to take place in vessel M-502, where acetone is slowly added to break any NMP-TPA salt complexes that will affect the quality of the end product. The amount of acetone added is calculated by CALC2 and is added at the same ratio as the NMP solvent. The mixture is then sent to section 7. The solid returns through S5-33 and is sent for an additional extraction in R-503.

The mass flow of NMP for the extraction in R-503 (calculated in CALC1 and entering stream S5-36) is 3.5 times the amount of TPA in stream S5-33. The solvent is heated to 105°C in E-503 before entering the complex-forming reactor. A portion of the solid (not dissolved in R-503) leaves in stream S5-34 with a purity equivalent to medium-quality TPA. The dissolved solid is cooled to 40°C to initiate crystallisation in vessel M-503. Acetone is added to the vessel at a mass rate 3.6 times greater than the mass rate of the TPA present in stream S5-32. The mixture is then sent to section 7 to remove the used solvents. S5-29 contains TPA with a purity equivalent to high-quality TPA.

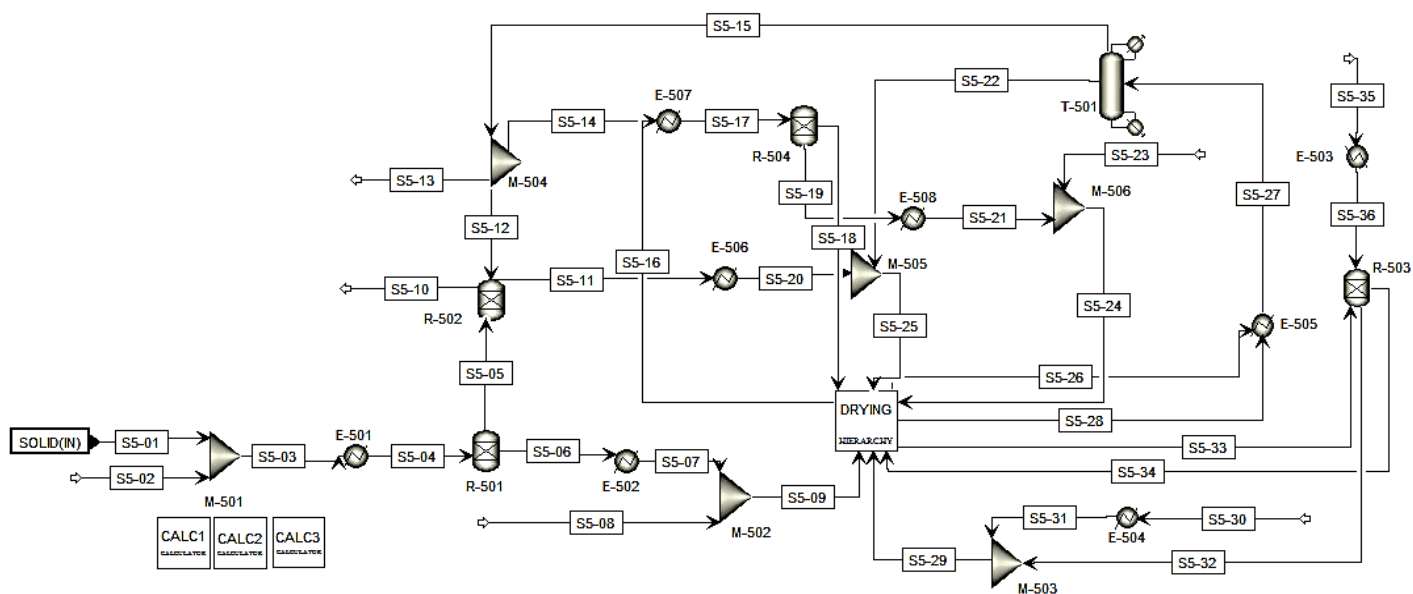


Figure 33: Pine Model TPA Purification

The purification sections for the *Eucalyptus* and PHR models (section 5 and section 4, respectively) were modelled in the same manner as the *Pine* model and is depicted in Figure 34 and Figure 35, respectively.

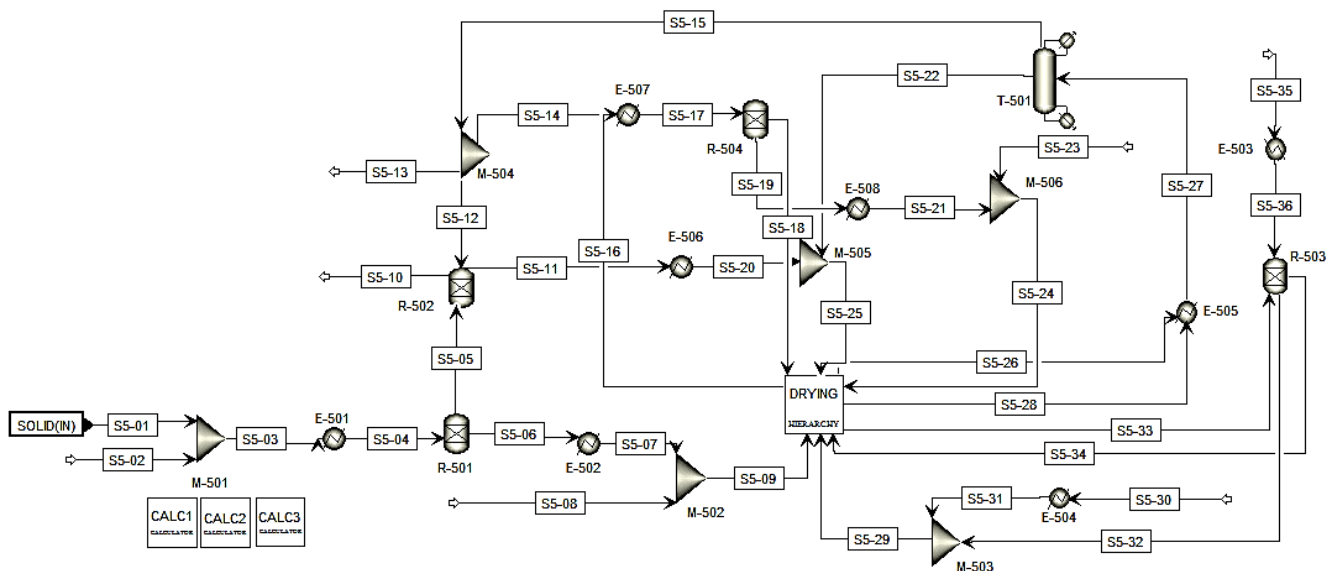


Figure 34: Eucalyptus Model TPA Purification

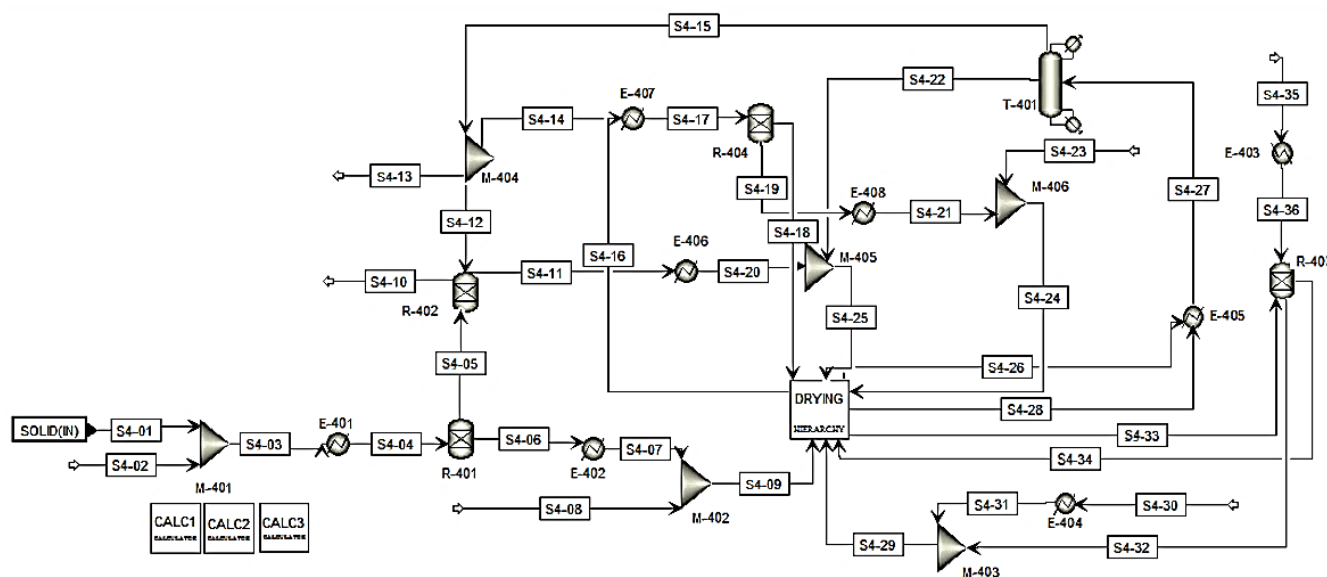


Figure 35: PHR Model TPA Purification

The solvents extracted (S5-28 and S5-26) from the drier section is cooled to 90°C in E-505 and separated in T-501. The tower's reflux rate and boil-up ratio was varied to achieve the best separation efficiency between the two solvents. A fraction of the NMP obtained from the tower bottom is allowed to flow from vessel M-504 to the second section of extractions. This fraction was calculated in CALC3 by determining the amount of NMP necessary for the extraction in R-502 and relating the amount to a fraction contained within M-504. The undissolved solids from reactor R-501 is sent to R-502. S5-10 can be added back to reactor R-501 (it is not at the required purity for medium-quality TPA). The mixture in stream S5-11 is cooled to 45°C to allow crystallisation in vessel M-505. The separated acetone from tower T-501 is added to the vessel to break any TPA-NMP salt formations. From M-505, the mixture is sent to section 7. The solid product (returning through stream S5-16) is cooled to 105°C and mixed with another fraction of NMP present in vessel M-506. The mass flow rate of NMP is 3.6 times the mass flow of the TPA available in stream S5-16 and was used to calculate the second fraction obtained from M-504 (calculated in CALC3). After a portion of solid is dissolved in R-504, the solvent mixture is then cooled to 40°C (in E-508). CALC2 calculates the amount of acetone added to vessel M-506 and is 3.6 times the mass flow rate of the TPA present in stream S5-21. The mixture is then sent to section 7. The solid product obtained in S5-24 has a purity equivalent to high-quality TPA.

Crystallised solids produced through reactors R-501 to R-504 are separated from NMP and acetone through driers (Y-701 to Y-704) operated at 210°C (shown in Figure 36). 80% of the flue gas produced in each drier is recycled (S7-04, S7-10, S7-15 and S7-20) back to complete the drying process and lower energy consumption.

High quality TPA received through Y-702 and Y-704 is collected within M-701, where after it is cooled in E-701 to 33°C for safer handling. Medium quality TPA retrieved from R-503 and R-504 is collected within M-702 and cooled to 33°C within E-702.

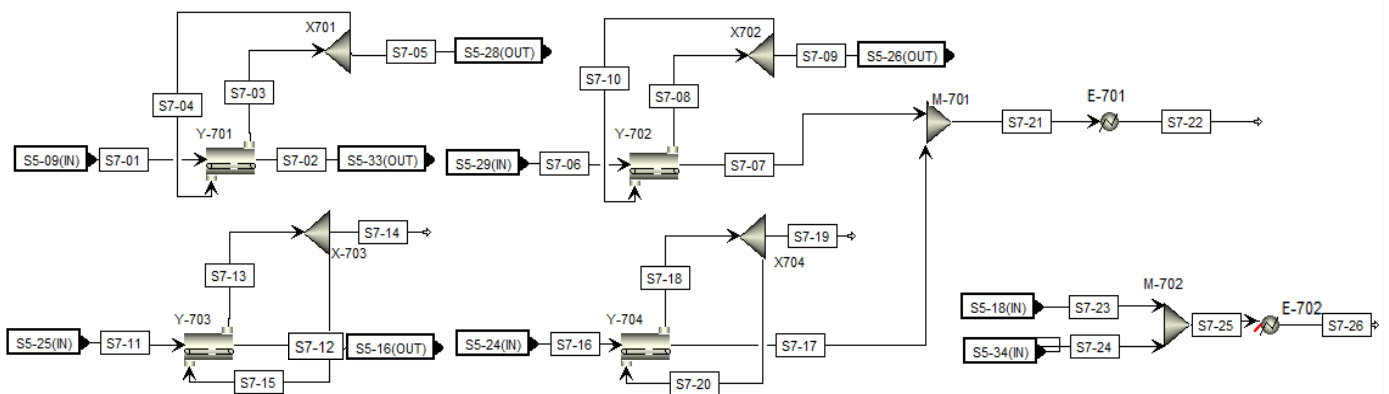


Figure 36: Pine Model TPA Powder Drying and Cooling

The drying and cooling sections for the *Eucalyptus* and PHR models (section 7 and section 5, respectively) were modelled in the same manner as the *Pine* model and is depicted in Figure 37 and Figure 38, respectively.

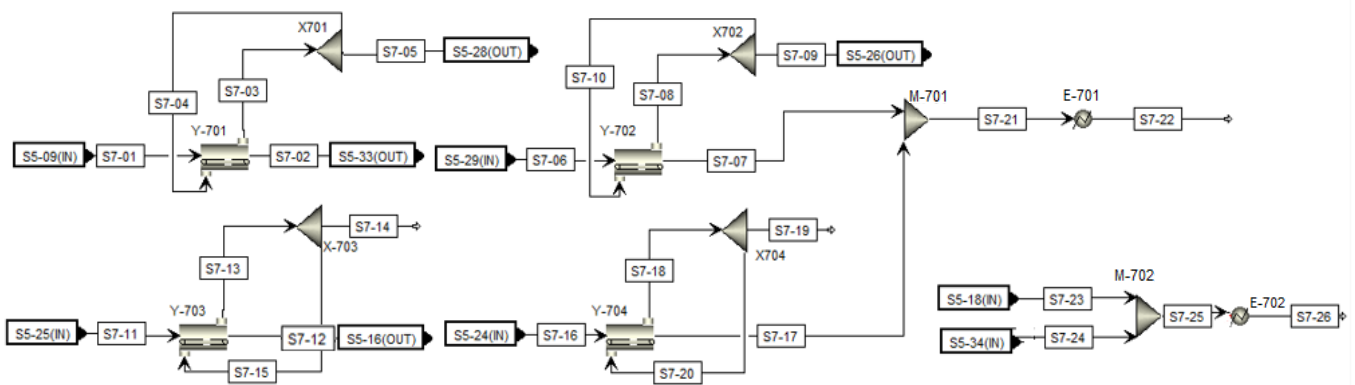


Figure 37: Eucalyptus Model TPA Drying and Cooling

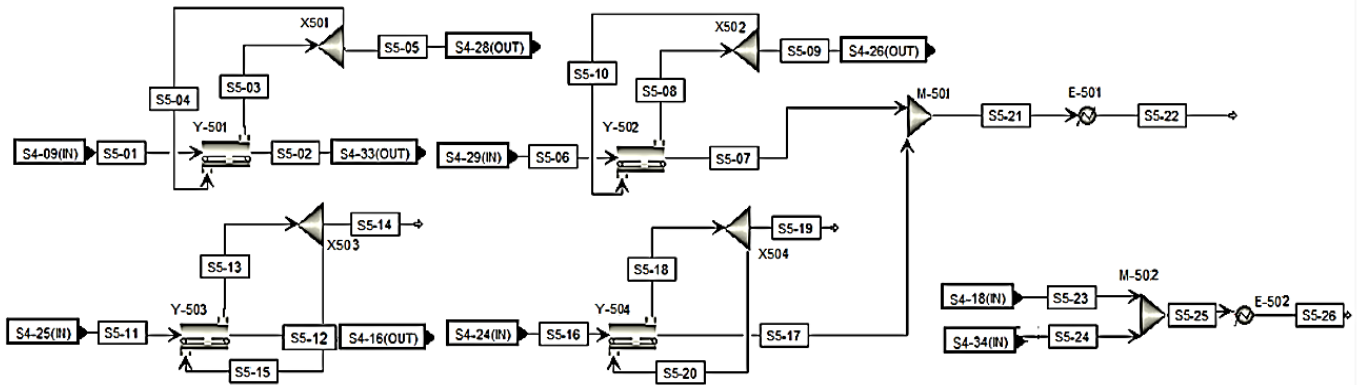


Figure 38: PHR Model TPA Drying and Cooling

4.4.7 Biomass Power Generation

The basis for the design of the biomass power generation sections was taken from Petersen (2015). The *Pine* biomass obtained from section 1 enters section 6 through S6-01 (shown in Figure 39) and is separated from a portion of water in filter F-601. The fraction of water filtered off is calculated by CALC1, this ensures that the biomass exiting the press filter has a moisture content of 50%. A moisture content of approximately 50% ensures that fine particles in the boiler do not cause an explosion. X601 is a separation unit to simplify combustion calculations by removing the small fraction of terpenes present in stream S6-03, which will not affect the energy balance in any significant manner. X604 recognises the composition of the solid portion (defined by its ultimate attribute) of the biomass and converts it to atomic components (carbon, hydrogen, nitrogen and oxygen) in CALC2. R-601 was simulated to identify possible products, while the amount of oxygen needed to produce these is calculated by CALC3 by a molar balance using air. 20% excess oxygen was specified to ensure complete combustion and to avoid the formation of carbon monoxide. The flue gas obtained from the boiler is utilised to heat up a pumped water stream (using P-601) in E-601. The amount of water (m_{water}) needed for the cycle was calculated by CALC4 that utilises the Equation 6.

$$\dot{m}_{\text{water}} = \dot{Q}_{X607} / [c_{p_l}(T_{\text{sat}} - T_{S6-08}) + H_{\text{vap}} + c_{p_v}(T_{S6-09} - T_{\text{sat}})] \quad (6)$$

Q_{X607} is the amount of heat transferred from the flue gas to the water, while the heat capacities of the vapour and liquid forms of water is denoted by c_{p_v} and c_{p_l} , respectively. T_{sat} , T_{S6-08} , T_{S6-09} and H_{vap} represents the saturation temperature, temperature of the water entering and exiting the heat exchanger and heat of evaporation of water, respectively.

The steam cycle is sectioned off in Figure 39 by dashed lines. The superheated steam obtained from E-601 is sent through a turbine (C-601), where the pressure drop (41 bar to 10 bar) is equivalent to a high-pressure turbine in a common biomass power generation steam-cycle. A low-pressure turbine follows that lowers the pressure from 10 bar to 1 bar. From each turbine, the power generated can be observed with work streams X608 and X609. The steam cycle closes with a cooling unit (E-602) to bring the steam back to ambient temperature water before being pumped again through P-601.

Oxygen needed during combustion, supplied by an air stream (S6-04), consumes energy from the flue gas (in E-602B and X-602A) after heating supplying energy to the steam cycle. This reduces the heat lost to the environment through S6-14. The mole flow of oxygen was calculated using a mole balance of the atomic components entering R-602 to create carbon dioxide and water (calculated in CALC3). The mole amount of oxygen present in the feed towards the reactor was subtracted from the oxygen supply in S6-04. The mole flow calculated was divided by 0.21 to determine the mole amount of air required and 20% was added as excess.

The modelling of flue gas purification as well as the gas stack was not included in this section, but is included in the cost of the boiler in Section 5.7.1.

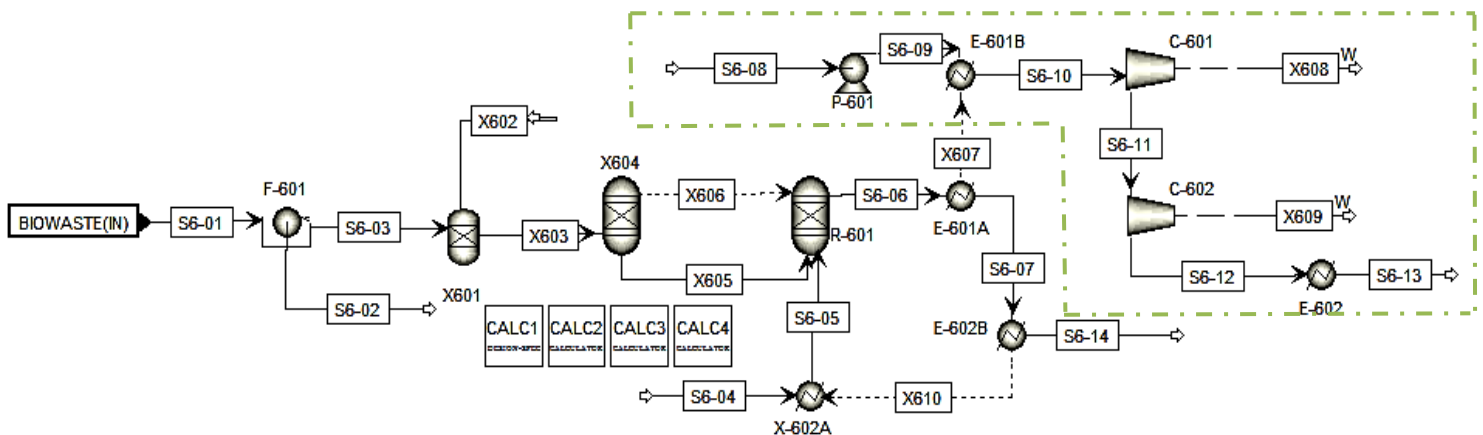


Figure 39: Pine Model Biomass Power Generation

The *Eucalyptus* biomass power generation (Figure 40) was modelled in the same manner as the *Pine* model, but differs in the sense that water is added through S6-01 to ensure 50% moisture content in stream S6-03. The biomass entering in S6-02, that was subjected to supercritical fluid extraction in section 1, has a moisture content less than 10%, therefore

water is added in this section to avoid a particle explosion within the boiler. Streams X605 and X606 reveals the amount of energy generated through the steam cycle. The amount of water needed in stream S6-09 is calculated in Equation 7.

$$\dot{m}_{water} = \dot{Q}_{X604} / [c_{p_l}(T_{sat} - T_{S6-09}) + H_{vap} + c_{p_v}(T_{S6-10} - T_{sat})] \quad (7)$$

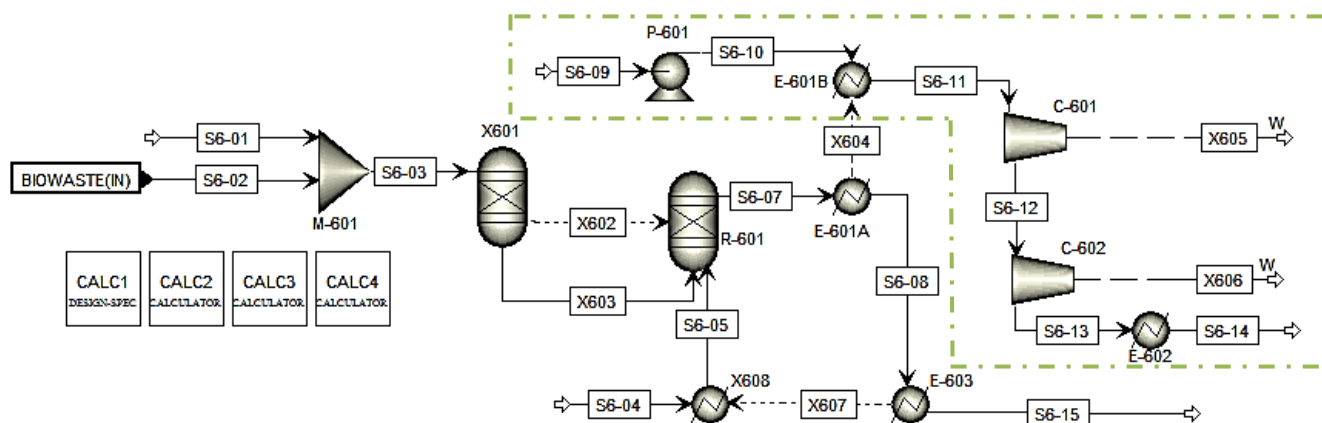


Figure 40: Eucalyptus Model Biomass Power Generation

4.4.8 *p*-Xylene Conversion and Purification of TPA

Figure 41 and Figure 42 depict the oxidation of the *p*-xylene product obtained from the CCEI process. The capacity of this process is 16 870 tonnes/annum of TPA, which requires 51 800 tonnes of starch per annum. The feed has a purity of 99.5% *p*-xylene (per mass) and approximately 0.5% n-tridecane.

p-Xylene enters the system at 300°C and 5.7 MPa (through stream S1-01) and is cooled to 200°C (in E-101) before entering the fluidised bed reactor (R-101). The amount of catalyst necessary for this reaction is determined by the turnover number, which is defined as the amount of *p*-xylene that is converted per mole of the catalyst. For the optimum selectivity of 99.6% for TPA, the turnover number is 33. Therefore, the mole flow of catalyst that enters S1-03 is calculated as the mole amount of *p*-xylene that enters S1-01 divided by 33 (calculated in CALC1). Aspen Plus® does not recognise the molecular complex form of the catalyst ($\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ and $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$), therefore the metal and water fraction of the catalyst were calculated as separate mole flow values and added to form stream X102. Air is introduced in stream S1-05, compressed to 550 psig (by C-101), and heated to 200°C (in E-102) before entering the reactor.

R-101 is a RYield type reactor, where the product composition was determined through mass balance calculations and utilising the given product selectivities. It is important to take note of the product composition as well as the types of chemical compounds present in the feed as it influences the product composition and purity of the final product. It is also important to include possible oxidation/decomposition of the feed compounds. For this specific reaction the formation of intermediates through oxidation is important, because it can directly affect the quality of your TPA powder and therefore also the final PET fibre, film or packaging.

The product exists R-101 through S1-08, where after the catalyst is separated from the liquid product in X103. In reality, the packing that contains the catalyst would remain within the reactor, which would be reactivated after a noticeable drop in conversion is detected. The liquid product is then dried in Y-101 and sent to the TPA purification stage. Similar impurities are present in the product liquid mentioned in Section 2.5.5, therefore washing steps with NMP is appropriate for the purification of the TPA powder. The amount of NMP necessary for each washing step is determined by the mass amount of TPA present in the feed stream before each filter (R-102 and R-103) and is calculated by CALC2. The amount of acetone, necessary to break any formed complexes and remove a small fraction of the impurities, depends on the amount of TPA present in each mixer feed (S1-13 and S1-24). The mole flow of acetone for each mixer (M-101 and M-103) is calculated by CALC2. After washing, the high quality TPA powder is dried (in Y-102 and Y-103) to remove any solvent.

Tower T-101 is integrated to recycle a portion of the solvents used in the first cycle for use in the second cycle. CALC3 calculates the amount of NMP that is necessary for the second cycle of washing, by bypassing the remaining solvent present in M-102.

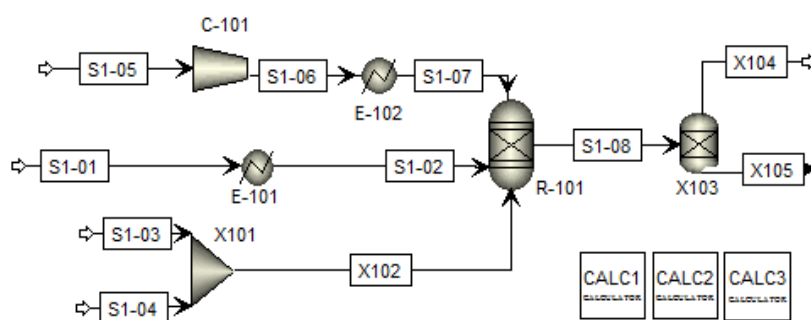


Figure 41: Starch-Based Model: Section One

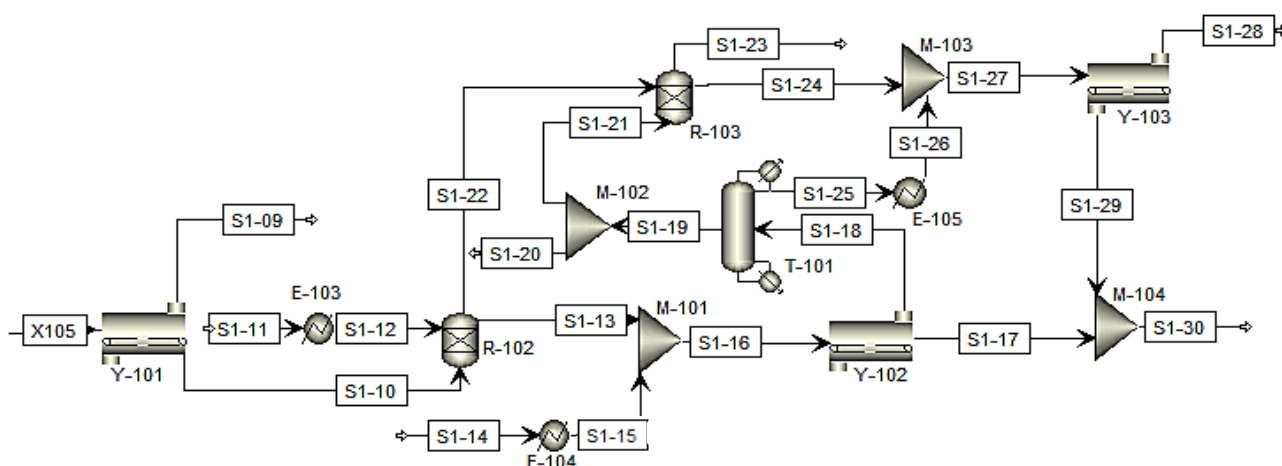


Figure 42: Starch-Based Model: Section Two

4.5 Heat Integration

The purpose of applying heat integration to a design process is to ensure maximum energy efficiency within the boundary of thermodynamics. Cost is also taken into account during the energy analysis, where the number of heat exchangers needs to be minimised together with the cost of utility addition. Utilities can include high or low-pressure steam, cooling water, air, flue gas or a refrigeration medium. Hot and cold utilities provides/consumes any additional energy to ensure that a stream reaches the set target temperature after the majority of heat was provided/consumed by another stream in the process.

Heat integration was applied to each modelled process through Aspen Energy Analyser. This tool utilises pinch analysis and requires some parameters, such as the approach temperature, to calculate the maximum energy saving potential. The approach temperature was chosen as 15°C, which is the average pinch temperature for chemical processing plants (Seider *et al.*, 2010). The sections of the process that is analysed can be defined; for the three base models (*Pine*, *Eucalyptus* and *PHR*), all sections were selected, excluding the power cycle sections. The energy analyser could not calculate energy solutions for the power cycle because of the manner in which it was modelled, by first breaking down the biomass into its atomic elements and then including the boiler and steam cycle. The option of only including the boiler and steam cycle was not given. Activating the energy analyser by selecting “Find Design Changes” gives solutions where heat exchangers can be added, modified or placed in a different location. After changes are made, the Energy Analysis Environment can be entered to view each process grid and to view the updated heat exchanger areas, which is used to define the cost of heat exchangers.

4.6 2G model results

Table 20 shows the production rate of TPA for the three 2G models. As mentioned in Chapter 2.1.3, the *Pine* and *Eucalyptus* biomass available varies annually, therefore a minimum, average and maximum was calculated from future biomass data. This resulted in a range of TPA production rates. In Chapter 4.3 an average value for the relief-gas feed was given, therefore the production rate of TPA is listed as an average.

Table 20: Base model TPA production rate

	Minimum	Average	Maximum
Pine model:			
Biomass available	710 ton/year	1030 ton/year	1350 ton/year
Biomass flow rate	80 kg/hr	120 kg/hr	150 kg/hr
Medium quality TPA	99 g/hr	119 g/hr	139 g/hr
High quality TPA	89 g/hr	108 g/hr	126 g/hr
PHR model:			
CST flow rate		20.5 kg/hr	
Medium quality TPA		730 g/hr	
High quality TPA		660 g/hr	
Eucalyptus Model:			
Biomass available	5900 ton/year	6800 ton/year	8000 ton/year
Biomass flow rate	660 kg/hr	760 kg/hr	900 kg/hr
Medium quality TPA	890 g/hr	1100 g/hr	1370 g/hr
High quality TPA	800 g/hr	1000 g/hr	1240 g/hr

From Table 20 it can be seen that there is on average 7 times more *Eucalyptus* biomass available than *Pine* biomass. Therefore, it is expected that the terpene capacity (approximately 3 wt% of the biomass) for *Eucalyptus* biomass should be larger. The PHR process has the highest terpene capacity, 20.5 kg/hr, compared to an average of 15.2 kg/hr and 2.4 kg/hr for the *Eucalyptus* and *Pine* processes, respectively.

Table 21: Pine model product composition

Product component	Mass flowrate (kg/hr)	Mass %	Limitation
Medium quality:			
Terephthalic acid	0.119	99.87%	99.9%
p-Toluic acid	4.39E-05	0.036% (360 ppm)	N/A
Cumic acid	3.65E-05	0.031% (310 ppm)	N/A
4-CBA	7.59E-05	0.063% (630 ppm)	< 400 ppm
High quality			
Terephthalic acid	0.108	99.99(35)%	99.9%
p-Toluic acid	2E-06	0.0019% (19 ppm)	< 150 ppm
Cumic acid	2.4E-06	0.0022% (22 ppm)	N/A
4-CBA	2.6E-06	0.0024% (24 ppm)	< 25 ppm

Table 21 shows the product composition of the Pine model. Due to the various washing steps, both medium and high quality TPA was produced. It can be seen that the medium quality TPA has a lower quality than conventional medium quality TPA. This particular product can still be sold for fibre production as dyes can be added to counter the colour produced by 4-CBA but the selling price will be reduced. The high quality TPA is well within the specification range and does not need further refining for liquid packaging production. Further investigation and optimisation is needed to lower the ppm value of 4-CBA in the medium quality TPA and to decrease TPA solid losses.

