UNIVERSITY OF
KWAZULU-NATAL

PLANT-BASED CARBON FLOW ANALYSIS OF SOUTH AFRICAN PULP MILLS

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A thesis submitted in fulfilment of the requirements of Masters of Science degree in Engineering, in the School of Chemical Engineering at the College of Agriculture, Engineering and Science, University of KwaZulu-Natal, Durban South Africa.

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July 2015

Key-words: MFA, Pulping, Carbon flows, Carbon transfer, Pulp mill, South Africa

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Acknowledgments

I would like to extend my deepest gratitude to the following individuals for their contributions towards this project:

1. My supervisors: Mr Iain Kerr and Prof. Chris Buckley for all the support they provided me. I could never have asked for better supervisors.
2. PAMSA for granting me this grand opportunity to conduct a study in the pulp and paper industry. I have learnt a lot and it is my wish to continue learning more in the industry.
3. The production managers and engineers at the pulp and paper mills for going out of their way to assist me with whatever data I requested.
4. My family for their unwavering support throughout my schooling years.
5. Everyone at PRG for making my time there, a memorable and pleasurable one.

Abstract

The aim of this study was to track and quantify the carbon flows from natural resources such as wood and bagasse, as it flows through the pulp mills of South Africa. This study is one of four projects aimed at conducting a complete carbon flow analysis for the entire forest products industry in order to assess the environmental sustainability of the industry with respect to carbon. The pulp mills investigated fall under the auspices of the Paper Manufactures Association of South Africa (PAMSA); and they belong to the parent companies: Sappi, Mondi and Mpact. This study is envisaged to provide decision makers in the pulp and paper industry with quantitative evidence on pulp mill carbon flows, which will aid them in deciding on the type of pulp mills to build in the future which will have the least effect with respect to solid and liquid effluent generation and climate change. It should also assist them in deciding on which type of raw material is best to use, be it wood or bagasse that will have the lowest environmental impacts.

From July 2016, the National Treasury of South Africa will be imposing a carbon tax at a rate of R120 per tonne of CO_2 emitted with an annual increase of 10% for the first five years, until 31st December 2019. There will be an initial 60% rebate on the tax (referred to as basic tax-free threshold) which will decline every year. The aim is to reduce the national greenhouse gas (GHG) emissions by 34% by 2020 and 42% by 2025 (Department Of National Treasury, 2013b). This was an undertaking which South Africa committed to at the Copenhagen climate change Conference of Parties (COP16) in December 2010.

To effectively track and quantify the flow of carbon, a material balance and hence a carbon balance over each of the pulp mills was conducted. The data used for generating the mass balances was sourced from each of the pulp mills investigated, and in some instances, estimations have been made from the literature. While the work focused on only carbon emanating from plant material used in the production of pulp, it is worth noting that there are other sources of carbon in the pulp and paper industry such as coal and natural gas which are significant.

Overall, the results indicate that about 39% of the original carbon stock ends up in the pulp, whilst the remaining 61% is lost through air emissions and solid and liquid effluents generated from the pulping processes. Furthermore, mechanical pulps served as a huge reservoir for the carbon because there was an 80% carbon transfer from the wood to these pulps. Dissolving pulp on the other hand, had the lowest carbon transfer (i.e. 36%). Finally, it was found that if the bigger pulp mills such as Mondi Richards Bay and Sappi Ngodwana were to increase the pulp yield on their kraft processes by 5%, this would increase the overall carbon stored in pulp by 2% for the South African pulp sector.

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Abbreviations

ADt	Air dry tonne
A. mearnsii	*Acacia mearnsii*
BDt	Bone dry tonne
BL	Black liquor
CE	Causticizing Efficiency
CO_2	Carbon-dioxide
DTPA	Diethylenetriaminepentaacetic acid
DNT	Department of National Treasury
E. grandis	*Eucalyptus grandis*
EDTA	Ethylenediaminetetraacetic acid
EU	European Union
FAO	Food and Agriculture Organisation
FSA	Forestry South Africa
FSC	Forest Stewardship Council
HW	Hardwood
IPCC	Intergovernmental Panel on Climate Change
ISO	International Organization for Standardization
LCA	Life Cycle Analysis
MFA	Material Flow Analysis
MIPS	Material intensity per unit service
ML/d	Mega litres per day
Mt	Megatonne (1Mt = 10^6 Kg)

NSSC	Neutral Sulphite Semi-chemical Pulping
P. patula	*Pinus patula*
PAMSA	The Paper Manufacturers Association of South Africa
SADC	Southern African Development Community
SASAQ	Semi Alkaline Sulphite Anthraquinone
SW	Softwood
t/ton	(metric) tonne
Tg	Teragram (1Tg = 10^9 Kg)
TMP	Thermo-Mechanical Pulping
UNFCCC	United Nations Framework Convention on Climate Change
VOCs	Volatile Organic Compounds

Glossary

Bagasse	Fibrous residue retained from sugarcane after the sugar juices have been extracted
Bark	Outermost layer of wood
Black liquor	White liquor with dissolved lignin and other wood degraded components
Brown-stock	Fibrous material suspended in dissolved lignin and water after leaving the digester
By-product	A secondary product other than the primary product produced from a manufacturing process
Carbon cycle	A cycle that describes the movement of carbon as it is used up by all ecosystems on earth and is eventually recycled back into the atmosphere
Carbon positive	Activities that reduce CO_2 emissions into the atmosphere
Carbon sink	A reservoir that absorbs more carbon than it emits
Causticizing efficiency	A measure of the degree to which causticizing reactions reach completion
Char	Solid material that remains after completion of pyrolysis
Clarifier	A large circular tank used for removing small quantities of fine solids to obtain a clear liquid
Coarseness	Defined as mass of fibre per unit length. Course fibres are good for strong paper manufacture but also promote uneven paper formation
Dead load	Inorganic chemicals that do not part take in the chemical reaction in the digester but rather circulate within the pulping and recovery loop
Debris	Non process related solids removed during screening

Delignification	Process where lignin is dissolved in cooking liquor
Digester	Pressurized vessel where chemical reactions involving lignin dissolution occur
Dissolving pulp	Pulp with very high cellulose content usually greater than 90%
Dregs	Dark insoluble material recovered from green liquor
Drum debarker	Relies on friction between logs to remove barks with the aid of a rotating drum. The degree of debarking is determined by the retention time in the debarker
Environmental management	Seeks to identify and minimise environmental issues emanating from human activities and their effect on the natural ecological systems
Exergy	The maximum theoretical work that can be obtained from an energy source by bringing it into equilibrium with its surroundings using a reversible process
Extractives	Light weighted organic compounds in woods usually responsible for turpentine production
Flocs	Fibres clumped together
Fluting	The wavy paper that is often seen in between the liners in corrugated board
Green liquor	Liquor produced by dissolving the smelt stream from the recovery boiler in water
Greenhouse effect	Increase in global temperatures as a result of gasses such as methane and carbon-dioxide trapping heat in the atmosphere
Grits	Oversized and unreacted lime from the recaustisizing plant that is sent for disposal
H-factor	A function combining time and temperature that is used to determine degree of delignification

Holocellulose	Carbohydrate portion of wood that includes the polysaccharides, cellulose and hemicellulose but not lignin and extractives
Hydraulic debarker	A debarker that removes bark and dirt from wood with high pressure water sprays (≥6.8atm)
Hypo number	A measure of lignin content of pulp using chlorine dioxide
Impregnation	Addition of active cooking chemicals to chips to ensure good penetration of liquor into the wood chip
K number	Also known as the permanganate number. It is a measure of the lignin content of pulp using permanganate to oxidize the residual lignin
Kappa number	A measure of lignin content defined by the volume of potassium permanganate consumed by one gram of dry pulp
Lignin	An organic chemical that binds the fibres in wood together and also imparts a dark colour to pulp after cooking
Lignosulphonate	Anionic polymer of lignin which is a by-product from sulphite pulping
Liquor penetration	Transfer of active cooking chemicals through the air-filled void within wood chips
Memo Items	Categories shown for the purposes of providing information but not to be included in national total greenhouse gas emissions (i.e. with respect to IPCC guidelines)
Methanogenic bacteria	Bacteria that produce methane from the decomposition of organic waste
Normal distribution	A continuous probability distribution symmetrical about the mean but never takes on the value zero
Opacity	Ability of pulp to resist light from penetrating through it

Pith	Non fibrous mass found in bagasse that contributes to excessive consumption of caustic during pulping and also affects pulp quality
Polymerization	Reaction of monomer molecules to form polymer chains
Pulp	A fibrous material produced either chemically or mechanically from wood, fibrous crops or recycled paper
Pulp consistency	Ratio of bone dry weight of pulp to the weight of pulp plus water
Pulp yield	The mass ratio of oven dry pulp to oven dry wood
Random variable	A variable that can take on different values each with a certain probability
Recovery boiler	Major process equipment in a kraft mill where black liquor solids are incinerated to recover the white liquor constituents and generate energy
Sequestration ratio	Ratio of the quantity of carbon stored in the biosphere to the carbon emitted into the atmosphere
Shives	Bundles of fibres that have not been separated
Substrate	A layer or substance on which bacteria grow
Suspended solids	Fine particles that remain in suspension while in water
Tall oil	An odorous by-product formed mainly from pulping softwoods by the kraft process
Tensile strength	Maximum stress a fibre can endure while stretched until the point it breaks
Trade balance	The difference between exports and imports
Turpentine	A volatile organic by-product produced during delignification in the digester.

Waste management	Refers to monitoring and managing wastes produced from industrial systems
White liquor	Strong alkaline solution used for kraft cooking comprised mainly of sodium hydroxide and sodium sulphide
Wood composition	Relates to the proportions of cellulose, hemicelluloses, lignin and extractives in wood

Chapter 1. Introduction

This section presents the general frame work for this research project. It will provide the reader with an overview of Material Flow Analysis, its relevance to the pulping sector and the goals and proposal of this study.

1.1 Material (carbon) Flow Analysis and carbon stocks and flows

Material flow analysis is a systematic approach to reconstructing the stocks and flows of a material, compound or element through an economic system and the environment (Hendriks *et al.*, 2000). It applies to substances (e.g. carbon) that raise particular concern regarding their sustainability. This Material Flow Analysis seeks to provide decision makers (e.g. Forestry South Africa and The Paper Manufacturers Association of South Africa [PAMSA]) with empirical data and evidence on carbon flows through pulp mills. This will enable them to make informed decisions regarding the efficient use of resources in pursuit of sustainable development.

Examples of environmental concerns facing our planet include ozone depletion and global warming. They are caused by the flow of materials through the economic system and the environment (Ščasný *et al*., 2003). For instance, the flow of carbon to the atmosphere exerts pressure on the environment, and as such, any increments in the carbon flows would cause an increase in environmental pressure. Figure 1.1 shows the exponential increase in atmospheric CO_2 since the beginning of the 17th century.

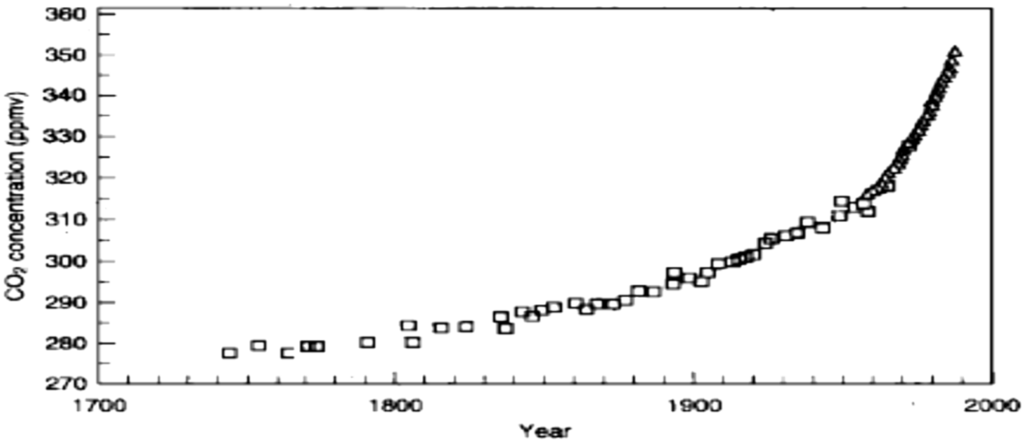

Figure 1.1: Exponential increase in atmospheric CO_2 (Gradel and Allenby, 1995)

As the concentration of CO_2 continues to climb, it is predicted that global temperatures will increase by 2 to 5 C° by the year 2050 (Gradel and Allenby, 1995). Also, the CO_2 emissions from forest harvesting and wood products on a global scale are tremendously significant. Using data from the Food and Agriculture Organisation (FAO), Winjum *et al*. (1998) estimated total carbon emissions at 980 Tg C/yr. The CO_2 emissions from wood based products are not to be included in the national totals for the energy sector (Pingoud *et al*., 2006), but rather labelled as 'memo items' for the purposes of quality assurance and control (QA/QC). The need to curb carbon emissions is imperative, especially in a dynamic industry such as the pulp and paper industry which receives its raw materials from carbon rich plantations.

It is interesting to note that there is an increasing trend observed in the carbon stored in wood products worldwide (see Figure 1.2). However, this increasing trend may not necessarily be significant in every country. This trend has been confirmed by various studies, and it has thus become important to monitor the changes in the carbon stored in wood products because this affects the natural carbon cycle.

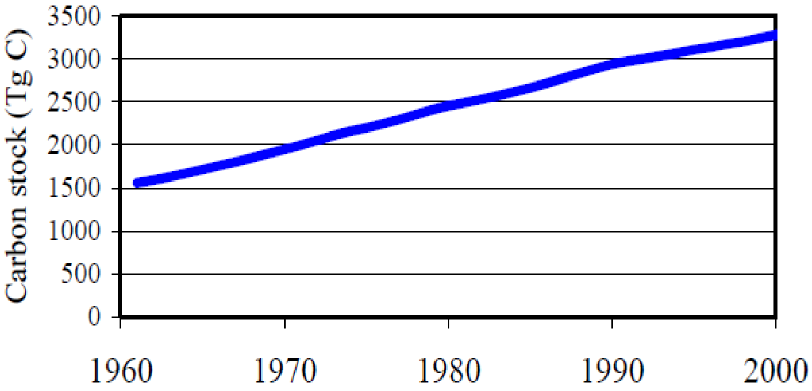

Figure 1.2: Global carbon stock in wood products from 1960 to 2000 (UNFCCC, 2003)

It has been reported that the carbon stocks in wood products increased from 1 500 Tg C in the year 1960 to 3 000 Tg C in the year 2000 (UNFCCC, 2003). Furthermore, it is estimated that this stock change amounts to about 2% of worldwide CO_2 emissions resulting from fossil fuel combustion (Brown *et al.*, 1998).

As a standard (Kyoto Protocol standard), CO_2 emissions from wood based carbon are not counted as emissions because it is assumed that the carbon is derived from sustainably grown forest plantations. Unfortunately, from July 2016, the National Treasury of South Africa will be imposing a tax of R120/tonne of CO_2 emitted from burning fossil fuels (coal, oil and gas) in addition to burning biomass such as black liquor and bark which are derived from wood (Department Of National Treasury, 2013b). The pulp and paper industry will however be given a tax free threshold of 60%, meaning that only 40% of the carbon emitted will be taxed.