Table 22: *Eucalyptus* model product composition

Product component	Mass flowrate (kg/hr)	Mass %	Limitation
Medium quality:			
Terephthalic acid	1.103	99.85%	99.9%
p-Toluic acid	4.07E-04	0.036% (368 ppm)	N/A
Cumic acid	3.85E-04	0.034% (348 ppm)	N/A
4-CBA	9.12E-04	0.082% (826 ppm)	< 400 ppm
High quality			
Terephthalic acid	0.998	99.99%	99.9%
p-Toluic acid	1.9E-05	0.0019% (19 ppm)	< 150 ppm
Cumic acid	2.3E-05	0.0023% (23 ppm)	N/A
4-CBA	2.5E-05	0.0025% (25 ppm)	< 25 ppm

Table 23: *PHR* model product composition

Product component	Mass flowrate (kg/hr)	Mass %	Limitation
Medium quality:			
Terephthalic acid	0.732	99.87%	99.9%
p-Toluic acid	2.71E-04	0.037% (370 ppm)	N/A
Cumic acid	2.25E-04	0.030% (306 ppm)	N/A
4-CBA	4.68E-04	0.063% (638 ppm)	< 400 ppm
High quality			
Terephthalic acid	0.663	99.99%	99.9%
p-Toluic acid	1.26E-05	0.0019% (19 ppm)	< 150 ppm
Cumic acid	1.52E-05	0.0023% (23 ppm)	N/A
4-CBA	1.66E-05	0.0025% (25 ppm)	< 25 ppm

Table 22 and Table 23 show the product composition of the *Eucalyptus* and *PHR* model product compositions, respectively. As with the Pine model, both these models produce medium quality TPA that is not up to standard when comparing the 4-CBA concentrations. The high quality TPA for both models is within specifications, because the concentrations of the by-products are less than the limitations given.

5 Process economics

5.1 General

The purpose for the development of these processing schemes through simulation and costing reveals the economics surrounding the production of TPA. The evaluation of process economics through costing of equipment, determination of fixed and variable costs as well as calculating certain economic parameters were performed, based on the methodological approach described by Humbird *et al.* (2011). This approach includes a discounted cash flow rate of return (DCFROR) analysis to determine the economic viability of the designed process schemes. This chapter focuses on the development and analysis of the process economics of the lignocellulosic and starch-based processes.

5.2 Sizing and costing of equipment

5.2.1 Total installed cost

The sizing and costing of the equipment chosen for each process was done with the aid of Aspen Plus[®] by retrieving certain outputs from the mass and energy balances, such as heat duty and volume, which defines the size of the specific equipment. These size factors are then applied cost formulae to determine the estimated purchase cost (PC). The total installed cost (TIC) for each piece of equipment was calculated by using the following:

$$TIC = PC \times MF \quad (8)$$

MF is the multiplying factor for each specific piece of equipment specified for each process (Peters & Timmerhaus, 2003). The value for these multipliers can be found in Appendix 8.3.1.

The biomass combustion and combined heat and power (CHP) unit purchased cost was estimated as a combined unit as opposed to costing individual pieces of equipment. The size of the unit is defined by the net power output of the unit and the purchased cost estimated at \$ 4 260/kW (IRENA, 2012).

5.2.2 Economy-of-scale

Certain specialised equipment cost was determined through literature by obtaining the cost of a similar piece of equipment and scaling to the appropriate size by using (Seider *et al.*, 2010):

$$\frac{\text{New Cost}}{\text{Base Cost}} = \left(\frac{\text{New Capacity}}{\text{Base Capacity}} \right)^m \quad (9)$$

The exponent m has an average value of 0.6, which is used in scaling-up sections of the chemical processing plant. For individual equipment costs, especially those obtained from quotes, the scaling exponents in Table 36 were utilised (Towler *et al.*, 2008).

5.2.3 Chemical Engineering Plant Cost Index

It is important to obtain cost estimates that relate to the current costing year (for this project the costing year was taken as 2016). Costs obtained relating to other costing years can be updated to the costing year by utilising the Chemical Engineering Plant Cost Index (CEPCI) (Equation 10).

$$2016 \text{ Cost} = \text{Base Cost} \left(\frac{2016 \text{ Index Value}}{\text{Base Index Value}} \right) \quad (10)$$

The average CEPCI value can be applied to all chemical processing industries and factors in fabrication, delivery and installation. Figure 43 shows how the average index value has varied annually since 2008. The index value for November 2016 was chosen as CEPCI value for the costing year and has a value of 533.9 (Chemical Engineering Online, 2016).

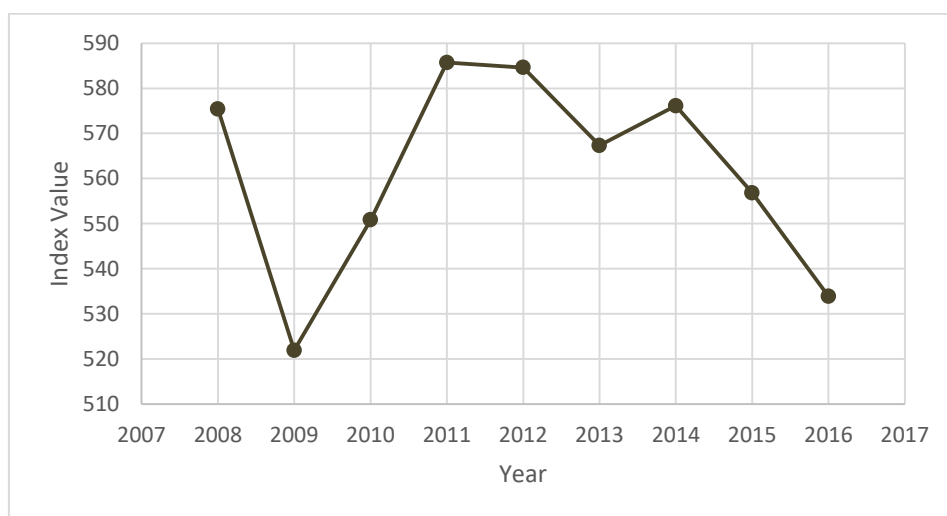


Figure 43: Annual average CEPCI values

5.3 Total capital investment

The costs associated with the design up to the installation and start-up of a new plant (or additional section of an existing plant) is included in the fixed capital investment (FCI). The total capital investment (TCI) is then calculated by adding the cost of land as well as working capital to the FCI. The value for the TCI was calculated in the manner shown in Table 24 (Humbird *et al.*, 2011).

Table 24: Total capital investment outline

	Installed cost
Total Equipment Installed Cost (TEIC)	TEIC
Warehouse	4% of ISBL
Site Development	9% of ISBL
Additional Piping	4.5% of ISBL
Total Direct Cost (TDC)	TEIC + 17.5% of ISBL
Prorateable Expenses	10% of TDC
Field Expenses	10% of TDC
Home Office & Construction	20% of TDC
Project Contingency	10% of TDC
Other Costs	10% of TDC
Total Indirect Cost (TIC)	70% of TDC
Fixed Capital Investment (FCI)	TDC+TIC
Location Factor	1
Corrected Fixed Capital Investment (CFCI)	1 x FCI
Working Capital (WC)	5% of CFCI
Total Capital Investment (TCI)	CFCI+WC

The total equipment installed cost is equal to the total installation cost of all equipment calculated in Chapter 5.2, while the inside battery limits (ISBL) investment accounts for all major equipment/sections of the designed process. The total direct cost consists of the total installed cost of all of the equipment as well as other costs relating to the preparation of the plant site, housing for process equipment as well as additional piping. The total indirect cost consists of employee fringe benefits, insurance relating to construction, construction tool, vehicle or facility purchase/rentals, construction of offices, permits, etc. The total indirect cost is calculated as a fraction of the total direct cost, while the FCI is the sum of the TIC and TDC. To correct the fixed capital investment figure according to the location of the retrieved cost data, a location factor is applied to the FCI. It is assumed that the majority of the cost data is of North American origin, where the location factor is one. To obtain the total capital investment, working capital (which is 5% of the CFCI) is added to the corrected fixed capital investment (Towler *et al.*, 2008).

5.4 Variable cost of production

The variable cost of production depends strongly on the rate of plant operations and includes the cost of raw materials, chemicals utilised during production, utilities such as pressurised steam and electricity and waste disposal.

The cost of the feedstock and chemicals used during production (given Appendix 8.3) were calculated by multiplying the cost of each type of feedstock or chemical with the mass flow rate given by Aspen Plus®. For each process there are certain chemicals that are recycled (marked as an asterisk in Table 40, Table 43 and Table 46 and costed as a base cost (mass flow times chemical cost) plus a 5% continuous chemical makeup cost.

As time progresses, the cost of these raw materials will vary. The inorganic chemical indices (ICI) can be used to give an estimation of how the cost will vary over the plant's lifetime (given in Figure 56). The trend-line obtained from the ICI data was used to estimate future raw material costs.

Cold Utilities are converted to electricity and subtracted from the electricity yield.

Waste disposal costs depend on the type of waste depending on the environmental hazard level or level of processing for safe discard. Categories include domestic, commercial, sanitary, construction, hazardous and non-hazardous industrial waste. The average cost of non-hazardous waste and hazardous waste disposal is \$11.6/tonne and \$46.4/tonne, respectively (Nahman *et al.*, 2014).

5.5 Fixed cost of production

The fixed cost of production does not depend on the production rate. Labour and supervision costs during operation as well as the labour burden for each employee are included in this calculation. The labour burden is approximated as 90% of the total labour and supervision cost, which was calculated using annual salaries (adjusted to 2016 costs using Figure 57) as well as the number of employees assigned to each position (shown in Table 39, Table 42, Table 45 and Table 48) (Humbird *et al.*, 2011).

The total labour and supervision cost is the sum of the product of the annual salary and the number of employees in the specific position. The number of employees was chosen by considering the size and number of sections of each process. The variation of the labour cost throughout the lifetime of the plant was estimated using the South African labour index given in Figure 57.

Other overhead costs include maintenance as well as property insurance and tax, which is 3% and 0.7% of the fixed capital investment, respectively. Adding this value to the labour and supervision cost and labour burden gives the total fixed operating cost.

5.6 Discounted Cash Flow Analysis

The calculation of the total capital investment as well as variable and fixed operating costs leads to the development of cash flow sheets, which is used during the discounted cash flow rate of return analysis. Table 25 shows the basic outline of the cash flow sheet that was created in Excel for each of the process schemes, which shares its structure with the cash flow sheet design done by (Humbird *et al.*, 2011). After completion of the cash flow sheets, the goal seek function is used to set the value of the net present value to zero by manipulating the selling price of TPA. The manipulated output value represents the minimum selling price of TPA.

It is assumed that two years will be sufficient for the construction of the plant, while the plant life was chosen as 25 years on an 8040 hours/year basis, with an economic analysis period of 20 years. Within the cost sheet, the year row had negative numbers to zero to indicate the construction period, where year one indicated the first year of operation. It is assumed that 50% of the production capacity is achieved in the first year to account for plant start-up and adjustments, while 75% of the variable operating cost is included for the same period. Fixed operating costs are not reliant on the production capacity of the plant, therefore 100% of this cost was included for year one. Full capacity is assumed after year two onwards (Humbird *et al.*, 2011).

This type of economic analysis requires a discount factor (DF) was calculated using:

$$DF = \frac{1}{(1 + DR)^{Year}} \quad (11)$$

The discount factor was calculated for each specific year with a discount rate (DR) of 10% (Luehrman, 1997).

Financial support through a loan is taken as 60% of the fixed capital investment, which is paid over ten years at an interest rate of 7% (News24Wire, 2016), while 40% of the plant cost would be supplied through equity. The annual loan payment with interest was calculated using the PMT function in Excel, assuming that the interest rate remains constant during the 10-year payment period. The loan principal represents the outstanding loan balance, from which the interest of the following year is calculated.

Table 25: Discounted cash flow sheet outline

Year	Current operating/construction year
Discount factor (DF)	Assures present value of annual cash income
Fixed capital investment	Calculated in Table 24
Working capital	Calculated in Table 24
Loan interest payment (LIP)	Annual interest payment
Loan principal	Outstanding loan balance
TPA price (\$/tonne)	Forecasted bio-TPA market price
TPA sales (TAS)	Annual TPA sales income
Feedstock price (\$/tonne)	Purchasing and transport of biomass price
Feedstock cost	Feedstock price x available biomass
Other Variable cost	Costs included in Chapter 5.4
Fixed Operating cost	Costs included in Chapter 5.5
Total Production cost (TPC)	Total of feedstock, variable and fixed cost
Annual depreciation	(zero salvage value at end of economic evaluation period)
Plant write-down	4% ^a
Depreciation charge (DC)	Plant write-down x FCI
Remaining value	FCI – total DC
Net revenue	TAS-LIP-TPC-DC
Income tax (IT)	28% on positive net revenue ^b
Annual cash income (ACI)	TAS-TPC-IT
Annual present value (APV)	ACI*DF
Total capital investment (including interest)	(FCI+WC+LIP) x DF
Net present value	Total APV - Total TCI (including interest)

^a Straight-line depreciation of industrial buildings and equipment (Crundwell, 2008)

^b South African income tax for companies (SARS, 2017)

Little information is given to the public on the market price and trend of fossil-based TPA. Figure 44 shows a few data points of the given/suggested prices of fossil-based TPA from January 2014 to November 2016. It can be seen that there has been a decline in the market price, which was initiated by the decline in the crude oil price and in turn affecting the price of fossil-derived *p*-xylene (the precursor for modern TPA production) (Velson, 2014). Since March 2017 there has been a slight stabilisation of the crude oil price (\$54.94 compared to \$29.78 in Jan 2016), but there is still uncertainty regarding future prices and complete stabilisation from the experienced decline (Knoema, 2017).

Due to the novelty of bio-TPA (no commercialisation at this time), it is uncertain whether fossil-based TPA prices will have any effect on bio-TPA prices. There is also uncertainty regarding the value of a green premium placed on the bio-based product. It is suggested that consumers are more likely to buy a more sustainable product when it is followed by a simplified backstory (Hermes, 2013). This should definitely be considered for the final bio-

PET product with a green premium of 125% predicted by Gevo (Lane, 2014). Green premium is defined as: “the additional price a market actor is willing to pay for the additional performance and/or the strategic performance of the intermediate or end product the buyer expects to get when choosing the bio-based alternative compared to the price of the conventional counterpart with the same technical performance” (Thielen, 2014). If an equal green premium is assumed for bio-TPA, then the expected market price for 2016 is \$1 575/tonne.

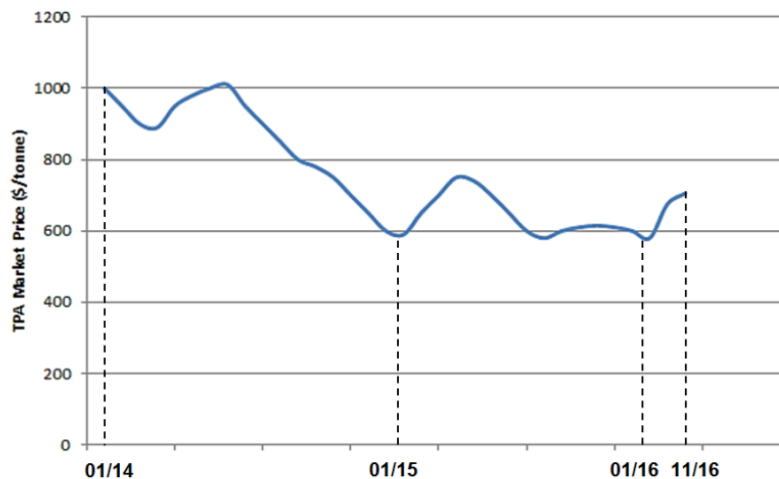


Figure 44: Fossil-based TPA market price: Jan 2014 - Nov 2016

The total production cost consists of the feedstock cost, variable operating cost as well as the fixed operating cost. The feedstock cost for both *Pine* needles and *Eucalyptus* leaves include transport cost that include the 300km radius discussed in Chapters 2.1.3.1 and 2.1.3.2. This cost is not available directly; therefore, an estimation was made based on the type and weight of the biomass, its moisture content and the average length of transport. This was done by using an application developed by the U.S. Forest Service (Extension, 2014). *Pine* needle and *Eucalyptus* leaf costs were estimated at \$7.5/tonne and \$5.1/tonne, respectively. The moisture content of *Pine* needles is approximately twice that of *Eucalyptus* leaves, which contribute to its higher price per tonne. There was no price assigned to the CST obtained from Ngodwana as it is assumed that the process will be integrated with the existing mill.

In the following sections (Chapters 5.7.1 to 5.7.3) the total capital investment results are given, that was used to construct cash flow sheets for each process scheme (*Pine*, *Eucalyptus* and PHR). The cash flow sheets were used to calculate indicators such as DCFROR and NPV that is used to compare each process scheme and to determine economic viability.

5.7 Scenario one: 2G process economics

This section looks at the economics of 2G feedstocks based on the amount of these feedstocks available in South Africa. A comparison of each 2G process per ton of TPA product can be found in Chapter 5.7.4.

5.7.1 *Pine* process economics

Table 26 shows a summary of the (rounded-off) costs associated with calculation of the total capital investment.

Table 26: *Pine* process total capital investment

	Installed cost (\$)	Installed cost (M\$/ton TPA) ^a
Total equipment installed cost (TEIC)	\$ 4 772 000	2.61
Warehouse	\$ 191 000	0.10
Site development	\$ 429 500	0.23
Additional piping	\$ 214 800	0.12
Total direct cost (TDC)	\$ 5 607 300	3.06
Prorateable expenses	\$560 800	0.31
Field expenses	\$560 800	0.31
Home office & construction	\$1 121 600	0.62
Project contingency	\$560 800	0.31
Other costs	\$560 800	0.31
Total indirect cost (TIC)	\$ 3 364 800	1.86
Fixed capital investment (FCI)	\$8 972 100	4.9
Location factor	1.00	
Corrected fixed capital investment (CFCI)	\$8 972 100	
Working capital (WC)	\$449 000	0.25
Total capital investment (TCI)	\$9 421 100	5.15

^a Annual TPA production: $(0.119+0.108)*8.04 = 1.83$ tonnes/annum

Table 27 depicts the variable and fixed operating costs of the *Pine* process, where the biomass includes the purchase and transport of *Pine* needles to the plant. The raw materials consist of all chemicals used during production. One reason for the high chemical cost is the use of pure oxygen in two major sections of the plant (oxidation of p-cymene and p-toluic acid). Air was supplied for the combustion of the biomass instead of pure oxygen because it is a minor section not contributing to the production of TPA and is commonly used in biomass combustion. This resulted in a lower chemical cost. The cost calculations for the feedstock and operating chemicals can be found in Table 40 (Appendix 8.3).

The total salaries were calculated in Table 39, by multiplying the number of employees with each specific salary, while the labour burden is 90% of the total salaries cost.

Maintenance is calculated as 3% of the ISBL, which includes all of the main sections of the plant and excluding the power generation section. Property insurance and tax is calculated as 0.7% of the fixed capital investment.

Table 27: Pine process variable and fixed operating costs

	Annual cost (\$)	Annual cost (M\$/ton TPA)
Variable operating cost:		
Biomass (including transport)	\$ 7 200	0.004
Operating chemicals	\$ 1 963 000	1.08
Waste disposal	\$ 27 000	0.01
Total variable operating cost	\$ 1 997 200	1.09
Fixed operating cost:		
Total salaries	\$ 1 019 000	0.56
Labour burden	\$ 917 000	0.50
Maintenance	\$ 603 000	0.33
Property insurance & tax	\$ 141 000	0.08
Total fixed operating cost	\$ 2 680 000	1.47

The total variable and fixed operating costs make up the total production cost, which is added to the discounted cash flow sheet as shown in Appendix 8.4.

After completing the cash flow sheet, the DCFROR could not be calculated because of the absence of a positive cash flow during the plant lifetime when assuming a selling price equivalent to the current fossil-based price of \$700/tonne. Using the expected green premium of 125% (\$1575/tonne) as selling price also revealed an incalculable DCFROR. At this small scale the cost of running the plant, including the purchase and maintenance of the plant, could not be overcome by the income generated by TPA sales. Small scale production usually leads to very high average production costs especially when considering specialised equipment. It is important to note that there is no short-term solution to increase this capacity. Pine species take years to mature (Chapter 2.1.3.1) and there are no growth-period commercial harvesting methods. In addition, new plantations will lead to the destruction of natural forests or other natural habitats, while changes in the genetics of *Pine* species to produce more terpenes will require years of research and defeats the main purpose of the plantation (wood harvesting for the manufacturing of packaging, paper, etc.).

5.7.2 *Eucalyptus* process economics

Table 28 shows a summary of the costs that were used to calculate the total capital investment for the *Eucalyptus* process.

The biomass cost includes the purchase and transport of the *Eucalyptus* leaves to the plant site, while the raw materials include all chemicals used during the production of the final product.

Table 28: *Eucalyptus* process total capital investment

	Installed cost (\$)	Installed cost (M\$/ton TPA) ^a
Total equipment installed cost (TEIC)	\$ 15 303 700	0.91
Warehouse	\$ 612 200	0.04
Site development	\$ 1 377 400	0.08
Additional piping	\$ 688 700	0.04
Total direct cost (TDC)	\$ 17 982 000	1.06
Prorateable expenses	\$ 1 798 200	0.11
Field expenses	\$ 1 798 200	0.11
Home office & construction	\$ 3 596 400	0.21
Project contingency	\$ 1 798 200	0.11
Other costs	\$ 1 798 200	0.11
Total indirect cost (TIC)	\$ 10 789 200	0.64
Fixed capital investment (FCI)	\$ 28 771 200	1.70
Location factor	1	
Corrected fixed capital investment (CFCI)	\$ 28 771 200	
Working capital (WC)	\$ 1 438 500	0.09
Total capital investment (TCI)	\$ 30 209 700	1.79

^a Annual TPA production: $(1.103+0.998)*8.04= 16.89$ tonnes/annum

The total salaries and labour burden was calculated in Table 42. Maintenance is calculated as 3% of the ISBL, which includes the supercritical fluid extraction, purifications and conversion sections towards the production of TPA. 0.7% of the fixed capital investment, listed in Table 28, equals the cost of property insurance and tax.

The total production cost included in the discounted cash flow sheet comprises of the total variable and fixed operating costs calculated in Table 29.

Table 29: *Eucalyptus* process variable and fixed operating costs

	Annual cost (\$)	Annual cost (M\$/ton TPA)
Variable operating cost:		
Biomass (including transport)	\$ 31 000	0.002
Operating chemicals	\$ 21 007 000	1.2
Waste disposal	\$ 50 000	0.003
Total variable operating cost	\$ 21 088 000	1.2
Fixed operating cost:		
Total salaries	\$ 1 227 000	0.07
Labour burden	\$ 1 104 000	0.06
Maintenance	\$ 863 000	0.05
Property insurance & tax	\$ 201 000	0.01
Total fixed operating cost	\$ 4 802 000	0.2

The cash flow sheet for this process can be found in Appendix 8.4. The goal seek function in Excel was used to determine the DCFROR value at net present value of zero. Due to the absence in positive cash flows, the DCFROR could not be determined and the process is deemed economically unviable at this scale. Similar to the *Pine* process, a *Eucalyptus* feedstock capacity increase has no short-term solution.

5.7.3 PHR process economics

Table 30 shows the costs associated with calculating the total capital investment for the PHR process.

Table 30: *PHR* process total capital investment

	Installed cost (\$)	Installed cost (M\$/ton TPA) ^a
Total equipment installed cost (TEIC)	\$ 13 021 000	1.16
Warehouse	\$ 520 900	0.05
Site development	\$ 1 172 000	0.02
Additional piping	\$ 586 000	0.05
Total direct cost (TDC)	\$ 15 300 000	1.36
Prorateable expenses	\$ 1 530 000	0.14
Field expenses	\$ 1 530 000	0.14
Home office & construction	\$ 3 060 000	0.27
Project contingency	\$ 1 530 000	0.14
Other costs	\$ 1 530 000	0.14
Total indirect cost (TIC)	\$ 9 180 000	0.82
Fixed capital investment (FCI)	\$ 24 480 000	2.18
Location factor	1	
Corrected fixed capital investment (CFCI)	\$ 24 480 000	
Working capital (WC)	\$ 1 224 000	0.11
Total capital investment (TCI)	\$ 25 704 000	2.29

^a Annual TPA production: $(0.732+0.663)*8.04= 11.22$

No feedstock cost was included in the calculation of the variable operating cost as it was assumed that the terpene oil and its source would be obtained from the existing mill through plant integration. The raw materials include all chemicals used during the production of TPA, while the utilities include mainly cooling water and low to medium pressure steam.

The total salaries and labour burden costs were calculated in Table 45. Maintenance costs were calculated as 3% of the ISBL, which included all sections of this process, while property insurance & tax were calculated as 0.7% of the fixed capital investment (Table 30).

Table 31: PHR process variable and fixed operating costs

	Annual cost (\$)	Annual cost (M\$/ton TPA)
Variable operating cost:		
Operating chemicals	\$ 22 070 000	1.98
Waste disposal	\$ 110 000	0.01
Total utilities	\$ 1 030 000	0.09
Total variable operating cost	\$ 23 210 000	2.08
Fixed operating cost:		
Total salaries	\$ 1 322 300	0.12
Labour burden	\$ 1 190 100	0.11
Maintenance	\$ 734 400	0.07
Property insurance & tax	\$ 171 400	0.02
Total fixed operating cost	\$ 3 418 200	0.30

The complete discounted cash flow sheet (Appendix 8.4) revealed negative cash flows throughout the lifespan of the plant. The DCFROR could therefore not be calculated and the process is deemed economically unviable at this scale.

The terpene feed to this process is dependent on an established process, where the mass flow of the biomass in the pre-cooking stage is dependent on the demands of that process. Scaling this TPA production process would be mill specific and would also rely on the type of pulping methods that may affect the composition of the CST. This process could be viable if alternative methods for cooling the water/terpene feed can be found that does not result in the loss of the volatile major terpene, together with funding and heat integration with the specific mill. Alternatively, these mills can investigate the possibility of TPA production from C5/C6 sugars from their feedstocks. This can prove advantageous when these mills replace their *Pine* feedstocks with *Eucalyptus*, because separation of cineole from the large amount of 'cooking water' in the CST will be impossible.

5.7.4 Scenario one economic comparison

Figure 45 shows the cost comparison of each 2G process in terms of the total equipment installed cost (TEIC), total capital investment (TCI) as well as the operating chemicals used during production. The Pine process shows the highest equipment cost and total capital investment. Some of the equipment had smaller size factors than the range suggested in the cost equation, for these the lowest figure in the range was chosen to determine the cost, which lead to higher equipment costs. In the cases where APEA could not determine the cost, the size factor was taken from the other tabs available in this section, such as TEMA HEX.

Comparing the Eucalyptus and PHR processes, it can be seen that the PHR process had the larger equipment cost and total capital investment. This means that the selection of the supercritical fluid extraction had a smaller impact on the TEIC than the cooling and separation of the terpene/water mixture together with desulphurisation used in the PHR process.

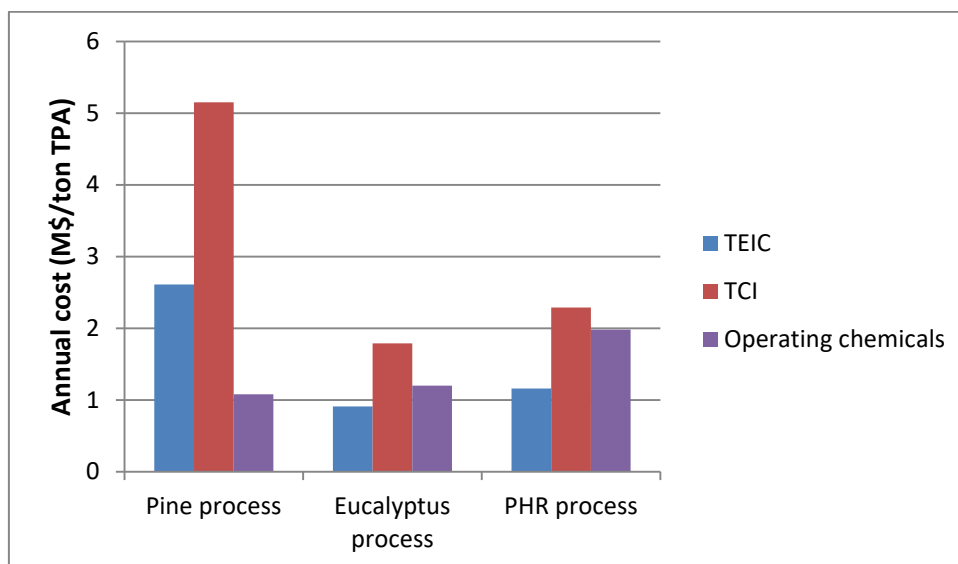


Figure 45: Scenario one annual cost comparison

As discussed in Chapters 5.7.1 to 5.7.3, these processes were deemed economically unviable due to the negative cash flows that prevented DCFROR calculations. The small production scale is limited by the amount of available feedstock in South Africa. Inclusion of branches and bark raised the capacity by a few percent, but was still considered a very small scale with a large average production cost (<0.01% PET market share).

High variable costs were due to the utilisation of pure oxygen, palladium-based catalysts and carbon dioxide.

Also comparing terpene-based feedstocks to starch-based feedstocks, it is important to note that terpene oils make up to a maximum of 3% of any section of conifers and eucalyptus species, where a maximum of 85% and 60% of the terpene oils contain either cineole or α -pinene, respectively. C5/C6 sugars are easier to access, through for example fermentation, and lead to a higher concentration of the TPA precursors (Panda, 2004).

It should also be considered that the selected processes have not yet been optimised specifically for the production of TPA through proper experimentation. Literature only provides efficiencies of conversions through selectivities and yields, which results in a larger probability of error in terms of the simulations. To more properly define the conversion sections, reaction kinetic data needs to be gathered together with all possible interactions from the multiple other terpenes and by-products present in the feed to each reactor. This problem inevitably echoes into the economics and minimum selling price, which further urges better defining of the conversion and purification of terpenes to TPA. During this project, a large amount of time was spent finding literature for each individual section and reviewing it further through simulation. Unfortunately, companies that are currently investigating a similar approach, withhold research information, due to the 'up and coming' nature of the bio-PET market. This also leads to less thorough comparisons of the simulated process.

5.8 Scenario two: 1G and 2G process economics

5.8.1 South African market share

With the introduction and rise of the "carbohydrate economy", it is important to determine a realistic figure of the market share of bio-plastics in South Africa. As the concern for the environment and awareness of wastes and pollutant emissions increases, so does the possibility of a larger market share in the global plastic consumption (Coles & Kirwan, 2011). For this analysis, a market share of 10% of the local PET market is assumed. Figure 46 shows the annual consumption of PET in South Africa, where an average annual growth of approximately 12 200 tonnes is experienced (Plastics SA, 2015). The estimated PET consumption for 2016 is 241 000 tonnes (Green Africa Directory, 2017). This equates to a bio-TPA production scale of 16 870 tonnes per annum, which will be used as scale during the following comparison between first and second-generation feedstock processes.

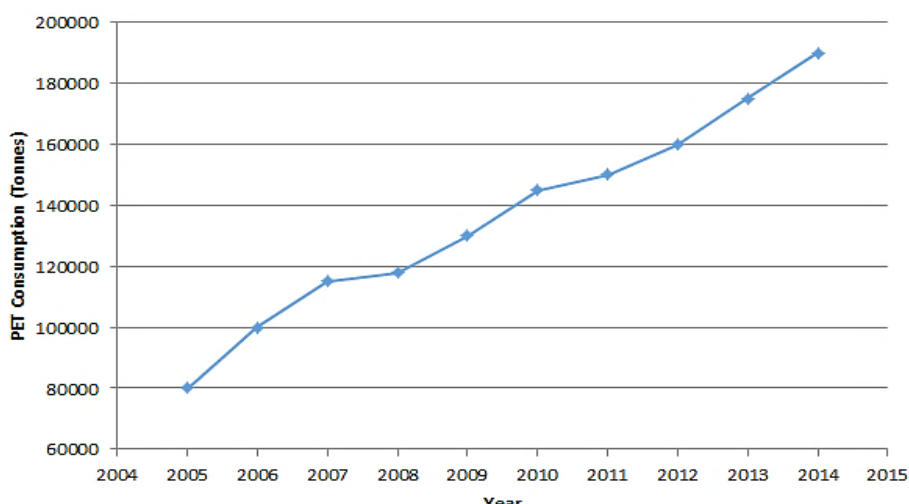


Figure 46: South African PET consumption

5.8.2 Starch-based process economic results

Table 32 shows the total capital investment of the starch-based process, which includes the costs associated with converting the starch source to p-xylene given in literature (Lin *et al.*, 2014). It also accounts for the costs calculated through the modelling of the conversion of p-xylene to TPA and the purification thereof. The total equipment cost for the starch-based bio-TPA production process is just over \$ 16 million for a production scale of 16 870 tonnes of bio-TPA per annum.

Table 32: Starch-based process total capital investment

	Installed cost (\$)
Total equipment installed cost (TEIC)	\$ 16 284 000
Warehouse	\$ 3 122 000
Site development	\$ 7 024 000
Additional piping	\$ 3 512 000
Total direct cost (TDC)	\$ 29 942 000
Prorateable expenses	\$ 2 994 000
Field expenses	\$ 2 994 000
Home office & construction	\$ 5 988 000
Project contingency	\$ 2 994 000
Other costs	\$ 2 994 000
Total indirect cost (TIC)	\$ 17 964 000
Fixed capital investment (FCI)	\$ 47 906 000
Location factor	1
Corrected fixed capital investment (CFCI)	\$ 47 906 000
Working capital (WC)	\$ 2 395 000
Total capital investment (TCI)	\$ 50 301 000

Table 33 shows the variable and fixed operating costs of the starch-based process, where the starch feed cost is estimated at \$310 per tonne (Esterhuizen, 2017).

Raw material costs include hydrogen (1500 tonnes/annum), ethylene (6200 tonnes/annum) and other catalysts (Sn-beta zeolite and Cu-Ru/C catalysts) and solvents, such as THF and NaCl. Waste disposal does not include all by-products and effluent streams, some un-purified by-products are sold for bioethanol fuel or natural gas equivalent, such as levulinic acid and hydrogen. Wastes include solid humins, which has no value for further processing.

The total salaries were calculated by multiplying the number of employees with the specific position salary (shown in Table 48). The number of employees in each position was determined by the size of the plant. The labour burden is 90% of the total salaries cost.

The maintenance cost is calculated as 3% of the ISBL, which includes all sections of the starch-based process, while property insurance and tax is calculated as 0.7% of the fixed capital investment calculated in Table 32.

Table 33: Starch-based variable and fixed operating costs

	Annual cost (\$)
Variable operating cost:	
Starch feed	\$ 1 508 000
Operating chemicals	\$ 19 311 000
Waste disposal	\$ 200 000
Total variable operating cost	\$ 21 019 000
Fixed operating cost:	
Total salaries	\$ 2 083 000
Labour burden	\$ 1 875 000
Maintenance	\$1 437 000
Property insurance & tax	\$ 335 000
Total fixed operating cost	\$ 5 730 000

With the assessment of the discounted cash flowsheet (found in Appendix 8.5), it was found that the minimum TPA selling price at a minimum hurdle rate (for nominal values) of 16% was \$1953/tonne. If the expected price for fossil-derived TPA in 2016 is \$700/tonne (Figure 44), then the green premium for this product would be 179%, which is 54% higher than the proposed green premium of 125% for bio-TPA. There is, however, potential for improvement on this process in terms of selecting optimal catalysts that will ensure maximum yield of an intermediate of product and lowering catalyst costs. There is also potential in improving processing and purification of the product and its intermediates to lower energy consumption, lower solvent consumption and maximise yield.

5.8.3 Scenario two economic comparison

This section draws a comparison between the 1G and 2G processes based on their minimum selling prices at a 10% South African PET market share. This comparison is done regardless of the feedstock limitations of the lignocellulosic-based processes and assumes that a sufficient supply can be provided (through importing or other). Each process was scaled using a scaling size, which is the size correlation between the original scale (used for simulation) and the new scale of 16 870 tonnes/annum. Using a scaling factor of 0.6 together with Equation 9, the equipment and variable cost at the new scale was calculated.

Table 34 depicts the individual minimum TPA selling price (MTSP) of each 1G and 2G process with their corresponding green premium percentage. A hurdle rate of 16% (for nominal values) was set as goal, while the minimum selling price was varied (an example can be seen in Appendix 8.5). It can be seen that the starch-based process has the lowest MTSP at \$1953/tonnes with a premium of 179%, while the 2G processes have much larger MTSP's. With the use of pure oxygen for two stages of oxidation, complex purifications, low concentrations of the major terpenes within the feedstock, multiple terpenes that affect conversion and contribute to by-product concentrations, a lower yield of biomass per hectare compared to starch-based feedstocks as well as high selling prices, the 2G processes are deemed economically unviable.

Table 34: Minimum selling price comparison

Process	Minimum selling price	Green premium
Pine	\$5 227/tonne	647%
Eucalyptus	\$22 443/tonne	3106%
PHR	\$38 114/tonne	5345%
Starch-based	\$1953/tonne	179%
FDCA	\$2130/tonne	204%

As previously mentioned, there are no comparable bio-TPA processes. There is, however a TPA alternative, called 2,5-Furandicarboxylic acid (FDCA), that is produced from starch-based feedstocks. This chemical is used to produce polyethylene furanoate (PEF), the biodegradable equivalent of PET, with a stronger O₂, CO₂ and liquid barrier than conventional PET. In recent years, VTT Finland has replaced their terpene research (Linnekoski *et al.*, 2014) to FDCA and has developed a process in which it can be produced at a selling price of \$2 130/tonne. They revealed that this selling price is promising and they will continue further research towards commercialisation after 2025 (Linnekoski *et al.*, 2017). This gives an indication that the starch-based process is worthwhile for further research, especially when considering triticale as feedstock in South Africa.

Figure 47 shows the sensitivity of the MTSP for the starch process. The effects of -30% to 30% on the fixed capital investment, CCEI equipment cost as well as the total catalyst and feedstock cost were analysed. The minimum selling price is represented by 0%.

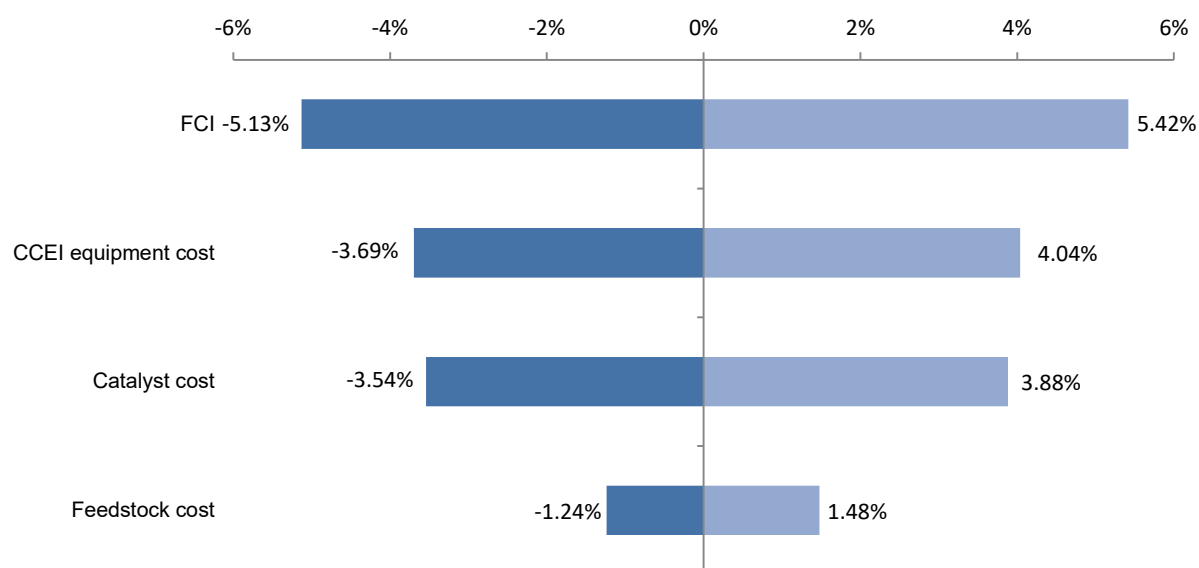


Figure 47: Starch process sensitivity analysis

The fixed capital investment has the largest effect on the MTSP, with a large contribution from the CCEI section (as can be seen from the second data bar). This is to be expected because the majority of the processing and purification is attributed to the CCEI section. Overall, the equipment cost of this process has the largest effect on the MTSP. The total catalyst cost has an average change of 3.7% on the MTSP, while the feedstock cost has the smallest effect on the MTSP (on average 1.36%).

The triticale cultivation growth might include a decrease in the feedstock price and would lower the green premium to a more realistic percentage. An advantage of using triticale rather than *Pine* and *Eucalyptus* components is that a larger amount of extractable starch exists in triticale (on average a starch content of 65.3%) than the amount of major terpene within any part of these species (Eudes, 2015). Further investigation on optimal catalysts might reveal less expensive catalysts that would perform similarly to the Sn-beta zeolite and copper-ruthenium-carbon catalysts used during the isomerisation of glucose and conversion of HMF to DMF. Lastly, improvements on the fixed capital investment can include an alternative to the purification of TPA that would require less washing equipment. Due to the nature of literature describing the CCEI process, heat integration could not be implemented and will have an effect on the utility cost, heat exchanger size and number.

6 Main conclusions

Processes towards the production of terephthalic acid from 1G and 2G feedstocks were successfully derived using available literature. Two scenarios were used to compare these processes in order to address the aim; firstly considering the amount of 2G feedstocks available in South Africa, and secondly considering a reasonable market share for novel chemicals in the short term using 1G and 2G feedstocks.

Through the determination of the 2G feedstock capacity in South Africa and the selection of appropriate literature, the simulation of the developed processes could be performed. It was determined that each 2G feedstock could produce high quality TPA at the correct specifications. Medium quality TPA was produced at a slightly lower quality, which will result in a lower selling price and application for fibre products rather than liquid containers. It was noted that the small production scale lead to high average costs of production, where the Pine process had the largest TEIC (M\$2.6/tonne TPA produced) and effectively also the largest TIC (M\$5.2/tonne). More comparable TEIC's were noted from the Eucalyptus and PHR processes (M\$0.9/tonne and M\$1.2/tonne, respectively). Ultimately, scenario one's approach delivered processes that are economically unviable (incalculable DCFROR's) with large feedstock capacity restrictions.

Scenario two was approached by literature review and modelling of the 1G process as well as the scale-up of the 2G processes in order to cost and analyse each process at a scale of 10% PET market share. The 2G processes were deemed economically unviable due to the high green premiums calculated for each process. In comparison with a TPA equivalent minimum selling price (FDCA) of \$2130/tonne, the starch process (MTSP of \$1953/tonne) has the potential to be economically viable when considering a starch-based source from where C5/C6 sugars can be obtained. A more realistic green premium can be reached through further research and optimisation, especially considering triticale as feedstock in South Africa. Fewer processing steps, more effective purification methods, optimal and less expensive catalysts and the introduction of by-product conversion for additional revenue will eventually lead to an MTSP that is closer to the expected green premium of 125%.

Lastly, considering the conventional steps from research to optimisation (recently seen through companies such as Coca-Cola and Virent aiming to produce fully bio-based TPA/PEF) several years are usually needed before commercialisation is possible. Therefore, an appropriate amount of time will be needed in order to optimise and eventually commercialise the production of fully bio-based TPA from starch-based feedstocks.

7 Recommendations for future work

The following recommendations apply to the developed processes for the production of TPA from 1G feedstocks:

- Determine potential for sweet sorghum and triticale as starch-based process feedstock.
- Identify the optimal parameters for each section of the processes through thorough experimentation.
- Investigate configurations for the production of bioethanol from certain by-product streams for additional sales.
- Investigate alternative catalysts that are less expensive but yield the same or improved selectivity to the appropriate intermediate/product.
- Perform heat integration on each optimised sections to increase energy efficiency.
- Perform market research analyses to determine consumer interest, acceptable green premium, etc.
- Perform a life-cycle assessment on the optimised processes to identify their full environmental impact.
- Determine international potential of the developed processes.

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8 Appendices

- Appendix A Introduction to terephthalic acid precursors
- Appendix B ASPEN Plus equipment models and flowsheets
- Appendix C Scenario one economic calculations
- Appendix D Scenario one Discounted Cash Flow Analysis sheets
- Appendix E Scenario two Discounted Cash Flow Analysis sheets

8.1 Appendix A: Introduction to terephthalic acid precursors

8.1.1 2G process scheme intermediate chemical compounds

This section introduces the intermediate chemical compounds involved in the production of TPA from lignocellulosic-based feedstocks (Figure 5). The major terpenes extracted from these feedstocks are alpha-pinene, the major terpene in *Pine* species, as well as cineole, the major terpene within *Eucalyptus* species. Both of these terpenes are categorised under the term oleoresins. Dehydrogenation of these terpenes under different reactor conditions using different catalysts produces the alkyl benzene p-cymene, which in turn can be oxidised to TPA.

Oleoresins

Oleoresins are liquids with very specific scents and are produced by organs within conifers. These liquids include terpenes, terpenoids (terpenes containing one or more oxygen molecule) and resinous acids. They are stored within the secretory and epidermis cells, resin channels and glandular trichomes of the wood. Approximately 90% of the essential oils found in conifers are made up of aromatic compounds. The main aromatic compounds are monoterpenes (terpenes with two isoprene units) and sesquiterpenes (terpenes with three isoprene units). α -Pinene and β -pinene are the most abundant monoterpenes, while 1, 8 – cineole is an abundant monoterpenoid in some essential oils (Flores, 2013). These compounds are further investigated in this study as possible precursors in the production of terephthalic acid.

Alpha-Pinene

Pinene is a primary terpene extracted from *Pine* trees and it has two isomers, alpha- and beta-pinene. α -pinene, also known as 2, 6, 6-trimethylbicyclo [3.1.1] hept-2-ene by its IUPAC name, is a colourless liquid solvent that is insoluble in water and has a boiling point of 156°C (National Centre for Biotechnology Information, 2009). Figure 48 shows the two dimensional structure of α -pinene.

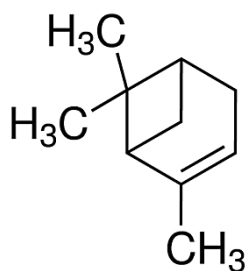


Figure 48: Two-dimensional structure of alpha-pinene

Studies have shown that alpha-pinene exhibits pharmaceutical properties, such as anti-inflammatory, anti-microbial, antioxidant and bronchodilator effects (Colbert, 2014). It has also exhibited anti-carcinogenic properties as it was shown to inhibit the growth of cancerous cells in mice by 40% (Kusuhara, *et al.*, 2012), which suggests that alpha-pinene can also be used as an antineoplastic drug. Monoterpenes, such as alpha-pinene, can also inhibit acetylcholinesterase activity. This discovery lead to new research regarding memory retention increases during the enzyme inhibition (Miyazawa & Yamafuji, 2005).

Alpha-pinene can be a precursor for TPA production because of the yield potential in commercial forest species and pulp mill residues in South Africa. Extraction methods from these sources are explained in more detail in Section 2.4.

1, 8-Cineole

Cineole (eucalyptol) is identified as a monoterpenoid and contributes to a large percentage of Eucalyptus oil content. It may have pharmaceutical importance as it exhibits analgesic, anti-inflammatory, decongestive, antioxidant and hepatoprotective properties (Lima *et al.*, 2013). Figure 49 shows the two-dimensional structure of cineole.

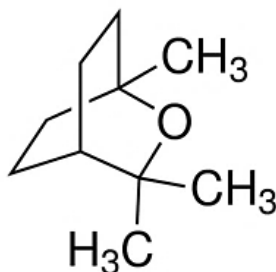


Figure 49: Two-dimensional structure of cineole

p-Cymene

p-Cymene is a secondary metabolite, and is found in foods, such as carrots, raspberries and spices and is used during the production of fungicides and pesticides. It can be used as a flavouring agent and possesses some pharmaceutical properties (analgesic and anti-inflammatory) (Quintans, *et al.*, 2013). Figure 50 shows the two dimensional structure of *p*-cymene.

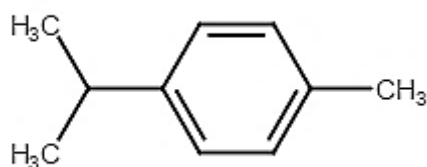


Figure 50: Two-dimensional structure of p-cymene

8.1.2 1G process scheme intermediate chemical compounds

This chapter provides an introduction to the intermediate chemical compounds involved in the production of TPA from starch-based feedstocks (Figure 13). Starch-based feedstocks can be utilised to extract starch and produce glucose from its polymers. The production of HMF from glucose leads to the production of a heterocyclic molecule called DMF, which is a precursor to the production of p-xylene. Lastly, p-xylene can be oxidised to form the desired product, TPA.

Starch

Starch polymers are produced within plants through photosynthesis and serves as carbohydrate reserves within sources such as wheat, barley, rice and other vegetables. Each polymer can contain up to 20 000 glucose molecules, which is used to sustain the plant and aid in reproduction. Extraction of starch and separation from the protein, oil and other insoluble portions of the plant involve manual refining, centrifuging, hydrolysis and/or drying (Fortescue, 2012). Figure 51 shows the structure of a starch molecule, where n represents the number of glucose molecules, which vary per polymer.

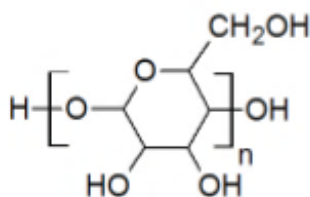


Figure 51: Starch molecular structure

Glucose

Glucose is classified as a monosaccharide, which means that it contains only one “sugar molecule”. The molecule can be either a chain (Fischer projection) or a ring and consists of five hydroxyl groups and one aldehyde group (Figure 52). In the human body, it is stored as glycogen in a similar manner as to which plants store starch polymers for energy reserves. Through glycolysis and the oxidation of glucose, energy in the form of adenosine triphosphate (ATP) is produced, while CO_2 and water form as by-products. Glucose is also used to manage hypoglycaemia, while the inability to regulate levels of glucose in the blood is experienced by patients with diabetes (Dunford & Doyle, 2012).

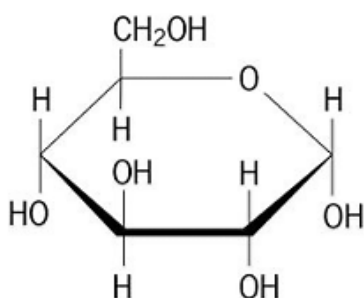


Figure 52: Glucose molecular structure

5-Hydroxymethylfurfural

5-Hydroxymethylfurfural (HMF) is an organic compound commonly produced in powder or crystalline form through the dehydration of glucose. It consists of a furan ring containing alcohol and aldehyde groups (Figure 53). HMF is highly soluble in water and has an average boiling point of 115°C . Various chemical compounds can be produced from HMF such as adipic acid, levulinic acid, DMF and caprolactam (which is used during the manufacturing of surgical sutures). HMF is also a natural component found coffee and honey and can be used as flavouring in certain beverages (Fischer, 2017).

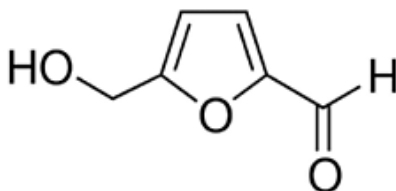


Figure 53: HMF molecular structure

2, 5-Dimethylfuran

2, 5-Dimethylfuran (DMF) is a heterocyclic molecule that is insoluble in water and has an average boiling point of 93°C (Figure 54). Recently it has gained attention because of its biofuel potential; it has a 40% greater energy density than ethanol and may consume only two thirds of the energy required to evaporate. There is also a lowered risk of explosion due to volatile gases but does require 20% more air than ethanol biofuel (Salazar, 2011).

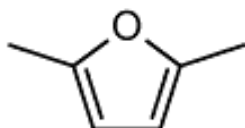


Figure 54: 2, 5-Dimethylfuran molecular structure

p-Xylene

The current industrial method for producing terephthalic acid, the Mid-Century process, utilises p-xylene (Figure 55) produced from crude oil in catalytic reformers. The product obtained from these reformers is called BTX, which is a mixture of benzene, toluene and isomers of the xylene group (ortho-, para- and meta-xylene). p-Xylene can also be used to produce benzoic acid, dimethyl esters and rubber products. The bio-based equivalent of p-xylene is identical in structure and characteristics to fossil-derived p-xylene and can therefore be used as precursor towards the production of bio-TPA (Abraham, 2017).

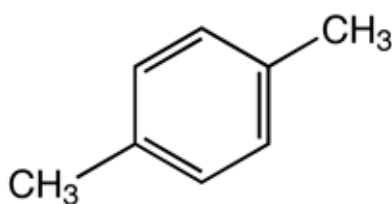












Figure 55: p-Xylene molecular structure

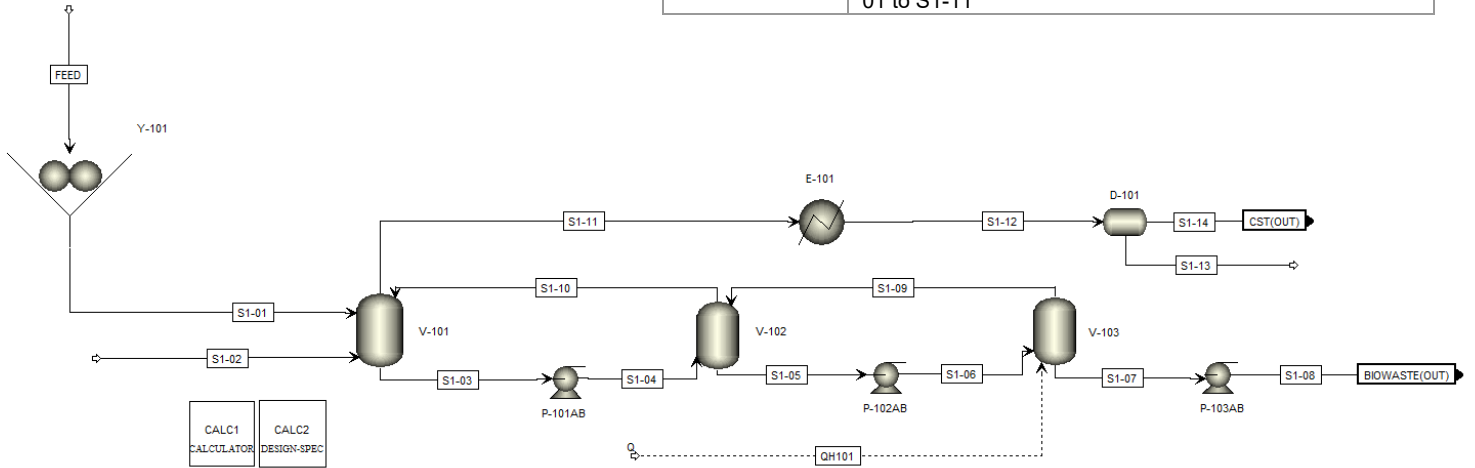
8.2 Appendix B: ASPEN Plus equipment models and flowsheets

ASPEN Plus block selection

Block type	Specifications	Block icon
Biomass mill	Type: rod mill Distribution function: Gates Gaudin Schuhmann Maximum particle diameter specified Power specification (process specific)	 Crusher
Terpene extraction vessel, flash vessel, minute component removal, fired heater, carrier gas removal	Duty: 0 kW /utility connection	 Flash2
Centrifugal pump, slurry pump	Discharge pressure (process specific) Pump and driver efficiencies: 0.85	 Pump
Heat exchanger, condenser	Pressure change: 0 atm Vapour fraction: 0 (condenser) Temperature (process specific)	 Heater
Decanter (terpene/water separation)	Key component in 2 nd liquid phase: water Pressure change: 0 atm	 Decanter
Compressor, turbine	Isentropic Discharge pressure (process specific)	 Compr
Conversion reactor	Temperature, pressure, inert components defined (process specific) Yields determined from selectivities	 RYield
Mixing vessel, liquid rerouting (via valves)	Pressure change: 0 atm	 Mixer
Stoichiometric reactor (CO ₂ treatment)	Pressure change: 0 atm Reaction: $\text{Ca(OH)}_2 + \text{CO}_2 \rightarrow \text{CaCO}_3 + \text{H}_2\text{O}$ Fractional conversion: 0.99 CO ₂	 RStoic
Solids dryer	Shortcut dryer Pressure change: 0 atm TPA powder dryer temperature: 210°C (due to NMP) 80% recycle of flue gas	 Dryer

Pine model

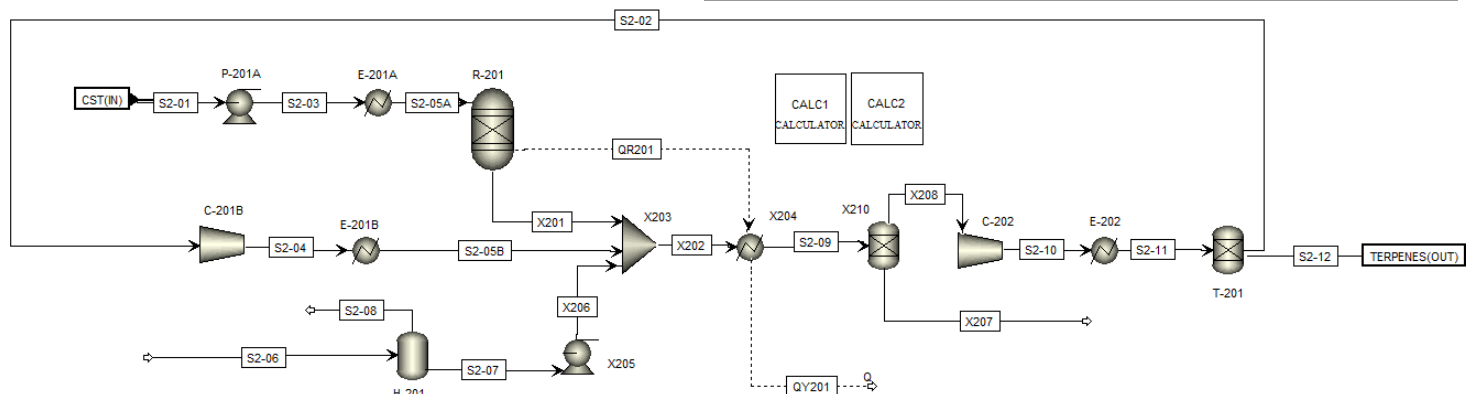
a) Pine hydro-distillation



Section 1	Units	S1-01	S1-02	S1-03	S1-08	S1-11	S1-12	S1-13	S1-14
From				V-101	P-103AB	V-101	E-101	D-101	D-101
To		V-101	V-101	P-101AB	SC-1	E-101	D-101		SC-3
Temperature	C	25	25	77.2	94.1	77.2	40.7	49.7	49.7
Pressure	bar	1	1	0.47	1	0.47	0.47	0.47	0.47
Mass Liquid Fraction		0.02	1	0.82	0.80	0	1	1	1
Mass Solid Fraction		0.98	0	0.18	0.20	0	0	0	0
Mass Flows	kg/hr	119.820	469.88	637.60	584.66	5.03	5.03	2.72	2.315
A-THUJEN	kg/hr	0.012	0	1.01E-04	2.20E-11	0.0121	0.0121	6.56E-07	0.012
TRICYCLE	kg/hr	0.056	0	4.12E-04	6.68E-11	0.0557	0.0557	3.35E-06	0.056
ALPHA-01	kg/hr	1.053	0	1.03E-02	2.93E-09	1.0528	1.0528	6.03E-05	1.053
A-FENCHO	kg/hr	0.015	0	3.09E-02	0.000298	0.0142	0.0142	5.74E-05	0.014
CARYOPH	kg/hr	0.017	0	8.30E-05	4.78E-12	0.0169	0.0169	5.84E-09	0.017
CAMPHENE	kg/hr	0.002	0	2.35E-05	6.50E-12	0.0024	0.0024	1.27E-07	0.002
TERP-4-O	kg/hr	0.010	0	3.24E-02	0.000857	0.0088	0.0088	3.08E-05	0.009
BETA-PIN	kg/hr	0.670	0	9.15E-03	5.05E-09	0.6704	0.6704	3.66E-05	0.670
TERP-4-Y	kg/hr	0.007	0	1.79E-03	2.89E-07	0.0073	0.0073	5.80E-07	0.007
A-TERPIN	kg/hr	0.191	0	8.09E-01	0.031362	0.1598	0.1598	5.32E-04	0.159
B-MYRCE	kg/hr	0.063	0	1.00E-03	8.41E-10	0.0629	0.0629	2.38E-06	0.063
CADINENE	kg/hr	0.012	0	4.33E-05	1.41E-12	0.0121	0.0121	3.70E-09	0.012
TERPINEN	kg/hr	0.002	0	4.99E-05	6.25E-11	0.0024	0.0024	1.23E-07	0.002
MSALICYL	kg/hr	0.005	0	5.17E-03	0.004826	0.0000	0.0000	9.45E-06	5.11E-06
D-LIM-01	kg/hr	0.077	0	1.62E-03	2.14E-09	0.0774	0.0774	3.32E-06	0.0774
PCYMENE	kg/hr	0.007	0	1.85E-02	0.006217	0.0010	0.0010	2.79E-05	0.0010
MUUROLOL	kg/hr	0.010	0	1.46E-02	6.79E-05	0.0096	0.0096	2.21E-07	0.0096
TERPI-01	kg/hr	0.039	0	1.48E-03	5.88E-09	0.0387	0.0387	2.29E-06	0.0387
T-CADINO	kg/hr	0.002	0	3.51E-03	1.52E-05	0.0024	0.0024	5.53E-08	0.0024
3-HEX-01	kg/hr	0.005	0	3.38E-03	4.06E-06	0.0048	0.0048	1.53E-05	0.0048
A-CADINO	kg/hr	0.034	0	4.91E-02	2.13E-04	0.0337	0.0337	7.76E-07	0.0337
WATER	kg/hr	0	469.88	519.1396	467.151	2.7287	2.7287	2.719	0.0097
NCPSD Sub									
BIOMASS	kg/hr	117.47	0	117.47	117.47	0	0	0	0

b) Dehydrogenation of α -pinene

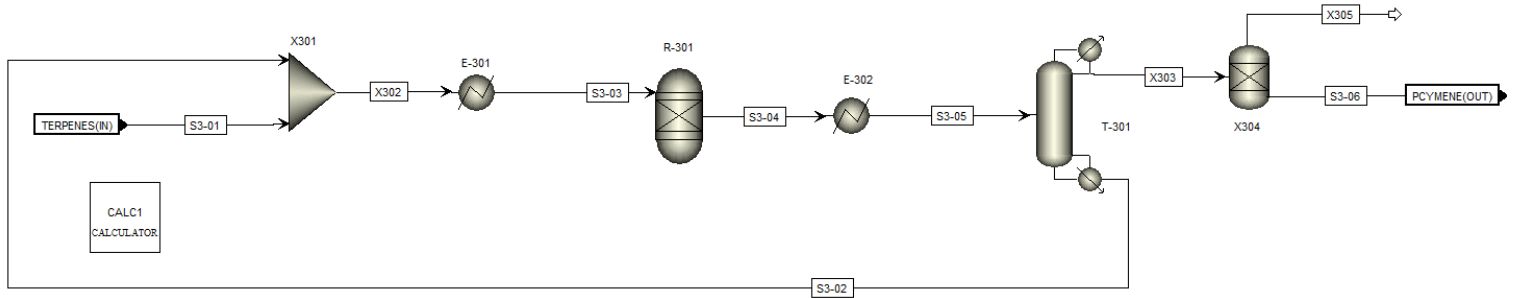
Block	Function
CALC1	Sets carrier gas volumetric feed (S2-02) as a function of terpene liquid mass feed (S2-01)
CALC2	Sets catalyst mass feed (S2-06) as a function of terpene liquid mass feed (S2-01)



Section 2	Units	S2-01	S2-02	S2-06	S2-09	S2-10	S2-11	S2-12
From		SC-4			X204	C-202	E-202	T-201
To		P-201A	C-201B	H-201	X210	E-202	T-201	SC-5
Temperature	C	60	60	25	275.5	186.5	60	60
Pressure	bar	0.47	1	1	5	1	1	1
Mass Vapour Frac		0	1	0	0.957	1	0.747	0
Mass Liquid Frac		1	0	1	0.043	0	0.253	1
Mass Flows	kg/hr	2.30	5.06	0.34	7.61	7.36	7.36	2.30
A-THUJEN	kg/hr	1.21E-02	0	0	0	0	0	0
TRICYCLE	kg/hr	5.57E-02	0	0	0	0	0	0
ALPHA-01	kg/hr	1.05	0	0	0	0	0	0
A-FENCHO	kg/hr	1.40E-02	0	0	1.47E-02	1.47E-02	1.47E-02	1.47E-02
CARYOPH	kg/hr	1.69E-02	0	0	1.77E-02	1.77E-02	1.77E-02	1.77E-02
CAMPHENE	kg/hr	2.42E-03	0	0	4.95E-02	4.95E-02	4.95E-02	4.95E-02
TERP-4-O	kg/hr	8.46E-03	0	0	0	0	0	0
BETA-PIN	kg/hr	6.70E-01	0	0	3.46E-01	3.46E-01	3.46E-01	3.46E-01
TERP-4-Y	kg/hr	7.26E-03	0	0	7.60E-03	7.60E-03	7.60E-03	7.60E-03
A-TERPIN	kg/hr	1.48E-01	0	0	1.54E-01	1.54E-01	1.54E-01	1.54E-01
B-MYRCE	kg/hr	6.29E-02	0	0	6.61E-02	6.61E-02	6.61E-02	6.61E-02
CADINENE	kg/hr	1.21E-02	0	0	0	0	0	0
PCYMENE	kg/hr	7.54E-04	0	0	7.95E-01	7.95E-01	7.95E-01	7.95E-01
MUUROLOL	kg/hr	9.58E-03	0	0	1.01E-02	1.01E-02	1.01E-02	1.01E-02
T-CADINO	kg/hr	2.40E-03	0	0	2.53E-03	2.53E-03	2.53E-03	2.53E-03
3-HEX-01	kg/hr	4.82E-03	0	0	5.07E-03	5.07E-03	5.07E-03	5.07E-03
A-CADINO	kg/hr	3.36E-02	0	0	3.52E-02	3.52E-02	3.52E-02	3.52E-02
WATER	kg/hr	0.01	0	0.09	0.01	0.01	0.01	0.01
NITROGEN	kg/hr	0	5.06	0	5.06	5.06	5.06	0
1-MET-02	kg/hr	0	0	0	0.0032	0.0032	0.0032	0.0032
1-MET-03	kg/hr	0	0	0	0.0839	0.0839	0.0839	0.0839
GUAIE-01	kg/hr	0	0	0	0.2419	0.2419	0.2419	0.2419
P-MEN-01	kg/hr	0	0	0	0.1792	0.1792	0.1792	0.1792
P-MEN-02	kg/hr	0	0	0	0.0412	0.0412	0.0412	0.0412
SODIU-01	kg/hr	0	0	0.0007	0.0007	0	0	0
CALCI-01	kg/hr	0	0	0.0093	0.0093	0	0	0
MAGNE-01	kg/hr	0	0	0.0021	0.0021	0	0	0
ALUMI-01	kg/hr	0	0	0.0585	0.0585	0	0	0
SILIC-01	kg/hr	0	0	0.1807	0.1807	0	0	0

b) p-Cymene purification

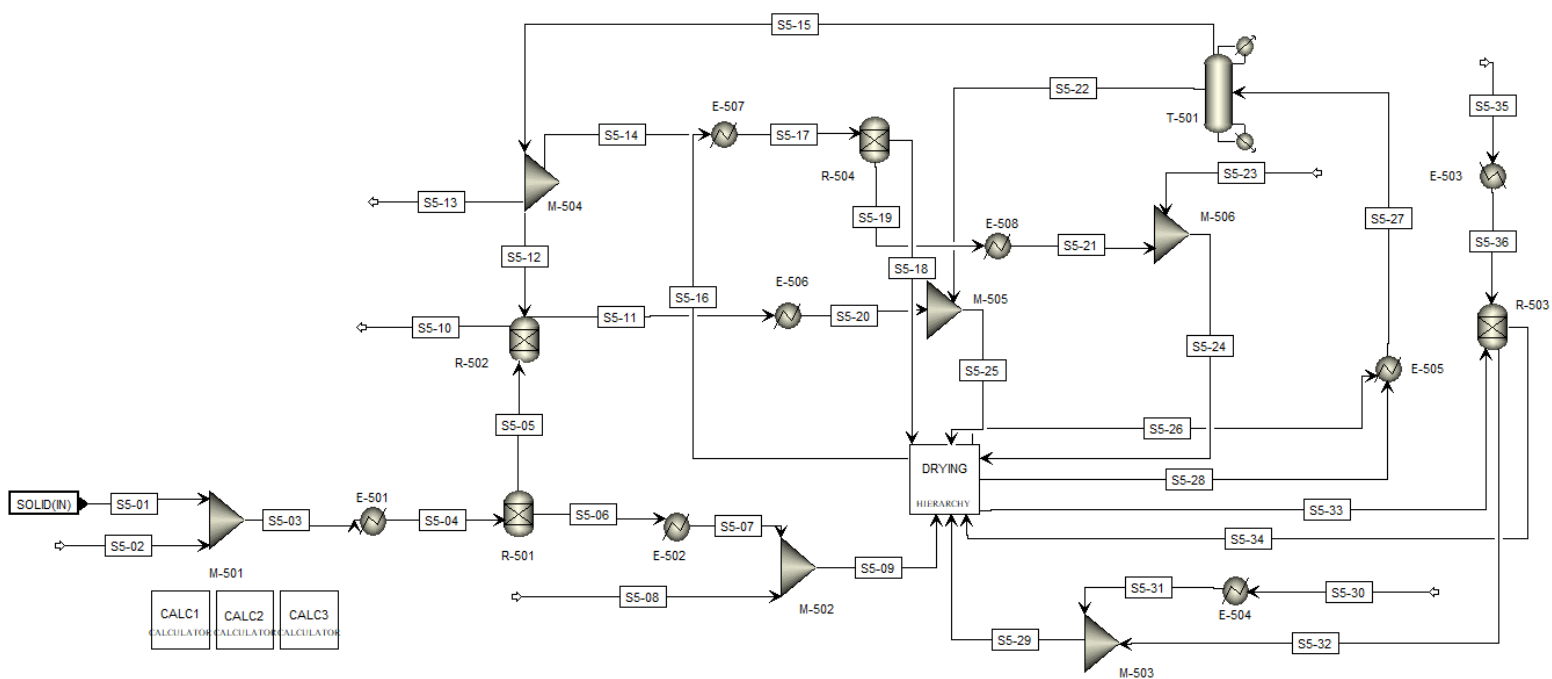
Block	Function
CALC1	Sets sulphuric acid mass feed (S3-02) as 25% of terpene liquid mass feed (S3-01)