These carbon taxes are being implemented as South Africa takes a bold and proactive approach to reducing its greenhouse gas emissions (GHG) by 34% by the year 2020 and 42% by the year 2025 (Department Of National Treasury, 2013a), in a drive towards establishing a green economy.

1.2 Overview of the pulp sector

South Africa is the 16th largest pulp producer in the world (Kerr, 2013). In 2011, the pulp and paper industry had the largest contribution (45%) to the GDP of the forest products sector which amounted to 606 billion US dollars (Lebedys and Li, 2014). More interestingly, the forestry, timber, pulp and paper sectors are viewed as contributing to black economic empowerment and the upliftment of poverty stricken communities in South Africa.

Raw materials for pulping are sourced from sustainably grown plantations certified by the Forest Stewardship Council. Pulping methods that are currently being used within the industry include: chemical, semi-chemical and mechanical pulping processes (described in detail in Section 3.3). Although some of the pulp is used domestically for paper related products, much of it is exported mostly to regions such as the EU, South and East Asia and the SADC. Figure 1.3 is a schematic representation of the value of pulps imported and exported by South Africa between the period 1998 and 2012 expressed in 2012 Rands.

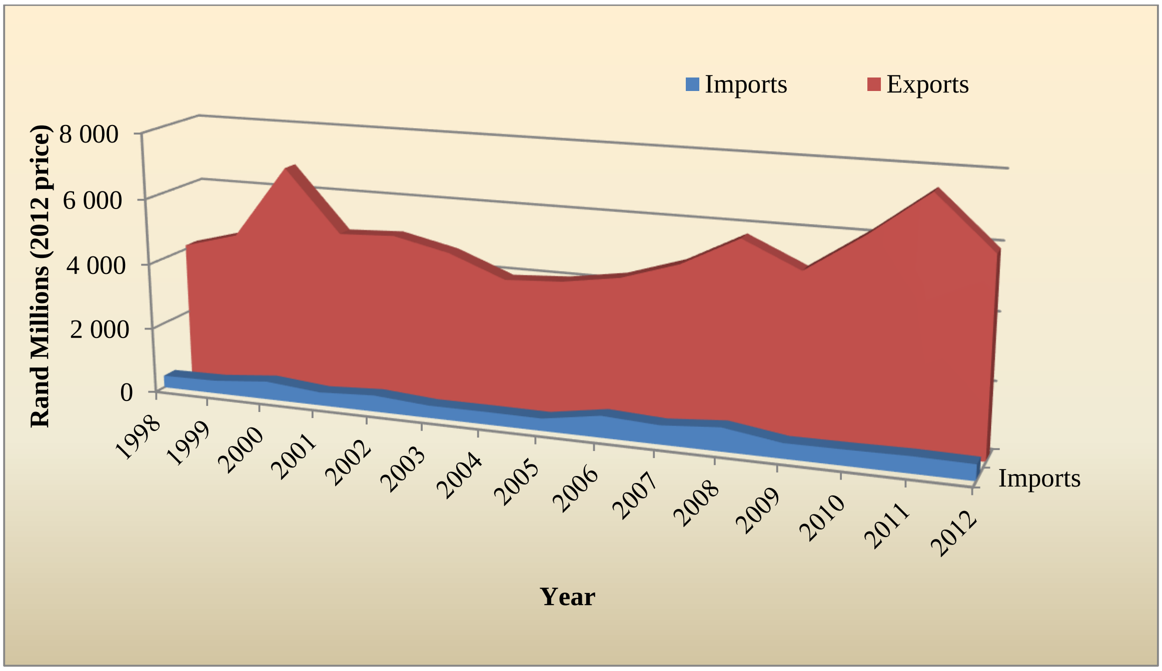

Figure 1.3: Value of imports and exports of pulp from 1998 to 2012

Figure 1.3 was reconstructed from data sourced from Forestry South Africa (see Appendix 7). The graph clearly reveals that over the past decade, South Africa has always had a positive trade balance since the exports exceed imports by a significant amount.

Pulp manufacturing is highly capital intensive and has thus resulted in only three companies holding a monopolist share in the South African pulp market. The companies are Mondi, Mpact and Sappi. Their respective pulp mills are as follows:

Mondi Mills: Mondi Richards Bay and Mondi Merebank

Mpact Mills: Mpact Piet Retief and Mpact Felixton

Sappi Mills: Sappi Saiccor, Sappi Ngodwana, Sappi Tugela and Sappi Stanger

Figure 1.4 illustrates the location of the pulp and paper mills in South Africa.

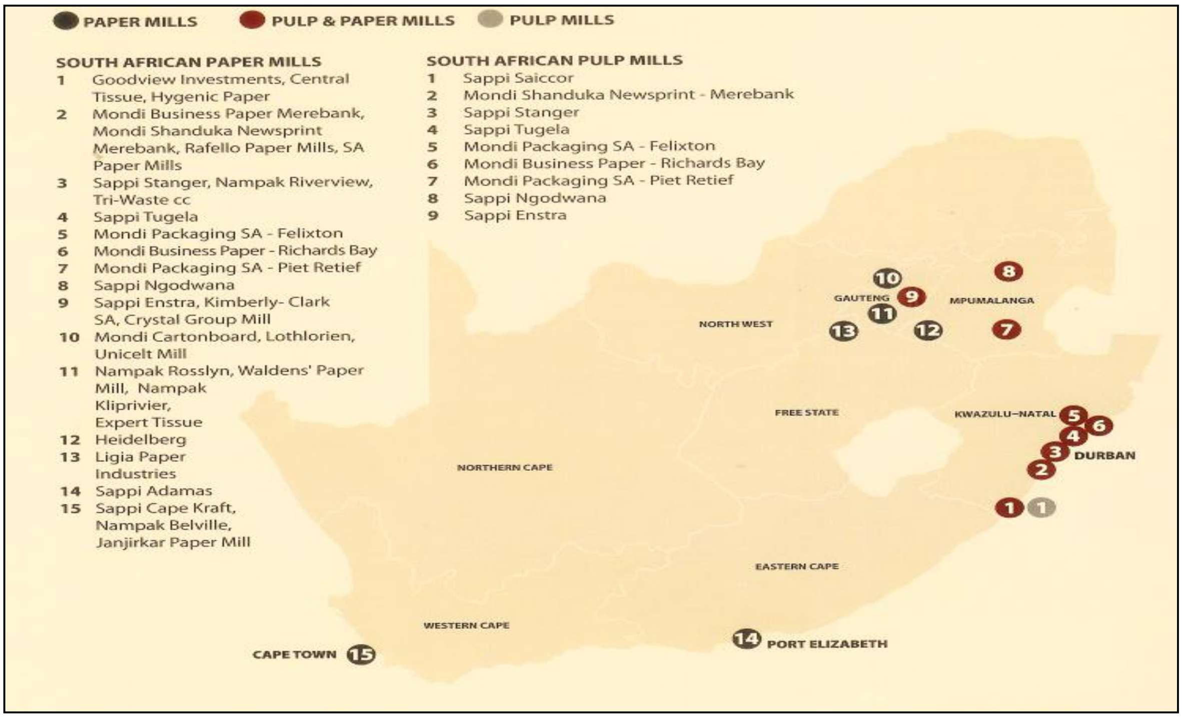

Figure 1.4: Location of pulp and paper mills in South Africa (Kerr, 2013)

From Figure 1.4, it is evident that many of the mills are located in the Mpumalanga and along the coast of KwaZulu-Natal. The locations are convenient since many of the tree plantations grow well in these geographical regions, while at the same time allowing easy access to ports for the export of pulp.

1.3 Focus of the study

In this study, a Material Flow Analysis with respect to elemental carbon will be conducted for the major pulp mills in South Africa. Carbon flows for all South African pulp mills which are members of the Paper Manufactures Association of South Africa will be quantified, culminating in a single integrated system from which the carbon flows will be analysed. Figure 1.5 is a typical example of a sankey diagram showing the different carbon inputs and the fate of the carbon.

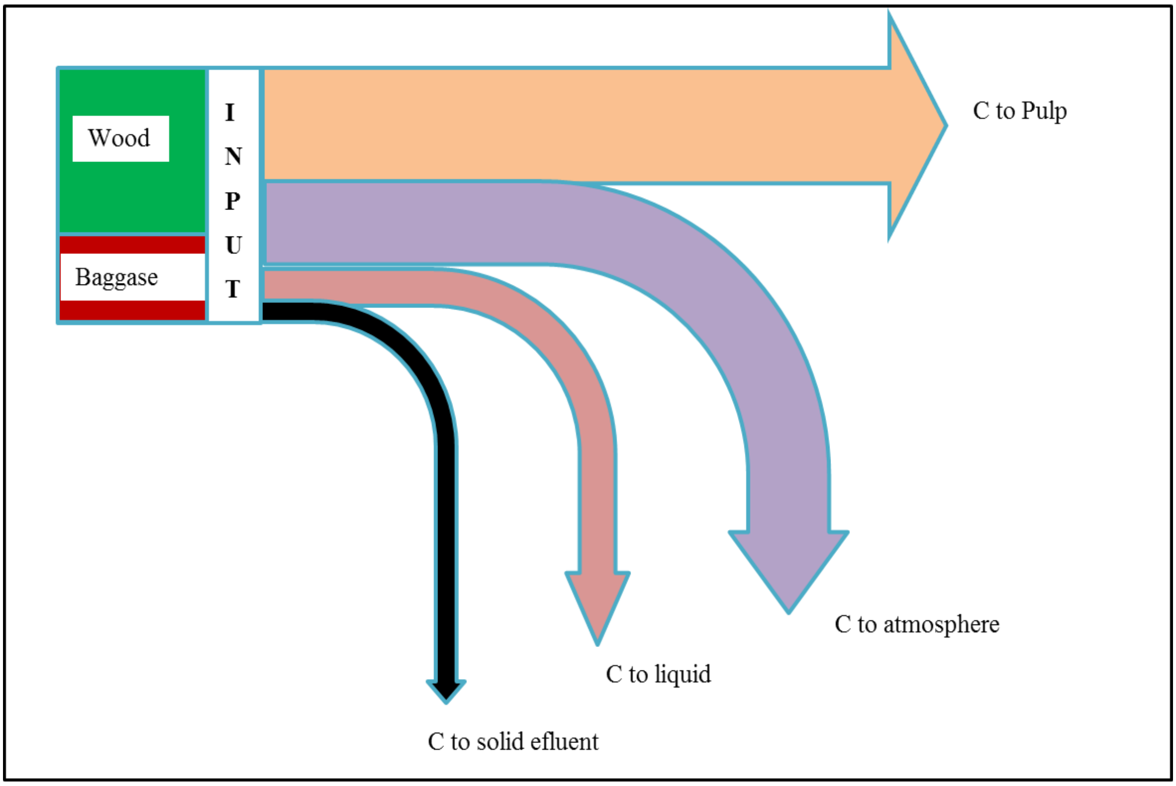

Figure 1.5: Sankey diagram showing the carbon inputs and outputs for the pulp sector

The primary source of carbon into the sector originates from wood, mostly *Eucalyptus grandis* and *Pinus patula*, as well as sugarcane bagasse. As wood and bagasse are transformed into pulp products, various by-products containing carbon are formed and subsequently emitted into the environment, either in the form of solid wastes sent to landfill (e.g. pulp mill rejects), gases emitted into the atmosphere (e.g. carbon-dioxide) or as organic fragments (e.g. lignin) in waste water drains.

The study will consider specifically only carbon inputs originating directly from plant resources (i.e. plant-based carbon) and also determine the fate of the carbon as it flows within the sector.

1.4 Importance of the study

The forestry, pulp and paper industry is associated with a substantial flow of carbon originating from extracted resources such as wood and bagasse. Though much of the carbon is locked up in the pulp produced, a significant portion is released directly into the environment as a result of pulping.

Once the flow of carbon into and out of the industrial sector and the environment is understood, the formulation of a strategic plan to utilise resources more efficiently can be sought. For instance, if a new pulp mill needs to be built, decision makers can make a decision with regard to mills that have the least environmental impact with respect to resource use, solid and liquid effluent generation and climate change.

This study is one of a series of projects aimed at compiling a complete Material Flow Analysis with respect to plant-based carbon over the entire forest products sector of South Africa (pulp, paper, printing, publishing, furniture, mining timber, charcoal etc.).

In the broader context, the fundamental idea is to determine if the forest products sector is a carbon sink. This is directly linked to the ability of the industry to absorb more carbon than it is emitting. This poses the fundamental question regarding whether the industry's activities are carbon positive, and whether the industry can be viewed as being environmentally sustainable with respective to carbon. The data gathered from this study can also facilitate a future Life Cycle Analysis for the entire forest products industry.

1.5 Aims

The aims of this research project are to:

- Track the wood and bagasse carbon flows and to determine the fate of the carbon as it flows through the South African pulp sector.
- Quantify all carbon inputs and outputs from each of the South African pulp mills.

1.6 Scope and limitations

The flow of carbon in forestry operations (e.g. carbon uptake by roots and absorption by trees and sugarcane, and decay of organic matter) will not be considered in this study. While some of the mills are integrated pulp and paper mills, this study will be restricted to investigating the flow of carbon through the pulping and bleaching processes only. Furthermore, as a point of reference, only data from the year 2011 will be used. The following related carbon flows will not be considered in the overall inputs or outputs of the system, however, they may be required in performing certain carbon balances. They are:

1. Carbon in coal used for electricity generation
2. Carbon in natural gas used to power the lime kilns
3. Carbon in calcium carbonate used in causticizing plants
4. Carbon in the salt cake fed to kraft recovery boilers

The reason they are not considered is because they are not part of the flow of carbon from the extracted resources (i.e. wood and bagasse).

1.7 Proposal

- The carbon flows in the major pulp mills in South Africa are affected by (or depend on) the type of raw materials (wood or bagasse) used and the pulping processes employed.

1.8 Structure and presentation of the dissertation

Chapter 2 describes the method of Material Flow Analysis as an environmental tool for resource management and how it compares with the Life Cycle Analysis. The section concludes with the theoretical basis of the error analysis employed in the study.

Chapter 3 looks at the different constituents that makeup wood and bagasse as well as their elemental composition. The chapter further explores the different pulping processes employed within the South African pulp sector. The chapter also gives a description of each of the individual mills regarding their production capacity, the type of raw materials used and the pulps produced.

Chapter 4 considers the application of MFA in the context of the pulp sector. It looks at different material flow related issues, the flow of lignin in the pulp sector and carbon flows to landfill. The chapter concludes with a list of material flow related studies that have been conducted in the forest products industry of which the pulp sector is a subsidiary.

Chapter 5 gives a description of the mass balance method conducted for each type of pulping process. Where similar methods to other pulping processes are to be applied have been highlighted.

Chapter 6 presents the results and discussions for each of the mills investigated. A material flow diagram and a bar graph showing the distribution of carbon is presented. The section concludes by comparing the different flows of carbon to air, liquid and solid effluents depending on the type of pulp produced and the raw materials used.

Chapter 7 summarises the carbon flows and shows how this ties up with the proposal of the study. A set of recommendations are given on how to improve on future carbon balance assessments and possible investigations into projects that lead to a lower carbon economy.

Chapter 2. Material Flow Analysis

This section presents a holistic overview of Material flow analysis, its strengths, how it compares with Life Cycle Analysis and a description of the procedures followed in conducting a Material Flow Analysis.

2.1 An Overview

Material Flow Analysis is a systematic reconstruction of the way an element, compound or material flows within an industrial system in a given space and time. It seeks to quantify the inputs and outputs of a given system based on physical units, usually reported in tonnes. Material Flow Analysis can be used not only as a tool to identify issues related to resource utilisation and environmental management, but also as a tool for making informed and knowledgeable decisions on the issues identified (Hendriks *et al*., 2000). Figure 2.1 is a simple model of a pulp sector Material Flow Analysis.

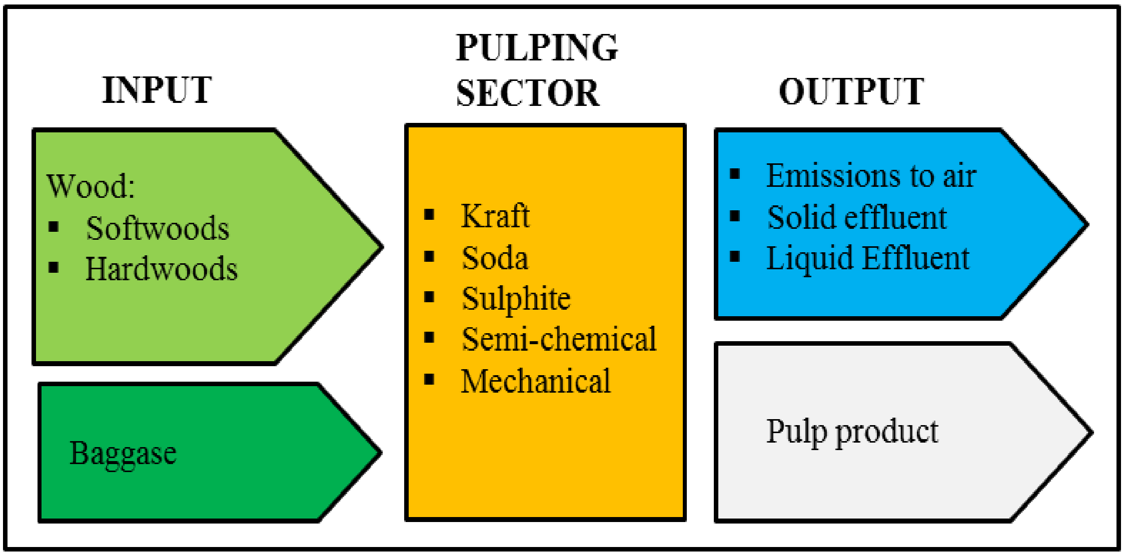

Figure 2.1: A simple model for Material Flow Analysis

The methodological platform of MFA can be divided into two groups: namely dematerialization and detoxification (Ščasný *et al*., 2003). Dematerialization looks at the metabolic efficiency of an industrial sector from a sustainable point of view with the aim of managing resources more efficiently. Conversely, detoxification analysis seeks to mitigate the environmental pressures resulting from a firm’s activities due to flows of substances with high environmental impact. The results from such a study are usually integrated into a model for risk assessment or mitigation.

2.2 Why Material Flow Analysis?

In order to abate and control potential environmental problems which may occur as a result of direct emissions from production systems (e.g. CO_2 and SO_2) or accumulation of hazardous waste in the environment (e.g. pulp mill rejects to landfills), it is important to analyse and evaluate the physical stocks and flows of materials through production systems.

Material Flow Analysis strives to quantify and identify the pathways and the fate of substances through production systems. In so doing; this allows the detection of relevant flows or control points within the system which show the greatest possibilities for improvement.

More importantly, the results of an MFA study can guide stakeholders and other interested parties in designing processes and products that steer towards resource conservation, environmental protection and waste minimisation.

One of the most powerful attributes of MFA as described by Brunner and Rechberger (2004) is the ability to recognise environmental problems that may occur in the future.

2.3 Material Flow Analysis vs. Life Cycle Analysis

The audience for MFA findings includes technical expects in the field of LCA and MFA. For this reason, it is worth discussing the relative differences between the two fields.

While MFA focuses on the analysis of the mass balance of a given industrial sector, LCA seeks to evaluate the various environmental impacts of a product from its point of extraction through to disposal (cradle to grave). Life Cycle Analysis strives for completeness by considering as many substances as possible, whereas MFA focuses on a single substance at a time to promote transparency and aid manageability (Brunner and Rechberger, 2004).

Material Flow Analysis by itself is inadequate in providing a comprehensive assessment on resource management, waste management and environmental management. Rochat *et al.* (2013) have discussed the application of an integrated MFA-LCA approach, which is a powerful combination that reveals a holistic view of the system in terms of material flows and also provides reliable data on environmental impacts. Material Flow Analysis can also be viewed as a method for developing an inventory for an LCA study. In this regard, it is clear that the starting point of an LCA is the MFA (Brunner and Rechberger, 2004).

In conducting either an MFA or LCA study, the first step is to define the goals and scope of the study. For MFA, indicator substances are carefully chosen in view of their environmental impacts. The flows of the indicator substances are quantified based on their concentration in a given stream and by applying mass conservation principles. The system is then analysed to identify weak points after which the results are presented in a clear and comprehensible format so that policy driven decisions can be drawn. The results may also include interpretation using scenario analysis.

For LCA, there is the life cycle inventory aspect that involves the compilation of data to quantify input and output flows, and also evaluate emissions and resource consumption. Life Cycle Analysis also makes use of functional units and procedural ISO standards all of which are uncommon and not formally defined in MFA studies. The information from the lifecycle inventory is used to evaluate the environmental effects and pressures posed by the substances investigated. An improvement assessment is then carried out to assess and reduce the environmental burden of substances or the processes investigated.

Table 2.1 provides a summary on the methodological differences between MFA and LCA as discussed.

Table 2.1: Differences between Material Flow Analysis and Life Cycle Analysis

MFA **(Montangero *et al.*, 2006)**	**LCA** **(Boguski *et al.*, 1996)**
1. Identification of material flow related issues	1. Goal definition and scoping
2. Selection of relevant substances, processes and system boundaries	2. Life cycle inventory
3. Quantification of mass flows of substance and stocks	3. Impact assessment
4. Identification of weak points within the system	4. Improvement assessment
5. Development and evaluation of scenarios	

2.4 Framework of Material Flow Analysis

In this section, the five components listed in Table 2.1 for conducting MFA will be elaborated.

2.4.1 Identification of material flow related issues

As discussed earlier, the pulp and paper industry is facing possible future carbon taxes for the CO_2 emitted into the atmosphere from process operations. Other considerations involve the disposal of liquid and solid effluents. These are all issues that need to be addressed in order to ensure that the effluents generated are within the assimilative capacity of the earth, and are thus sustainable.

2.4.2 Selection of relevant substances, processes and system boundaries

One of the key objectives of MFA is to develop a simplified model that is a trustworthy representation of reality. This can be achieved by reducing the complexity of the system while at the same time extracting as much information as possible with minimum effort (Brunner and Rechberger, 2004). Additionally, a simplified system promotes transparency and aids manageability.

2.4.3 Quantification of substance mass flows and stocks

The law of conservation of mass, also commonly referred to as the first law of thermodynamics is the fundamental principle applied in all MFA studies. It states that the total mass of inputs into a system must be equal to the total mass of outputs and the mass accumulation within the system. The law can be described by Equation (2.1).

$$\sum \dot{m}_{\mathrm{inputs}} = \sum \dot{m}_{\mathrm{outputs}} + \dot{m}_{\mathrm{accumulation}} \qquad (2.1)$$

The law holds for the overall system and sub processes within the system. If the concentration of a particular substance in a given stream is known, the substance flow rate (X_i) is determined by multiplying the concentration (c_i) by the stream flow rate (m_i) as shown by Equation (2.2).

$$X_i = c_i \times m_i \qquad (2.2)$$

Where i = stream number

Mass conservation must holds for each substance. If not, this can be attributed to flows omitted in error or simply incorrect concentrations. An additional technique to aid in mass balancing is the use of the so called ‘proxy data’ which allows data estimation of a given system by comparing with similar systems (Brunner and Rechberger, 2004).

Data for the mass balance can be sourced from the literature, national reports, different companies, and by contacting engineers at the pulp mills.

2.4.4 Identification of weak points in the system

Information drawn from the mass balances can be used to identify critical processes or flows within the system. Scenario based approaches can then be employed to minimise environmental degradation or improve resource consumption.

2.4.5 Presentation and evaluation of results

The results from a Material Flow Analysis study need to be clear and understandable so that stakeholders can interpret them and make decisions based on them. Evaluation methods are used to interpret the results of the mass balance and to measure the environmental performance of the system. Next, the evaluation methods for MFA will be discussed.

2.5 Evaluation methods for Material Flow Analysis

Material Flow Analysis generates a mass balance for a system where mass flows and concentrations of the substance to be investigated are calculated for each stream within the system. Very often, the results of an MFA forms the basis for evaluating a system, however, it is possible to take an extra step forward by considering applicable evaluation methods for MFA. Such methods include: Statistical Entropy Analysis, Material intensity per unit service, exergy, anthropogenic vs geogenic flows, cost benefit analysis etc. Three of the evaluation methods will be discussed next.

2.5.1 Statistical Entropy Analysis (SEA)

Statistical Entropy Analysis is a method used for quantifying the degree to which a substance is concentrated or diluted as it is transformed within a system and it forms an integral part of any material flow system (Brunner and Rechberger, 2004). It was developed at the Vienna University of Technology and is the only evaluation method that was specifically developed for MFA results. Unlike the other evaluation methods, SEA provides a comprehensive assessment of a system by utilising all the information (i.e. mass flows and concentrations of the substance of interest) drawn from an MFA without the need for extra computation.

The entropy introduced in this section is referred to as Shannon’s statistical entropy, denoted ‘H’ (which is different from thermodynamic entropy). It is used in the field of information systems to measure the loss or gain of information within a system. It is defined as a positive function that measures the variance in a finite probability distribution (Brunner and Rechberger, 2004), as shown in Equation (2.3).

$$\mathrm{H}(\mathrm{P_i}) = -\lambda \sum_{\mathrm{i}=1}^{\mathrm{k}} \mathrm{P_i} \ln(\mathrm{P_i}) \geq 0 \qquad \text{for} \sum_{\mathrm{i}=1}^{\mathrm{k}} \mathrm{P_i} = 1 \tag{2.3}$$

Where $\lambda = 1/\ln(2)$ *and* P_i *is the probability of event ‘i’.*

Equation (2.3) is identical to the H-theorem proposed by Ludwig Boltzmann in 1872 from the field of statistical mechanics which seeks to provide a statistical description of a set of particles in space as a function of their position, time and momentum. Shannon's statistical entropy is also similar in formal definition to the thermodynamic entropy (S [J/mol/K]) proposed by Rudolph Clausius in the early 1850's, however, the physical interpretation of the two are different.

Through SEA, a new metric called the 'Substance Concentrating Efficiency' is derived, this metric measures the ability of a system to concentrate or dilute a substance. In the context of carbon flows within the pulp and paper sector, it gives a measure of how efficient the industry is in locking up carbon in products and thereby preventing them from reaching the atmosphere or receiving waters.

2.5.2 Efficiency of the life cycle stages indicator

This indicator has been suggested by van der Voet (1996) particularly for applications in substance flow analysis. If the pulping sector is modelled as a single independent life cycle stage in the life span of carbon, the leakage of carbon can be determined and expressed as a fraction of the total carbon input (i.e. Total losses/total inputs). The inverse of this leakage fraction is the efficiency which can then be compared across different pulping processes to establish their appropriateness. The leakage in this regard can be considered as all carbon flows that ultimately end up in the environment and not in the final pulp product.

2.5.3 Material intensity per service unit (MIPS)

Material intensity per unit service as an indicator for analyzing MFA results has been suggested by Brunner and Rechberger (2004). It is defined as the mass of input resources consumed per unit of service or final product formed. Material intensity per service unit can be summarized by Equation (2.4).

$$\mathrm{MIPS} = \frac{\mathrm{X}}{\mathrm{Y}} \tag{2.4}$$

Where: X = input raw materials consumed

Y = mass of desired product formed

In the context of this research project, MIPS can be defined as the mass of logs required to produce 1 tonne of pulp. A combination of MIPS with scenario analysis of the system would be instrumental in tackling the environmental aspect of sustainable development.

2.6 Propagation of Uncertainty

The mass balancing and estimation techniques needed to quantify material flows will be prone to a certain level of uncertainty which needs to be quantified. Two simple methods for calculating the propagation of error in MFA studies have been proposed by Brunner and Rechberger (2004). The methods are Gauss's law of error propagation and the Monte Carlo simulation and they will be considered next.

2.6.1 Gauss's law of error propagation

Gauss's law calculates the variance associated with a function (f) whose arguments consists of random input variables X_1, X_2..,X_n. This is achieved by first expanding the function using the Taylor series terminated at the linear term. The expansion provides a linear approximation to the function at some chosen input parameters. The difference between the value approximated with the Taylor expression and the mean value of the function provides a measure of uncertainty in the mean. Equation (2.5) presents the mathematical formula for the uncertainty.

$$\mathrm{Var(Y)} \approx \sum_{\mathrm{i=1}}^{\mathrm{n}} \left(\mathrm{Var(X_i)} \cdot \left[\frac{\partial \mathrm{Y}}{\partial \mathrm{X_i}}\right]^2_{\mathrm{X=\mu}} \right) + 2 \cdot \sum_{\mathrm{j=1}}^{\mathrm{n}} \sum_{\mathrm{j=i+1}}^{\mathrm{n}} \left(\mathrm{Cov}[\mathrm{X_i, X_j}] \cdot \left[\frac{\partial \mathrm{Y}}{\partial \mathrm{X_i}}\right]_{\mathrm{X=\mu}} \cdot \left[\frac{\partial \mathrm{Y}}{\partial \mathrm{X_j}}\right]_{\mathrm{X=\mu}} \right) \tag{2.5}$$

For $Y = f(X_1, X_2, \ldots, X_n)$

And where: $\mu_i = E(X_i) = mean\ value\ of\ X_i$

$Var\ (X_i) = variance\ in\ X_i$

$Cov\ (X_i, X_j) = co - variance\ in\ X_i and\ X_j$

Equation (2.5) provides reliable results only if the random input variables are normally distributed and also for small deviations in the mean.

Suppose the output flow rate of a system (Y_1) is a fraction (TC_1, also known as the *'Transfer coefficient'*) of the input flow rate (X), then Equation (2.6) holds.

$$Y_1 = TC_1 \cdot X \Rightarrow E(TC_1) \cdot E(X) \tag{2.6}$$

Recalling that Y_1 is a function of TC_1 and X, and applying Equation (2.5) on Equation (2.6), the variance in Y_1 can be expressed by Equation (2.7):

$$Var(Y_1) \approx [E(X)^2 \cdot Var(TC_1)] + [E(TC_1)^2 \cdot Var(X)] + [2 \cdot E(TC_1) \cdot E(X) \cdot Cov(TC_1, X)] \tag{2.7}$$

If it is assumed that TC_1 and X are independent of each other, then the covariance is zero and thus, the last term drops off, leading to Equation (2.8):

$$Var(Y_1) \approx [E(X)^2 \cdot Var(TC_1)] + [E(TC_1)^2 \cdot Var(X)] \tag{2.8}$$

This means that if the error in the input flow rate and the transfer coefficient is known, then it is possible to estimate the associated error in the output flow.