	Units	S3-01	S3-02	S3-03	S3-04	S3-05	S3-06
From		ŞC-6		E-301	R-301	E-302	X304
To		X301	X301	R-301	E-302	T-301	ŞC-8
Temperature	C	60	25	110	110	80	140
Pressure	bar	1	1	1	1	1	0.9
Mass Vapour Fraction		0	0	0	0	0	0.014
Mass Liquid Fraction		1	1	1	1	1	0.986
Mass Flows	kg/hr	2.304	0.576	2.880	2.880	2.880	0.565
A-FENCHO	kg/hr	0.015	0	0.015	0	0	0
2-NOR-01	kg/hr	0.042	0	0.042	0	0	0
CARYOPH	kg/hr	0.018	0	0.018	0	0	0
CAMPHENE	kg/hr	0.050	0	0.050	0	0	0
BETA-PIN	kg/hr	0.346	0	0.346	0	0	0
TERP-4-Y	kg/hr	0.008	0	0.008	0	0	0
A-TERPIN	kg/hr	0.154	0	0.154	0	0	0
B-MYRCE	kg/hr	0.066	0	0.066	0	0	0
TERPINEN	kg/hr	0.058	0	0.058	0	0	0
BPELLLAN	kg/hr	0.041	0	0.041	0	0	0
GTERPINE	kg/hr	0.045	0	0.045	0	0	0
PCYMENE	kg/hr	0.795	0	0.795	0.56	0.56	0.56
MUUROLOL	kg/hr	0.010	0	0.010	0	0	0
TERPI-01	kg/hr	0.055	0	0.055	0	0	0
T-CADINO	kg/hr	0.003	0	0.003	0	0	0
3-HEX-01	kg/hr	0.005	0	0.005	0	0	0
A-CADINO	kg/hr	0.035	0	0.035	0	0	0
WATER	kg/hr	0.011	0.029	0.040	1.73E-03	1.73E-03	1.73E-03
1-MET-02	kg/hr	0.003	0	0.003	0	0	0
1-MET-03	kg/hr	0.084	0	0.084	0	0	0
GUAIE-01	kg/hr	0.242	0	0.242	0	0	0
P-MEN-01	kg/hr	1.79E-01	0	1.79E-01	2.59E-03	2.59E-03	2.59E-03
P-MEN-02	kg/hr	4.12E-02	0	4.12E-02	5.76E-04	5.76E-04	5.76E-04
SULFU-01	kg/hr	0	0.547145	0.547145	1.265	1.265	0
ISOPRESS	kg/hr	0	0	0	0.548	0.548	0
CEMBRENE	kg/hr	0	0	0	0.014	0.014	0
ELLIOTIN	kg/hr	0	0	0	0.488	0.488	0
Volume Flow	l/min	0.045	0.006	0.052	0.036	0.035	0.091

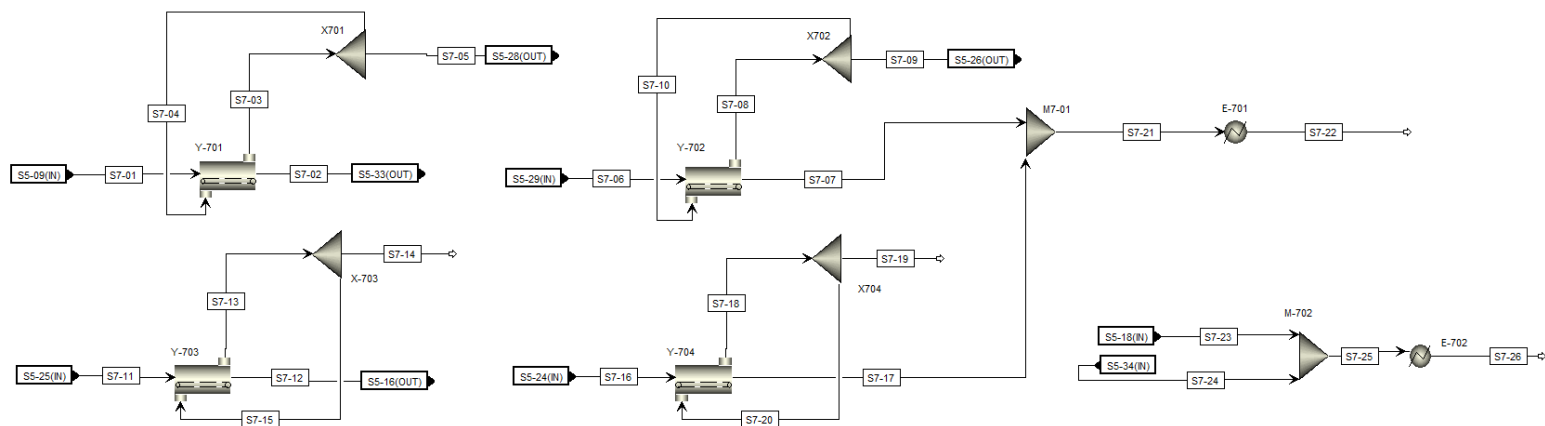
d) TPA purification and drying

Block	Function
CALC1	Sets NMP mass feed (S5-02) as 3 times the TPA mass feed (S5-01) (2 nd wash stage R-502: 3.6 times)
CALC2	Sets acetone mass feed (S5-08 and S5-30) as 3 and 3.6 times the TPA mass in S5-07 and S5-32, respectively
CALC3	Calculates fraction bypass in M-504 for correct amount of NMP to R-504



	Units	S5-01	S5-02	S5-03	S5-04	S5-05	S5-06	S5-07	S5-08	S5-09	S5-10	S5-11	S5-12
From		SC-10		M-501	E-501	R-501	R-501	E-502		M-502	R-502	R-502	M-504
To		M-501	M-501	E-501	R-501	R-502	E-502	M-502	M-502	SC-3		E-506	R-502
Temperature	C	90	25	40.21	160	160	160	45	25	39.57	189.38	189.38	199.18
Pressure	bar	12	1	1	1	1	1	1	1	1	0.9	0.9	0.9
Mass Vap Frac		0	0	0	0	0	0	0	0	0	0	0	0
Mass Liq Frac		0	1	0.694	0.694	0	0.905	0.905	1	0.926	0	0.905	1
Mass Sol Frac		1	0	0.306	0.306	1	0.095	0.095	0	0.074	1	0.095	0
Mass Flows	kg/hr	0.562	1.278	1.840	1.840	0.428	1.412	1.412	0.403	1.815	0.336	0.967	0.875
N-MET-01	kg/hr	0	1.278	1.278	1.278	0	1.278	1.278	0	1.278	0	0.875	0.875
ACETO-01	kg/hr	0	0	0	0	0	0	0	0.403	0.403	0	0	0
Volume Flow	l/min	0.006	0.021	0.027	0.030	0.005	0.025	0.023	0.009	0.031	0.004	0.018	0.017
CIPSD Sub													
Temperature	C	90		40.21	160	160	160	45		39.57	189.38	189.38	
Pressure	bar	12		1	1	1	1	1		1	0.9	0.9	
Molar Liq Fraction		0		0	0	0	0	0		0	0	0	
Molar Sol Fraction		1		1	1	1	1	1		1	1	1	
Mass Liq Fraction		0		0	0	0	0	0		0	0	0	
Mass Sol Fraction		1		1	1	1	1	1		1	1	1	
Average MW		159.55		159.55	159.55	157.60	166.12	166.12		166.12	155.42	166.12	
Mass Flows	kg/hr	0.562		0.562	0.562	0.428	0.134	0.134		0.134	0.336	0.092	
TEREP-02	kg/hr	0.426		0.426	0.426	0.292	0.134	0.134		0.134	0.200	0.092	
P-TOL-02	kg/hr	0.101		0.101	0.101	0.101	2.73E-05	2.73E-05		2.73E-05	0.100602	1.87E-05	
CUMIC-01	kg/hr	0.029		0.029	0.029	0.029	2.03E-05	2.03E-05		2.03E-05	0.029273	1.87E-05	
4-CAR-01	kg/hr	6.36E-03		6.36E-03	6.36E-03	6.30E-03	5.99E-05	5.99E-05		5.99E-05	6.28E-03	1.87E-05	
	Units	S5-13	S5-14	S5-15	S5-16	S5-17	S5-18	S5-19	S5-20	S5-21	S5-22	S5-23	S5-24
From		M-504	M-504	T-501	SC-5	E-507	R-504	R-504	E-506	E-508	T-501		M-506
To			E-507	M-504	E-507	R-504	SC-10	E-508	M-505	M-506	T-501	M-506	SC-9
Temperature	C	199.18	199.18	199.18	210	105	105	105	45	40	124.43	25	34.64
Pressure	bar	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9	1	0.9

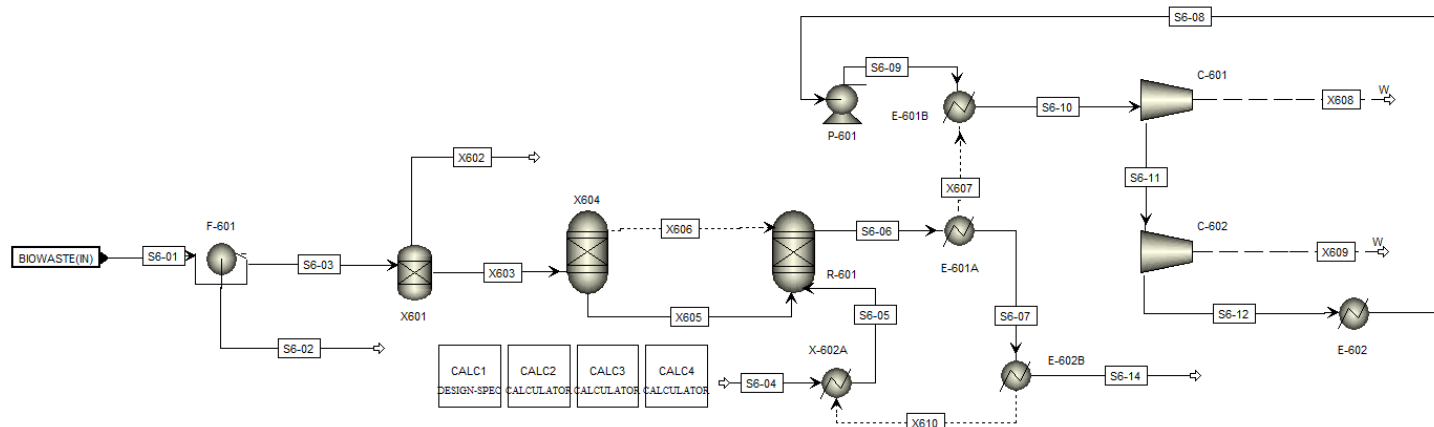
Mass Vap Fraction		0	0	0	0	0	0	0	0	0	1	0	0
Mass Liq Fraction		1	1	1	0	0.783	0	0.883	0.905	0.883	0	1	0.918
Mass Sol Fraction		0	0	0	1	0.217	1	0.117	0.095	0.117	0	0	0.082
Mass Flows	kg/hr	0.437	0.331	1.643	0.092	0.423	0.048	0.375	0.967	0.375	0.736	0.157	0.532
N-MET-01	kg/hr	0.437	0.331	1.643	0	0.331	0	0.331	0.875	0.331	0.104	0	0.331
ACETO-01	kg/hr	0	0	0	0	0	0	0	0	0	0.632	0.157	0.157
Vol Flow	l/min	0.008	0.006	0.032	0.001	0.007	0.001	0.006	0.015	0.006	7.305	0.003	0.009
CIPSD Sub													
Temperature	C				210	105	105	105	45	40			34.64
Pressure	bar				0.9	0.9	0.9	0.9	0.9	0.9			0.9
Molar Liq Fraction					0	0	0	0	0	0			0
Molar Sol Fraction					1	1	1	1	1	1			1
Mass Liq Fraction					0	0	0	0	0	0			0
Mass Sol Fraction					1	1	1	1	1	1			1
Average MW					166.1218	166.1218	166.1125	166.1321	166.1218	166.1321			166.1321
Mass Flows	kg/hr				9.20E-02	9.20E-02	4.83E-02	4.37E-02	9.20E-02	4.37E-02			4.37E-02
TEREP-02	kg/hr				9.19E-02	9.19E-02	4.83E-02	4.37E-02	9.19E-02	4.37E-02			4.37E-02
P-TOL-02	kg/hr				1.87E-05	1.87E-05	1.79E-05	8.31E-07	1.87E-05	8.31E-07			8.31E-07
CUMIC-01	kg/hr				1.87E-05	1.87E-05	1.77E-05	1.00E-06	1.87E-05	1.00E-06			1.00E-06
4-CAR-01	kg/hr				1.87E-05	1.87E-05	1.76E-05	1.09E-06	1.87E-05	1.09E-06			1.09E-06
	Units	S5-25	S5-26	S5-27	S5-28	S5-29	S5-30	S5-31	S5-32	S5-33	S5-34	S5-35	S5-36
From		M-505	ŠC-7	E-505	ŠC-1	M-503		E-504	R-503	ŠC-2	R-503		E-503
To		ŠC-6	E-505	T-501	E-505	ŠC-8	E-504	M-503	M-503	R-503	ŠC-4	E-503	R-503
Temperature	C	108.54	210	90	210	83.38	25	40	123.64	210	123.64	25	105
Pressure	bar	0.9	1	1	1	1	1	1	1	1	1	1	1
Mass Vap Fraction		0.320	1	0.041	1	0.045	0	0	0	0	0	0	0
Mass Liq Fraction		0.626	0	0.959	0	0.872	1	1	0.880	0	0	1	1
Mass Sol Fraction		0.054	0	0	0	0.084	0	0	0.120	1	1	0	0
Mass Flows	kg/hr	1.704	0.699	2.379	1.680	0.763	0.229	0.229	0.533	0.134	0.071	0.470	0.470
N-MET-01	kg/hr	0.980	0.470	1.747	1.278	0.470	0	0	0.470	0	0	0.470	0.470
ACETO-01	kg/hr	0.632	0.229	0.632	0.403	0.229	0.229	0.229	0	0	0	0	0
Volume Flow	l/min	5.377	5.816	0.881	13.270	0.300	0.005	0.005	0.009	0.001	0.001	0.008	0.008
CIPSD Subs													
Temperature	C	108.54				83.38			123.64	210	123.64		
Pressure	bar	0.9				1			1	1	1		
Molar Liq Fraction		0				0			0	0	0		
Molar Sol Fraction		1				1			1	1	1		
Mass Liq Fraction		0				0			0	0	0		
Mass Sol Fraction		1				1			1	1	1		
Average MW		166.1218				166.1321			166.1321	166.1176	166.1046		
Mass Flows	kg/hr	9.20E-02				6.37E-02			6.37E-02	1.34E-01	7.05E-02		
TEREP-02	kg/hr	9.19E-02				6.37E-02			6.37E-02	1.34E-01	7.04E-02		
P-TOL-02	kg/hr	1.87E-05				1.21E-06			1.21E-06	2.73E-05	2.61E-05		
CUMIC-01	kg/hr	1.87E-05				1.47E-06			1.47E-06	2.03E-05	1.88E-05		
4-CAR-01	kg/hr	1.87E-05				1.59E-06			1.59E-06	5.99E-05	5.83E-05		



	Units	S7-01	S7-02	S7-03	S7-04	S7-05	S7-06	S7-07	S7-08	S7-09	S7-10	S7-11	S7-12	S7-13
From		TPA.ŞC-3	Y-701	Y-701	X701	X701	TPA.ŞC-1	Y-702	Y-702	X702	X702	TPA.ŞC-6	Y-703	Y-703
To		Y-701	TPA.ŞC-2	X701	Y-701	TPA.ŞC-1	Y-702	M7-01	X702	TPA.ŞC-7	Y-702	Y-703	TPA.ŞC-5	X-703
Temperature	C	39.6	210	210	210	210	83.4	210	210	210	210	108.5	210	210
Pressure	bar	1	1	1	1	1	1	1	1	1	1	0.9	0.9	0.9
Mass Vap Frac		0	0	1	1	1	0.045	0	1	1	1	0.320	0	1
Mass Liq Frac		0.926	0	0	0	0	0.872	0	0	0	0	0.626	0	0
Mass Sol Frac		0.074	1	0	0	0	0.084	1	0	0	0	0.054	1	0
Mass Flows	kg/hr	1.815	0.134	8.402	6.721	1.680	0.763	0.064	3.495	0.699	2.796	1.704	0.092	8.058
N-MET-01	kg/hr	1.278	0	6.389	5.111	1.278	0.470	0	2.348	0.470	1.878	0.980	0	4.898
ACETO-01	kg/hr	0.403	0	2.013	1.610	0.403	0.229	0	1.147	0.229	0.918	0.632	0	3.160
Vol Flow	l/min	3.09E-02	1.48E-03	66.35	53.08	13.27	0.300	7.03E-04	29.08	5.82	23.27	5.38	1.01E-03	77.23
CIPSD Sub														
Mass Flows	kg/hr	0.134278	0.134278				6.37E-02	6.37E-02				9.20E-02	9.20E-02	
TEREP-02	kg/hr	0.13417	0.13417				6.37E-02	6.37E-02				9.19E-02	9.19E-02	
P-TOL-02	kg/hr	2.73E-05	2.73E-05				1.21E-06	1.21E-06				1.87E-05	1.87E-05	
CUMIC-01	kg/hr	2.03E-05	2.03E-05				1.47E-06	1.47E-06				1.87E-05	1.87E-05	
4-CAR-01	kg/hr	5.99E-05	5.99E-05				1.59E-06	1.59E-06				1.87E-05	1.87E-05	
	Units	S7-14	S7-15	S7-16	S7-17	S7-18	S7-19	S7-20	S7-21	S7-22	S7-23	S7-24	S7-25	S7-26
From		X-703	X-703	TPA.ŞC-9	Y-704	Y-704	X704	X704	M7-01	E-701	TPA.ŞC-10	TPA.ŞC-4	M-702	E-702
To			Y-703	Y-704	M7-01	X704		Y-704	E-701		M-702	M-702	E-702	
Temperature	C	210	210	34.6	210	210	210	210	210	33	105	123.6	116.2	33
Pressure	bar	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9	1	0.9	0.9
Mass Vap Frac		1	1	0	0	1	1	1	0	0	0	0	0	0
Mass Liq Frac		0	0	0.917886	0	0	0	0	0	0	0	0	0	0
Mass Sol Frac		0	0	0.082114	1	0	0	0	1	1	1	1	1	1
Mass Flows	kg/hr	1.612	6.446	0.532	0.044	2.440	0.488	1.952	0.107	0.107	0.048	0.071	0.119	0.119
N-MET-01	kg/hr	0.980	3.919	0.331	0	1.654	0.331	1.323	0	0	0	0	0	0
ACETO-01	kg/hr	0.632	2.528	0.157	0	0.786	0.157	0.629	0	0	0	0	0	0
Vol Flow	l/min	15.45	61.78	9.17E-03	4.82E-04	22.48	4.50	17.98	1.1E-03	1.1E-03	5.33E-04	7.78E-04	1.31E-03	1.3E-03
CIPSD Sub														
Mass Flows	kg/hr			0.0437	0.0437				0.1074	0.1074	0.0483	0.0705	0.1188	0.1188
TEREP-02	kg/hr			0.0437	0.0437				0.1074	0.1074	0.0483	0.0704	0.1187	0.1187
P-TOL-02	kg/hr			8.31E-07	8.31E-07				2.0E-06	2.0E-06	1.79E-05	2.61E-05	4.39E-05	4.3E-05
CUMIC-01	kg/hr			1.00E-06	1.00E-06				2.4E-06	2.4E-06	1.77E-05	1.88E-05	3.65E-05	3.6E-05
4-CAR-01	kg/hr			1.09E-06	1.09E-06				2.6E-06	2.6E-06	1.76E-05	5.83E-05	7.59E-05	7.5E-05

e) Biomass power and heat generation

Block	Function
CALC1	Varies F-601 frac for 40% liquid (mixed) in S6-03
CALC2	Combines water from proximate and ultimate, breaks down ultimate composition into individual fractions: YH=U(2)/100*(1-YW); H-atoms (the 2 nd entry of ultimate composition) fraction times all other atoms excluding H in water fraction
CALC3	Calculates air mole flow: AIRC=((C)+(H*0.5)+(N*2)-(O))/0.21
CALC4	Energy balance to determine water flow in steam cycle: WFLOW = QP/((4.535*(251.71-TIN))+1706.7+(3.268*(455.8-251.71)))

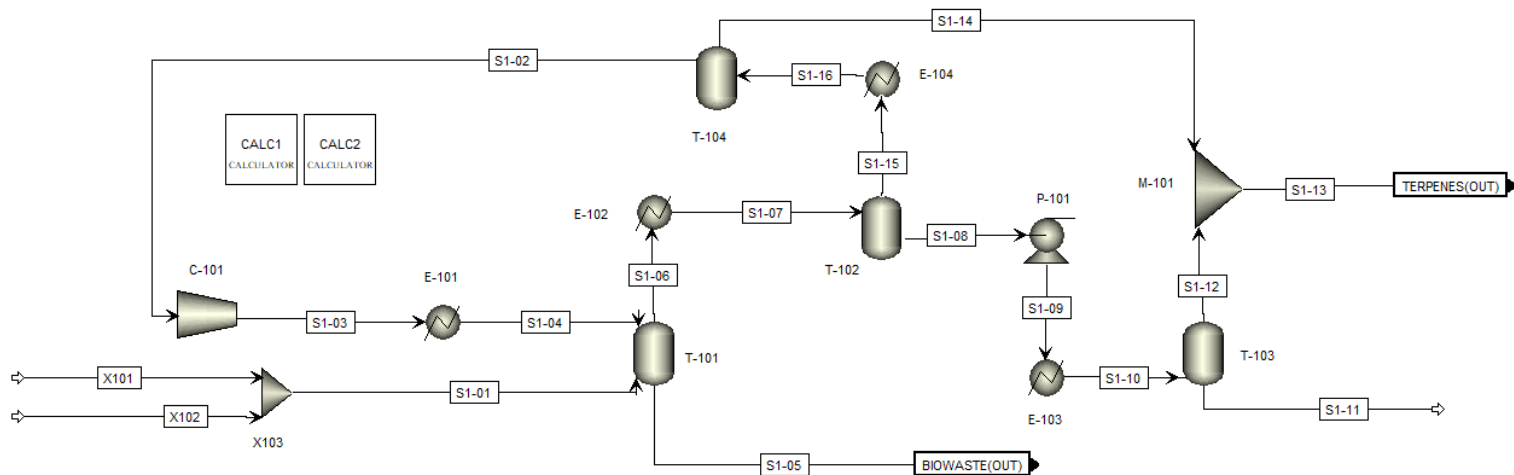


	Units	S6-01	S6-02	S6-03	S6-05	S6-06	S6-07	S6-08	S6-09	S6-10	S6-11	S6-12
From		SC-2	F-601	F-601	X-602A	R601	E-601A		P-601	E-601B	C-601	C-602
To		F-601		X601	R601	E-601A	E-602B	P-601	E-601B	C-601	C-602	E-602
Stream Class		MCINCPD	MCINCPD	MCINCPD	MCINCPD	MCINCPD	MCINCPD	MCINCPD	MCINCPD	MCINCPD	MCINCPD	MCINCPD
Temperature	C	94.2	94.2	94.2	222.8	1007.7	230.0	40.0	43.3	512.5	332.8	116.0
Pressure	bar	1	1	1	1	1	1	1	41	41	10	1
Mass Vap Frac		0	0	0	1	0.99	0.99	0	0	1	1	1
Mass Liq Frac		0.80	1	0.40	0	0	0	1	1	0	0	0
Mass Sol Frac		0.20	0	0.60	0	0.006	0.006	0	0	0	0	0
Density	gm/cc	0.98	0.92	1.11	7.00E-04	2.58E-04	6.56E-04	0.98	0.98	0.01	0.00	0.00
Enthalpy	cal/sec	-582274	-402393	-179880	7624.77	-172254	-225968	-254602	-254380	-200666	-206686	-213516
Mass Flows	kg/hr	585.43	389.64	195.79	569.02	764.80	764.80	242.85	242.85	242.85	242.85	242.85
A-THUJEN	kg/hr	3.17E-11	2.64E-11	5.30E-12	0	0	0	0	0	0	0	0
TRICYCLE	kg/hr	9.63E-11	8.02E-11	1.61E-11	0	0	0	0	0	0	0	0
ALPHA-01	kg/hr	4.22E-09	3.52E-09	7.07E-10	0	0	0	0	0	0	0	0
A-FENCHO	kg/hr	4.29E-04	3.57E-04	7.18E-05	0	0	0	0	0	0	0	0
2-NOR-01	kg/hr	1.87E-09	1.56E-09	3.14E-10	0	0	0	0	0	0	0	0
CARYOPH	kg/hr	6.98E-12	5.81E-12	1.17E-12	0	0	0	0	0	0	0	0
CAMPHENE	kg/hr	9.38E-12	7.81E-12	1.57E-12	0	0	0	0	0	0	0	0
TERP-4-O	kg/hr	1.20E-03	9.95E-04	2.00E-04	0	0	0	0	0	0	0	0
BETA-PIN	kg/hr	7.29E-09	6.07E-09	1.22E-09	0	0	0	0	0	0	0	0
B-MYRCE	kg/hr	1.21E-09	1.01E-09	2.03E-10	0	0	0	0	0	0	0	0
D-LIM-01	kg/hr	3.08E-09	2.57E-09	5.16E-10	0	0	0	0	0	0	0	0
PCYMENE	kg/hr	6.49E-03	5.40E-03	1.09E-03	0	0	0	0	0	0	0	0
MUUROLOL	kg/hr	9.89E-05	8.24E-05	1.66E-05	0	0	0	0	0	0	0	0
TERPI-01	kg/hr	8.52E-09	7.09E-09	1.43E-09	0	0	0	0	0	0	0	0
T-CADINO	kg/hr	2.22E-05	1.85E-05	3.72E-06	0	0	0	0	0	0	0	0
3-HEX-01	kg/hr	5.88E-06	4.90E-06	9.85E-07	0	0	0	0	0	0	0	0
WATER	kg/hr	467.90	389.59	78.31	0.00	149.47	149.47	242.85	242.85	242.85	242.85	242.85
BIOMASS	kg/hr	117.47	0	117.47	0	0	0	0	0	0	0	0
OXYGE-01	kg/hr	0	0	0	132.53	3.19	3.19	0	0	0	0	0
CARBO-01	kg/hr	0	0	0	0.00	169.76	169.76	0	0	0	0	0
NITROGEN	kg/hr	0	0	0	436.49	437.88	437.88	0	0	0	0	0
HYDROGEN	kg/hr	0	0	0	0	1.73E-05	1.73E-05	0	0	0	0	0
SIO2	kg/hr	0	0	0	0	4.49	4.49	0	0	0	0	0
Volume Flow	l/min	9.96	7.02	2.93	13555.93	49495.01	19442.29	4.13	4.15	357.93	1131.87	7269.26
Average MW		18.02	18.02	18.02	28.85	27.27	27.27	18.02	18.02	18.02	18.02	18.02
Mole Flows	kmol/hr	25.97	21.63	4.35	19.72	27.89	27.89	13.48	13.48	13.48	13.48	13.48
Mass Flows	kg/hr	467.96	389.64	78.32	569.02	760.31	760.31	242.85	242.85	242.85	242.85	242.85
Volume Flow	l/min	8.44	7.02	1.41	13555.93	49494.99	19442.26	4.13	4.15	357.93	1131.87	7269.26

Eucalyptus model

a) SCF extraction

Block	Function
CALC1	Sets CO ₂ volume feed (S1-02) as 25 times the biomass mass feed (S1-01)

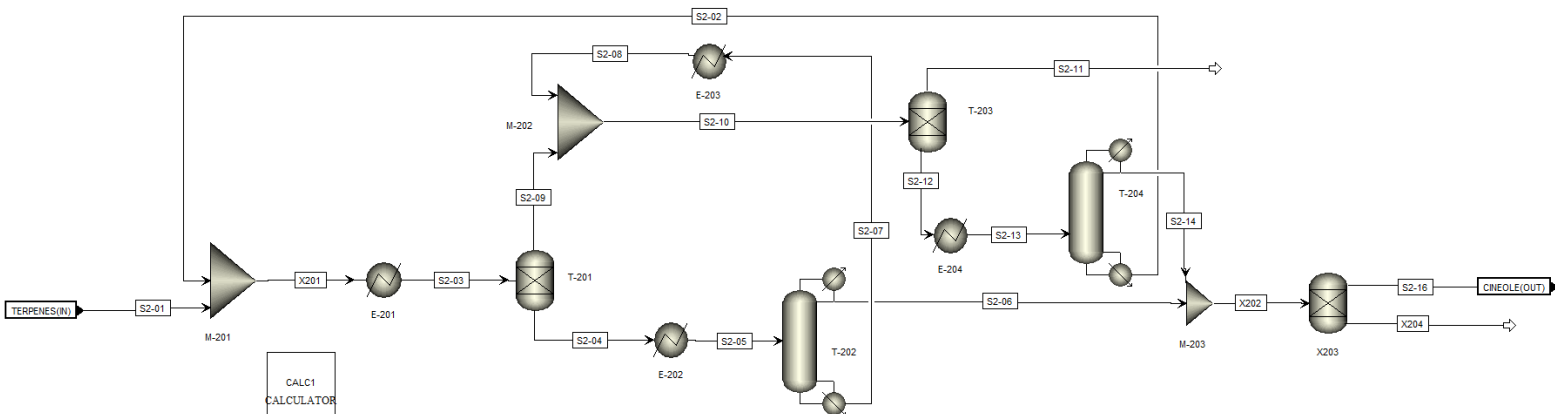


	Units	S1-01	S1-02	S1-03	S1-04	S1-05	S1-06	S1-07	S1-08	S1-09
From		X103		C-101	E-101	T-101	T-101	E-102	T-102	P-101
To		T-101	C-101	E-101	T-101	SC-1	E-102	T-102	P-101	E-103
Temperature	C	25.0	80	80.1	80	80	80	160	160	156.9
Pressure	bar	1	163.9	164	164	164	164	164	164	1
MIXED Substream										
Phase		Liquid	Vapour	Vapour	Vapour		Vapour	Mixed	Liquid	Liquid
Temperature	C	25.0	80	80.1	80		80	160	160	156.9
Pressure	bar	1	163.9	164	164		164	164	164	1
Molar Vap Frac		0	1	1	1		1	0.974	0	0
Molar Liq Frac		1	0	0	0		0	0.026	1	1
Molar Sol Frac		0	0	0	0		0	0	0	0
Mass Vap Frac		0	1	1	1		1	0.935	0	0
Mass Liq Frac		1	0	0	0		0	0.065	1	1
Average MW		178.75	44.01	44.01	44.01		46.07	46.07	117.35	117.35
Mass Flows	kg/hr	19.90	315.75	315.75	315.75		335.65	335.65	21.92	21.92
ALPHA-01	kg/hr	1.274	0	0	0		1.274	1.274	1.015	1.015
BETA-01	kg/hr	0.198	0	0	0		0.198	0.198	0.165	0.165
BETA-01	kg/hr	0.275	0	0	0		0.275	0.275	0.233	0.233
1-MET-01	kg/hr	0.924	0	0	0		0.924	0.924	0.803	0.803
D-LIM-01	kg/hr	2.169	0	0	0		2.169	2.169	1.891	1.891
GAMMA-01	kg/hr	0.415	0	0	0		0.415	0.415	0.369	0.369
TERPI-01	kg/hr	0.461	0	0	0		0.461	0.461	0.415	0.415
ALPHA-02	kg/hr	0.184	0	0	0		0.184	0.184	0.178	0.178
SPATHULE	kg/hr	1.147	0	0	0		1.147	1.147	1.143	1.143
A-EUDESME	kg/hr	0.215	0	0	0		0.215	0.215	0.215	0.215
CADINEDI	kg/hr	0.292	0	0	0		0.292	0.292	0.291	0.291
1:8-C-01	kg/hr	7.667	0	0	0		7.667	7.667	6.651	6.651
3-CAR-01	kg/hr	0.015	0	0	0		0.015	0.015	0.013	0.013
CAMPH-01	kg/hr	0.026	0	0	0		0.026	0.026	0.025	0.025
SABINYLA	kg/hr	0.015	0	0	0		1.54E-02	1.54E-02	1.04E-02	1.04E-02
ALLOAROM	kg/hr	0.015	0	0	0		0.015	0.015	0.015	0.015
AMITEOL	kg/hr	0.077	0	0	0		0.077	0.077	0.077	0.077
CARBO-01	kg/hr	0	315.74	315.74	315.74		315.74	315.74	3.884	3.884
N-NON-01	kg/hr	1.484	0	0	0		1.484	1.484	1.484	1.484
N-DOT-01	kg/hr	1.291	0	0	0		1.291	1.291	1.291	1.291
N-PEN-01	kg/hr	0.614	0	0	0		0.614	0.614	0.614	0.614
N-HEX-01	kg/hr	1.140	0	0	0		1.140	1.140	1.140	1.140
NCPSD Substream										