2.6.2 Monte Carlo simulation

While the propagation of error using Gauss's law requires that random variables are normally distributed, the Monte Carlo simulation is suited to random variables that do not necessarily follow a normal distribution, however, their statistical distribution (i.e. mean and variance) must be known. For each input variable, a computer algorithm assigns a random number to the variables in line with their relative distributions. The random numbers are used to calculate the result of some function (f) with input parameters X_1, X_2 .., X_n , by repeating the procedure a 1000 times, the mean and standard deviation of the function can be determined.

The problem with using the Monte Carlo simulation is that some variables may be bounded and hence, the random variables generated by the computer may lie outside the required range. This situation is addressed by determining the probability that the value lies outside a given range which can be analyzed using Equation (2.9).

$$c = \left|\frac{z - \mu_z}{\sigma_z}\right| \tag{2.9}$$

Where: c = *how far the standard deviation is from the mean*

μ_z = *mean of random variable*

σ_z = *standard deviation of random variable*

z = *limit of random variable*

The value of 'c' corresponds to some probability reported in Table 2.2.

Table 2.2: Probability that observations lie outside μ+(c+σ)
(Brunner and Rechberger, 2004)

c	**Probability (%)**
1	15.866
2	2.275
3	0.135
4	0.003

When 'c' is greater than 4, the probability that a randomly created value stretches outside the limits of the random variable is 0.003% which means that the value may not likely be created.

Chapter 3. Pulping

This section will cover the nature of wood and bagasse used for pulping in South Africa, their composition and various pulping technologies particularly with respect to those used within the South African pulp sector.

3.1 Wood

Not only is wood a rich source of fibre, it is also the source of a substantial fraction of carbon entering the pulping sector with carbon content of about 50%. Table 3.1 gives the elemental composition of wood.

Table 3.1: Elemental analysis of wood (Biermann, 1996)

Element	Dry weight composition [%]
Carbon	49-50.5
Oxygen	43.5-44.5
Hydrogen	5.8-6.1
Nitrogen	0.2-0.5

There are various metal ions in wood such as potassium and calcium; however, their fractions are relatively small compared to carbon, oxygen, hydrogen, and nitrogen.

3.1.1 Types of wood

Trees can be divided into two general categories, namely: softwoods and hardwoods. Softwoods belong to a group of plants called gymnosperms while hardwoods belong to a group called angiosperms. Botanically, softwoods are classified as conifers because their seeds are not enclosed within the ovaries of their flowers. In contrast, the seeds of hardwoods are covered in the ovaries. Anatomically, hardwoods are porous, as they have vessel structures made up of cells that permit the transportation of water through the tree, however these vessel-like structures are absent in softwoods.

In general, softwoods have longer and thinner fibres which are good for high tensile strength pulps, while hardwoods have shorter and thicker fibres for increased opacity.

Many species of trees are used for pulping in South Africa; however, *Pinus patula (P. patula)* is by far the most commonly used softwood species while *Eucalyptus grandis (E. grandis)* and *Acacia mearnsii* (*A. mearnsii)* are the common hardwood species used. A description of the three species is presented next.

3.1.1.1 Pinus patula

P. patula is the most important softwood species used both from an economical and industrial point of view. It was introduced in South Africa in 1907 by Sir David Hutchins. Since then, about 300 000 ha of land has been afforested with this species (SAPPI, 2012). *P. patula* is a fast growing, high elevation species indigenous to Mexico but is however regarded as an alien species in South Africa. It averages 30 m at maturity and grows at a rate of 1 m/year until it reaches an age of 25 years (Wright, 1994).

P. patula is suitable for pulping due to its high wood quality (e.g. resin content, moisture content, extent of debarking etc.) which is particularly important as it affects various aspects such as pulp yield, liquor consumption and the extent of pulp bleaching, all of which depend on the composition of wood.

3.1.1.2 Eucalyptus grandis

E. grandis is the most dominant of all hardwood species planted in South Africa. It is renowned for its superior fibre and pulping properties especially for kraft and dissolving pulp. In contrast to *P. patula*, *E. grandis* has thick and coarse fibres which offer increased opacity, essential for manufacturing high quality fine papers.

3.1.1.3 Acacia mearnsii

A. mearnsii, commonly known as Black wattle, is another prominent hardwood species which is mostly used together with other wood species for the production of dissolving pulp in South Africa. Although an alien and widespread species in South Africa, it is indigenous to Australia. Studies conducted by Yadav *et al.* (2007) who investigated the pulping characteristics of *A. mearnsii* found that the species has a low lignin content; and it is possible to achieve 88% pulp brightness after bleaching unbleached kraft pulp from the species.

Table 3.2 provides a summary of the differences between soft and hardwood species grown in South Africa.

Table 3.2: Differences between hard and softwoods grown in South Africa

	Softwoods	**Hardwoods**
Wood species	Mainly *P. patula*	Mainly *E. grandis and A. mearnsii*
Fibre dimensions	long and thin fibres	Short and thick fibres
End products	low opacity	High opacity
Pulping characteristics	High lignin content	Low lignin content
	High extractive content	Low extractive content

3.1.2 Chemical constituents of wood

Wood has a relatively simple structure both physically and chemically. It is made up of three primary substances: cellulose, hemicellulose and lignin. Of these three, cellulose is the most abundant comprising about 45% of the dry weight of wood. The hemicellulose content differs according to wood species. For instance, hardwoods have more hemicellulose than softwoods, which is 35% and 25% for hard and softwoods respectively. Cellulose and hemicellulose together make up the carbohydrate portion of wood which consists of the fibres required for paper making. Lignin on the other hand, is a complex polyphenol responsible for binding the wood fibres together. Its content is higher in softwoods (25%) than hardwoods (21%). Wood also contains a small fraction of extractives (2 to 4%) which are responsible for the production of by-products such as turpentine and tall oil from the pulping process. Figure 3.1 is a schematic showing the composition of wood.

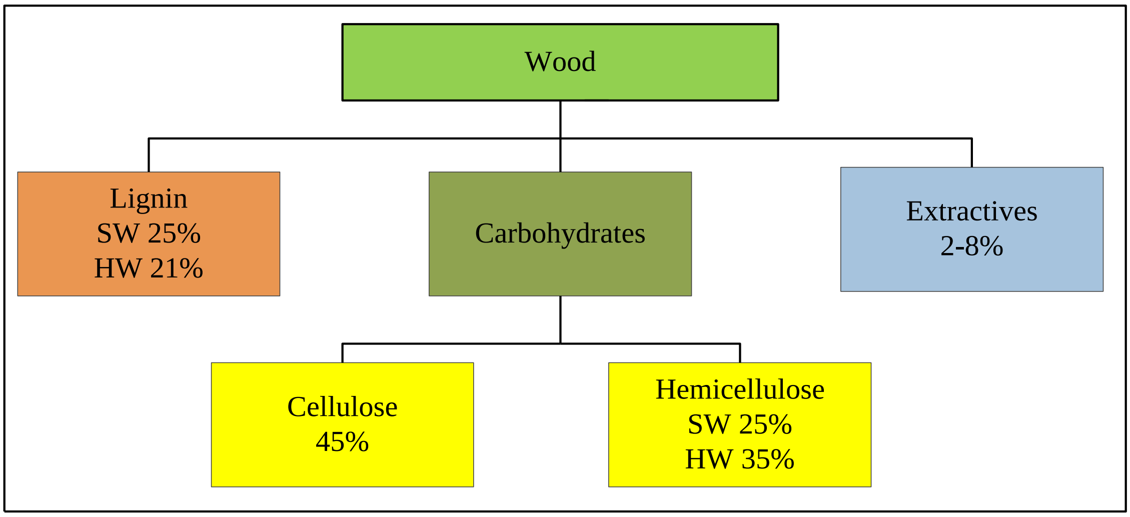

Figure 3.1: Composition of wood (Kerr, 2013)

3.1.3 Wood bark

Wood is delivered to pulp mills usually as logs, sometimes with bark. The amount of bark on wood depends on the age, location and the altitude where the trees are grown. Bark content of *P. patula* grown in South Africa has been reported to be 11.8 wt. % on a dry basis (Wright, 1994).

A significant fraction of bark comprises lignin, extractives (mainly resin and fatty acids), phenolic acids and holocellulose. Studies undertaken by Psotta (1979) revealed the composition of bark in *P. patula* grown in South Africa to be 30.5% lignin, 21.2% phenolic acid, 20.8% extractives and 25% holocellulose.

3.1.4 Preparation of wood for pulping

Wood preparation begins with debarking then chipping and screening.

3.1.4.1 Debarking

Debarking is an operation where bark is removed from wood. Bark is removed because it affects the bleachability of pulp and also because it contain extractives that neutralise cooking chemicals which results in an increase in cooking time. Furthermore, there is very little or no useful fibre in bark. It can be removed either by passing through a drum or hydraulic debarker which can achieve bark removal efficiency as high as 98%. The debarker separates the bark waste from the clean wood, which is thereafter transported to a wood waste fuel system for energy generation.

3.1.4.2 Chipping and Screening

After debarking, the wood is reduced to smaller sizes to increase the surface area of contact with pulping chemicals in the digester where lignin is liberated from the carbohydrates. If the sizes of chips are non-homogeneous, this results in different proportions of overcooked and undercooked chips. To overcome this problem, the chips are screened to remove oversized and undersized chips.

3.2 Bagasse

Bagasse is the secondary source of fibre after wood. It is the fibrous mass that results from the crushing and processing of sugarcane from which sugar juices have been extracted. When suitable pulping processes are employed, it is possible to produce bagasse pulps with similar properties to *Eucalyptus* pulps. This can be linked to the morphological similarities between the two. Bagasse fibres range from 1 to 1.5 mm in length and 20 micron in diameter, which is comparable with *Eucalyptus* species with 0.7 to 1.3 mm in length and 20 to 30 micron diameter (Covey *et al.*, 2005).

3.2.1 Chemical composition of bagasse

The composition of bagasse has been reported by various authors (see Table 3.3).

Table 3.3: Composition of bagasse

	Walford (2008)	**Alves *et al.* (2010)**	**Rainey (2009)**	**Hemmasi *et al.* (2011)**
Cellulose (%)	37	41	47	55.75
Hemicellulose (%)	28	24	27	20.5
Lignin (%)	21	24	23	3.25
Ash (%)	unreported	2.1	1	1.85

Using the composition reported by Walford (2008), a first estimate of the carbon content in bagasse can be determined.

Cellulose has the chemical formula, $(C_6H_{10}O_5)_n$, with a carbon fraction of 44% regardless of the value of 'n'. Lignin is built up of three main compounds, namely: coniferyl alcohol, synapyl alcohol, and coumaryl alcohol (Ismail, 2003, Walford, 2008). The structure of lignin in bagasse is loose and flexible which implies that a less rigorous pulping process can be employed (i.e. low temperatures and chemical charge) to achieve a desired kappa number and still maintain good pulp quality. Table 3.4 shows the composition of bagasse lignin and the carbon content of each of the three main components.

Table 3.4: Composition of lignin

Composition of lignin	**Molecular formula**	**Molar mass [g/mol]**	**Carbon [%]**
Coniferyl alcohol	$C_{10}H_{12}O_3$	180	66.7
Sinapyl alcohol	$C_{11}H_{14}O_4$	210	62.9
Coumaryl alcohol	$C_9H_{10}O_2$	150	72.0
Total			67.2

Taking an average of the three components, the overall carbon content of lignin is estimated to be 67.2% on a mass basis. It is assumed that there is no carbon in the ash. Xylose ($C_5H_{10}O_5$) contains 40% carbon and it is the backbone of the bagasse hemicellulose polymer. The xylose is branched with glucose ($C_6H_{12}O_6$) and arabinose ($C_5H_{10}O_5$) each of which contains 40% carbon. Thus, the carbon in bagasse hemicellulose is 40%. Taking all these numbers into account, the carbon fraction in bagasse is estimated to be 42% which differs from the carbon in wood (i.e. 50%) by 8%.

3.2.2 Depithing of bagasse

Bagasse contains a non-fibrous material low in cellulose called pith. Pith comprises about 30 to 35% of the weight of bagasse (Covey *et al*., 2005) and does not contribute to paper fibre but rather results in a significant consumption of pulping chemicals and also results in a lower draining pulp. Thus, it is necessary to remove pith prior to pulping. According to Dixit *et al*. (2010), pith removal efficiency of more than 75% can be achieved with residual pith content in the range of 5 to 7%.

3.2.3 Problems with using bagasse for making pulp

Using bagasse for pulp manufacture has the following related issues:

1. The South African government is exploring the use of bagasse as a renewable energy source in the production of ethanol. This has resulted in bagasse being phased out.
2. Bagasse contains a moderate proportion of silica (0.5%) which is twenty times more than in *Eucalyptus* (Covey *et al*., 2005). This silica has the potential to cause tremendous wear of process equipment especially at the paper machines. It also causes evaporator fouling and makes the

black liquor very viscous at high solids content. For these reasons, efforts are made to reduce the silica content.

3. Bagasse is a seasonal crop, which means that it is available about six months in a year. Hence, significant quantities need to be stored to ensure continuous production of pulp. Furthermore, because bagasse is susceptible to microbial invasion and degradation, storage has led to the excessive use of pulping chemicals and a loss in pulp yield.

3.3 Types of pulping processes

From a general point of view, pulping can be regarded as a process through which fibrous mass is liberated from any fibrous material (e.g. wood and bagasse). The type of pulping processes used within the South African pulp industry includes: Chemical, Mechanical and Semi-chemical pulping processes. The sections to follow will discuss the different pulping processes prevailing particularly in the South African pulp sector.

3.3.1 Chemical Pulping

Chemical pulping falls under the primary category of pulping. Its objective is to dissolve as much lignin as possible while keeping carbohydrate degradation at a minimum. Lignin dissolution is achieved through the addition of aqueous liquor which contains ions that render the lignin soluble while leavening much of the cellulose intact. This is because cellulose is made up of insoluble polysaccharides which have a predominantly crystalline structure. Among the prominent chemical pulping processes are the soda, kraft, and sulphite processes.

3.3.1.1 Soda Pulping

Soda pulping is an alkaline pulping process that uses sodium hydroxide solution as the active chemical ingredient for delignification, and it has been noted as the first successful industrial scale chemical pulping technique. It is suitable for pulping non-wood plants such as bagasse, straw, grass and bamboo. Recent developments in the soda process make use of caustic soda combined with small amounts of an additive called anthraquinone, usually at about 0.05% on wood (Sixta *et al*., 2006). Anthraquinone acts as a catalyst that improves the chemical reaction kinetics and decreases the extent of carbohydrate degradation which results in an increase in pulp yield. Nonetheless, anthraquinone is an expensive material that results in poor bleachability of alkali-pulps (Hamzeh *et al.*, 2009).

3.3.1.2 Kraft Pulping

Kraft (or sulphate) pulping is an improvement on the soda process. The active pulping chemicals are sodium hydroxide (140 to 170 mg/L) and sodium sulphide at a pH greater than 12 and temperature range of 160°C to 180°C for about 0.5 to 3 hours. (Biermann, 1996). Under these conditions, most of the lignin within the wood is dissolved. Kraft pulping is characterised by strong pulps, high tolerance to different species of wood and a high recovery of pulping chemicals.

3.3.1.3 Sulphite pulping

Sulphite pulping emerged not too long after the soda process was discovered. Its popularity grew for over five decades after the discovery of soda pulping simply because the pulp produced was easier to bleach compared to kraft and soda pulps. There are different types of sulphite pulping processes, but they differ according to the pH operation range and the choice of chemicals used for delignification. Some of the common sulphite pulping processes will be discussed next.

Calcium bisulphite pulping

Limestone ($CaCO_3$), which is relatively inexpensive, is the raw material used in the process. It is reacted with sulphur dioxide to form calcium bisulphite ($Ca(HSO_3)_2$) which is the chief constituent of the cooking liquor. At the cooking temperature, calcium bisulphite degenerates into calcium sulphite and hydrated sulphur dioxide as illustrated by Equation (3.1).

$$\mathrm{Ca(HSO_3)_2 \rightarrow CaSO_3 + SO_2 \cdot H_2O} \tag{3.1}$$

The process has two main demerits. Firstly, in order to keep calcium sulphite from precipitating onto the fibre, an excessive amount of sulphur dioxide has to be added together with a reduction in both pH (< 2.3) and temperature (<130ºC). A lower temperature leads to increased residence time (8 to 10 hours) in the digester, hence the design capacity of digesters need to be increased (Macdonald, 2004) to accommodate a higher feed input to produce more pulp in compensation for the lag time. Secondly, the incineration of calcium sulphite in the chemical recovery leads to calcium sulphate whose thermochemical properties dictate that it decomposes to calcium oxide and sulphur dioxide only at extreme temperatures (1200ºC) therefore recovery of the liquor is not practical (Sixta *et al*., 2006).

Magnesium bisulphite pulping

Using magnesium as opposed to calcium as a base presents some great benefits. Firstly of all, the magnesium base allows delignification at slightly higher pH (5 to 6) making it essential for increased pulp strength. Secondly, unlike calcium sulphite, magnesium sulphite ($MgSO_3$) decomposes at a lower temperature and the magnesium sulphate formed reacts readily with carbon to generate magnesium oxide, sulphur dioxide and carbon-dioxide as shown by Equation (3.2).

$$\mathrm{MgSO_4 + C \rightarrow MgO + SO_2 + CO_2} \tag{3.2}$$

Magnesium oxide is combined with sulphur dioxide to form magnesium bisulphite ($Mg(HSO_3)_2$) in the cooking liquor.

3.3.2 Mechanical Pulping

Mechanical pulping uses grinding or refining to reduce wood to a fibrous mass. It is characterised by a high specific energy consumption and high yields usually in the range 85% to 95% (Sixta, 2006), mostly due to increased retention of lignin and cellulose. The pulps produced are low in strength but cheaper to produce compared to chemical pulps. Mechanical pulps are used for making newspapers and printing papers all of which do not require a high tensile strength. Ground wood and thermomechanical pulps are the two types of mechanical pulps produced within the industry.

3.3.2.1 Ground wood pulping

In ground wood pulping, fibres are separated from the wood matrix by pressing debarked logs against a rotating grinding stone which is sprayed with water to reduce friction of the logs against the stone. Pressure-ground wood and stone-ground wood pulping are the two methods commonly used for producing ground wood pulps in South Africa.

3.3.2.2 Thermo-mechanical pulping (TMP)

In the case of thermomechanical pulping, the logs are reduced to chips and thereafter pre-heated with steam to soften the fibres before refining. The steam pressure is about 3 to 5 bar at a temperature of 140 to 155 ^{o}C. The process is more suitable for softwoods due to the long fibre lengths which impart high strength properties to the resultant pulps. In general, Thermo-mechanical pulps are stronger than groundwood pulps but weaker than chemical pulps.

3.3.3 Semi-chemical pulping

Two semi-chemical pulping processes, namely: Neutral Sulphite Semi-Chemical (NSSC) pulping and Semi Alkaline Sulphite Anthraquinone (SASAQ) pulping will be discussed in the sections to follow.

3.3.3.1 Neutral sulphite semi-chemical pulping

Sodium sulphite and sodium carbonate are the active pulping chemicals in this process. Neutral Sulphite Semi-Chemical pulps are used for making unbleached products where stiffness and strength are important. Such products include bond paper, grease-proof paper and corrugating medium. The yield is dependent on the type of wood species used, which ranges from 70 to 80%.The operating pH is 7 to 9 with a sodium base (Scott *et al*., 2005).

3.3.3.2 Semi Alkaline sulphite Anthraquinone

Semi Alkaline Sulphite Anthraquinone is an advanced pulping method where semi alkaline sulphite pulp is produced. The key strength of this process is that it results in high yields, usually 10 to 15% greater than conventional kraft yield (Macdonald, 2004), while at the same time results in comparatively strong pulps which are also easy to bleach.

Table 3.5 presents a summary of the pulping processes discussed.

Table 3.5: Summary of pulping processes used in South Africa (Mokebe, 2007)

Classification	**Process Name**	**Wood Used**	**Yield range [%]**
Chemical	Kraft	Hard and Soft	40-50
	Sulphite	Hard and Soft	45-55
	Soda	Hardwood	45-55
Mechanical	Groundwood	Softwood (mostly)	90-95
	Thermomechanical	Softwood	90-96
Semi-chemical	NSSC	Hardwood	65-80
	SASAQ	Hardwood	50-65

3.4 Chemistry of lignin

The chemistry of lignin varies depending on the chemical treatment employed. This section will consider the lignin chemistry for kraft and sulphite processes respectively.

3.4.1 Kraft delignification reaction kinetics

Delignification can be divided into three phases, namely: initial phase, bulk phase and residual phase. In the initial phase, the reaction rate is first order with respect to lignin and zero order with respect to hydroxide and hydrosulphide ions. Although the initial phase is shorter, the rate of pulping is much faster.

The bulk phase is not as fast as the initial phase, however much of the lignin (90%) is dissolved in this phase (Gustavsson, 2007).

The residual phase is marked by slow reaction kinetics, loss in pulp yield and a high consumption of alkali per unit of lignin dissolved.

3.4.2 Sulphite delignification reactions

With sulphite pulping, delignification can be divided into three phases, namely: sulphonation, hydrolysis and condensation.

Sulphonation occurs when excess sulphurous acid reacts with lignin to form lignosulphonic acid which combines with the base element to form a soluble lignosulphonate salt. This reaction renders the lignin hydrophilic.

Hydrolysis leads to the disintegration of lignin into smaller fragments that easily dissolve in liquor. Condensation reactions interfere with sulphonation reactions leading to high molecular weight compounds which reduce the solubility of lignin. High residual lignin in the range of 15 to 20% (i.e. 100 to 133 kappa) can be achieved for NSSC pulp with yield in the range of 75 to 85% (Biermann, 1996).

3.5 Pulp bleaching

Bleaching is the addition of chemicals to improve pulp brightness by dissolving residual lignin. Increased brightness implies a high visual quality and increased economic value of paper produced from the pulp. Kappa number is the main control variable for bleaching provided delignification is the aim for bleaching. The kappa number for bleachable grades of pulp is 12 to 18 for hardwoods and 20 to 35 for softwoods (Biermann, 1996). For brown pulps that are not going to be bleached, the range is 40 to 100 due to high lignin content.

Table 3.6 provides a list of the commonly used bleaching chemicals.

Table 3.6: Chemicals used in bleaching

Chemicals	Formula	Symbol
Oxidising agents		
Chlorine	Cl_2	C
Ozone	O_3	Z
Hydrogen peroxide	H_2O_2	P
Sodium peroxide	Na_2O_2	
Chlorine dioxide	ClO_2	D
Sodium hypochlorite	NaOCl	H
Reducing agents		
Sodium dithionate	$Na_2S_2O_4$	Y
Other chemicals		
Sodium hydroxide	NaOH	E
Sulphur dioxide	SO_2	S
Enzymes	xylanases	X
Chelants	EDTA, DTPAD	Q

3.6 Pulp mills in South Africa

The following sections present the different pulp mills in South Africa. A description of the processes as well as the raw materials used for pulp production will be provided.

3.6.1 Mondi Richards Bay

Raw materials:
Mondi Richards Bay uses *E. grandis* to produce bleached hardwood kraft pulps while *P. patula* is used for unbleached pulps. The *Eucalyptus* wood is debarked in the forest while pine is debarked on site with a drum debarker.

Description:
The mill comprises of two main fibre lines. The first line pulps softwood via a batch digester while the second line pulps hardwoods via a continuous digester. Black liquor from the two lines are mixed and sent through the same recovery circuit. Bleaching of hardwood pulp is achieved with an OODE-$_o$DED bleaching sequence. A blend of bleached and unbleached pulps are used for kraft liners; which is a two-ply product where the top layer is comprised of bleached *Eucalyptus* fibres while the bottom layer is composed of unbleached pine fibres.

3.6.2 Mondi Merebank

Raw materials:
Mondi Merebank uses softwood pine species sourced from forest plantations certified by the Forest Stewardship Council (FSC).

Description:
Mondi Merebank is an integrated pulp and paper mill. The pulp mill is a TMP plant which is the only plant in South Africa that produces TMP pulp. The mill produces newsprint, and printing and writing papers.

3.6.3 Sappi Saiccor

Raw materials:
Hardwoods from the genera *Eucalyptus* and *Acacia* (especially *A. mearnsii*) are preferred for manufacturing dissolving pulp at Sappi Saiccor due to the high cellulose content. The wood is sourced from sustainably grown forests owned by Sappi and local small growers.

Description:
The pulp mill is comprised of three fibre lines. The first line is a calcium sulphite line whose spent liquor is unrecoverable. Some of the liquor is sent to Lignotech for lignosulphonate recovery, while the remainder is piped out to sea. The second and third lines use the magnesium bisulphite pulping

process with a recovery boiler where magnesium oxide is recovered and subsequently converted to magnesium bisulphite which is recycled to the digester. The bleaching sequence is an ODE$_o$DH.

3.6.4 Sappi Ngodwana

Raw materials:
Softwood species used include *Pinus patula*, *Pinus elliottii* and *Pinus taeda*. The hardwood species used is mainly *Eucalyptus.*

Description:
Sappi Ngodwana is one of two mills in South Africa after Mondi Merebank that produces groundwood pulp from softwoods. The mill also uses the standard kraft process with vertical continuous digesters via two kraft fibre lines, one for hardwoods and the other for softwoods. The mill added 210 000 t/y of dissolving pulp to its pulp production in June 2013. The pulps are bleached with the OZDED bleaching sequence.

3.6.5 Sappi Tugela

Raw materials:
The source of virgin fibre is soft and hardwoods acquired from Sappi owned forests in the KwaZulu-Natal province.

Description:
The pulp mill comprises the kraft pulping process which has a capacity to produce 200 000 t/y of softwood pulp and 100 000 t/y hardwood NSSC pulp. The recovery of kraft liquor is achieved in a recovery boiler while a Copeland reactor is used to produce a sodium carbonate/sulphate mixture as a by-product from the NSSC recovery circuit, some of which is recycled as salt cake to the kraft recovery boiler, and the balance sold off to the market. The resultant pulp is used to manufacture containers and fluting boards.

3.6.6 Sappi Stanger

Raw materials:
Bagasse is the primary source of fibre which is obtained from local sugarcane processing supplies. Sappi Stanger is the only mill in Africa that uses bagasse to produce coated and uncoated wood free papers (Botha, 2003). The mill also produces tissue wadding.

Description:
The mill has the capacity to produce 60 000 t/y of pulp using continuous soda pulping. The spent liquor is treated in a Copeland reactor to recover Sodium carbonate which is often sold off.

3.6.7 Mpact Piet Retief

Raw materials:
Mpact Piet Retief receives softwoods and hardwood from timber plantations in the KwaZulu-Natal and Mpumalanga provinces.

Description:
Mpact Piet Retief produces NSSC pulp using vertical continuous digesters with yield in the range of 70 to 85% (Sauer, 2012). The recovery of sodium carbonate/sulphate from the spent liquor is achieved with a Copeland reactor. The pulp is used to manufacture linerboard and corrugating medium.

3.6.8 Mpact Felixton

Raw materials:
Bagasse is the primary source of virgin fibre; however, the mill also makes use of recycled fibre.

Description:
Mpact Felixton manufactures pulp from the continuous soda process. Due to lack of recovery equipment, the spent cooking liquor is piped out to sea.

In 2007, Mondi initiated Project Khulisa to expand the capacity of Felixton mill from 110 000 to 155 000 t/y (Mondi Felixton, 2009). The pulp is used for corrugating packaging material for goods in transit.

A summary of South African pulp mills is presented in Table 3.7.

Table 3.7: Summary of mills, processes, raw material, recovery and products manufactured

Mill	Process	Raw material	Recovery	Product
Mondi				
Richards Bay	Kraft	*E. grandis and P. patula*	Recovery furnace	Linerboard
Merebank	TMP	Softwoods	None	Printing writing paper etc.
Mpact				
Piet Retief	NSSC	Hardwoods and softwoods	Copeland reactor	Linerboards and corrugating mediums
Felixton	Soda	Bagasse	None	Corrugating and packaging material
Sappi				
Saiccor	Acid and Mg Sulphite	*Eucalyptus* and *Acacia*	Recovery furnace	Chemical cellulose
Ngodwana	Kraft	Softwoods and hardwoods	Recovery furnace	News print and linerboard
Tugela	Kraft and NSSC	Softwoods and hardwoods	Recovery furnace Copeland reactor	Container and fluting boards
Stanger	Soda	Bagasse	Copeland reactor	Uncoated wood free paper

Chapter 4. Material flow analysis in the pulp sector

This section will address some of the material flow related issues in the pulp and paper industry, the boundaries of the system to be investigated, the flow of lignin and carbon flow to landfill. The section concludes by highlighting some of the Material Flow Analysis studies with respect to carbon that have been undertaken particularly in the forest products industries on other continents.

Although the methodological context of MFA is still at a developmental stage, some MFA studies have been initiated particularly in the forest products sector (inclusive of pulp and paper sector) mostly in the United States (Ruth and Harrington, 1997, Côté *et al*., 2002), Europe (Sundin *et al*., 2001, Korhonen *et al*., 2001) and Asia (Hashimoto and Moriguchi, 2004, Kayo *et al.*, 2013). In many instances, the study is spurred by a public outcry that prompts the forest products sector to steer its operations towards cleaner production. This can be achieved by first considering the pathways and the flows of the materials or substances that pose an environmental threat, in order to pave the way forward towards developing measures to mitigate the threat.

4.1 Material flow related issues in the pulp sector

As discussed in Chapter 1, the pulp sector is faced with issues related not only to the disposal of by-product waste streams, but also related to the consumption of primary resources to ensure that environmental degradation is kept at a minimum.

Particular issues include:

1. The disposal of pulp mill rejects, organic liquids and solid effluents to landfills can trigger the production of methane and carbon-dioxide upon decomposition. Methane is 25 times more potent than carbon-dioxide and very efficient in absorbing ultraviolet radiation which consequently leads to the greenhouse effect.
2. The recovery of by-products such as tall oils and crude turpentine has a given degree of energy use that needs to be explored.
3. Wastewater from bleaching operations often contains lignin and an organic substance known as hexenuronic acid particularly when hardwoods are pulped. The quantities of these substances in bleach effluent drains depend on the bleaching efficiency and may have negative ecological effects.

4.2 System Analysis

The fibrous material in wood and bagasse is very rich in carbon and is the primary material that flows within the pulp sector. Tracking the pathways and the carbon flow would therefore provide the necessary information required to tackle these issues. The flow of carbon can be tracked quite simply by considering the following five processes which are at the heart of most pulp manufacturing processes.