BIOMASS	kg/hr	755.03				755.03				
	Units	S1-10	S1-11	S1-12	S1-13	S1-14	S1-15	S1-16		
From		E-103	T-103	T-103	M-101	T-104	T-102	E-104		
To		T-103		M-101	SC-5	M-101	E-104	T-104		
Temperature	C	200	200	200	157.4848	80	160	80		
Pressure	bar	1	1	1	1	163.9	164	164		
MIXED Substream										
Phase		Mixed	Liquid	Vapour	Mixed	Liquid	Vapour	Mixed		
Temperature	C	200	200	200	157.5	80	160	80		
Pressure	bar	1	1	1	1	163.9	164	164		
Molar Vap Frac		0.877	0	1	0.996	0	1	0.983		
Molar Liq Frac		0.123	1	0	0.004	1	0	0.017		
Molar Sol Frac		0	0	0	0	0	0	0		
Mass Vap Frac		0.689	0	1	0.991	0	1	0.979		
Mass Liq Frac		0.311	1	0	0.009	1	0	0.021		
Average MW		117.35	297.03	92.20	76.56	54.91	44.19	44.19		
Mass Flows	kg/hr	21.923	6.814	15.109	21.606	6.497	313.725	313.725		
ALPHA-01	kg/hr	1.015	0.065	0.949	1.205	0.255	0.260	0.260		
BETA-01	kg/hr	0.165	0.013	0.152	0.185	0.033	0.033	0.033		
BETA-01	kg/hr	0.233	0.017	0.216	0.258	0.042	0.043	0.043		
1-MET-01	kg/hr	0.803	0.076	0.727	0.847	0.120	0.121	0.121		
D-LIM-01	kg/hr	1.891	0.184	1.707	1.983	0.276	0.278	0.278		
GAMMA-01	kg/hr	0.369	0.040	0.330	0.375	0.046	0.046	0.046		
TERPI-01	kg/hr	0.415	0.048	0.367	0.413	0.046	0.046	0.046		
ALPHA-02	kg/hr	0.178	0.039	0.139	0.146	6.79E-03	6.79E-03	0.007		
SPATHULE	kg/hr	1.143	0.798	0.346	0.349	3.16E-03	3.16E-03	3.16E-03		
A-EUDES	kg/hr	0.215	0.151	0.064	0.065	5.48E-04	5.48E-04	5.48E-04		
CADINEDI	kg/hr	0.291	0.183	0.107	0.109	1.35E-03	1.35E-03	1.35E-03		
1:8-C-01	kg/hr	6.651	0.588	6.064	7.073	1.009	1.015	1.015		
3-CAR-01	kg/hr	0.013	0.001	0.012	0.014	2.25E-03	2.27E-03	2.27E-03		
CAMPH-01	kg/hr	0.025	4.22E-03	2.03E-02	2.19E-02	1.62E-03	1.62E-03	1.62E-03		
SABINYLA	kg/hr	1.04E-02	2.89E-04	1.01E-02	1.50E-02	4.89E-03	4.97E-03	4.97E-03		
ALLOAROM	kg/hr	0.015	5.33E-03	9.78E-03	1.00E-02	2.61E-04	2.61E-04	2.61E-04		
AMITEOL	kg/hr	0.077	7.36E-02	3.27E-03	3.28E-03	1.66E-05	1.66E-05	1.66E-05		
CARBO-01	kg/hr	3.884	2.43E-03	3.882	8.531	4.649	311.864	311.864		
N-NON-01	kg/hr	1.484	1.481	2.97E-03	2.97E-03	1.37E-06	1.37E-06	1.37E-06		
N-DOT-01	kg/hr	1.291	1.291	7.21E-04	7.21E-04	1.85E-07	1.85E-07	1.85E-07		
N-PEN-01	kg/hr	0.614	0.614	8.49E-05	8.49E-05	1.66E-08	1.66E-08	1.66E-08		
N-HEX-01	kg/hr	1.140	1.140	1.18E-08	1.18E-08	1.18E-08	1.18E-08	1.18E-08		

b) Cineole purification

Block	Function
CALC1	Sets HQ mass feed (S2-02) as 34.5% of the terpene mass feed (S2-01)

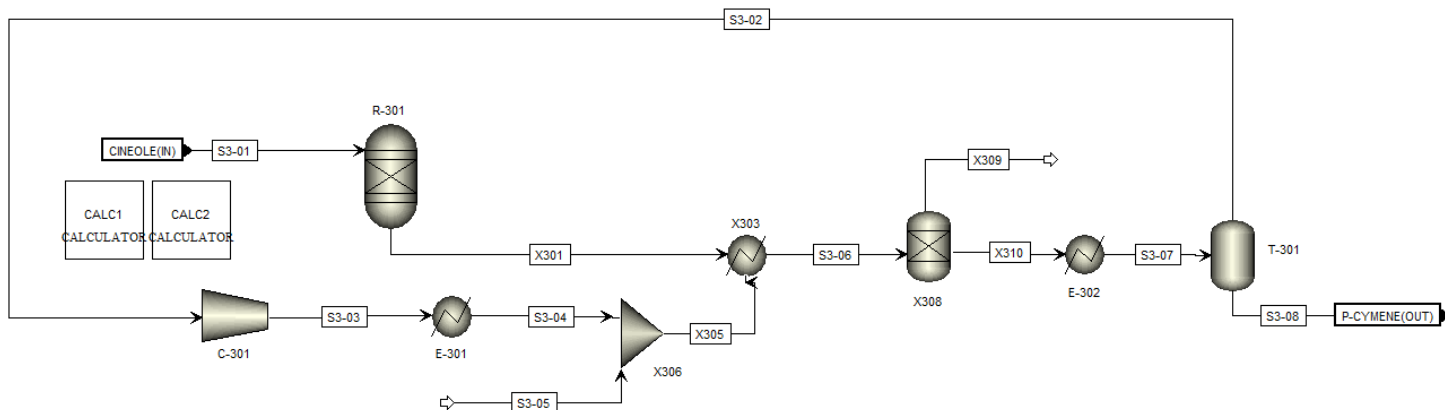


	Units	S2-01	S2-02	S2-03	S2-04	S2-05	S2-06	S2-07	S2-08
From		SC-3		E-201	T-201	E-202	T-202	T-202	E-203
To		M-201	M-201	T-201	E-202	T-202	M-203	E-203	M-202
MIXED Substream									
Phase		Mixed	Liquid	Mixed	Liquid	Liquid	Liquid	Liquid	Liquid
Temperature	C	157.5	25	-5	-5	50	171.5	286.6	-5
Pressure	bar	1	1	1	1	1	0.9	1.1	1.1
Molar Vap Frac		0.996	0	0.616	0	0	0	0	0
Molar Liq Frac		0.004	1	0.384	1	1	1	1	1
Molar Sol Frac		0	0	0	0	0	0	0	0
Mass Vap Frac		0.991	0	0.343	0	0	0	0	0
Mass Liq Frac		0.009	1	0.657	1	1	1	1	1
Average MW		76.56	110.11	79.01	133.05	133.05	153.24	110.59	110.59
Mass Flows	kg/hr	21.606	2.439	24.045	6.287	6.287	3.813	2.474	2.474
ALPHA-01	kg/hr	1.205	0	1.205	0.060	0.060	0.060	0.000	0.000
BETA-01	kg/hr	0.185	0	0.185	0	0	0	0	0
BETA-01	kg/hr	0.258	0	0.258	0	0	0	0	0
1-MET-01	kg/hr	0.847	0	0.847	0.110	0.110	0.109	9.49E-04	9.49E-04
D-LIM-01	kg/hr	1.983	0	1.983	0	0	0	0	0
GAMMA-01	kg/hr	0.375	0	0.375	0	0	0	0	0
TERPI-01	kg/hr	0.413	0	0.413	0	0	0	0	0
ALPHA-02	kg/hr	0.146	0	0.146	0	0	0	0	0
SPATHULE	kg/hr	0.349	0	0.349	0	0	0	0	0
A-EUDESME	kg/hr	0.065	0	0.065	0	0	0	0	0
CADINEDI	kg/hr	0.109	0	0.109	0	0	0	0	0
1:8-C-01	kg/hr	7.073	0	7.073	3.678	3.678	3.641	0.037	0.037
3-CAR-01	kg/hr	0.014	0	0.014	0	0	0	0	0
CAMP-01	kg/hr	0.022	0	0.022	0	0	0	0	0
SABINYLA	kg/hr	0.015	0	0.015	0	0	0	0	0
ALLOAROM	kg/hr	0.010	0	0.010	0	0	0	0	0
AMITEOL	kg/hr	3.28E-03	0	3.28E-03	0	0	0	0	0
CARBO-01	kg/hr	8.531	0	8.531	0	0	0	0	0
N-NON-01	kg/hr	2.98E-03	0	2.98E-03	0	0	0	0	0
N-DOT-01	kg/hr	7.21E-04	0	7.21E-04	0	0	0	0	0
N-PEN-01	kg/hr	8.49E-05	0	8.49E-05	0	0	0	0	0
N-HEX-01	kg/hr	1.10E-04	0	1.10E-04	0	0	0	0	0
P-HYD-01	kg/hr	0	2.439	2.439	2.439	2.439	0.002	2.436	2.436
	Units	S2-09	S2-10	S2-11	S2-12	S2-13	S2-14	S2-16	
From		T-201	M-202	T-203	T-203	E-204	T-204	X203	
To		M-202	T-203		E-204	T-204	M-203	SC-4	
Phase		Mixed	Mixed	Mixed	Liquid	Liquid	Liquid	Mixed	
Temperature	C	-5	-4.8	-4.8	-4.8	40	171.8	171.6	
Pressure	bar	1	1	1	1	1	0.9	0.9	
Molar Vap Frac		0.739	0.676	0.777	0	0	0	0.290	
Molar Liq Frac		0.261	0.324	0.223	1	1	1	0.710	
Molar Sol Frac		0	0	0	0	0	0	0	

Mass Vap Frac		0.471	0.411	0.526	0	0	0	0.290	
Mass Liq Frac		0.529	0.589	0.474	1	1	1	0.710	
Average MW		69.07	72.40	65.05	125.37	125.37	153.58	153.40	
Mass Flows	kg/hr	17.758	20.232	15.963	4.269	4.269	1.817	5.625	
ALPHA-01	kg/hr	1.145	1.145	1.133	0.011	0.011	0.011	0.072	
BETA-01	kg/hr	0.185	0.185	0.185	0	0	0	0	
BETA-01	kg/hr	0.258	0.258	0.258	0	0	0	0	
1-MET-01	kg/hr	0.737	0.738	0.701	0.037	0.037	0.037	0.146	
D-LIM-01	kg/hr	1.983	1.983	1.983	0	0	0	0	
GAMMA-01	kg/hr	0.375	0.375	0.375	0	0	0	0	
TERPI-01	kg/hr	0.413	0.413	0.413	0	0	0	0	
ALPHA-02	kg/hr	0.146	0.146	0.146	0	0	0	0	
SPATHULE	kg/hr	0.349	0.349	0.349	0	0	0	0	
A-EUDESME	kg/hr	0.065	0.065	0.065	0	0	0	0	
CADINEDI	kg/hr	0.109	0.109	0.109	0	0	0	0	
1:8-C-01	kg/hr	3.395	3.432	1.647	1.784	1.784	1.767	5.408	
3-CAR-01	kg/hr	0.014	0.014	0.014	0	0	0	0	
CAMPH-01	kg/hr	0.022	0.022	0.022	0	0	0	0	
SABINYLA	kg/hr	0.015	0.015	0.015	0	0	0	0	
ALLOAROM	kg/hr	0.010	0.010	0.010	0	0	0	0	
AMITEOL	kg/hr	3.28E-03	3.28E-03	3.28E-03	0	0	0	0	
CARBO-01	kg/hr	8.531	8.531	8.531	0	0	0	0	
N-NON-01	kg/hr	2.98E-03	2.98E-03	2.98E-03	0	0	0	0	
N-DOT-01	kg/hr	7.21E-04	7.21E-04	7.21E-04	0	0	0	0	
N-PEN-01	kg/hr	8.49E-05	8.49E-05	8.49E-05	0	0	0	0	
N-HEX-01	kg/hr	1.10E-04	1.10E-04	1.10E-04	0	0	0	0	
P-HYD-01	kg/hr	0	2.436	0	2.436	2.436	0.002	0	

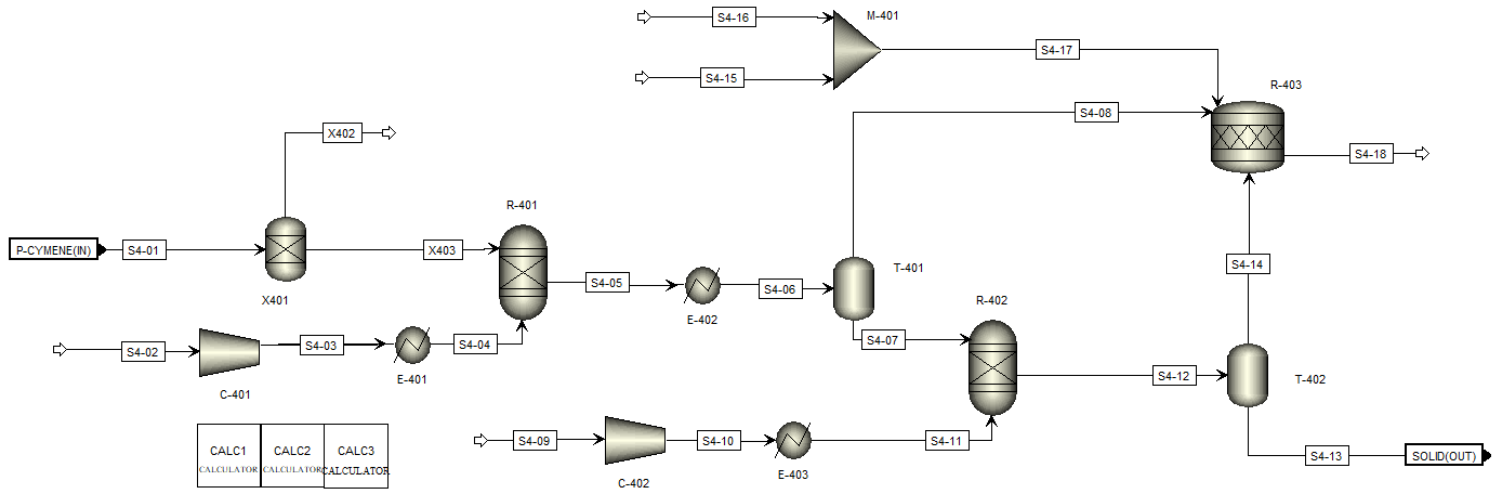
c) Cineole dehydrogenation

Block	Function
CALC1	Sets carrier gas volume flow (S3-02) as 2.5 times the cineole volume feed flowrate (S3-01)
CALC2	Sets catalyst mass flow (S3-05) as 5% of the terpene mass flowrate (S3-01)



	Units	S3-01	S3-02	S3-03	S3-04	S3-05	S3-06	S3-07	S3-08
From		SC-6		C-301	E-301		X303	E-302	T-301
To		R-301	C-301	E-301	X306	X306	X308	T-301	SC-7
Temperature	C	171.6	25	26.4	280	25	276.6	60	60
Pressure	bar	0.9	1	1.01	1.01	1	1	1	1
Mass Vapour Fraction		0.290	1	1	1	0	0.980	0.691	0
Mass Liquid Fraction		0.710	0	0	0	1	0.020	0.309	1
Mass Flows	kg/hr	5.625	10.657	10.657	10.657	0.445	16.727	16.282	5.038
ALPHA-01	kg/hr	0.072	0	0	0	0	0.067	0.067	0.054
1-MET-01	kg/hr	0.146	0	0	0	0	5.509	5.509	4.939
1:8-C-01	kg/hr	5.408	0	0	0	0	0.049	0.049	0.043
HYDROGEN	kg/hr	0	0	0	0	0	5.62E-05	5.62E-05	2.03E-09
OXYGEN	kg/hr	0	0.778	0.778	0.778	0	0.778	0.778	2.25E-04
ALUMI-01	kg/hr	0	0	0	0	0.322	0.322	0	0
PALLA-01	kg/hr	0	0	0	0	1.23E-01	1.23E-01	0	0
ARGON	kg/hr	0	9.879	9.879	9.879	0	9.879	9.879	0.003

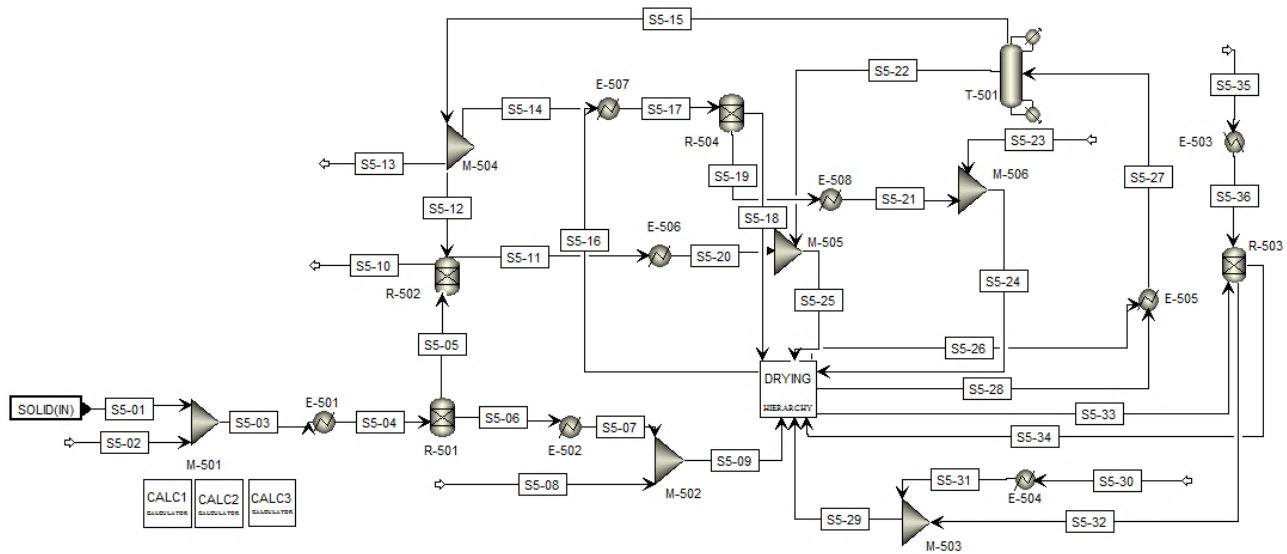
d) p-Cymene oxidation



	Units	S4-01	S4-02	S4-03	S4-04	S4-05	S4-06	S4-07	S4-08	S4-09
From		ŞC-8		C-401	E-401	R-401	E-402	T-401	T-401	
To		X401	C-401	E-401	R-401	E-402	T-401	R-402	R-403	C-402
MIXED Substream										
Phase		Liquid	Vapour	Vapour	Vapour	Mixed	Vapour		Vapour	Vapour
Temperature	C	60	25	474.3	140	140	210		210	25
Pressure	bar	1	1	20	20	20	20		10	1
Molar Vap Frac		0	1	1	1	0.628	1		1	1
Molar Liq Frac		1	0	0	0	0.372	0		0	0
Molar Sol Frac		0	0	0	0	0	0		0	0
Mass Vap Frac		0	1	1	1	0.761	1.		1	1
Mass Liq Frac		1	0	0	0	0.239	0		0	0
Mass Flows	kg/hr	5.038	7.064	7.064	7.064	6.672	6.672		6.672	6.392
ALPHA-01	kg/hr	0.054	0	0	0	0	0		0	0
1-MET-01	kg/hr	4.939	0	0	0	0	0		0	0
1:8-C-01	kg/hr	0.043	0	0	0	0.044	0.044		0.044	0.000
WATER	kg/hr	0	0	0.000	0.000	1.912	1.912		1.912	0
OXYGEN	kg/hr	2.25E-04	7.064	7.064	7.064	1.324	1.324		1.324	6.392
CARBO-01	kg/hr	0	0	0	0	3.326	3.326		3.326	0
ARGON	kg/hr	2.56E-03	0	0	0	0	0		0	0
A-PINOX	kg/hr	0	0	0	0	0.040	0.040		0.040	0
(S)-C-01	kg/hr	0	0	0	0	0.027	0.027		0.027	0
CALCI-01	kg/hr	0	0	0	0	0	0		0	0
CALCI-02	kg/hr	0	0	0	0	0	0		0	0
CIPSD Substream										
Temperature	C					140	210	210		
Pressure	bar					20	20	10		
Molar Liq Frac						0	0	0		
Molar Sol Frac						1	1	1		
Mass Liq Frac						0	0	0		
Mass Sol Frac						1	1	1		
Mass Flows	kg/hr					5.428	5.428	5.428		
TEREP-02	kg/hr					2.322	2.322	2.322		
4-CAR-01	kg/hr					0	0	0		
CUMIC-02	kg/hr					0.302	0.302	0.302		
P-TOL-02	kg/hr					2.804	2.804	2.804		
Units		S4-10	S4-11	S4-12	S4-13	S4-14	S4-15	S4-16	S4-17	S4-18
From		C-402	E-403	R-402	T-402	T-402	R-403	M-401	M-401	R-403
To		E-403	R-402	T-402	ŞC-9	R-403	M-401	M-401	R-403	
MIXED Substream										
Phase		Vapour	Vapour	Vapour		Vapour	Liquid	Liquid	Liquid	Mixed
Temperature	C	375.5	190	190		190	25	25	25	25
Pressure	bar	12	12	12		1	1	1	1	1

Molar Vap Frac		1	1	1		1	0	0	0	0.022
Molar Liq Frac		0	0	0		0	1	1	1	0.978
Molar Sol Frac		0	0	0		0	0	0	0	0
Mass Vap Frac		1	1	1		1	0	0	0	0.034
Mass Liq Frac		0	0	0		0	1	1	1	0.966
Mass Flows	kg/hr	6.392	6.392	6.227		6.227	25.617	173.489	199.107	212.005
ALPHA-01	kg/hr	0	0	0		0	0	0	0	0
1-MET-01	kg/hr	0	0	0		0	0	0	0	0
1:8-C-01	kg/hr	0	0	0		0	0	0	0	0.044
WATER	kg/hr	0	0	0.119		0.119	0	173.489	173.489	176.882
OXYGEN	kg/hr	6.392	6.392	6.107		6.107	0	0	0	7.431
CARBO-01	kg/hr	0	0	0		0	0	0	0	0
ARGON	kg/hr	0	0	0		0	0	0	0	0
A-PINOX	kg/hr	0	0	0		0	0	0	0	0.040
(S)-C-01	kg/hr	0	0	0		0	0	0	0	0.027
CALCI-01	kg/hr	0	0	0		0	5.600	0	5.600	0
CALCI-02	kg/hr	0	0	0		0	20.017	0	20.017	27.582
CIPSD Substream										
Temperature	C			190	190					
Pressure	bar			12	1					
Molar Liq Frac				0	0					
Molar Sol Frac				1	1					
Mass Liq Frac				0	0					
Mass Sol Frac				1	1					
Mass Flows	kg/hr			5.593	5.593					
TEREP-02	kg/hr			3.960	3.960					
4-CAR-01	kg/hr			0.074	0.074					
CUMIC-02	kg/hr			0.306	0.306					
P-TOL-02	kg/hr			1.253	1.253					

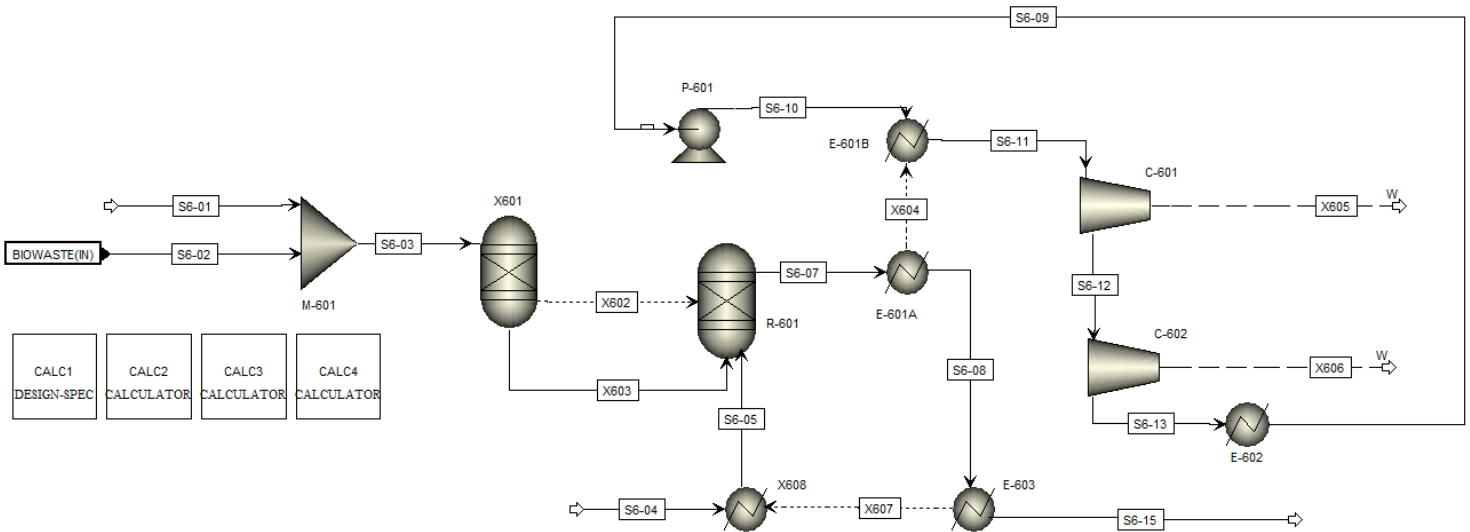
e) TPA purification and drying



	Units	S5-01	S5-02	S5-03	S5-04	S5-05	S5-06	S5-07	S5-08	S5-09	S5-10	S5-11
From		S5-10		M-501	E-501	R-501	R-501	E-502		M-502	R-502	R-502
To		M-501	M-501	E-501	R-501	R-502	E-502	M-502	M-502	Y-501		E-506
MIXED Sub												
Phase			Liquid	Liquid	Vapour		Vapour	Liquid	Liquid	Liquid	Vapour	Liquid
Temperature	C		25	67.5	160		160	45	25	39.9	75.3	75.3
Pressure	bar		1	1	1		1	1	1	1	0.9	0.9
Mass Flows	kg/hr		11.879	11.879	11.879		11.879	11.879	3.742	15.621	0.013	8.124
ACETO-01	kg/hr		0	0	0		0	0	3.742	3.742	0.013	0
N-MET-01	kg/hr		11.879	11.879	11.879		11.879	11.879	0	11.879	0	8.124
CIPSD Sub												
Mass Flows	kg/hr	5.593		5.593	5.593	4.345	1.248	1.248		1.248	3.490	0.855
TEREP-02	kg/hr	3.960		3.960	3.960	2.712	1.247	1.247		1.247	1.858	0.854
4-CAR-01	kg/hr	0.074		0.074	0.074	0.074	5.56E-04	5.56E-04		5.56E-04	0.074	3.81E-04
CUMIC-02	kg/hr	0.306		0.306	0.306	0.306	2.42E-04	2.42E-04		2.42E-04	0.306	1.66E-04
P-TOL-02	kg/hr	1.253		1.253	1.253	1.253	2.53E-04	2.53E-04		2.53E-04	1.253	1.73E-04
	Units	S5-12	S5-13	S5-14	S5-15	S5-16	S5-17	S5-18	S5-19	S5-20	S5-21	S5-22
From		M-504	M-504	M-504	T-501	Y-503	E-507	R-504	R-504	E-506	E-508	T-501
To		R-502		E-507	M-504	E-507	R-504		E-508	M-505	M-506	M-505
MIXED Sub												
Phase		Liquid	Liquid	Liquid	Liquid		Vapour	Vapour	Vapour	Liquid	Liquid	Vapour
Temperature	C	75.3	75.3	75.3	75.3		105	105	105	45	40	53.2
Pressure	bar	0.9	0.9	0.9	0.9		0.9	0.9	0.9	0.9	0.9	0.9
Mass Flows	kg/hr	8.137	4.907	3.076	16.120		3.076	4.92E-03	3.071	8.124	3.071	6
ACETO-01	kg/hr	0.013	7.85E-03	4.92E-03	0.025797		4.92E-03	4.92E-03	0	0	0	5.849
N-MET-01	kg/hr	8.124	4.899	3.071	16.094		3.071	0	3.071	8.124	3.071	0.151
CIPSD Sub												
Mass Flows	kg/hr					0.855	0.855	0.449	0.406	0.855	0.406	
TEREP-02	kg/hr					0.854	0.854	0.449	0.406	0.854	0.406	
4-CAR-01	kg/hr					3.81E-04	3.81E-04	3.71E-04	1.01E-05	3.81E-04	1.01E-05	
CUMIC-02	kg/hr					1.66E-04	1.66E-04	1.56E-04	9.33E-06	1.66E-04	9.33E-06	
P-TOL-02	kg/hr					1.73E-04	1.73E-04	1.65E-04	7.71E-06	1.73E-04	7.71E-06	
	Units	S5-25	S5-27	S5-28	S5-29	S5-30	S5-31	S5-32	S5-33	S5-34	S5-35	S5-36
From		M-505	E-505	Y-502	M-503		E-504	R-503	Y-501	R-503		E-503
To		Y-503	T-501	E-505	Y-502	E-504	M-503	M-503	R-503		E-503	R-503
MIXED Sub												
Temperature	C	62.8	90	210	69.4	25	40	126.6			25	105
Pressure	bar	0.9	1	1	1	1	1	1			1	1
Mass Flows	kg/hr	14.124	22.120	6.499	6.499	2.133	2.133	4.366			4.366	4.366
ACETO-01	kg/hr	5.849	5.875	2.133	2.133	2.133	2.133	0			0	0
N-MET-01	kg/hr	8.275	16.245	4.366	4.366	0	0	4.366			4.366	4.366
CIPSD Sub												
Mass Flows	kg/hr	0.855			0.593			0.593	1.248	0.656		
TEREP-02	kg/hr	0.854			0.592			0.592	1.247	0.655		
4-CAR-01	kg/hr	3.81E-04			1.48E-05			1.48E-05	5.56E-04	5.42E-04		
CUMIC-02	kg/hr	1.66E-04			1.36E-05			1.36E-05	2.42E-04	2.28E-04		
P-TOL-02	kg/hr	1.73E-04			1.13E-05			1.13E-05	2.53E-04	2.42E-04		

f) Biomass power and heat generation

Block	Function
CALC1	Vary water mass flow (S6-01) for 40% MIXED (liquid) mass flowrate in S6-03