- Pulp digestion or grinding
- Cleaning and screening
- Bleaching
- Evaporation
- Black liquor incineration and recovery.

Figure 4.1: is a simplified model showing the boundaries of the system of study.

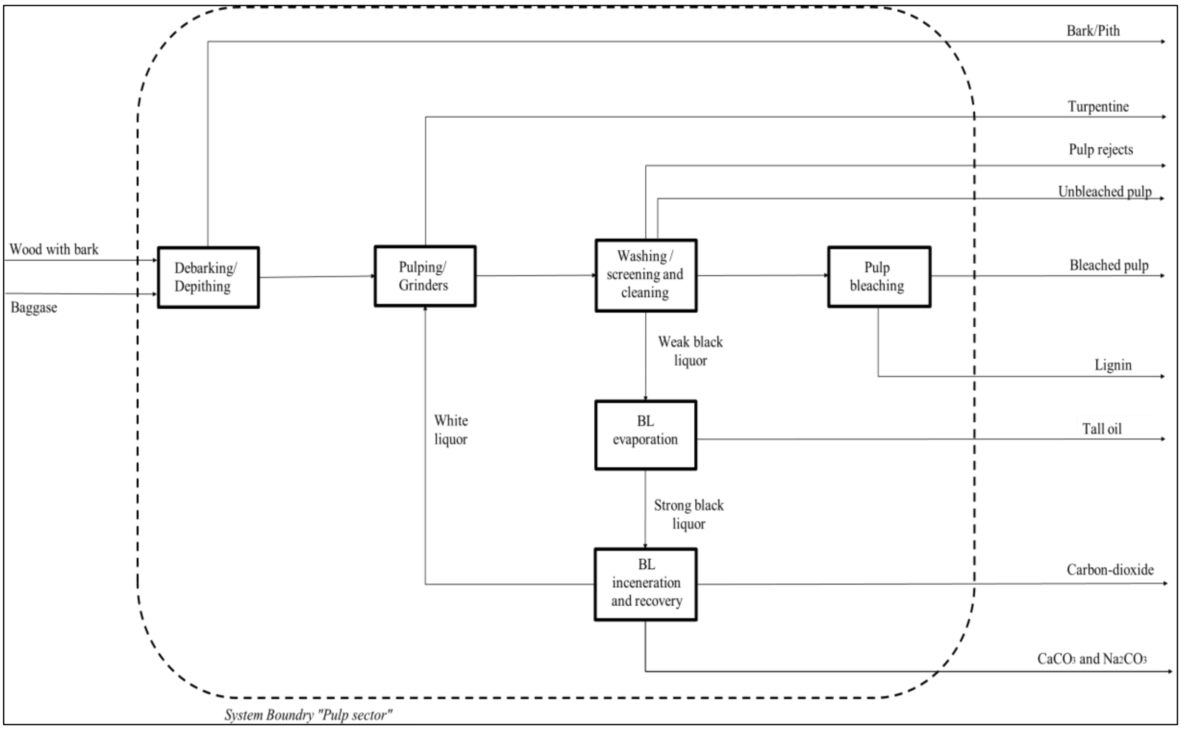

Figure 4.1 Relevant processes and carbon flows through pulp sector

The boundaries of the system are limited to all plant-based carbon sources and sinks as illustrated in Figure 4.1. In other words, the material flows in Figure 4.1 relate to carbon flows originating directly from extracted fibre resources (i.e. wood and bagasse).

Next, the time dimension for material flows needs to be chosen. The approach adopted in this study was to quantify all material flows within a calendar year with 2011 being chosen as the base year. Choosing a time base of one year is also convenient as national reports on pulp production are often published annually and also because a time base of one year is consistent across many MFA related studies (van der Voet, 2002). In some MFA studies, data is reconstructed over several years from which conclusions are drawn based on the trends observed. However, this approach will not be adopted in this study mainly due to the dynamic nature of the South African pulp and paper industry which is characterized by continuous technological advancement, construction of new plants and the expansion and sometimes closure of old plants, all of which makes it difficult to obtain reliable and relevant data.

4.3 Material flow of wood species and lignin

Using either softwoods or hardwoods for pulping may have different effects on material flows because their composition is not the same. For instance, softwoods in general have more lignin but less carbohydrate than hardwoods. Supposing equal quantities of softwoods and hardwoods are pulped chemically and separately, and that the same amounts of carbohydrates are degraded in both cases. If both woods are pulped to the same kappa number, then the pulp yield for the hardwood process would be higher. This is often the case since high yields are achieved with hardwoods. However, more lignin would be extracted from the softwoods than hardwoods into the recovery process, which has obvious environmental implications after incineration.

Alternatively, if the pulp yield after digestion is kept constant for both situations, then to achieve the same kappa number in each case after bleaching, much more lignin needs to be extracted from the softwood process, thus putting pressure on the bleaching stages through increased consumption of bleaching chemicals. At some mills in South Africa such as Mondi Richards Bay mill for instance, pulps produced from softwoods are not bleached.

4.4 Carbon flow to Landfills

Solid effluents sent to landfill include: green liquor dregs, lime slaker grits and even pulp mill rejects. Also, suspended solids from wastewater treatment plants are often sent to landfill and are regarded as contributing to greenhouse gas emissions upon decomposition.

The organic materials placed in landfills are susceptible to attack by both aerobic and anaerobic bacteria. Initially, aerobic bacteria degrade the organic material in the presence of oxygen until the oxygen has been exhausted. At this point, anaerobic bacteria become activated and proceed to degrade the remaining material into short chain organic molecules which methanogenic bacteria feed on. Methanogenic bacteria are responsible for producing methane found in the biogas from landfills.

4.5 Material flow analysis studies in forest products industry

Numerous studies of material flow analyses in the forests products sector have been conducted all over the world (North America, Europe and Asia) in recent years. Some of the findings of these studies are presented next.

4.5.1 North America

Côté *et al*. (2002) developed a carbon accounting (assessment) method to establish the sequestration of forest carbon at an integrated pulp and paper mill in the United States of America. The study took into consideration the harvesting of wood, manufacturing and the final disposal of both solid effluents and paper based products. The approach adopted in this dissertation is closely aligned with the work of Côté *et al*. (2002) particularly in the assessment of carbon in the pulp sector. The contrast is that this thesis does not consider carbon derived from the combustion of fossil fuels in the Material Flow Analysis.

They showed that carbon sequestration ratios (i.e. the ratio of carbon sequestered to carbon emitted) greater than 1 can be achieved for the forests products industry even with the most conservative assumptions; and this clearly revealed that the industry is environmentally sustainable with respect to carbon.

Calculation results of a carbon balance over a kraft mill performed by Manning and Tran (2010) reveals that about 48% of the carbon in wood ends up in the pulp produced, while 52% reports to the black liquor stream which is subsequently burned for energy (see Figure 4.2).

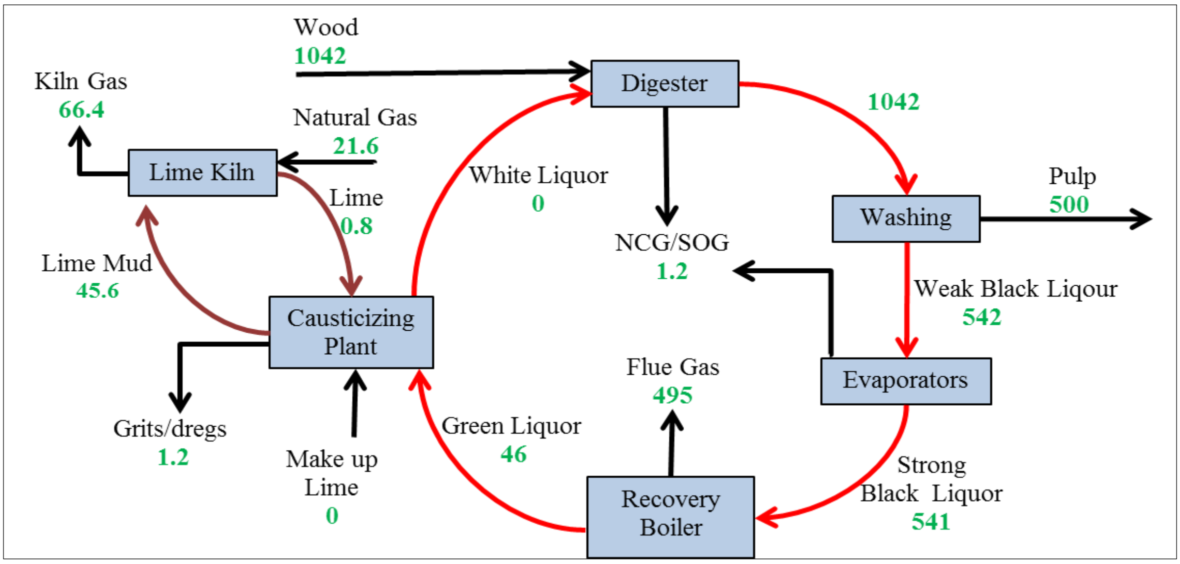

Figure 4.2: Calculation results of a carbon balance in t/d of C for a 1000 t/d kraft pulp mill (Manning and Tran, 2010)

For this kraft mill, softwood was pulped to 48% pulp yield (the kappa number was not stated in the text). Although not explicitly stated in the text, it is likely that the carbon flow rate of 1042 t/d for wood refers to debarked wood which means that the carbon in bark was not accounted for. If the carbon in bark was taken into account, this would cause both the carbon that reported to the pulp (52%) and black liquor (42%) to decrease because the bark content of softwood is significant (.i.e. about 11%. see Section 3.1.3).

4.5.2 Europe

Korhonen *et al.* (2001) analysed the material and energy flows through the forest industry (including pulp and paper sector) of Finland for the year 1997. They assert that the goals of industrial ecology pertaining to carbon are linked to the goals associated with energy flows. What this means is that the consumption of geological or fossil fuels must be reduced either through the use of solar or other renewable energy sources and intern, the natural ecosystem and oceans must be able to absorb the carbon released into the atmosphere as a result of burning fuels for domestic and industrial purposes.

Figure 4.3 shows the carbon flows in the Finnish pulp and paper industry which has been extracted from the work of Korhonen *et al*. (2001).

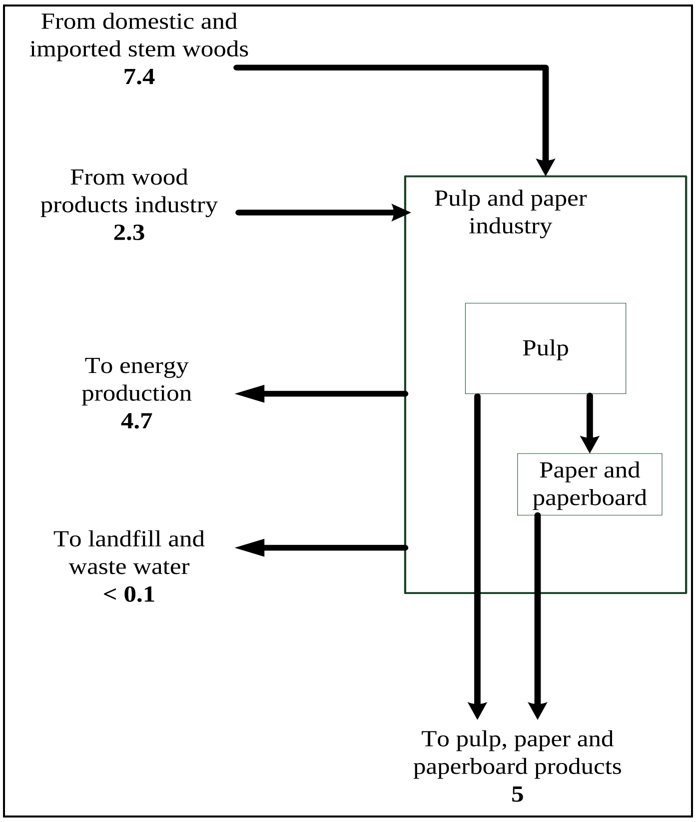

Figure 4.3: Carbon flows in the Finnish pulp and paper industry in millions of tonnes of C for the year 1997 (Korhonen *et al.*, 2001)

A closer look at the Finnish pulp and paper industry shows that there is nearly a 50% split in the carbon that reports to the pulp and the carbon burned for energy. It is important to note that this split greatly depends on the pulp yield; this means that the flow of carbon to pulp increases with increasing pulp yield. Additionally, the carbon that reported to landfill and wastewater was about 1% of the total carbon from wood.

4.5.3 Asia

Hashimoto and Moriguchi (2004) have compiled a data book of material and carbon flows in the forest industry of Japan using data from the year 1960 to 2000. Carbon stocks and flows were estimated from the literature and the changes monitored on a year to year basis. Kayo *et al*. (2013) also conducted a carbon balance assessment for harvested wood products for pulp/paper, furniture, buildings and energy. They developed a dynamic model to predict carbon emissions in three regions in Japan using data from the work of Hashimoto and Moriguchi (2004) and projected them till the year 2050. They found that the carbon stock in wood products of which paper and paperboard products are included decreased from 280 MtC in 2004 to 254MtC in 2050.

Cha *et al*. (2010) used both LCA and MFA to assess the potential of using domestic wood as a resource for increasing the carbon stock and decreasing greenhouse gases in South Korea. Nearly two thirds of South Korea is covered by forest (i.e. 6.4 million ha of forest). Nonetheless, the country is a net importer of wood because the forests have not matured, and also because it is not economically viable to produce wood domestically. Of the total wood harvested, a third of it is abandoned in the forest and becomes a potential greenhouse emitter, while 60% of the wood collected is used for producing pulp and fibreboard. The study looked at the effect of using wood as a material to substitute concrete for building a house and it was found that the wooden house stored 38.3 tCO_2 and resulted in a reduction of 54.3 tCO_2e. While the LCA was used to evaluate the global warming potential of the wooden house and a concrete house, the MFA was used as a means to quantify the consumption of wood resources in addition to the carbon stock in the forest sector in the year 2009, which was found to be increasing.

In the context of the preceding study, it is clear that one of the major contrasts between MFA and LCA is in the evaluation of greenhouse gas emissions (i.e. CO_2, CH_4 and N_2O) of a product (i.e. wooden or concrete house) over the life-cycle stages of the product. Furthermore, a combination of MFA and LCA can be a powerful way of assessing the sustainability of producing one product over another in as far as the consumption rate of resources and the effect on global warming is concerned.

Chapter 5. Methodology

This section is concerned with the data gathering and the mass balancing method of approach used to achieve the objectives of this study. For each type of pulping process, the method of data collection and carbon mass balancing principles will be presented.

Kraft, soda, sulphite, semi-chemical and mechanical pulping processes will be considered in this section.

5.1 Kraft pulping

The following mills produce kraft pulp:

- Mondi Richards Bay
- Sappi Ngodwana
- Sappi Tugela

5.1.1 Process description of a typical kraft mill

Debarking and chipping

Very often, wood is debarked either at the forest or at the mill prior to chipping. This is usually achieved with a drum debarker with a debarking efficiency as high as 98%. The bark collected is often burnt to generate energy, but can sometimes be used for composting. After debarking, the wood is chipped to a uniform size before feeding to the digester or refiner. Chip screening ensures that oversized chips are recycled while undersized chips are sent to rejects, then later burnt for energy or used for composting in some cases.