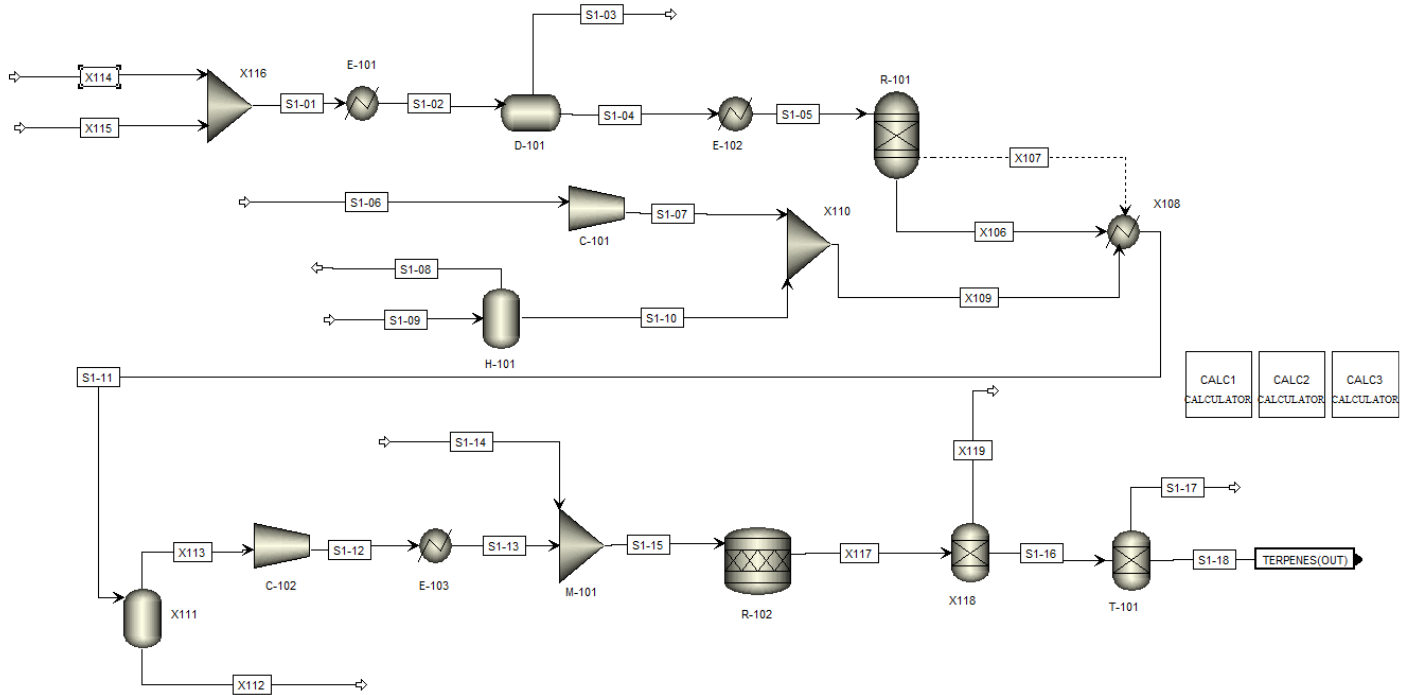


	Units	S6-01	S6-02	S6-04	S6-05	S6-07	S6-08	S6-09	S6-10	S6-11	S6-12	S6-13	S6-15
From			SC-2		X608	R-601	E-601A		P-601	E-601B	C-601	C-602	E-603
To		M-601	M-601	X608	R-601	E-601A	E-603	P-601	E-601B	C-601	C-602	E-602	
Temperature	C	25	80	25	161.1	320.1	230	40	43.2	512.3	332.7	170.9	105
Pressure	bar	1	1	1	1	1	1	2	41	41	10	2	1
Mass Vap Frac		0	0	1	1	1	1	0	0	1	1	1	1
Mass Liq Frac		1	0	0	0	0	0	1	1	0	0	0	0
Mass Sol Frac		0	1	0	0	0	0	0	0	0	0	0	0
Mass Flows	kg/hr	302.01	755.03	19588.58	19588.58	20645.63	20645.63	603.96	603.96	603.96	603.96	603.96	20645.63
WATER	kg/hr	302.01	0	0	0	895.79	895.79	603.96	603.96	603.96	603.96	603.96	895.79
BIOMASS	kg/hr	0	755.03	0	0	0	0	0	0	0	0	0	0
NITROGEN	kg/hr	0	0	15026.07	15026.07	14012.46	14012.46	0	0	0	0	0	14012.46
OXYGEN	kg/hr	0	0	4562.51	4562.51	0	0	0	0	0	0	0	0
NO2	kg/hr	0	0	0	0	4323.69	4323.69	0	0	0	0	0	4323.69
CARBO-01	kg/hr	0	0	0	0	1413.69	1413.69	0	0	0	0	0	1413.69

PHR Model

a) Dehydrogenation and desulphurisation

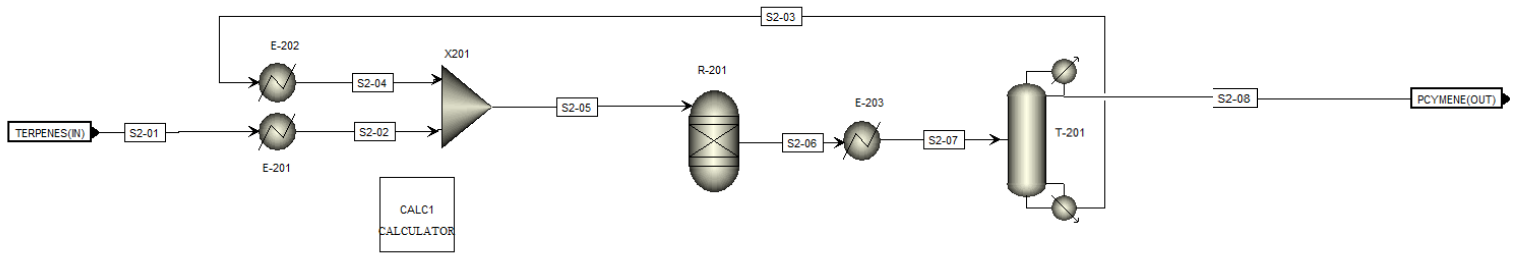
Block	Function
CALC3	Sets hydrogen peroxide mass flow (S1-14) as 1.5 times the H2S and C2H6S2 mass flowrates (S1-13)



	Units	S1-01	S1-02	S1-03	S1-04	S1-05	S1-06	S1-07	S1-08	S1-09
From		X116	E-101	D-101	D-101	E-102		C-101	H-101	
To		E-101	D-101		E-102	R-101	C-101	X110		H-101
MIXED Substream										
Phase		Vapour	Liquid	Liquid	Liquid	Vapour	Vapour	Vapour	Vapour	Liquid
Temperature	C	175	30	30	30	300	60	345.5	500	25
Pressure	bar	1	1	1	1	1	1	5.5	1	5.5
Molar Vap Frac		1	0	0	0	1	1	1	1	0
Molar Liq Frac		0	1	1	1	0	0	0	0	1
Molar Sol Frac		0	0	0	0	0	0	0	0	0
Mass Vap Frac		1	0	0	0	1	1	1	1	0
Mass Liq Frac		0	1	1	1	0	0	0	0	1
Mass Flows	kg/hr	4120.5	4120.5	4104.0	16.5	16.5	450.35	450.35	8.5	30.8
ALPHA-01	kg/hr	8.508	8.508	0.069	8.438	8.438	0	0	0	0
CAMPHENE	kg/hr	0.267	0.267	0.002	0.265	0.265	0	0	0	0
BETA-PIN	kg/hr	4.1	4.1	0.031	4.069	4.069	0	0	0	0
TERP-4-Y	kg/hr	0	0	0	0	0	0	0	0	0
A-TERPIN	kg/hr	0.267	0.267	0.118	0.148	0.148	0	0	0	0
B-MYRCE	kg/hr	0.267	0.267	1.21E-03	0.265	0.265	0	0	0	0
D-LIM-01	kg/hr	0.267	0.267	1.34E-03	0.265	0.265	0	0	0	0
BPHELLAN	kg/hr	2.932	2.932	0.015	2.916	2.916	0	0	0	0
GTERPINE	kg/hr	0	0	0	0	0	0	0	0	0
PCYMENE	kg/hr	0	0	0	0	0	0	0	0	0
TERPI-01	kg/hr	0	0	0	0	0	0	0	0	0
WATER	kg/hr	4100	4100	4099.96	0.037	0.037	0	0	8.390	8.395
NITROGEN	kg/hr	0	0	0	0	0	450.347	450.347	0	0
GUAIE-01	kg/hr	0	0	0	0	0	0	0	0	0
SODIU-01	kg/hr	0	0	0	0	0	0	0	0	0.062
CALCI-01	kg/hr	0	0	0	0	0	0	0	0	0.830
MAGNE-01	kg/hr	0	0	0	0	0	0	0	0	0.185

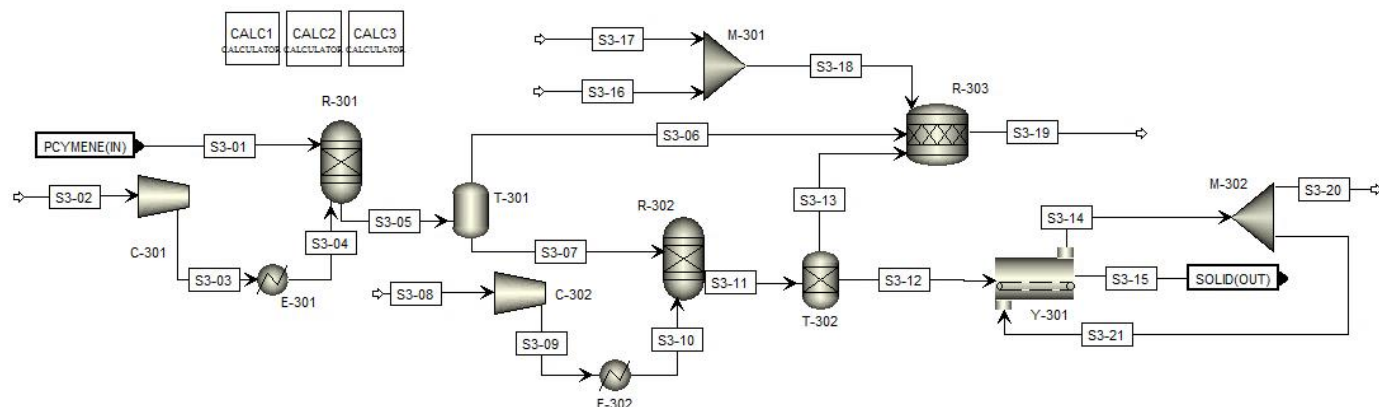
ALUMI-01	kg/hr	0	0	0	0	0	0	0	0	5.203
SILIC-01	kg/hr	0	0	0	0	0	0	0	0	16.076
MERCAPTA	kg/hr	0.82	0.82	0.818	1.62E-03	1.62E-03	0	0	0	0
DIMETS	kg/hr	1.989	1.989	1.983	5.13E-03	5.13E-03	0	0	0	0
DIMDIS	kg/hr	1.087	1.087	0.951	0.136	0.136	0	0	0	0
	Units	S1-10	S1-11	S1-12	S1-13	S1-14	S1-15	S1-16	S1-17	S1-18
From		H-101	X108	C-102	E-103		M-101	X118	T-101	T-101
To		X110	X111	E-103	M-101	M-101	R-102	T-101		ŞC-5
MIXED Substream										
Phase		Liquid	Mixed	Vapour	Mixed	Liquid	Mixed	Mixed	Mixed	Liquid
Temperature	C	500	352.5	137.2	25	25	24.5	25	25	25
Pressure	bar	1	5	1	1	1	1	1	1	1
Molar Vap Frac		0	0.998	1	1	0	1	1	1	0
Molar Liq Frac		1	2.08E-03	0	1.47E-04	1	1.98E-04	4.41E-04	2.19E-04	1
Molar Sol Frac		0	0	0	0	0	0	0	0	0
Mass Vap Frac		0	0.995	1	0.999	0	0.999	0.998	1.000	0
Mass Liq Frac		1	4.89E-03	0	9.99E-04	1	1.12E-03	1.61E-03	2.73E-04	1
Mass Flows	kg/hr	22.3	489.177	466.877	466.877	1.8	468.677	468.677	452.677	15.9
ALPHA-01	kg/hr	0	0	0	0	0	0	0	0	0
CAMPHENE	kg/hr	0	0.215	0.215	0.215	0	0.215	0.215	0	0.215
BETA-PIN	kg/hr	0	3.309	3.304	3.304	0	3.304	3.304	0	3.304
TERP-4-Y	kg/hr	0	0.579	0.571	0.571	0	0.571	0.571	0	0.571
A-TERPIN	kg/hr	0	0.215	0.214	0.214	0	0.214	0.214	0	0.214
B-MYRCE	kg/hr	0	0.215	0.215	0.215	0	0.215	0.215	0	0.215
D-LIM-01	kg/hr	0	0.215	0.215	0.215	0	0.215	0.215	0	0.215
BPHELLAN	kg/hr	0	2.366	2.361	2.361	0	2.361	2.361	0	2.361
GTERPINE	kg/hr	0	0.116	0.116	0.116	0	0.116	0.116	0	0.116
PCYMENE	kg/hr	0	1.357	1.354	1.354	0	1.354	1.354	0	1.354
TERPI-01	kg/hr	0	0.298	0.297	0.297	0	0.297	0.297	0	0.297
WATER	kg/hr	5.16E-03	5.16E-03	5.16E-03	5.16E-03	0	5.16E-03	1.288	0	1.288
NITROGEN	kg/hr	0	450.347	450.345	450.345	0	450.345	450.345	450.345	0
GUAIE-01	kg/hr	0	3.905	3.874	3.874	0	3.874	3.874	0	3.874
SODIU-01	kg/hr	0.062	0.061	0	0	0	0	0	0	0
CALCI-01	kg/hr	0.830	0.830	0	0	0	0	0	0	0
MAGNE-01	kg/hr	0.185	0.185	0	0	0	0	0	0	0
ALUMI-01	kg/hr	5.203	5.203	0	0	0	0	0	0	0
SILIC-01	kg/hr	16.076	16.076	0	0	0	0	0	0	0
MERCAPTA	kg/hr	0	0	0	0	0	0	0	0	0
DIMETS	kg/hr	0	0.430	0.430	0.430	0	0.430	0	0	0
DIMDIS	kg/hr	0	0	0	0	0	0	0	0	0
M-CYMENE	kg/hr	0	0.017	0.017	0.017	0	0.017	0.017	0	0.017
O-CYMENE	kg/hr	0	0.529	0.529	0.529	0	0.529	0.529	0	0.529
MENTHENE	kg/hr	0	1.109	1.107	1.107	0	1.107	1.107	0	1.107
MENTHANE	kg/hr	0	0.265	0.264	0.264	0	0.264	0.264	0	0.264
H2S	kg/hr	0	1.191	1.191	1.191	0	1.191	0.095	0.095	0
CH4	kg/hr	0	0.215	0.215	0.215	0	0.215	0.215	0.215	0
H2O2	kg/hr	0	0	0	0	1.787	1.787	0.458	0.458	0
S	kg/hr	0	0	0	0	0	0	1.031	1.031	0
DIMETSO	kg/hr	0	0	0	0	0	0	0.541	0.541	0

b) p-Cymene purification



	Units	S2-01	S2-02	S2-03	S2-04	S2-05	S2-06	S2-07	S2-08
From		ŞC-6	E-201		E-202	X201	R-201	E-203	T-201
To		E-201	X201	E-202	X201	R-201	E-203	T-201	ŞC-8
Temperature	C	25	70	25	70	70.4	110	150	180.9
Pressure	bar	1	1	1	1	1	1	1	0.9
Mass Vapour Fraction		0	0	0	0	0	0	0	0
Mass Liquid Fraction		1	1	1	1	1	1	1	1
Mass Solid Fraction		0	0	0	0	0	0	0	0
Mass Flows	kg/hr	15.94	15.94	3.98	3.98	19.92	19.92	19.92	6
CAMPHENE	kg/hr	0.215	0.215	0	0	0.215	0	0	0
BETA-PIN	kg/hr	3.304	3.304	0	0	3.304	0	0	0
TERP-4-Y	kg/hr	0.571	0.571	0	0	0.571	0	0	0
A-TERPIN	kg/hr	0.214	0.214	0	0	0.214	0	0	0
B-MYRCE	kg/hr	0.215	0.215	0	0	0.215	0	0	0
D-LIM-01	kg/hr	0.215	0.215	0	0	0.215	0	0	0
BPHELLAN	kg/hr	2.361	2.361	0	0	2.361	0	0	0
GTERPINE	kg/hr	0.116	0.116	0	0	0.116	0	0	0
PCYMENE	kg/hr	1.354	1.354	0	0	1.354	3.875	3.875	3.873
TERPI-01	kg/hr	0.297	0.297	0	0	0.297	0	0	0
WATER	kg/hr	1.288	1.288	0.199	0.199	1.488	0.012	0.012	0.012
GUAIE-01	kg/hr	3.874	3.874	0	0	3.874	0	0	0
P-MEN-01	kg/hr	0	0	0	0	0	0.018	0.018	0.018
P-MEN-02	kg/hr	0	0	0	0	0	0.004	0.004	0.004
H2SO4	kg/hr	0	0	3.786	3.786	3.786	8.755	8.755	1.480
ISOPRESS	kg/hr	0	0	0	0	0	3.790	3.790	1.23E-39
CEMBRENE	kg/hr	0	0	0	0	0	0.096	0.096	4.66E-20
ELLIOTIN	kg/hr	0	0	0	0	0	3.375	3.375	0.612
M-CYMENE	kg/hr	0.017	0.017	0	0	0.017	0	0	0
O-CYMENE	kg/hr	0.529	0.529	0	0	0.529	0	0	0
MENTHENE	kg/hr	1.107	1.107	0	0	1.107	0	0	0
MENTHANE	kg/hr	0.264	0.264	0	0	0.264	0	0	0

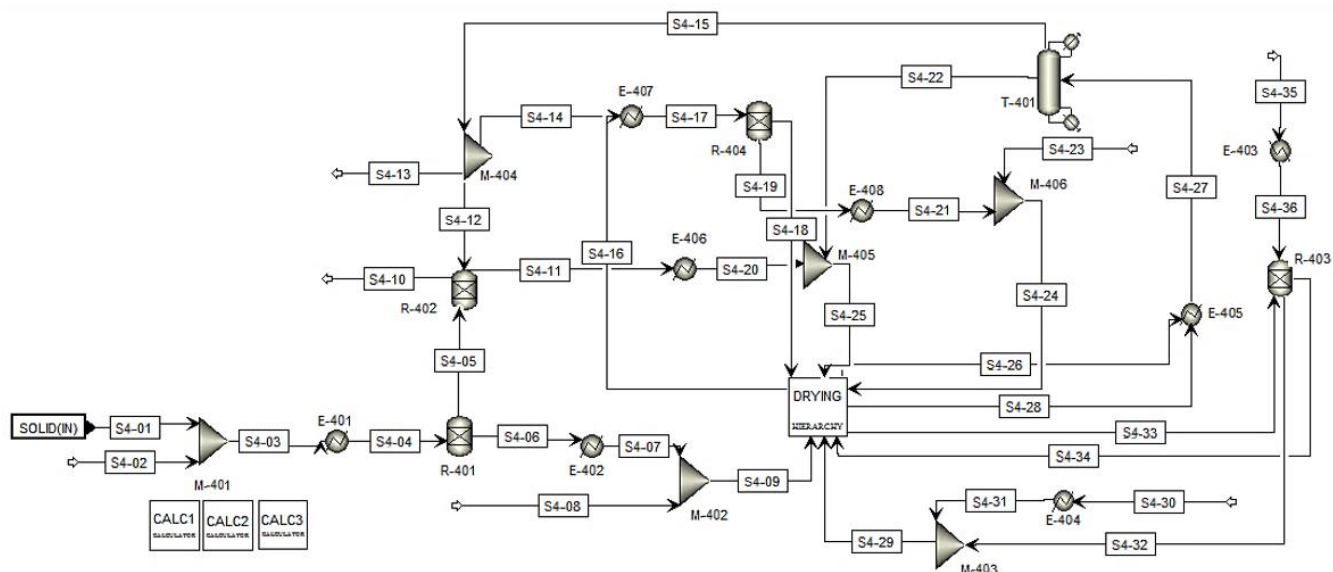
c) p-Cymene oxidation



	Units	S3-01	S3-02	S3-03	S3-04	S3-05	S3-06	S3-07	S3-08	S3-09	S3-10	S3-11
From		ŞC-9		C-301	E-401	-301	V-301	V-301		C302	E-402	R-302
To		R-301	C-301	E-401	R-301	V-301	R-303	R-302	C302	E-402	R-302	V-302
MIXED Sub												
Phase		Liquid	Vapour	Vapour	Vapour	Mixed	Vapour	Liquid	Vapour	Vapour	Vapour	Vapour
Temperature	C	166.2	25	532.5	140	140	140	140	25	420.9	190	190
Pressure	bar	0.9	1	20	20	20	20	20	1	12	12	12
Molar Vap Frac		0	1	1	1	0.630	1	0	1	1	1	1
Molar Liq Frac		1	0	0	0	0.370	0	1	0	0	0	0
Mass Vap Frac		0	1	1	1	0.764	1	0	1	1	1	1
Mass Liq Frac		1	0	0	0	0.236	0	1	0	0	0	0
Mass Flows	kg/hr	6	6.784	6.784	6.784	7.039	5.381	1.658	0.6	0.6	0.6	4.534
PCYMENE	kg/hr	4.796	0	0	0	0	0	0	0	0	0	0
WATER	kg/hr	0.015	0	0	0	2.024	0.475	1.548	0	0	0	0.873
OXYGE-01	kg/hr	0	6.784	6.784	6.784	1.401	1.394	0.007	0.6	0.6	0.6	3.582
CARBO-01	kg/hr	0	0	0	0	3.528	3.476	0.053	0	0	0	0.030
P-MEN-01	kg/hr	0.022	0	0	0	0.069	0.029	0.040	0	0	0	0.039
P-MEN-02	kg/hr	4.93E-03	0	0	0	0.017	7.11E-03	9.51E-03	0	0	0	9.60E-03
H2SO4	kg/hr	0.774	0	0	0	0	0	0	0	0	0	0
ISOPRESS	kg/hr	2.37E-40	0	0	0	0	0	0	0	0	0	0
CEMBRENE	kg/hr	1.74E-20	0	0	0	0	0	0	0	0	0	0
ELLIOTIN	kg/hr	0.388	0	0	0	0	0	0	0	0	0	0
CA(OH)2	kg/hr	0	0	0	0	0	0	0	0	0	0	0
CALCI-02	kg/hr	0	0	0	0	0	0	0	0	0	0	0
CIPSD Sub												
Mass Flows	kg/hr					5.745		5.745				3.469
TPA	kg/hr					2.457		2.457				2.628
P-TOLUIC	kg/hr					2.967		2.967				0.621
CUMIC-A	kg/hr					0.321		0.321				0.181
4-CBA	kg/hr					0		0				0.039
	Units	S3-12	S3-13	S3-14	S3-15	S3-16	S3-17	S3-18	S3-19	S3-20	S3-21	
From		V-302	V-302	Y-301	Y-301			M-303	R-303	M-302	M-302	
To		Y-301	R-303	M-302	ŞC-7	M-303	M-303	R-303			Y-301	
MIXED Sub												
Phase		Vapor	Vapor	Liquid		Liquid	Liquid	Liquid	Mixed	Liquid	Liquid	
Temperature	C	190	190	90		25	25	25	25	90	90	
Pressure	bar	12	12	12		1	1	1	1	12	12	
Molar Vap Frac		1	1	0		0	0	0	0.026	0	0	
Molar Liq Frac		0	0	1		1	1	1	0.974	1	1	
Mass Vap Frac		1	1	0		0	0	0	0.042	0	0	
Mass Liq Frac		0	0	1		1	1	1	0.958	1	1	
Mass Flows	kg/hr	0.922	3.612	4.610		5.901	100.356	106.257	115.250	0.922	3.688	
PCYMENE	kg/hr	0	0	0		0	0	0	0	0	0	
WATER	kg/hr	0.873	0	4.366		0	100.356	100.356	102.266	0.873	3.493	
OXYGE-01	kg/hr	0	3.582	0		0	0	0	4.976	0	0	
CARBO-01	kg/hr	0	0.030	0		0	0	0	0	0	0	
P-MEN-01	kg/hr	0.039	0	0.196		0	0	0	0.029	0.039	0.157	
P-MEN-02	kg/hr	9.60E-03	0	0.048		0	0	0	7.11E-03	9.60E-03	0.038415	
H2SO4	kg/hr	0	0	0		0	0	0	0	0	0	
ISOPRESS	kg/hr	0	0	0		0	0	0	0	0	0	

CEMBRENE	kg/hr	0	0	0		0	0	0	0	0	0	
ELLIOTIN	kg/hr	0	0	0		0	0	0	0	0	0	
CA(OH)2	kg/hr	0	0	0		5.901	0	5.901	0	0	0	
CALCI-02	kg/hr	0	0	0		0	0	0	7.971	0	0	
CIPSD Sub												
Mass Flows	kg/hr	3.469			3.469							
TPA	kg/hr	2.628			2.628							
P-TOLUIC	kg/hr	0.621			0.621							
CUMIC-A	kg/hr	0.181			0.181							
4-CBA	kg/hr	0.039			0.039							

d) TPA purification and drying

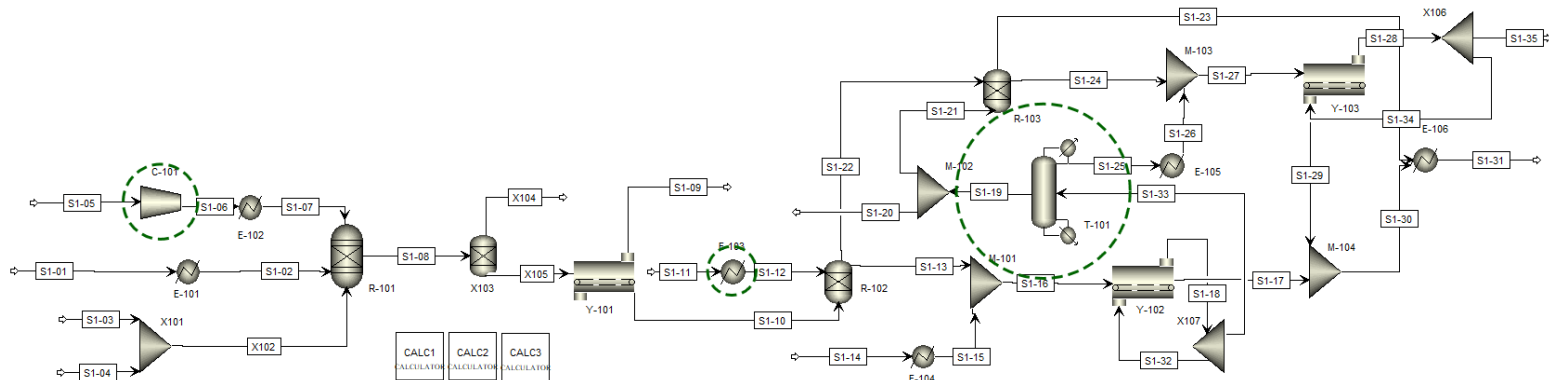


	Units	S4-01	S4-02	S4-03	S4-04	S4-05	S4-06	S4-07	S4-08
From		ŞC-10		M-401	E-401	R-401	R-401	E-402	
To		M-401	M-401	E-401	R-401	R-402	E-402	M-402	M-402
MIXED Sub									
Phase			Liquid	Liquid	Liquid		Liquid	Liquid	Liquid
Temperature	C		25	40.2	160		160	45	25
Pressure	bar		1	1	1		1	1	1
Molar Vap Frac			0	0	0		0	0	0
Molar Liq Frac			1	1	1		1	1	1
Mass Vap Frac			0	0	0		0	0	0
Mass Liq Frac			1	1	1		1	1	1
Mass Flows	kg/hr		7.885	7.885	7.885		7.885	7.885	2.484
NMP	kg/hr		7.885	7.885	7.885		7.885	7.885	0
ACETONE	kg/hr		0	0	0		0	0	2.484
CIPSD Sub									
Mass Flows	kg/hr	3.469		3.469	3.469	2.641	0.829	0.829	
TPA	kg/hr	2.628		2.628	2.628	1.800	0.828	0.828	
P-TOLUIC	kg/hr	0.621		0.621	0.621	0.621	1.68E-04	1.68E-04	
CUMIC-A	kg/hr	0.181		0.181	0.181	0.181	1.25E-04	1.25E-04	
4-CBA	kg/hr	0.039		0.039	0.039	0.039	3.70E-04	3.70E-04	
Units		S4-09	S4-10	S4-11	S4-12	S4-13	S4-14	S4-15	S4-16
From		M-402	R-402	R-402	M-404	M-404	M-404	T-401	Y-403
To		Y-401		E-406	R-402		E-407	M-404	E-407
MIXED Sub									
Phase		Liquid		Liquid	Liquid	Liquid	Liquid	Liquid	
Temperature	C	39.6		189.4	199.2	199.2	199.2	199.2	
Pressure	bar	1		0.9	0.9	0.9	0.9	0.9	
Molar Vap Frac		0		0	0	0	0	0	
Molar Liq Frac		1		1	1	1	1	1	
Mass Vap Frac		0		0	0	0	0	0	
Mass Liq Frac		1		1	1	1	1	1	
Mass Flows	kg/hr	10.368		5.401	5.401	1.908	2.042	9.351	
NMP	kg/hr	7.885		5.401	5.401	1.908	2.042	9.351	
ACETONE	kg/hr	2.484		0	8.23E-43	2.91E-43	3.11E-43	1.43E-42	
CIPSD Sub									
Mass Flows	kg/hr	0.829	2.073	0.567					0.567
TPA	kg/hr	0.828	1.233	0.567					0.567
P-TOLUIC	kg/hr	1.68E-04	0.621	1.15E-04					1.15E-04
CUMIC-A	kg/hr	1.25E-04	0.181	1.15E-04					1.15E-04

4-CBA	kg/hr	3.70E-04	0.039	1.15E-04					1.15E-04
	Units	S4-17	S4-18	S4-19	S4-20	S4-21	S4-22	S4-25	S4-27
From		E-407	R-404	R-404	E-406	E-408	T-401	M-405	E-405
To		R-404		E-408	M-405	M-406	M-405	Y-403	T-401
MIXED Sub									
Phase		Liquid		Liquid	Liquid	Liquid	Vapor	Mixed	Mixed
Temperature	C	105		105	45	40	142.4	123.4	90
Pressure	bar	0.9		0.9	0.9	0.9	0.9	0.9	1
Molar Vap Frac		0		0	0	0	1	0.466	0.058
Molar Liq Frac		1		1	1	1	0	0.534	0.942
Mass Vap Frac		0		0	0	0	1	0.364	0.041
Mass Liq Frac		1		1	1	1	0	0.636	0.959
Mass Flows	kg/hr	2.042		2.042	5.401	2.042	5.331	10.732	14.682
NMP	kg/hr	2.042		2.042	5.401	2.042	1.431	6.832	10.782
ACETONE	kg/hr	3.11E-43		0	0	0	3.899	3.899	3.899
CIPSD Sub									
Mass Flows	kg/hr	0.567	0.298	0.269	0.567	0.269		0.567	
TPA	kg/hr	0.567	0.298	0.269	0.567	0.269		0.567	
P-TOLUIC	kg/hr	1.15E-04	1.10E-04	5.13E-06	1.15E-04	5.13E-06		1.15E-04	
CUMIC-A	kg/hr	1.15E-04	1.09E-04	6.19E-06	1.15E-04	6.19E-06		1.15E-04	
4-CBA	kg/hr	1.15E-04	1.08E-04	6.73E-06	1.15E-04	6.73E-06		1.15E-04	
	Units	S4-28	S4-29	S4-30	S4-31	S4-32	S4-33	S4-35	S4-36
From		Y-402	M-403		E-404	R-403	Y-401		E-403
To		E-405	Y-402	M-403	M-403	E-404	E-403	R-403	R-403
MIXED Sub									
Phase		Vapor	Liquid	Liquid	Liquid	Liquid		Liquid	
Temperature	C	210	34.6	25	40	38.2		25	
Pressure	bar	1	1	1	1	1		1	
Molar Vap Frac		1	0	0	0	0		0	
Molar Liq Frac		0	1	1	1	1		1	
Mass Vap Frac		1	0	0	0	0		0	
Mass Liq Frac		0	1	1	1	1		1	
Mass Flows	kg/hr	4.313	4.313	1.416	2.898	2.898		2.898	
NMP	kg/hr	2.898	2.898	0	2.898	2.898		2.898	
ACETONE	kg/hr	1.416	1.416	1.416	0	0		0	
CIPSD Sub									
Mass Flows	kg/hr		0.393		0.393	0.393	0.829		0.829
TPA	kg/hr		0.393		0.393	0.393	0.828		0.828
P-TOLUIC	kg/hr		7.48E-06		7.48E-06	7.48E-06	1.68E-04		1.68E-04
CUMIC-A	kg/hr		9.05E-06		9.05E-06	9.05E-06	1.25E-04		1.25E-04
4-CBA	kg/hr		9.83E-06		9.83E-06	9.83E-06	3.70E-04		3.70E-04

Starch Model

p-Xylene conversion



	Units	S1-01	S1-02	S1-03	S1-04	S1-05	S1-06	S1-07	S1-08	S1-09	S1-10	S1-11	S1-12	S1-13
Description														
From			E-101				C-101	E-102	R-101	Y-101	Y-101		E-103	R-102
To		E-101	R-101	X101	X101	C-101	E-102	R-101	X103		R-102	E-103	R-102	M-101
MIXED Sub														
Phase		Liquid	Vapor	Liquid	Liquid	Vapor	Vapor	Vapor	Mixed	Vapor		Liquid	Vapor	Vapor
Temperature	C	300	200	25	25	25	696.5	200	200	200		25	105	124.3
Pressure	bar	57	1	1	1	1	38.93	38.93	38.93	38.93		1	1	1
Molar Vap Frac		0	1	0	0	1	1	1	0.53	1		0	1	1
Molar Liq Frac		1	0	1	1	0	0	0	0.47	0		1	0	0
Mass Vap Frac		0	1	0	0	1	1	1	0.41	1		0	1	1
Mass Liq Frac		1	0	1	1	0	0	0	0.59	0		1	0	0
Molar Enthalpy	kcal/mol	11.1	10.8	-165.1	-68.3	-8.90E-16	5.2	1.3	-48.5	1.1		-10	3.47E-01	9.90E-01
Mass Enthalpy	kcal/kg	104.2	102.0	-943.1	-3789.1	-2.78E-14	161.5	39.2	-1409.8	35.0		-116	4.08	11.62
Molar Entropy	cal/mol-K	-70.5	-65.8	-191.8	-39.0	2.61E-02	1.7	-3.9	-28.2	-4.4		-145	-115.88	-114.22
Mass Entropy	cal/gm-K	-0.7	-0.6	-1.1	-2.2	8.17E-04	0.1	-0.1	-0.8	-0.1		-2	-1.36	-1.34
Enthalpy Flow	Gcal/hr	2.3	2.3	-11.4	-37.8557	-4.49E-16	2.6	0.6	-45.1	0.3		-12	0.41	1.17
Mass Flows	kg/hr	22413.8	22413.8	12132.8	9990.6	16132.2	16132.2	16132.2	31969.7	9886.1		100855	100855	100855
P-XYLENE	kg/hr	22301.7	22301.7	0	0	0	0	0	0	0		0	0	0
OXYGEN	kg/hr	0	0	0	0	16132.2	16132.16	16132.16	9773.84	9773.84		0	0	0
CO(CH-01	kg/hr	0	0	6135.64	0	0	0	0	6121.542	0		0	0	0
MN(CH-01	kg/hr	0	0	5997.167	0	0	0	0	5988.07	0		0	0	0
WATER	kg/hr	0	0	0	9990.622	0	0	0	9974.049	0		0	0	0
BENZO-01	kg/hr	0	0	0	0	0	0	0	3.03347	3.03347		0	0	0
N-TRI-01	kg/hr	112.0691	112.0691	0	0	0	0	0	109.2049	109.2049		0	0	0
N-MET-01	kg/hr	0	0	0	0	0	0	0	0	0		100855	100855	100855
ACETO-01	kg/hr	0	0	0	0	0	0	0	0	0		0	0	0
CISOLID Sub														
Mass Sol Frac									1	1				1
Molar Enthalpy	kcal/mol								-208.90	-208.90				-193.13
Mass Enthalpy	kcal/kg								-1258.43	-1258.43				-
Molar Entropy	cal/mol-K								-707.48	-707.48				1162.52
Mass Entropy	cal/gm-K								-4.26	-4.26				-649.95
Enthalpy Flow	Gcal/hr								-36.12	-36.12				-3.91
Mass Flows	kg/hr								28700	28700				-15.79
P-XYLENE	kg/hr								0	0				13582
P-TOLUIC	kg/hr								103.14	103.14				0
4-CBA	kg/hr								6.067	6.067				0.883
TEREP-01	kg/hr								28590.45	28590.45				0.340
Units		S1-14	S1-15	S1-16	S1-17	S1-18	S1-19	S1-20	S1-21	S1-22	S1-23	S1-24	S1-25	S1-26
Description														
From			E-104	M-101	Y-102	Y-102	T-101	M-102	M-102	R-102	R-103	R-103	T-101	E-105
To		E-104	M-101	Y-102	M-104	X107	M-102		R-103	R-103	E-106	M-103	E-105	M-103
MIXED Sub														
Phase		Liquid	Liquid	Mixed		Vapor	Liquid	Liquid	Liquid			Mixed	Liquid	Liquid
Temperature	C	25	40	69.5		150	75.4	75.4	75.4			75.4	52.9	40

Pressure	bar	1	1	1		1	0.9	0.9	0.9			0.9	0.9	0.9
Molar Vap Frac		0	0	0.71		1	0	0	0			0.05	0	0
Molar Liq Frac		1	1	0.29		0	1	1	1			0.95	1	1
Mass Vap Frac		0	0	0.69		1	0	0	0			0.05	0	0
Mass Liq Frac		1	1	0.31		0	1	1	1			0.95	1	1
Molar Enthalpy	kcal/mol	-58.96	-58.52	-23.62		-19.24	-7.88	-7.88	-7.88			-7.54	-57.36	-57.75
Mass Enthalpy	kcal/kg	-1015.20	-1007.57	-319.66		-260.28	-92.60	-92.60	-92.60			-88.52	-980.43	-987.25
Molar Entropy	cal/mol-K	-74.19	-72.76	-94.71		-82.61	-139.11	-139.11	-139.11			-138.11	-72.49	-73.70
Mass Entropy	cal/gm-K	-1.28	-1.25	-1.28		-1.12	-1.63	-1.63	-1.63			-1.62	-1.24	-1.26
Enthalpy Flow	Gcal/hr	-49.63	-49.26	-47.87		-194.87	-9.24	-4.23	-5.00			-4.78	-49.02	-49.36
Mass Flows	kg/hr	48890	48890	149745			99744.88	45708.93	54035.96			54035	50000	50000
P-XYLENE	kg/hr	0	0	0		0	0	0	0			0	0	0
OXYGEN	kg/hr	0	0	0		0	0	0	0			0	0	0
CO(CH-01	kg/hr	0	0	0		0	0	0	0			0	0	0
MN(CH-01	kg/hr	0	0	0		0	0	0	0			0	0	0
WATER	kg/hr	0	0	0		0	0	0	0			0	0	0
BENZO-01	kg/hr	0	0	0		0	0	0	0			0	0	0
N-TRI-01	kg/hr	0	0	0		0	0	0	0			0	0	0
N-MET-01	kg/hr	0	0	100855.2		504276.1	99724.43	45699.55	54024.88			54024.88	1130.75	1130
ACETO-01	kg/hr	48889.68	48889.68	48889.68		244448.4	20.45352	9.372994	11.08052			11.08	48869.25	48869
CISOLID Sub														
Mass Sol Frac				1	1					1	1	1		
Molar Enthalpy	kcal/mol			-195.82	-191.73					-231.39	-267.86	-195.55		
Mass Enthalpy	kcal/kg			-1178.71	-1154.08					-1394.93	-1616.99	-1177.07		
Molar Entropy	cal/mol-K			-657.22	-646.53					-778.27	-898.98	-656.43		
Mass Entropy	cal/gm-K			-3.96	-3.89					-4.69	-5.43	-3.95		
Enthalpy Flow	Gcal/hr			-16.01	-15.67					-21.09	-12.92	-8.39		
Mass Flows	kg/hr			13582	13582					15118	7988	7130		
P-XYLENE	kg/hr			0	0					0	0	0		
P-TOLUIC	kg/hr			0.883	0.883					102.26	101.79	0.463		
4-CBA	kg/hr			0.340	0.340					5.727	5.549	0.178		
TEREP-01	kg/hr			13580.47	13580.47					15009.99	7880.24	7129.74		
	Units	S1-27	S1-28	S1-29	S1-30	S1-31	S1-32	S1-33	S1-34	S1-35				
Description														
From		M-103	Y-103	Y-103	M-104	E-106	X107	X107	X106	X106				
To		Y-103	X106	M-104	E-106		Y-102	T-101	Y-103					
MIXED Sub														
Phase		Mixed	Vapor				Vapor	Vapor	Vapor	Vapor				
Temperature	C	59.9	150				150	150	150	150				
Pressure	bar	0.9	0.9				1	1	0.9	0.9				
Molar Vap Frac		0.01	1				1	1	1	1				
Molar Liq Frac		0.99	0				0	0	0	0				
Mass Vap Frac		0.01	1				1	1	1	1				
Mass Liq Frac		0.99	0				0	0	0	0				
Molar Enthalpy	kcal/mol	-36.34	-26.85				-19.24	-19.24	-26.85	-26.85				
Mass Enthalpy	kcal/kg	-520.16	-384.34				-260.28	-260.28	-384.34	-384.34				
Molar Entropy	cal/mol-K	-99.80	-72.28				-82.61	-82.61	-72.28	-72.28				
Mass Entropy	cal/gm-K	-1.43	-1.03				-1.12	-1.12	-1.03	-1.03				
Enthalpy Flow	Gcal/hr	-54.12	-199.93				-155.90	-38.97	-159.94	-39.99				
Mass Flows	kg/hr	104036	520179.8				598979.6	149744.9	416143.8	104036				
P-XYLENE	kg/hr	0	0				0	0	0	0				
OXYGEN	kg/hr	0	0				0	0	0	0				
CO(CH-01	kg/hr	0	0				0	0	0	0				
MN(CH-01	kg/hr	0	0				0	0	0	0				
WATER	kg/hr	0	0				0	0	0	0				
BENZO-01	kg/hr	0	0				0	0	0	0				
N-TRI-01	kg/hr	0	0				0	0	0	0				
N-MET-01	kg/hr	55155.63	275778.2				403420.9	100855.2	220622.5	55155.63				
ACETO-01	kg/hr	48880.33	244401.6				195558.7	48889.68	195521.3	48880.33				
CISOLID Sub														
Mass Sol Frac		1		1		1								
Molar Enthalpy	kcal/mol	-196.24		-191.73	-23.90	-217.66								
Mass Enthalpy	kcal/kg	-1181.26		-1154.08	166.13	-1311.22								
Molar Entropy	cal/mol-K	-658.47		-646.53	124.67	-730.04								
Mass Entropy	cal/gm-K	-3.96		-3.89		-4.40								
Enthalpy Flow	Gcal/hr	-8.42		-8.23		-37.63								
Mass Flows	kg/hr	7130		7130	20712.1	28700								
P-XYLENE	kg/hr	0		0	0	0								
P-TOLUIC	kg/hr	0.463		0.463	1.346179	103.14								
4-CBA	kg/hr	0.178		0.178	0.517755	6.067								
TEREP-01	kg/hr	7129.74		7129.74	20710.21	28590.45								

8.3 Appendix C: Scenario one economic calculations

8.3.1 General Indexes and multipliers

8.3.1.1 Installation cost multipliers

Table 35: Installation cost multipliers

Equipment Type	MF
Boiler	1.8
Compressors, motor driven	1.6
Cooling tower	1.5
Distillation columns, stainless steel	2.4
Heat exchangers, shell & tube, stainless steel	2.2
Heat exchangers, air-cooled	2.8
Skidded equipment	1.8
Solids handling equipment (incl. filters)	1.7
Pressure vessels, carbon steel	3.1
Pressure vessels, stainless steel	2
Pre-treatment reactor system	1.5
Pumps, stainless steel	2.3
Pumps, carbon steel	3.1
Tanks, field-erected, carbon steel	1.7
Tanks, storage, plastic	3
Tanks, storage, carbon steel	2.6
Turbogenerator	1.8

8.3.1.2 Scaling Exponents for Individual Equipment

Table 36: Scaling exponents

Equipment	Exponent
Agitators	0.5
Compressors, Motor Driven	0.6
Distillation Columns	0.6
Heat Exchangers	0.7
Inline Mixers	0.5
Package Quotes/ Skidded Equipment	0.6
Pressure Vessels	0.7
Pumps	0.8
Tanks, Atmospheric	0.7
Solids Handling Equipment	0.8

8.3.1.3 Heat transfer area calculation

Table 37: Heat transfer area calculation

$A = Q/(U \cdot T_M)$	
A	Heat exchanger area (ft ²)
Q	Heat transfer rate (Btu/hr): retrieved from ASPEN
U	Overall heat transfer coefficient (Btu/lb.°F)
T_M	Log mean temperature difference (°F): shell and tube temperatures retrieved from ASPEN

8.3.1.4 Inorganic chemical index

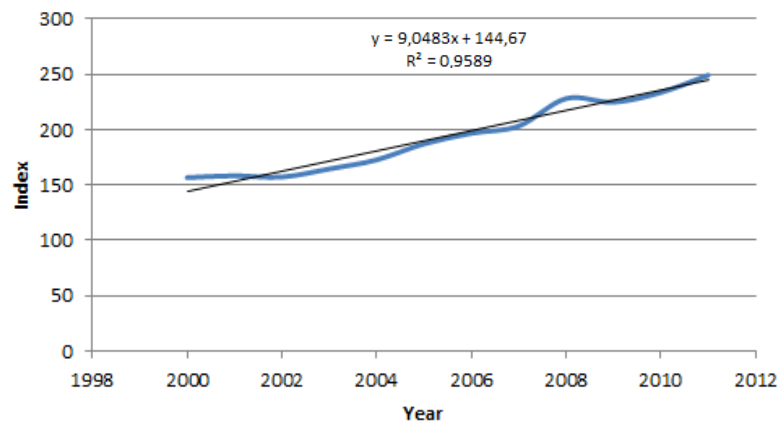


Figure 56: Inorganic chemical index

8.3.1.5 South African Labour Index

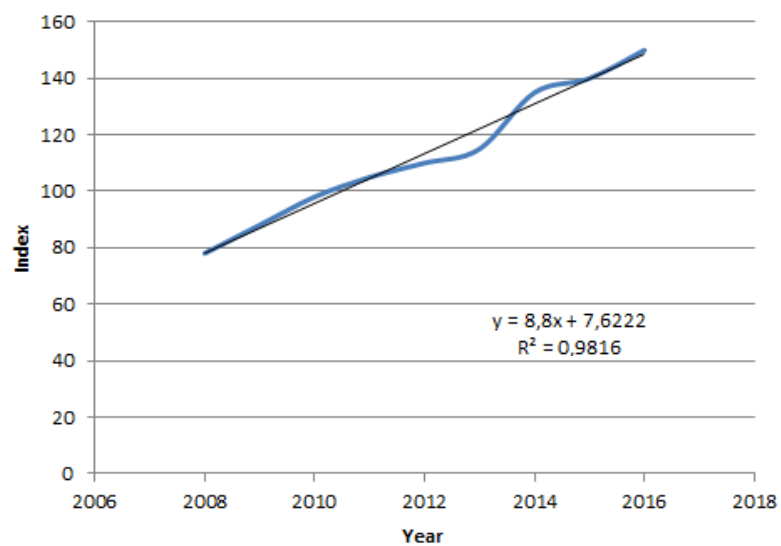


Figure 57: South African labour index

8.3.1.6 Raw material costs

Table 38: Variable costs of raw materials

Chemical	Price (\$/kg)	Reference
Sulphuric Acid	79.55	Sigma Aldrich
Calcium Hydroxide	5.57	Sigma Aldrich
Nitrogen	179.60	BOC Online
Na-Based Zeolite Y	800	Riogen Inc. (Enquiry)
Water	0.00157	Ethekwini Municipality
NMP	163.38	Sigma Aldrich
Acetone	52.95	Science Company
Oxygen	147.00	BOC Online
Carbon Dioxide	116.70	BOC Online
Hydroquinone	107.20	Sigma Aldrich
Argon	273.13	BOC Online
Pd Alumina (0.38% Pd)	1300	Riogen Inc. (Enquiry)
T(<i>p</i> -Cl)PPMnCl	29 850	PorphyChem (Enquiry)
Hydrogen Peroxide	26.36	Science Company

8.3.2 Pine process

Table 39: Pine process: total annual salary cost

Position Salary	2015 Salary (R/y)	Salary (\$/y)	Number of Employees	Total Annual Salary (2016)
Plant Manager	981 000	71 345	1	\$68 411
Plant Engineer	958 000	69 673	2	\$133 614
Maintenance Supervisor	679 000	49 382	1	\$47 351
Maintenance Technician	195 000	14 182	6	\$81 591
Laboratory Manager	679 000	49 382	1	\$47 351
Laboratory Technician	195 000	14 182	5	\$67 993
Shift Supervisor	679 000	49 382	4	\$189 403
Shift Operators	195 000	14 182	12	\$163 183
Yard Employees	460 000	33 455	3	\$96 236
Clerks & Secretaries	592 000	43 055	3	\$123 851
	(Alimandegari, 2017)		Total	\$1 020 000
			Labour Burden (90%)	\$918 000

Table 40: Pine process: feedstock and chemical cost

Feedstock/chemical	Flowrate (kg/hr)	Density (kg/m ³)	Volume (m ³)	Mass (per Cylinder) (kg)	Cost (\$/kg)	\$/annum
Biomass	120				0.0075	\$964 800
Sulphuric Acid*	0.55	1480	0.0001	0.148	79.55	\$17 541
Oxygen	1.2	2210	0.0001	0.221	147	\$1 464 349
Nitrogen *	5.1	1.251	0.1316	0.16	179.64	\$366 367
Na Zeolite Y *	4.1				800	\$3 317
Calcium Hydroxide	0.56	1.429	0.075	0.10	5.57	\$4 045
Water *	570.4				0.001567	\$360
NMP *	1.28	1047	0.0005	0.52	163.38	\$84 129
Acetone *	1.03		0.0037		52.95	\$22 075
				Total		\$2 930 000

Table 41: Pine process: equipment purchase cost

Equipment code	Equipment type	Size factor	Cost formula	Purchase cost (\$)	Reference
Section 1					
V-101	Stainless steel vessel	V = 250 gal	$C = 1\,980\,V^{0.58}$	\$135 200	
V-102					
V-103					
P-101	Slurry pump (costed as centrifugal)	$S = QH^{0.5}$ Q = 4.1 gal/min H = 4.6 ft	$C = \exp[9.7171 - 0.6019\ln(S) + 0.0519\ln(S^2)]$	\$28 100	
P-102					
P-103					
E-101	Shell and tube heat exchanger (U-tube/stainless steel)	A = 6.9 ft ² (heat transfer area)	$C = \exp[11.147 - 0.9186\ln(A) + 0.0979\ln(A^2)]$	\$84 000	
D-101				\$100 000	Alibaba (enquiry)
Size reduction	Rod mill	W = 120 kg/hr		\$155 800	APEA
				Total	\$830 000
Section 2					
R-201				\$ 155 000	APEA
H-201	Fired heater (stainless steel)			\$108 000	APEA
C-201	Compressor (screw/stainless steel)	P = 15.6 Hp	$C = \exp[8.1238 + 0.7243\ln(P)]$	\$182 000	
E-201	Shell and tube heat exchanger (U-tube/stainless steel)	A = 2.8 ft ²	$C = \exp[11.147 - 0.9186\ln(A) + 0.0979\ln(A^2)]$	\$45 500	
E-202		A = 2.3 ft ²		\$98 400	
C-202	Gas expander	P = 20 Hp (power extracted)	$C = 530\,P^{0.81}$	\$11 500	
T-201				\$110 500	APEA
				Total	\$711 000
Section 3					
R-301				\$150 200	APEA
E-301	Shell and tube heat exchanger (U-tube/stainless steel)	A = 2.9 ft ²	$C = \exp[11.147 - 0.9186\ln(A) + 0.0979\ln(A^2)]$	\$45 000	
E-302		A = 1.9 ft ²		\$34 000	
T-301				\$ 171 400	APEA
				Total	\$400 600
Section 4					
R-401				\$190 000	APEA
R-402				\$111 000	
R-403				\$160 000	
E-401	Shell and tube heat exchanger (U-tube/stainless steel)	A = 1.2 ft ²	$C = \exp[11.147 - 0.9186\ln(A) + 0.0979\ln(A^2)]$	\$ 46 000	
E-402		A = 1.5 ft ²		\$ 38 000	
C-401				\$235 500	APEA
C-402				\$192 000	
V-401	Stainless steel vessel	V = 6.5 gal	$C = 1\,980\,V^{0.58}$	\$ 16 300	
V-402		V = 22.4 gal		\$33 400	
V-403		V = 27.1 gal		\$37 300	
Y-401				\$23 200	APEA
				Total	\$1 083 000
Section 5					
R-501				\$117 300	APEA

R-502				\$120 800	
R-503				\$115 700	
R-504				\$121 900	
M-501	Stainless steel vessel	V = 0.43 gal	$C = 1\,980\,V^{0.58}$	\$3 400	
M-502		V = 0.49 gal		\$3 600	
M-503		V = 4.76 gal		\$13 600	
M-504		V = 0.5 gal		\$3 700	
M-505		V = 15.2 gal		\$26 700	
M-506		V = 0.15 gal		\$1 800	
E-501	Shell and tube heat exchanger (U-tube/stainless steel)	A = 4.7 ft ²	$C = \exp[11.147 - 0.9186\ln(A) + 0.0979\ln(A^2)]$	\$ 79 500	
E-502		A = 3.7 ft ²		\$71 100	
E-503		A = 2.7 ft ²		\$43 100	
E-504		A = 3.0 ft ²		\$53 100	
E-505		A = 3.5 ft ²		\$67 400	
E-506		A = 2.9 ft ²		\$45 900	
E-507		A = 4.3 ft ²		\$74 700	
E-508		A = 8.3 ft ²		\$83 300	
T-501				\$183 200	
				Total	\$1 230 000
Section 6					
Power generation		W = 45.73 kW	$C = 4\,264/W$	\$340 200	
				Total	\$340 200
Section 7					
Y-701				\$17 600	Alibaba (enquiry)
Y-702					
Y-703					
Y-704					
E-701	Shell and tube heat exchanger (U-tube/stainless steel)	A = 5.7 ft ²	$C = \exp[11.147 - 0.9186\ln(A) + 0.0979\ln(A^2)]$	\$54 200	
E-702		A = 5.7 ft ²		\$54 200	
				Total	\$179 000
				Grand total	\$ 4 774 000

8.3.3 Eucalyptus process

Table 42: Eucalyptus process: total annual salary cost

Position Salary	2015 Salary (R/y)	Salary (\$/y)	Number of Employees	Total Annual Salary (2016)
Plant Manager	981 000	71 345	1	\$68 411
Plant Engineer	958 000	69 673	3	\$200 422
Maintenance Supervisor	679 000	49 382	1	\$47 351
Maintenance Technician	195 000	14 182	8	\$108 788
Laboratory Manager	679 000	49 382	1	\$47 351
Laboratory Technician	195 000	14 182	5	\$67 993
Shift Supervisor	679 000	49 382	4	\$189 403
Shift Operators	195 000	14 182	15	\$203 978
Yard Employees	460 000	33 455	4	\$128 315
Clerks & Secretaries	592 000	43 055	4	\$165 135
	(Alimandegari, 2017)		Total	\$1 230 000
			Labour Burden (90%)	\$1 107 000

Table 43: Eucalyptus process: feedstock and chemical cost

Feedstock/chemical	Flowrate (kg/hr)	Density (kg/m ³)	Volume (m ³)	Mass (per Cylinder) (kg)	Cost (\$/kg)	\$/annum
Biomass	755.03				0.0051	\$30 959
Carbon Dioxide *	315.75	1.98	0.07	0.14	116.70	\$36 849
Hydroquinone *	2.44				107.2	\$105 351
Argon *	9.88	1.784	0.1316	0.23	273.13	\$1 087 329
Oxygen *	14.23	1.429	0.075	0.11	146.96	\$16 817 714
Pd Alumina *	3.88				1300	\$5 042
Water*	1041.54				0.001567	\$13 124
Calcium Hydroxide	5.60				5.57	\$250 300
Mn/Fe *	5.50				2.03	\$89 620
PPCI *	0.09				298500	\$28 143
NMP *	16.24	1047	0.0005	0.52	163.38	\$1 069 449
Acetone *	70.49		0.0038		52.95	\$1 504 189
						\$21 100 000

Table 44: Eucalyptus process: equipment purchase cost

Equipment code	Equipment type	Size factor	Cost formula	Purchase cost (\$)	Reference
Section 1					
T-101				\$757 600	APEA
T-102				\$630 000	
T-103				\$108 100	
T-104				\$460 000	
M-101	Stainless steel vessel	V = 2700 gal	$C = 1\,980 V^{0.58}$	\$533 000	
P-101	Liquid expander	P = 150 Hp	$C = 1\,400 P^{0.70}$	\$1 021 000	
E-101	Shell and tube heat exchanger (U-tube/stainless steel)	A = 4.0 ft ²	$C = \exp[11.147 - 0.9186\ln(A) + 0.0979\ln(A^2)]$	\$411 000	
E-102		A = 6.6 ft ²		\$282 600	
E-103		A = 4.0 ft ²		\$140 600	
E-104		A = 10.8 ft ²		\$89 700	
C-101	Compressor (centrifugal/stainless steel)	P = 200 Hp	$C = \exp[7.58 + 0.8\ln(P)]$	\$725 000	
Size reduction	Rod mill	W = 760 kg/hr		\$ 393 000	APEA
				Total	\$5 552 000
Section 2					
E-201	Shell and tube heat exchanger (U-tube/stainless steel)	A = 8.1 ft ²	$C = \exp[11.147 - 0.9186\ln(A) + 0.0979\ln(A^2)]$	\$34 000	
E-202		A = 5.8 ft ²		\$52 500	
E-203		A = 2.7 ft ²		\$128 500	
E-204		A = 5.5 ft ²		\$55 500	
T-201				\$102 700	APEA
T-202				\$87 200	
T-203				\$101 000	
T-204				\$76 400	
M-202	Stainless steel vessel	V = 1200 gal	$C = 1\,980 V^{0.58}$	\$129 000	
M-203		V = 120 gal		\$88 300	
				Total	\$855 100
Section 3					
R-301				\$648 700	APEA
E-301	Shell and tube heat exchanger (U-tube/stainless steel)	A = 1.9 ft ²	$C = \exp[11.147 - 0.9186\ln(A) + 0.0979\ln(A^2)]$	\$180 300	
E-302		A = 5.5 ft ²		\$56 000	
T-301				\$201 000	APEA
C-301				\$1 086 000	APEA
				Total	\$2 172 000
Section 4					
R-401				\$289 000	APEA
R-402				\$300 900	
R-403				\$270 000	
E-401	Shell and tube heat exchanger (U-tube/stainless steel)	A = 6.7 ft ²	$C = \exp[11.147 - 0.9186\ln(A) + 0.0979\ln(A^2)]$	\$59 000	
E-402		A = 3.8 ft ²		\$75 300	
E-403		A = 6.4 ft ²		\$36 700	
C-401				\$1 006 400	APEA
C-402				\$936 100	
M-401	Stainless steel vessel	V = 52 gal	$C = 1\,980 V^{0.58}$	\$ 54 400	
T-401		V = 120 gal		\$88 300	
T-402		V = 168 gal		\$107 400	
				Total	\$3 224 000
Section 5					
R-501				\$180 300	APEA

R-502				\$330 500	
R-503				\$213 000	
R-504				\$159 500	
M-501	Stainless steel vessel	V = 5.1 gal	$C = 1\,980\,V^{0.58}$	\$14 200	
M-502		V = 5.2 gal		\$16 100	
M-503		V = 470.8 gal		\$213 200	
M-504		V = 5.3 gal		\$15 500	
M-505		V = 719 gal		\$204 400	
M-506		V = 1.6 gal		\$7 700	
E-501	Shell and tube heat exchanger (U-tube/stainless steel)	A = 5.6 ft ²	$C = \exp[11.147 - 0.9186\ln(A) + 0.0979\ln(A^2)]$	\$69 100	
E-502		A = 5.8 ft ²		\$42 600	
E-503		A = 9.2 ft ²		\$22 200	
E-504		A = 5.6 ft ²		\$75 700	
E-505		A = 5.1 ft ²		\$56 600	
E-506		A = 5.8 ft ²		\$34 600	
E-507		A = 6.3 ft ²		\$48 600	
E-508		A = 2.6 ft ²		\$182 800	
T-501				\$762 500	APEA
				Total	\$2 650 000
Section 6					
Power generation		W = 98.74 kW	$C = 4\,264/W$	\$408 200	
				Total	\$408 200
Section 7					
Y-701				\$35 500	Alibaba (enquiry)
Y-702					
Y-703					
Y-704					
E-701	Shell and tube heat exchanger (U-tube/stainless steel)	A = 2.5 ft ²	$C = \exp[11.147 - 0.9186\ln(A) + 0.0979\ln(A^2)]$	\$106 600	
E-702		A = 2.4 ft ²		\$196 600	
				Total	\$445 200
				Grand total	\$ 15 306 500

8.3.4 PHR process

Table 45: PHR process: total annual salary cost

Position Salary	2015 Salary (R/y)	Salary (\$/y)	Number of Employees	Total Annual Salary (2016)
Plant Manager	981 000	71 345	1	\$71 345
Plant Engineer	958 000	69 673	3	\$209 018
Maintenance Supervisor	679 000	49 382	1	\$49 382
Maintenance Technician	195 000	14 182	8	\$113 455
Laboratory Manager	679 000	49 382	1	\$49 382
Laboratory Technician	195 000	14 182	5	\$70 909
Shift Supervisor	679 000	49 382	4	\$197 527
Shift Operators	195 000	14 182	18	\$255 273
Yard Employees	460 000	33 455	4	\$133 818
Clerks & Secretaries	592 000	43 055	4	\$172 218
	(Alimandegari, 2017)		Total	\$1 323 000
			Labour Burden (90%)	\$1 191 000

Table 46: PHR process: feedstock and chemical cost

Feedstock/chemical	Flowrate (kg/hr)	Density (kg/m ³)	Volume (m ³)	Mass (per Cylinder) (kg)	Cost (\$/kg)	\$/annum
Sulphuric Acid*	3.79	1480	0.0001	0.148	79.55	\$1 211 000
Calcium hydroxide	5.90	2210	0.0001	0.221	5.57	\$264 200
Nitrogen *	450.35	1.251	0.1316	0.16	179.64	\$5 935 000
Na Zeolite Y *	30.75				800	\$2 002 400
Oxygen	7.38	1.429	0.075	0.10	147	\$4 365 000
NMP *	10.78	1047	0.0005	0.52	163.38	\$7 083 000
Acetone *	3.90		0.0037		52.95	\$830 200
Hydrogen peroxide	1.79				26.36	\$379 000
					Total	\$22 070 000

Table 47: PHR process: equipment purchase cost

Equipment code	Equipment type	Size factor	Cost formula	Purchase cost (\$)	Reference
Section 1					
R-101				\$365 000	APEA
R-102				\$167 000	
H-101	Fired heater (stainless steel)			\$321 000	
C-101				\$1 145 000	
E-101	Shell and tube heat exchanger (U-tube/stainless steel)			\$605 500	
E-102				\$196 300	
C-102				\$91 600	
M-101	Stainless steel vessel	V = 1053 gal	$C = 1\,980\,V^{0.58}$	\$311 400	
D-101	Oil/water decanter			\$687 000	Alibaba (enquiry)
T-101				\$128 300	APEA
				Total	\$4 018 100
Section 2					
R-201				\$150 700	APEA
E-201	Shell and tube heat exchanger (U-tube/stainless steel)	A = 2.1 ft ²	$C = \exp[11.147 - 0.9186\ln(A) + 0.0979\ln(A^2)]$	\$240 600	
E-202		A = 1.8 ft ²		\$269 900	
T-201				\$170 000	APEA
				Total	\$831 200
Section 3					
R-301				\$325 600	APEA
R-302				\$367 800	
R-303				\$317 000	
E-301	Shell and tube heat exchanger (U-tube/stainless steel)	A = 2.1 ft ²	$C = \exp[11.147 - 0.9186\ln(A) + 0.0979\ln(A^2)]$	\$429 800	
E-302		A = 2.7 ft ²		\$209 900	
C-301				\$1 527 000	APEA
C-302				\$1 099 800	
V-301	Stainless steel vessel	V = 38.6 gal	$C = 1\,980\,V^{0.58}$	\$31 700	
V-302		V = 83.6 gal		\$49 600	
V-303		V = 84 gal		\$49 700	
Y-301				\$57 000	Alibaba (enquiry)
				Total	\$4 464 900
Section 4					
R-401				\$301 100	APEA
R-402				\$307 200	
R-403				\$299 800	
R-404				\$306 000	
M-401	Stainless steel vessel	V = 3.4 gal	$C = 1\,980\,V^{0.58}$	\$10 400	
M-402		V = 4.4 gal		\$12 200	
M-403		V = 8.3 gal		\$17 600	
M-404		V = 3.9 gal		\$11 500	
M-405		V = 31.7 gal		\$38 200	
M-406		V = 2.9 gal		\$9 700	
E-401	Shell and tube heat exchanger (U-tube/stainless steel)	A = 5.1 ft ²	$C = \exp[11.147 - 0.9186\ln(A) + 0.0979\ln(A^2)]$	\$124 900	
E-402		A = 4.2 ft ²		\$100 200	
E-403		A = 2.9 ft ²		\$144 700	
E-404		A = 3.3 ft ²		\$228 200	

E-405		$A = 3.8 \text{ ft}^2$		\$125 100	
E-406		$A = 3.1 \text{ ft}^2$		\$118 500	
E-407		$A = 4.4 \text{ ft}^2$		\$121 000	
E-408		$A = 9.3 \text{ ft}^2$		\$63 300	
T-401				\$979 000	APEA
				Total	\$3 318 600
Section 5					
Y-501				\$57 000	Alibaba (enquiry)
Y-502					
Y-503					
Y-504					
E-501	Shell and tube heat exchanger (U-tube/stainless steel)	$A = 6.2 \text{ ft}^2$	$C = \exp[11.147 - 0.9186\ln(A) + 0.0979\ln(A^2)]$	\$97 000	
E-502		$A = 6.1 \text{ ft}^2$		\$63 600	
				Total	\$388 600
				Grand total	\$13 021 400

8.3.5 Starch process

Table 48: Starch process: total annual salary cost

Position Salary	2015 Salary (R/y)	Salary (\$/y)	Number of Employees	Total Annual Salary (\$/y)
Plant Manager	981 000	71 345	2	\$142 691
Plant Engineer	958 000	69 673	4	\$278 691
Maintenance Supervisor	679 000	49 382	2	\$98 764
Maintenance Technician	195 000	14 182	8	\$113 455
Laboratory Manager	679 000	49 382	2	\$98 764
Laboratory Technician	195 000	14 182	10	\$141 818
Shift Supervisor	679 000	49 382	8	\$395 055
Shift Operators	195 000	14 182	25	\$354 545
Yard Employees	460 000	33 455	6	\$200 727
Clerks & Secretaries	592 000	43 055	6	\$258 327
	(Alimandegari, 2017)		Total	\$2 083 000
			Labour Burden (90%)	\$1 875 000

Table 49: Starch process CCEI costs

	Annual costs (\$/tonne p-xylene)
Feedstock	\$310/tonne
Catalysts	\$1425/tonne
Purchased equipment	\$185/tonne
Equipment setting	\$26/tonne

Table 50: Starch process: equipment purchase cost

Equipment code	Equipment type	Size factor	Cost formula	Purchase cost (\$)	Reference
Section 1					
R-101				\$254 400	APEA
R-102				\$259 700	
R-103				\$185 400	
E-101	Shell and tube heat exchanger (U-tube/stainless steel)			\$198 000	
E-102				\$156 900	
E-103				\$174 300	
E-104				\$62 300	
E-105				\$85 700	
C-101				\$3 117 300	
M-101	Stainless steel vessel			\$105 200	
M-102				\$99 800	
M-103				\$95 700	
M-104				\$113 300	
Y-101				\$652 900	
Y-102				\$310 900	
Y-103				\$155 400	
T-101				\$10 256 000	
				Total	\$16 283 200