Cooking in the digester

The digester is the main chemical reactor on a kraft mill where lignin is liberated from wood. Before initiating the cook, the chips are usually pre-steamed for approximately 30 minutes until the temperature of the chips reach 100^oC. Pre-steaming is required to remove the trapped air within the pores of the chips; this promotes uniform liquor penetration through the pores during impregnation. The chemical charge is achieved by pumping white liquor (140 to 170 mg/L) at 80^oC to 100^oC through the bottom of the digester such that the ratio of dry chips to total liquor is 4:1 on a mass basis. Usually, a combination of regenerated white liquor and spent black liquor after the cook is used during chip impregnation since black liquor is understood to accelerate the rate of delignification (Gustavsson, 2007).

Lignin is extracted from the chips by cooking in liquor at 160^oC to 170^oC with the temperature being maintained either by direct steam or indirectly via a steam liquor heat exchanger. Volatile organic compounds (VOCs) are produced during the cook and are constantly purged to prevent pressure build up within the digester. The VOCs are thereafter condensed to recover chemicals such as turpentine $(C_5H_6)_n$. During the cook, it is desired to remove as much lignin as possible while keeping carbohydrate degradation at a minimum, thus, the cook is halted when a given kappa number usually between 15 to 20 for hardwood pulp is reached. The 'H factor', which is a function of time and temperature, allows the prediction of kappa number and hence the completion of the cook.

The product from the digester - also called 'brown stock' - is cooled to below 100^oC before discharging into a blow tank which serves two purposes. Firstly, it separates steam and gases from the pulp. Secondly, it dilutes the pulp to a low consistency, enabling it to be pumped to the next unit. Diluting the pulp also reduces the rigidity in the fibre network and eliminates pulp flocs.

Washing, screening and cleaning

From the blow tank, the pulp is sent for washing and screening. During the washing phase, residual liquor from the digester, which contains both lignin and inorganic pulping chemicals, is recovered by adding minimal amounts of dilution water to the pulp to clean it effectively. It is essential to keep dilution water to a minimum to decrease the load on the evaporators downstream. Screening and cleaning removes impurities within the pulp such as: bark, shives, debris, dirt and plastics so that the resulting pulp is of good quality for paper production. Hydrocyclones are used to effect cleaning through the use of centripetal forces in the gravitational field of the hydrocyclone. A combination of centrifugal action and the gravitational field causes the solid impurities (which have higher density than fibres) to lose momentum on the inside wall of the hydrocyclone (Biermann, 1996). Solid impurities report to the underflow because they settle much faster than fibres while cleaned fibres report to the overflow.

Evaporation and black liquor burning

The recovered spent liquor, referred to as 'weak black liquor' has solid content of about 10 to 15%. It is concentrated in multiple effect evaporators to about 65% solids or more to increase the calorific value of the liquor, now termed 'strong black' liquor after evaporation. Strong black liquor is burnt by spraying droplets into a recovery furnace that serves two functions. The first is to combust all the organic substances in the black liquor to carbon-dioxide and water and to convert the sodium sulphate added to the furnace to sodium sulphide (Na_2S). Some of the sodium reacts in the presence of oxygen and carbon-dioxide to form sodium carbonate (Na_2CO_3). It must be noted that the sodium and sulphur in black liquor presents another source of sodium sulphide. Sodium carbonate and sodium sulphide are the primary components of the inorganic smelt at the bottom of the furnace. The smelt stream is dissolved in weak white liquor and then clarified and filtered to remove impurities that would otherwise affect the subsequent processes to follow; it forms the so called 'green liquor'.

Recausticizing

Green liquor is contacted with calcium oxide which has been slaked to calcium hydroxide. Calcium hydroxide reacts with sodium carbonate to form sodium hydroxide and a precipitate of calcium carbonate, this reaction is the recausticizing reaction. The result is a mixture of sodium hydroxide and sodium sulphide in the fresh ‘white liquor’ that is pumped to the digester for delignification. Calcium carbonate is filtered and sent to the lime kiln where it is burnt (usually with natural gas) to calcium oxide to be used in the recausticizer after slaking.

Figure 5.1 below is a block flow diagram representing the flow of material through a typical kraft mill. The area demarcated by the red line represents the spent liquor recovery line.

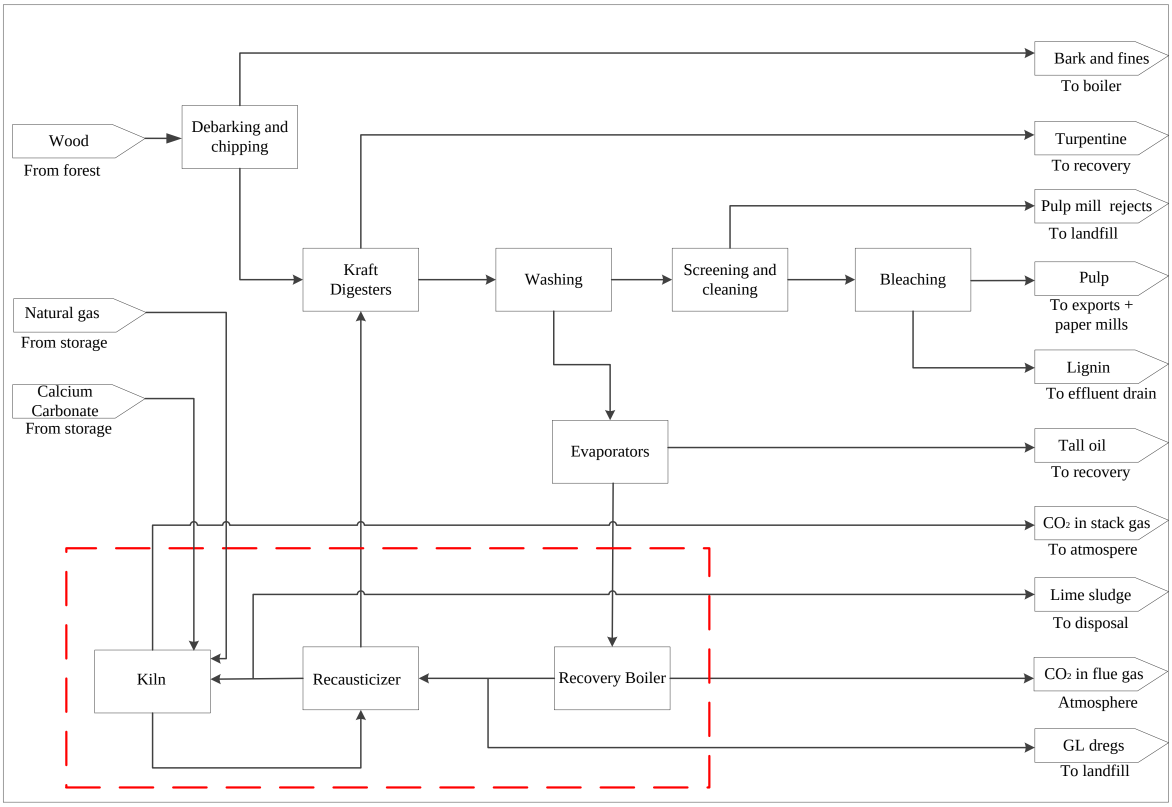

Figure 5.1: Block flow diagram of a conventional kraft pulp mill

5.1.2 Data collection

This section deals with the data collected from each mill in order to perform the required material balances. A list of some of the essential data collected is as follows:

1. Mass of wood transported to pulp mills for pulp production and their moisture content
2. Mass of bark removed or the debarking efficiency if the wood was debarked at the mill
3. Screening efficiency for chips
4. Mass of turpentine produced and other non-condensable gasses
5. Mass of pulp mill rejects
6. Mass of pulp produced, either bleached or unbleached pulp

7. Pulp yield before bleaching and after bleaching
8. Kappa number between different stages of bleaching
9. Mass of black liquor solids, solids content and elemental composition
10. Mass of salt cake make-up to recovery boiler and the composition
11. Smelt reduction efficiency of recovery boiler
12. Causticizing efficiency
13. Mass of lime slaker grits and green liquor dregs

5.1.3 Mass balancing

A mass balance was performed at each of the major process units, namely: debarking and chipping, digesters, washers, evaporators, recovery furnaces, causticizing plants and lime kilns as illustrated in Figure 5.1. Based on the information from the literature, the carbon content in addition to a carbon mass balance was performed. It will be shown how the balances were completed for each unit.

5.1.3.1 Debarking and chipping

Wood bark comprises about 11.8% of the dry weight of wood (Wright, 1994). Bark contains about 50% carbon (Gavrilescu, 2008) just about the same as for wood. Because the green weight of wood is usually provided by the mills, the moisture content has to be subtracted to convert it to bone-dry tonnes; this is given by Equation (5.1).

$$\mathrm{DWW} = \mathrm{GW}(1 - \mathrm{MC}) \tag{5.1}$$

Where: DWW = dry weight of wood
GW = Green weight
MC = Moisture content

The dry weight of wood after debarking prior to chipping can be expressed by Equation (5.2).

$$\mathrm{DW} = \mathrm{DWW}(1 - \mathrm{DE}) \tag{5.2}$$

Where: DW = debarked wood
DE = debarking efficiency

The mass of bark removed is obviously $[DWW \times DE]$.

In practice, not all the wood that is chipped falls within the same size class. Undersized chips (fines) are often discarded or burnt and usually fall in the range of 50 to 100 kg per tonne of oven dry pulp (Gavrilescu, 2008). The mass of fine chips will decrease the total mass of chips sent for pulping, hence it is subtracted from the mass of debarked wood. At this point, the carbon content of all quantities calculated is assumed to be 50 % carbon by mass because no chemical reactions have taken place yet.

5.1.3.2 Digesters

Carbon flow to the digester originates primarily from chipped wood. There is also carbon in white liquor in the form of sodium carbonate and potassium carbonate from the liquor recovery loop, however, the latter chemicals constitute a small fraction (assumed to be zero) of white liquor which is composed essentially of sodium sulphide and sodium hydroxide.

Carbon exits the digester in the brown stock; with spent liquor, as non-condensable gases and as turpentine. Turpentine is produced from the volatile fraction of wood extractives, and although the quantities produced are extremely small, it is nevertheless reported to be in the order of 5 to10 kg per tonne of pulp produced (Sixta *et al*., 2006). Turpentine comprises mainly of monoterpenes ($C_{10}H_{16}$) which contain 88% carbon by mass. The difference between carbon in wood and the turpentine produced is equivalent to carbon in the pulp and spent liquor [Equation (5.3)].

$$\text{C in pulp and liqour} = \text{C in dry wood} - \text{C in turpentine} \tag{5.3}$$

5.1.3.3 Washing and screening

Pulp is washed, screened and cleaned prior to storage. However, there are pulp mill rejects generated from both coarse and fine screening as well as final stage cleaners, which are often discarded to landfill. Uncooked chips, bark particles and knots from wood form the bulk of pulp mill rejects which are in the order of 25 to70 kg per tonne of pulp or 2 to 6% of unscreened pulp (Gavrilescu, 2008). In most instances, uncooked chips are continuously recycled back to the digester to further extract the fibres in them.

Before performing a carbon balance over the washer, a balance based on solids alone is required to determine the mass of black liquor solids (BLS), provided this value is not given by the mill. This is possible since the mass of pulp produced forms part of the essential data needed [Equation (5.4)].

$$\text{wt. of BL solids} = \text{wt. of solids in wood} - \text{wt. of dry unbleached pulp} \tag{5.4}$$

While the mass of black liquor solids is often provided by the mills, the exact elemental composition is rarely known and it varies depending on the pulp yield, wood species and the alkali charge (Fakhrai, 2002). Fortunately, there are numerous publications where the composition of black liquor solids has been reported (Cardoso *et al*., 2009, Gavrilescu, 2008, Saturnino, 2012, Gonçalves *et al*., 2004, Krotscheck and Sixta, 2006). Black liquor compositions from kraft mills in Brazil and Scandinavia are presented in Table 5.1.

Table 5.1: Black liquor characterisation (Gonçalves *et al*., 2004)

Elemental Composition [%]								
Wood type: Hardwood								
Mill location	**Kappa no.**	**C**	**H**	**N**	**Na**	**K**	**S**	**Cl**
Brazil/Plant A	17	33.9	3.6	0.01	22.6	1.8	3.7	4.5
Brazil Plant B	17	35.4	3.7	0	20.9	1.1	3	4.3
Brazil Plant C	17	29.5	3.6	0	18.6	1.2	4.4	2.6
Brazil Plant D	17	34.8	3.4	0.04	18.4	1	3.6	3.2
Wood type: Softwood								
Mill location	**Kappa no.**	**C**	**H**	**N**	**Na**	**K**	**S**	**Cl**
Scandinavia	27	35.8	3.6	0.06	19.6	1.8	4.6	0.5
Scandinavia	26	34.6	3.3	0.07	19.8	1.4	5.2	0.5
Scandinavia	25	34.6	3.4	0.07	17.2	3.2	5.4	0.3
Scandinavia	24	33.9	3.3	0.07	19.6	3.2	5.7	0.3

Based on the data shown in Table 5.1 it is possible to analyse and show that there is no statistical difference in the mean carbon content of hardwood and softwood black liquors from Brazil and Scandinavia respectively. The parameters shown in Table 5.1 have been calculated at the 95% confidence level.

Table 5.2: Statistical parameters for analysing the difference in carbon content

	Hardwood BL	Softwood BL
Mean [%]	33.4	34.725
Variance	7.14	0.6225
F Statistic	11.5	
F Critical one-tail	9.28	
t Statistic	0.951	
t Critical one-tail	2.13	
t Critical two-tail	2.78	

Before a comparison between the two means (using a t test) can proceed, it must be determined if there is statistical difference between the variance (using the F test). The calculated F statistic (11.5) is greater than F critical (9.28) which suggests that there is a significant difference between the two variances. In other words; the null hypothesis that there is no statistical difference in the variance must be rejected. Therefore, a t-test with unequal variance must be applied. From the t-test, the calculated t statistic (0.951) is less than t critical for both the one-tail (2.13) and two-tail (2.78). This means that the null hypothesis which states that there is no significant difference between the two means cannot be rejected and thus, it is concluded that there no statistical difference between the mean carbon content of hardwood and softwood black liquors from Brazil and Scandinavia respectively.

5.1.3.4 Evaporators

Tall oil soaps may be produced at the evaporators only when softwood is pulped. They come from the non-volatile components of wood extractives usually in the order of 30 to 50 kg per tonne of pulp (Sixta *et al*., 2006). Very often, the soaps are sent for vacuum distillation for further purification where the main fractions collected are resin acids and fatty acids, with a mass split ranging from 33.3 to 66.6% or 66.6 to 33.3% respectively depending on the geological location where the trees were grown (Panda, 2007). However, since the *Pinus* species of wood grown in South Africa are known to be non-resinous (Wright, 1994), it was decided to use 33.3% as the fraction of resin acids in the tall oil. This value was then used to estimate the carbon in tall oil. Table 5.3 shows the different fractions of resin and fatty acids in tall oil.