8.4 Appendix D: Scenario one Discounted Cash Flow Analysis sheets

Scenario one: Pine process (1)

Total Capital Investment															
	Discount Rate	2016	2017	2018	2019	2020	2021	2022	2023	2024	2025	2026	2027	2028	2029
Total Installed Cost	13.52%														
Warehouse	5.70%														
Site Development	28%														
Additional Piping	4.0%														
Total Direct Cost (TDC)	7%														
Loan Term	10														
Protable Expenses															
Field Expenses															
Home Office & Construction															
Project Contingency															
Other Costs															
Total Indirect Cost															
Fixed Capital Investment (FCI)															
South African Location Factor	8.03														
Electricity Production (kWh)	793950														
Working Capital															
Total Capital Investment															
Selling price															
Year	-2	-1	0	1	2	3	4	5	6	7	8	9	10	11	12
Discount Factor	1.28667904	1.1352													
Fixed Capital Investment	\$0.00	\$0.00	\$3 588 647	\$448 581											
Working Capital															
Loan Payment															
Loan Interest Payment	0	0	\$ 376 808	\$ 376 808	\$ 349 535	\$ 320 354	\$ 289 130	\$ 255 720	\$ 219 971	\$ 181 720	\$ 140 792	\$ 96 988	\$ 50 139	\$ -	\$ -
Loan Principal	0	0	\$ 5 382 970	\$ 4 993 364	\$ 4 576 485	\$ 4 130 426	\$ 3 653 142	\$ 3 142 448	\$ 2 596 006	\$ 2 011 312	\$ 1 385 690	\$ 716 275	\$ -	\$ -	\$ -
TPA Price (\$/tonne)			700	705.25	710.539375	715.8684203	721.2374335	726.6467142	732.0965646	737.5872888	743.1191935	748.6925674	754.3077818	759.9650902	765.6648284
TPA Sales			\$ -	\$ 5 660	\$ 5 702	\$ 5 745	\$ 5 788	\$ 5 832	\$ 5 875	\$ 5 920	\$ 5 964	\$ 6 009	\$ 6 054	\$ 6 099	\$ 6 145
Electricity Price (\$/kWh)				\$ 0.09	\$ 0.10	\$ 0.11	\$ 0.11	\$ 0.12	\$ 0.13	\$ 0.13	\$ 0.14	\$ 0.15	\$ 0.16	\$ 0.17	\$ 0.18
Electricity Sales			\$ -	\$ 75 528	\$ 79 834	\$ 84 384	\$ 89 194	\$ 94 278	\$ 99 632	\$ 105 332	\$ 111 336	\$ 117 682	\$ 124 380	\$ 131 460	\$ 138 975
Total Annual Sales			\$ -	\$ 81 168	\$ 85 556	\$ 90 129	\$ 94 982	\$ 100 110	\$ 105 527	\$ 111 252	\$ 117 300	\$ 123 691	\$ 130 444	\$ 137 579	\$ 145 119
Annual Manufacturing Cost															
Operating Cost			\$ 1 969 419	\$ 2 087 213	\$ 2 098 429	\$ 2 129 644	\$ 2 160 859	\$ 2 192 074	\$ 2 223 290	\$ 2 254 505	\$ 2 285 720	\$ 2 316 936	\$ 2 348 151	\$ 2 379 366	\$ 2 410 581
Fixed Operating Cost			\$ 2 268 021	\$ 2 359 124	\$ 2 401 236	\$ 2 443 348	\$ 2 485 460	\$ 2 527 572	\$ 2 569 685	\$ 2 611 797	\$ 2 653 909	\$ 2 696 021	\$ 2 738 133	\$ 2 780 246	\$ 2 822 358
Total Production Cost			\$ 4 237 440	\$ 4 359 124	\$ 4 468 449	\$ 4 541 777	\$ 4 615 104	\$ 4 688 432	\$ 4 761 759	\$ 4 835 087	\$ 4 908 414	\$ 4 981 742	\$ 5 055 069	\$ 5 128 397	\$ 5 201 724
Annual Depreciation															
Plant Writedown			4%	4%	4%	4%	4%	4%	4%	4%	4%	4%	4%	4%	4%
Depreciation Charge			\$358 865	\$358 865	\$358 865	\$358 865	\$358 865	\$358 865	\$358 865	\$358 865	\$358 865	\$358 865	\$358 865	\$358 865	\$358 865
Remaining Value			\$8 612 752	\$7 895 023	\$7 536 158	\$7 177 893	\$6 818 429	\$6 459 564	\$6 100 699	\$5 741 835	\$5 382 970	\$5 024 105	\$4 665 241	\$4 306 376	\$3 947 511
Net Revenue			\$ -	\$ -	\$ -	\$ -	\$ -	\$ -	\$ -	\$ -	\$ -	\$ -	\$ -	\$ -	\$ -
Income Tax			\$ -	\$ -	\$ -	\$ -	\$ -	\$ -	\$ -	\$ -	\$ -	\$ -	\$ -	\$ -	\$ -
Annual Cash Income			\$ -	\$ -	\$ -	\$ -	\$ -	\$ -	\$ -	\$ -	\$ -	\$ -	\$ -	\$ -	\$ -
Annual Present Value			\$ -	\$ -	\$ -	\$ -	\$ -	\$ -	\$ -	\$ -	\$ -	\$ -	\$ -	\$ -	\$ -
TCI + Interest			\$ -	\$ -	\$ -	\$ -	\$ -	\$ -	\$ -	\$ -	\$ -	\$ -	\$ -	\$ -	\$ -
Net Present Value			\$ -	\$ -	\$ -	\$ -	\$ -	\$ -	\$ -	\$ -	\$ -	\$ -	\$ -	\$ -	\$ -
IRR			#NUM!												

Scenario one: Pine process (2)

	2029	2030	2031	2032	2033	2034	2035	2036	2037	2038	2039	2040	2041
	13	14	15	16	17	18	19	20	21	22	23	24	25
	0.1923	0.1694	0.1492	0.1315	0.1158	0.1020	0.0899	0.0792	0.0697	0.0614	0.0541	0.0477	0.0420
\$	-	-	-	-	-	-	-	-	-	-	-	-	-
\$	-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
\$	771.4073146	777.1928694	783.021816	788.8944796	794.8111882	800.772721	806.7780641	812.8288996	818.9251164	825.0670547	831.2550576	837.4894706	843.7706416
\$	6.191	6.237	6.284	6.331	6.379	6.427	6.475	6.523	6.572	6.622	6.671	6.721	6.771
\$	0.19	0.20	0.21	0.22	0.23	0.24	0.26	0.27	0.29	0.30	0.32	0.34	0.36
\$	146.896	155.269	164.120	173.474	183.362	193.814	204.862	216.539	228.881	241.928	255.717	270.293	285.700
\$	153.087	161.507	170.404	179.806	189.741	200.241	211.336	223.062	235.454	248.549	262.389	277.015	292.472
\$	2.410 581	2.441 797	2.473 012	2.504 227	2.535 443	2.566 658	2.597 873	2.629 089	2.660 304	2.691 519	2.722 734	2.753 950	2.785 165
\$	2.864 470	2.906 582	2.948 694	2.990 807	3.032 919	3.075 031	3.117 143	3.159 255	3.201 368	3.243 480	3.285 592	3.327 704	3.369 816
\$	5.275 052	5.348 379	5.421 707	5.495 034	5.568 361	5.641 689	5.715 016	5.788 344	5.861 671	5.934 999	6.008 326	6.081 654	6.154 981
	4%	4%	4%	4%	4%	4%	4%	4%	4%	4%	4%	4%	4%
\$358 865	\$358 865	\$358 865	\$358 865	\$358 865	\$358 865	\$358 865	\$358 865	\$358 865	\$358 865	\$358 865	\$358 865	\$358 865	\$358 865
\$3 947 511	\$3 588 647	\$3 229 782	\$2 870 917	\$2 512 053	\$2 153 188	\$1 794 323	\$1 435 459	\$1 076 594	\$717 729	\$358 865	\$0	\$0	\$0
\$-5480 829	\$-5 545 737	\$-5 610 167	\$-5 674 093	\$-5 737 485	\$-5 800 313	\$-5 862 545	\$-5 924 147	\$-5 985 082	\$-6 045 314	\$-6 104 802	\$-6 163 504	\$-6 222 206	\$-6 280 908
\$	-5 121 964	-5 186 872	-5 251 303	-5 315 228	-5 378 620	-5 441 448	-5 503 680	-5 565 282	-5 625 218	-5 686 450	-5 745 938	-5 804 639	-5 862 510
\$	-985 135	-878 804	-783 757	-698 818	-622 932	-555 152	-494 627	-440 595	-392 371	-349 340	-310 954	-276 718	-246 192

Scenario one: Eucalyptus process (1)

Total Capital Investment									
Total Installed Cost	\$15 303 647.42								
Warehouse	\$ 612 145.90								
Site Development	\$ 1 377 328.27								
Additional Piping	\$ 688 664.13								
Total Direct Cost (TDC)	\$17 981 785.71								
Proratable Expenses									
Field Expenses	\$1 798 178.57								
Home Office & Construction	\$3 596 357.14								
Project Contingency	\$1 798 178.57								
Other Costs	\$1 798 178.57								
Total Indirect Cost	\$10 789 071.43								
Fixed Capital Investment (FCI)	\$28 770 857.14								
South African Location Factor	1								
Corrected FCI	\$28 770 857.14								
Working Capital	\$1 438 542.86								
Total Capital Investment	\$30 209 400.00								
MSP									
Year	-2								
Discount Factor	1.289								
Fixed Capital Investment	\$0.00								
Working Capital									
Loan Payment									
Loan Interest Payment	0								
Loan Principal	0								
TPA Price (\$/tonne)									
TPA Sales									
Electricity Price (\$/kWh)									
Electricity Sales									
Total Annual Sales									
Other Variable Cost									
Fixed Operating Cost									
Total Production Cost									
Annual Depreciation									
Plant Writedown									
Depreciation Charge									
Remaining Value									
Net Revenue									
Income Tax									
Annual Cash Income									
Annual Present Value									
TCI + Interest									
Net Present Value									
IRR									

Scenario one: Eucalyptus process (2)

	2026	2027	2028	2029	2030	2031	2032	2033	2034	2035	2036	2037	2038	2039	2040	2041
	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25
	0.281	0.248	0.218	0.192	0.169	0.149	0.131	0.116	0.102	0.090	0.079	0.070	0.061	0.054	0.048	0.042
\$	2 457 794	\$	\$	\$	\$	\$	\$	\$	\$	\$	\$	\$	\$	\$	\$	\$
\$	160 790	\$	\$	\$	\$	\$	\$	\$	\$	\$	\$	\$	\$	\$	\$	\$
\$	843	\$	\$	\$	\$	\$	\$	\$	\$	\$	\$	\$	\$	\$	\$	\$
\$	142 396	\$	\$	\$	\$	\$	\$	\$	\$	\$	\$	\$	\$	\$	\$	\$
\$	0.17	\$	\$	\$	\$	\$	\$	\$	\$	\$	\$	\$	\$	\$	\$	\$
\$	1 353 966	\$	\$	\$	\$	\$	\$	\$	\$	\$	\$	\$	\$	\$	\$	\$
\$	1 496 352	\$	\$	\$	\$	\$	\$	\$	\$	\$	\$	\$	\$	\$	\$	\$
\$	24 750 375	\$	\$	\$	\$	\$	\$	\$	\$	\$	\$	\$	\$	\$	\$	\$
\$	4 100 041	\$	\$	\$	\$	\$	\$	\$	\$	\$	\$	\$	\$	\$	\$	\$
\$	28 850 416	\$	\$	\$	\$	\$	\$	\$	\$	\$	\$	\$	\$	\$	\$	\$
4%		4%	4%	4%	4%	4%	4%	4%	4%	4%	4%	4%	4%	4%	4%	4%
\$1 150 834	\$1 150 834	\$1 150 834	\$1 150 834	\$1 150 834	\$1 150 834	\$1 150 834	\$1 150 834	\$1 150 834	\$1 150 834	\$1 150 834	\$1 150 834	\$1 150 834	\$1 150 834	\$1 150 834	\$1 150 834	\$1 150 834
\$16 111 680	\$14 960 846	\$13 810 011	\$12 659 177	\$11 508 343	\$10 357 509	\$9 206 674	\$8 055 840	\$6 905 006	\$5 754 171	\$4 603 337	\$3 452 503	\$2 301 669	\$1 150 834	\$0.00	\$0.00	\$0.00
\$-28 665 688	\$-28 809 200	\$-29 107 548	\$-29 399 550	\$-29 684 790	\$-29 962 826	\$-30 233 185	\$-30 505 361	\$-30 777 537	\$-31 049 713	\$-31 321 889	\$-31 594 065	\$-31 866 241	\$-32 138 417	\$-32 410 593	\$-32 682 769	\$-32 954 945
\$	\$	\$	\$	\$	\$	\$	\$	\$	\$	\$	\$	\$	\$	\$	\$	\$
\$-29 811 857	\$-27 658 366	\$-27 956 713	\$-28 248 715	\$-28 533 956	\$-28 811 962	\$-29 082 350	\$-29 344 527	\$-29 597 885	\$-29 842 152	\$-30 076 418	\$-30 300 684	\$-30 524 950	\$-30 749 216	\$-30 973 482	\$-31 197 748	\$-31 422 014
\$-8 388 131	\$-6 855 361	\$-6 104 942	\$-5 433 225	\$-4 834 467	\$-4 300 189	\$-3 823 591	\$-3 398 573	\$-3 019 668	\$-2 681 976	\$-2 381 105	\$-2 113 122	\$-1 874 506	\$-1 662 106	\$-1 473 101	\$-1 304 969	\$-1 146 835

Scenario one: PHR process (1)

[illegible]

Scenario one: PHR process (2)

[illegible]

Scenario two: Pine process (2)

	2028	2029	2030	2031	2032	2033	2034	2035	2036	2037	2038	2039	2040	2041
	12	13	14	15	16	17	18	19	20	21	22	23	24	25
	0.218	0.192	0.169	0.149	0.131	0.116	0.102	0.090	0.079	0.070	0.051	0.054	0.048	0.042
\$	\$	\$	\$	\$	\$	\$	\$	\$	\$	\$	\$	\$	\$	\$
\$	-0.00	-0.00	-0.00	-0.00	-0.00	-0.00	-0.00	-0.00	-0.00	-0.00	-0.00	-0.00	-0.00	-0.00
\$	-0.00	-0.00	-0.00	-0.00	-0.00	-0.00	-0.00	-0.00	-0.00	-0.00	-0.00	-0.00	-0.00	-0.00
	5718	5761	5804	5847	5891	5935	5980	6025	6070	6115	6161	6208	6254	6301
	96373871	97095675	97824900	98558587	99297776	100042509	100792828	101548774	102310390	103077718	103850801	104629682	105414405	106205013
\$	234 324 490	\$ 237 398 631	\$ 240 472 772	\$ 243 546 913	\$ 246 621 054	\$ 249 695 195	\$ 252 769 336	\$ 255 843 477	\$ 258 917 618	\$ 261 991 759	\$ 265 065 900	\$ 268 140 041	\$ 271 214 181	\$ 274 288 322
\$	2 822 358	\$ 2 864 470	\$ 2 906 582	\$ 2 948 694	\$ 2 990 807	\$ 3 032 919	\$ 3 075 031	\$ 3 117 143	\$ 3 159 255	\$ 3 201 368	\$ 3 243 480	\$ 3 285 592	\$ 3 327 704	\$ 3 369 816
\$	237 146 848	\$ 240 263 101	\$ 243 379 354	\$ 246 495 607	\$ 249 611 861	\$ 252 728 114	\$ 255 844 367	\$ 258 960 620	\$ 262 076 873	\$ 265 193 126	\$ 268 309 379	\$ 271 425 633	\$ 274 541 886	\$ 277 658 139
	4%	4%	4%	4%	4%	4%	4%	4%	4%	4%	4%	4%	4%	4%
\$	\$35 341 672	\$35 341 672	\$35 341 672	\$35 341 672	\$35 341 672	\$35 341 672	\$35 341 672	\$35 341 672	\$35 341 672	\$35 341 672	\$35 341 672	\$35 341 672	\$35 341 672	\$35 341 672
\$	\$424 100 062	\$388 758 390	\$353 416 719	\$318 075 047	\$282 733 375	\$247 391 703	\$212 050 031	\$176 708 359	\$141 366 687	\$106 025 016	\$70 683 344	\$35 341 672	\$0.00	\$0.00
\$	115 759 858	\$ 130 003 256	\$ 145 200 375	\$ 161 405 309	\$ 178 675 233	\$ 197 070 580	\$ 216 655 223	\$ 237 496 677	\$ 259 666 301	\$ 283 239 520	\$ 308 296 056	\$ 334 920 173	\$ 363 200 937	\$ 428 574 159
\$	32 412 760	\$ 36 400 912	\$ 40 656 105	\$ 45 193 486	\$ 50 029 065	\$ 55 179 762	\$ 60 663 463	\$ 66 499 070	\$ 72 706 564	\$ 79 307 065	\$ 86 322 896	\$ 93 777 648	\$ 101 695 262	\$ 120 000 764
\$	118 688 770	\$ 128 944 016	\$ 139 885 942	\$ 151 553 494	\$ 163 987 840	\$ 177 232 489	\$ 191 333 433	\$ 206 339 279	\$ 222 301 408	\$ 239 274 126	\$ 257 314 832	\$ 276 484 196	\$ 296 846 346	\$ 308 573 394
\$	25 914 393	\$ 24 800 488	\$ 23 700 675	\$ 22 619 355	\$ 21 560 237	\$ 20 528 402	\$ 19 520 367	\$ 18 544 138	\$ 17 599 266	\$ 16 688 902	\$ 15 807 835	\$ 14 962 547	\$ 14 151 241	\$ 12 958 326

Scenario two: Eucalyptus process (1)

Total Capital Investment									
Total Installed Cost	\$242 546 466.11	Discount Rate	13.52%						
Warehouse	\$ 9 701 858.64	Inflation Rate	6.60%						
Site Development	\$ 21 625 181.95	Income Tax	28%						
Additional Piping	\$ 10 914 590.97	Equity %	40%						
Total Direct Cost (TDC)	\$284 992 097.68	Interest Rate	7%						
Protable Expenses	\$28 499 209.77	Loan Term	10	n					
Field Expenses	\$28 499 209.77	Annual Payment	\$38 953 404.64	Size factor	100				
Home Office & Construction	\$56 998 419.54	Construction							
Project Contingency	\$28 499 209.77	% Spent: Year -2	0%						
Other Costs	\$28 499 209.77	% Spent: Year -1	0%						
Total Indirect Cost	\$170 995 258.61	% Spent: Year 0	100%						
Fixed Capital Investment (FCI)	\$455 987 356.29	TPA Production (tonnes/yr)	16893.65						
South African Location Factor	1	Electricity Production (kWh)	79395000						
Corrected FCI	\$455 987 356.29								
Working Capital	\$22 799 367.81								
Total Capital Investment	\$478 786 724.10	MSP	\$ 22 443	Green Premium	3106%				
Year									
Discount Factor	1.28867904	-1	2016	2017	2018	2019	2020	2021	2022
Fixed Capital Investment	\$0.00	1.1352	0	1	2	3	4	5	6
Working Capital	\$0.00	\$0.00	\$182 394 942.51	0.880902044	0.775988411	0.683569777	0.602158013	0.530442225	0.46726764
Loan Payment	0	0	\$22 799 367.81						
Loan Interest Payment	0	0	\$19 151 468.96						
Loan Principal	0	0	\$273 592 413.77						
TPA Price (\$/tonne)			22442 61914						
TPA Sales		\$	\$ 381 981 240.76	\$ 389 620 865.68	\$ 397 413 282.89	\$ 405 361 548.54	\$ 413 468 779.52	\$ 421 738 155.11	\$ 430 172 918.21
Electricity Price (\$/kWh)		\$	\$ 0.09	\$ 0.10	\$ 0.10	\$ 0.11	\$ 0.12	\$ 0.12	\$ 0.13
Electricity Sales		\$	\$ 7 617 166.30	\$ 8 119 888.62	\$ 8 655 801.26	\$ 9 227 084.15	\$ 9 836 071.70	\$ 10 485 252.43	\$ 11 177 279.09
Total Annual Sales		\$	\$ 389 596 397.06	\$ 397 740 754.19	\$ 406 069 084.15	\$ 414 588 632.69	\$ 423 304 851.22	\$ 432 223 407.54	\$ 441 350 197.30
Other Variable Cost		\$	\$ 333 430 963.65	\$ 344 703 076.06	\$ 349 987 956.83	\$ 355 272 837.61	\$ 360 557 718.38	\$ 365 842 599.16	\$ 371 127 479.93
Fixed Operating Cost		\$	\$ 3 396 101.23	\$ 3 532 517.49	\$ 3 595 575.68	\$ 3 658 633.87	\$ 3 721 692.06	\$ 3 784 750.25	\$ 3 847 808.44
Total Production Cost		\$	\$ 336 827 064.88	\$ 348 235 593.56	\$ 353 583 532.52	\$ 358 931 471.48	\$ 364 279 410.45	\$ 374 975 288.37	\$ 380 323 227.34
Annual Depreciation		\$	\$ 18 239 494.25	\$ 18 239 494.25	\$ 18 239 494.25	\$ 18 239 494.25	\$ 18 239 494.25	\$ 18 239 494.25	\$ 18 239 494.25
Plant Writedown		\$	\$ 18 239 494.25	\$ 18 239 494.25	\$ 18 239 494.25	\$ 18 239 494.25	\$ 18 239 494.25	\$ 18 239 494.25	\$ 18 239 494.25
Depreciation Charge		\$	\$ 437 741 862.04	\$ 437 741 862.04	\$ 437 741 862.04	\$ 437 741 862.04	\$ 437 741 862.04	\$ 437 741 862.04	\$ 437 741 862.04
Remaining Value		\$	\$ -205 194 310.33	\$ -205 194 310.33	\$ -205 194 310.33	\$ -205 194 310.33	\$ -205 194 310.33	\$ -205 194 310.33	\$ -205 194 310.33
Net Revenue		\$	\$ 3 971 840.29	\$ 8 152 393.95	\$ 12 615 949.93	\$ 17 374 546.04	\$ 22 440 901.19	\$ 27 828 459.43	\$ 33 551 436.97
Income Tax		\$	\$ 1 112 115.28	\$ 2 282 670.31	\$ 3 532 465.98	\$ 4 864 872.89	\$ 6 283 452.33	\$ 7 791 968.64	\$ 9 394 402.35
Annual Cash Income		\$	\$ 1 297 883.59	\$ 2 921 146.73	\$ 4 651 742.05	\$ 6 490 944.72	\$ 8 440 644.84	\$ 10 502 745.89	\$ 12 679 162.98
Annual Present Value		\$	\$ 186 311 726.34	\$ 224 345 779.29	\$ 266 776.01	\$ 3 179 790.27	\$ 3 908 574.38	\$ 4 477 274.42	\$ 5 218 959.27
TCI + Interest		\$	\$ -	\$ -	\$ -	\$ -	\$ -	\$ -	\$ -
Net Present Value		\$	\$ -38 034 052.95	\$ -38 034 052.95	\$ -38 034 052.95	\$ -38 034 052.95	\$ -38 034 052.95	\$ -38 034 052.95	\$ -38 034 052.95
IRR			16%						

Scenario two: Eucalyptus process (2)

	2027	2028	2029	2030	2031	2032	2033	2034	2035	2036	2037	2038	2039	2040	2041
\$ 39,535,405	\$ -	\$ -	\$ -	\$ -	\$ -	\$ -	\$ -	\$ -	\$ -	\$ -	\$ -	\$ -	\$ -	\$ -	\$ -
\$ 2,548,354	\$ -	\$ -	\$ -	\$ -	\$ -	\$ -	\$ -	\$ -	\$ -	\$ -	\$ -	\$ -	\$ -	\$ -	\$ -
\$ 27,562,009	\$ -	\$ -	\$ -	\$ -	\$ -	\$ -	\$ -	\$ -	\$ -	\$ -	\$ -	\$ -	\$ -	\$ -	\$ -
\$ 455,502,942	\$ 465,633,001	\$ 474,945,661	\$ 484,444,574	\$ 494,133,465	\$ 504,016,135	\$ 514,096,457	\$ 524,378,986	\$ 534,855,954	\$ 545,556,773	\$ 556,474,530	\$ 567,040,030	\$ 578,956,110	\$ 590,535,732	\$ 602,345,937	\$ 614,392,856
\$ 15,339,658	\$ 14,433,276	\$ 16,401,372	\$ 17,483,828	\$ 18,637,751	\$ 19,867,863	\$ 21,179,131	\$ 22,576,945	\$ 24,067,033	\$ 25,655,457	\$ 27,348,717	\$ 29,153,733	\$ 31,077,879	\$ 33,120,019	\$ 35,316,534	\$ 37,661,534
\$ 470,042,601	\$ 480,068,271	\$ 490,331,533	\$ 500,825,914	\$ 511,617,984	\$ 522,653,896	\$ 533,964,318	\$ 545,567,301	\$ 557,442,909	\$ 569,630,307	\$ 582,129,966	\$ 594,757,435	\$ 608,109,843	\$ 621,611,112	\$ 635,474,956	\$ 649,708,778
\$ 392,287,003	\$ 397,551,884	\$ 402,831,645	\$ 408,121,526	\$ 413,406,526	\$ 418,691,407	\$ 423,978,288	\$ 429,261,168	\$ 434,446,049	\$ 439,630,930	\$ 445,115,811	\$ 450,400,692	\$ 455,685,572	\$ 460,970,453	\$ 466,255,334	\$ 471,540,215
\$ 1,400,041	\$ 1,463,089	\$ 1,428,216	\$ 1,352,274	\$ 1,415,332	\$ 1,478,390	\$ 1,541,449	\$ 1,604,507	\$ 1,667,565	\$ 1,730,623	\$ 1,793,681	\$ 1,856,739	\$ 1,919,798	\$ 1,982,856	\$ 2,045,914	\$ 2,108,972
\$ 396,367,044	\$ 401,711,983	\$ 407,062,922	\$ 412,410,861	\$ 417,758,800	\$ 423,106,739	\$ 428,454,678	\$ 433,802,617	\$ 439,150,556	\$ 444,498,495	\$ 449,846,434	\$ 455,194,373	\$ 460,542,312	\$ 465,890,251	\$ 471,238,190	\$ 476,586,129
\$ 18,239,494	\$ 18,239,494	\$ 18,239,494	\$ 18,239,494	\$ 18,239,494	\$ 18,239,494	\$ 18,239,494	\$ 18,239,494	\$ 18,239,494	\$ 18,239,494	\$ 18,239,494	\$ 18,239,494	\$ 18,239,494	\$ 18,239,494	\$ 18,239,494	\$ 18,239,494
\$ 255,920,920	\$ 237,113,425	\$ 250,634,437	\$ 262,394,943	\$ 274,155,448	\$ 285,916,954	\$ 297,678,460	\$ 309,439,966	\$ 321,199,471	\$ 332,959,977	\$ 344,720,483	\$ 356,480,989	\$ 368,241,495	\$ 379,999,001	\$ 391,756,507	\$ 403,514,013
\$ 5,887,709	\$ 60,111,800	\$ 65,029,117	\$ 70,955,559	\$ 75,619,320	\$ 81,307,663	\$ 87,270,138	\$ 93,515,407	\$ 100,052,858	\$ 106,892,318	\$ 114,044,068	\$ 121,518,800	\$ 129,328,037	\$ 137,483,367	\$ 145,997,272	\$ 173,122,282
\$ 14,008,568	\$ 16,831,304	\$ 19,028,153	\$ 19,654,756	\$ 21,173,320	\$ 22,766,146	\$ 24,435,639	\$ 26,184,314	\$ 28,014,800	\$ 29,929,649	\$ 31,932,339	\$ 34,025,866	\$ 36,211,850	\$ 38,495,343	\$ 40,870,236	\$ 48,474,233
\$ 19,013,593	\$ 61,519,900	\$ 65,600,458	\$ 68,780,286	\$ 72,685,745	\$ 76,791,014	\$ 81,075,994	\$ 85,570,587	\$ 90,277,552	\$ 95,201,963	\$ 100,351,223	\$ 105,733,088	\$ 111,355,681	\$ 117,227,518	\$ 123,357,530	\$ 124,648,028
\$ 5,603,067	\$ 15,240,252	\$ 14,205,238	\$ 13,228,880	\$ 12,342,945	\$ 11,459,564	\$ 10,619,971	\$ 9,910,465	\$ 9,377,366	\$ 8,555,997	\$ 7,944,655	\$ 7,373,088	\$ 6,841,006	\$ 6,344,023	\$ 5,880,693	\$ 5,234,408

Scenario two: Starch process (1)

Total Capital Investment									
Total Installed Cost	\$ 316 283 351.60								
Wirehouse	\$ 3 121 654.00								
Site Development	\$ 7 023 744.00								
Additional Piping	\$ 3 511 872.00								
Total Direct Cost (TDC)	\$ 29 840 631.60								
Proratable Expenses	\$ 2 994 063.16								
Field Expenses	\$ 2 994 063.16								
Home Office & Construction	\$ 5 988 126.32								
Project Contingency	\$ 2 994 063.16								
Other Costs	\$ 2 994 063.16								
Total Indirect Cost	\$ 17 964 376.96								
Fixed Capital Investment (FCI)	\$ 47 905 010.57								
South African Location Factor	1								
Corrected FCI	\$ 47 905 010.57								
Working Capital	\$ 2 395 250.53								
Total Capital Investment	\$ 50 300 261.08								
Year	-2								
Discount Factor	1.289								
Fixed Capital Investment	\$ 0.00								
Working Capital	\$ 0.00								
Loan Payment	0								
Loan Interest Payment	0								
Loan Principal	0								
TPA (Rhone)	0								
TPA Sales	0								
Breakdown Sales	0								
Total Annual Sales	0								
Other Variable Cost	0								
Fixed Operating Cost	0								
Total Production Cost	0								
Annual Depreciation	0								
Plant Writedown	0								
Depreciation Charge	0								
Remaining Value	0								
Net Revenue	0								
Income Tax	0								
Annual Cash Income	0								
Annual Present Value	0								
TCI + Interest	0								
Net Present Value	0								
RR	16%								

Scenario two: Starch process (2)

	2028	2029	2030	2031	2032	2033	2034	2035	2036	2037	2038	2039	2040	2041
	12	13	14	15	16	17	18	19	20	21	22	23	24	25
	0.218	0.192	0.169	0.149	0.131	0.116	0.102	0.090	0.079	0.070	0.061	0.054	0.046	0.042
\$	\$	\$	\$	\$	\$	\$	\$	\$	\$	\$	\$	\$	\$	\$
\$	-0.00	-0.00	-0.00	-0.00	-0.00	-0.00	-0.00	-0.00	-0.00	-0.00	-0.00	-0.00	-0.00	-0.00
\$	-0.00	-0.00	-0.00	-0.00	-0.00	-0.00	-0.00	-0.00	-0.00	-0.00	-0.00	-0.00	-0.00	-0.00
\$	2.453	2.502	2.552	2.603	2.655	2.708	2.762	2.817	2.874	2.931	2.980	3.050	3.111	3.173
\$	41 394 193	42 211 876	43 056 114	43 917 236	44 795 581	45 691 993	46 605 322	47 537 429	48 488 171	49 457 941	50 447 100	51 456 042	52 485 163	53 534 866
\$	917 169	926 340	935 604	944 960	954 509	963 953	973 593	983 329	993 162	1 003 094	1 013 125	1 023 256	1 033 489	1 043 823
\$	42 301 361	43 138 217	43 991 718	44 862 196	45 749 900	46 655 446	47 578 915	48 520 758	49 481 340	50 461 035	51 460 225	52 479 298	53 518 651	54 578 689
\$	25 152 731	25 882 714	26 612 697	27 342 680	28 072 662	28 802 645	29 532 628	30 262 611	30 992 593	31 722 576	32 452 559	33 182 542	33 912 525	34 642 507
\$	9 116 163	9 252 185	9 398 206	9 524 228	9 660 250	9 796 271	9 932 293	10 068 314	10 204 336	10 340 358	10 476 379	10 612 401	10 748 422	10 884 444
\$	34 268 892	34 734 889	35 200 903	35 666 908	36 132 912	36 598 916	37 064 921	37 530 925	37 996 929	38 462 934	38 928 938	39 394 943	39 860 947	40 326 951
\$	4%	4%	4%	4%	4%	4%	4%	4%	4%	4%	4%	4%	4%	4%
\$	\$1 916 200	\$1 916 200	\$1 916 200	\$1 916 200	\$1 916 200	\$1 916 200	\$1 916 200	\$1 916 200	\$1 916 200	\$1 916 200	\$1 916 200	\$1 916 200	\$1 916 200	\$1 916 200
\$	\$22 694 405	\$21 075 205	\$19 162 004	\$17 245 804	\$15 329 603	\$13 413 403	\$11 497 203	\$9 581 002	\$7 664 802	\$5 748 601	\$3 832 401	\$1 916 200	\$0.00	\$0.00
\$	6 116 266	6 487 117	6 874 614	7 279 068	7 700 678	8 140 329	8 597 794	9 073 632	9 568 210	10 081 901	10 615 086	11 168 155	11 741 504	12 331 736
\$	1 712 553	1 616 393	1 524 892	1 438 145	1 355 246	1 275 292	1 198 382	1 124 617	1 054 099	9 879 532	9 222 224	8 592 053	7 992 621	7 425 467
\$	6 319 912	6 586 925	6 865 922	7 157 144	7 460 832	7 777 237	8 106 612	8 449 216	8 805 311	9 175 169	9 559 062	9 957 272	10 370 683	10 801 251
\$	1 379 884	1 266 898	1 163 263	1 068 204	980 910	900 730	827 059	759 346	697 103	639 673	587 250	536 860	494 362	450 914