Table 5.3: The fractions of resin acids and fatty acids in tall oil

Name	Molecular Formula	Mass fraction	Carbon fraction	Molar weight
Resin Acid				
1. Abeitic Acid	$C_{20}H_{30}O_2$	85-90%	79.5%	302
2. Pimaric Acid	$C_{20}H_{30}O_2$	10-15%	79.5%	302
Fatty Acids				
1. Palmitic Acid	$C_{16}H_{32}O_2$	15%	75%	256
2. Oleic Acid	$C_{18}H_{34}O_2$	48%	76.6%	282
3. Linoleic Acid	$C_{18}H_{32}O_2$	37%	77.1%	280

When the numbers shown in Table 5.3 are taken into perspective together with the 33.33% to 66.6% split, the fraction of carbon in tall oil is about 78% on average.

5.1.3.5 Recovery furnaces

As discussed previously, the primary function of the recovery boiler is to economize the flow of cooking liquor by regenerating the inorganic constituents (such as sodium sulphide) which is later recycled to the digester. Its secondary function is to produce steam and electrical power to be used in the mill, while excess electricity generated is sold to the national grid. The feed to the recovery boiler comprises black liquor, salt cake (sodium sulphate) and air, while the main outputs are the flue gases and smelt streams.

There are other inputs and outputs into and out of the recovery boiler, however the aforementioned inputs and outputs have been considered for the purposes of tracking the plant-based carbon flow and hence to perform a carbon balance over the recovery furnace. It is worth mentioning at this stage that the material balance is complicated by the multiple input and output streams into the furnace, as well as the various chemical reactions that occur.

Black liquor is composed of organic and inorganic fractions. The organic portion is presumed to follow the general equation for the complete combustion of organic compounds [Equation (5.5)].

$$\text{Organic Matter}(\mathrm{C, H, O}) + \mathrm{O_2} \rightarrow \mathrm{CO_2} + \mathrm{H_2O} \tag{5.5}$$

Reactions involving the inorganics lead to the formation of inorganic substances which report to the smelt stream at the bottom of the furnace. These reactions can be represented by Equation (5.6).

$$\text{Inorganic Matter}(\mathrm{Na, O, S, K, Cl}) + \mathrm{O_2} \rightarrow \mathrm{Na_2S} + \mathrm{Na_2SO_4} + \mathrm{NaCl} + \mathrm{Na_2CO_3} + \mathrm{K_2CO_3} \tag{5.6}$$

Carbon exits the recovery boiler substantially in the form of carbon-dioxide through the stack gas; however minimal amounts of carbon-monoxide are also formed as a result of incomplete combustion of carbon. The second output is the recovery boiler smelt stream which comprises sodium and potassium carbonates as well as unburned carbon.

In order to perform an accurate material balance over the recovery boiler, the standard method for conducting recovery boiler performance calculations as introduced by Tappi (1995) was followed. The standard method is a detailed and properly structured algorithm that takes into account black liquor solids flow rate and solids content in addition to other boiler operating parameters as the inputs, and then generates the mass of effluent gases and smelt as outputs. This algorithm was incorporated into an Excel spread sheet together with all the other balances to calculate the different outflows from the recovery boiler.

Some authors have made modifications and simplifications to the recovery boiler balance. Typical examples include the work of Saturnino (2012) who developed a model on chemical balances in a kraft mill, as well as the simplified approach presented in the work of Krotscheck and Sixta (2006) who introduced a simplified method for conducting a material balance over a recovery boiler, however, their method does not account for unburned carbon in the smelt.

5.1.3.6 Causticizing plants

Unburned carbon is usually removed with the green liquor dregs. Dregs are produced at 5 to 6 kg per tonne of unbleached pulp with a carbon content in the range 3 to 5 wt. % (Sanchez and Tran, 2005). The causticizing plant receives its feed from the slaker where calcium oxide is hydrolysed to calcium hydroxide (slaked lime) in an exothermic reaction as shown by Equation (5.7).

$$CaO + H_2O \rightarrow Ca(OH)_2 \quad \Delta H = -65\ kJ/kmol \tag{5.7}$$

$$\text{Molar mass: } 56\mathrm{g} + 18\mathrm{g} \rightarrow 74\mathrm{g}$$

Slaked lime reacts with sodium carbonate to regenerate sodium hydroxide which is recycled to the digester. This reaction is reversible but is limited by equilibrium [Equation (5.8)].

$$\mathrm{Ca(OH)_2 + Na_2CO_3 \rightleftharpoons 2NaOH + CaCO_3 \quad \Delta H = {\sim}0\ kJ/kmol} \tag{5.8}$$

$$\text{Molar mass: } 74\mathrm{g} + 106\mathrm{g} \rightarrow 80\mathrm{g} + 100\mathrm{g}$$

Equilibrium causticizing efficiency (CE) ranges from 85 to 90%, however, the average achievable CE is 3 to 10% less than the equilibrium efficiency (Sixta *et al.*, 2006). The efficiency can be increased by adding more lime or by increasing the retention time in the causticizer; however the addition of excessive lime leads to poor washing of sodium hydroxide from lime mud.

The amount of sodium hydroxide or calcium carbonate produced from the causticizing reaction is calculated by determining the stoichiometric amount of calcium hydroxide required while taking into account the causticizing efficiency (about 83%) as in Equation (5.9)

$$\mathrm{CaCO_3\ formed = Na_2CO_3 \times CE \times \frac{M_r(CaCO_3)}{M_r(Na_2CO_3)}} \tag{5.9}$$

Because the causticizing reaction $\mathrm{Ca(OH)_2 + Na_2CO_3 \rightleftharpoons 2NaOH + CaCO_3}$ never reaches completion due to equilibrium limitations, some sodium carbonate is left unreacted. The unreacted amount is found according to Equation (5.10):

$$\mathrm{Unreacted\ Na_2CO_3 = Na_2CO_3 \times (1 - CE)} \tag{5.10}$$

Unreacted sodium carbonate ends up circulating within the pulping and recovery cycle together with other inorganic compounds such as potassium carbonate ($\mathrm{K_2CO_3}$), sodium thiosulphate ($\mathrm{Na_2S_2O_3}$) and sodium chloride (NaCl) all of which are characterised as dead load chemicals. About 20% of the recovered inorganic chemicals end up as dead load (Grace and Tran, 2009) while the remaining 80% is assumed to be purged in the lime slaker grits in order to avoid an infinite build-up of dead load chemicals, which would otherwise have an adverse effect on the functioning of process equipment and also result in a rise in white liquor consumption.

5.1.3.7 Lime kilns

The aim for conducting a carbon balance over the lime kiln is to determine the amount of carbon in the calcium carbonate formed that is released as carbon-dioxide into the atmosphere. Calcium carbonate is separated from sodium hydroxide and thereafter combusted in the lime kiln at high temperatures (above 820^{o}C). At this temperature, carbon-dioxide and calcium oxide are formed in an endothermic calcination reaction as in Equation (5.11).

$$\mathrm{CaCO_3 \rightarrow CaO + CO_2 \quad \Delta H = 178\ kJ/kmol} \tag{5.11}$$

$$\text{Molar mass: } 100\mathrm{g} \rightarrow 56\mathrm{g} + 44\mathrm{g}$$

It is assumed that all carbon in the calcium carbonate is released as carbon-dioxide after burning. The amount formed is calculated as in Equation (5.12).

$$\mathrm{CO_2\ formed = CaCO_3\ formed} \times \frac{\mathrm{M_r(CO_2\ )}}{\mathrm{M_r(CaCO_3)}} \tag{5.12}$$

5.1.3.8 *Bleach plant*

The feed to the bleach plant is washed pulp. Most of the carbon in the pulp is locked up in the cellulose, hemicellulose, residual lignin and hexenuronic acid which are often produced in large amounts in *Eucalyptus* kraft pulps. Bleaching results in loss of fibre and hence a reduction in yield. The weight loss over a bleach plant is about 4 to 8% all of which was assumed to be lignin for simplicity in the work of Côté *et al.* (2002).

Knowing the yield for bleached and unbleached pulps, the percentage losses over the bleached plant can be estimated by the Equation (5.13) whose formulation is shown in Appendix 6.

$$\%\ \mathrm{loss}\ = \left(1 - \frac{\mathrm{Yeild(bleached\ pulp)}}{\mathrm{Yeild(unbleached\ pulp)}}\right) \times 100\ \% \tag{5.13}$$

Table 5.4 provides a summary of the process parameters discussed in this section, some of which were used in completing the mass balance.

Table 5.4: Summary of the process parameters

	Values	**Reference**
Wood moisture content	47%	(FAO, 2013)
Bark content of wood	11.8%	(Wright, 1994)
Debarking efficiency	98%	(Kerr, 2013)
Turpentine production	5-10 kg/t pulp	(Sixta *et al.*, 2006)
Chips to rejects	50-100 kg/t pulp	(Gavrilescu, 2008)
Tall oil production	30-50 kg/t pulp	(Sixta *et al.*, 2006)
Salt cake makeup	3% of BL solids	(Saturnino, 2012)
Carbon: green liquor dregs	3-5%	(Sanchez and Tran, 2005)
Causticizing efficiency	83%	(Grace and Tran, 2009)

5.2 Sulphite pulping

In 2011, the Sappi Saiccor pulp mill was the only mill in South Africa that produced dissolving pulp using calcium and magnesium bases in the form of calcium and magnesium sulphite respectively. Of recent (2013), Sappi Ngodwana has introduced dissolving pulp into their process.

5.2.1 Process description of a typical sulphite pulping process

Sulphite pulping is intolerant to species with high levels of extractives (e.g. pine) because they interfere with the sulphite chemical reactions in the digester. The spent liquor is referred to as red or brown liquor from which cooking chemicals may be recovered depending on the choice of base (i.e. magnesium or calcium) used. As previously highlighted in Section 3.3.1.3, the calcium bisulphite process does not permit recovery of pulping chemicals. This has resulted in the spent liquor being used for lignosulphonate production as well as some being discharged to sea. Nonetheless, using magnesium as a base presents the opportunity to recover magnesium oxide for recycling into fresh liquor.

5.2.2 Data collection

A list of some of the essential data required is as follows:

1. Mass of wood transported to pulp mills for pulp production and their moisture content
2. Mass of bark removed or the debarking efficiency if the wood was debarked at the mill
3. Screening efficiency for chips
4. Mass of pulp mill rejects
5. Mass of bleached pulp produced
6. Pulp yield before bleaching and after bleaching
7. K number of pulp before and after bleaching
8. Mass of spent liquor, solids content and elemental composition

5.2.3 Mass balancing

A detailed mass balance with assumptions is presented in Appendix 3.

5.3 Soda pulping

The following mills make use of the soda process:

- Sappi Stanger
- Mpact Felixton

5.3.1 Process description of a typical soda pulping process

Sodium hydroxide is the chief pulping chemical for the soda process. The major problem with soda pulping is the treatment of spent liquor. The Felixton mill discharges the spent liquor to sea, while the Stanger mill incinerates the liquor in a Copeland fluidised bed reactor that is operated at temperatures as high as 700ºC. Bagasse is the main source of fibre used in the process.

5.3.2 Data collection

A list of some of the essential data required is as follows:

1. Mass of bagasse transported to pulp mills and the amount of pulp produced from it
2. Moisture content of bagasse
3. The pith fraction of bagasse and the pith removal efficiency
4. The kappa number of the pulp before and after bleaching
5. Mass of salt cake produced (if the liquor was burned in the Copeland)

5.3.3 Mass balancing

A sample calculation for the mass balance has been presented in Appendix 5.

5.4 Semi-Chemical Pulping

The following pulp mills produce NSSC pulp:

- Sappi Tugela
- Mpact Piet Retief

5.4.1 Process description of semi-chemical pulping process

The various pulping processes differ with respect to the chemical treatment required to degrade lignin. For instance, in NSSC pulping, sodium sulphite is introduced to degrade lignin while sodium carbonate is added as a buffer to control pH by neutralising organic acids produced from wood (Antonides, 2000). In the case of SASAQ, in addition to sodium sulphite and sodium carbonate, anthraquinone is also added as a catalyst which greatly increases the rate of delignification due to high selectivity for lignin, leading to high yields (10% > kraft) at a given kappa number.

As with the soda process, the spent liquor is either discarded to sea or incinerated in a Copeland reactor where the organic constituents are oxidised to carbon-dioxide while the inorganic components are converted to a mixture of sodium sulphate (Na_2SO_4) and sodium carbonate (Na_2CO_3), which is sold off as a by-product. The effluent gases leaving the Copeland reactor are passed through a scrubber to remove particulate matter to acceptable levels before releasing into the atmosphere.

5.4.2 Data collection

1. Mass of wood and the moisture content
2. Mass of bark removed or the debarking efficiency if the wood was debarked at the mill
3. Screening efficiency for chips
4. Mass of turpentine if softwood was pulped
5. Mass of pulp mill rejects
6. Mass of pulp produced
7. Kappa number of pulp
8. Mass of spent liquor, solids content and elemental composition
9. If the liquor was incinerated in a recovery boiler, then data required for recovery boiler calculations apply
10. Mass of salt cake

5.4.3 Mass balancing

Similar to kraft pulping, refer to Section 5.1.3.

5.5 Mechanical pulping

The following pulp mills produce mechanical pulp:

- Sappi Ngodwana (Groundwood pulping)
- Mondi Merebank (Thermomechanical pulping)

5.5.1 Process description of mechanical pulping processes

In stone ground wood for instance, logs are pressed against a rotating grinder which softens and strips the fibres from wood. The resultant pulp is screened to remove fibres that have not been adequately separated, while screened pulp is cleaned and sometimes sent for bleaching. Mechanical pulping has little direct contribution to environmental degradation since much of the organic components are locked up in the pulp produced. However, the greatest drawback of the process is the significant amount of energy (about 1300 kWh/tonne) required to rotate the grinders.

In thermomechanical pulping, wood is chipped and pre-steamed to soften the lignin before being sent through a two stage refining process. In the first refining step, the chips are sandwiched between two disk refiners at high temperatures (110 to 130^{o}C) and high pressure to promote the generation of longer fibres (essential for the production of strong paper) and to minimize fines at the paper machines. In the second refining step, the refiners are operated at ambient temperature and pressure to prepare the fibres for the paper machines. The main operating variable for the primary refiner is the consistency which must be maintained between 20 to 30% (Biermann, 1996). Lower consistencies can damage the fibres while higher consistencies lead to plugging of the refiner. While thermomechanical pulping is the most important of all mechanical pulping processes due to the greater strength of the resultant pulp, the process has a slightly higher energy demand in the range of 1900 to 2900 kWh/tonne (Biermann, 1996) compared to the stone groundwood pulping process.

5.5.2 Data collection

1. Mass of wood and the moisture content
2. Mass of bark removed or the debarking efficiency if the wood was debarked at the mill
3. Screening efficiency for chips and mass of chips sent to rejects
4. Mass of pulp produced
5. Flow rate of effluent and the solids content

5.5.3 Mass balancing

A sample calculation is presented in Appendix 2.

5.5.4 Error Analysis

The errors where calculated using Gauss’s law of error propagation (discussed in Section 2.6.1). Because the underlying assumption for Gauss’s law states that the errors can be modelled quite adequately by assuming a normal distribution, it was imperative to challenge this assumption. This was done by using the Monte Carlo simulator which showed that the errors could be approximated by assuming a normal distribution. This comes as no surprise because the normal distribution works sufficiently well in modelling the probability distribution in most real life systems, whether in the realm of finance or process engineering. As a default from the literature, a 10% error (Pingoud *et al.*, 2006) was taken to be associated with assuming 50% carbon in the dry weight of wood. Equation (2.8) from Section 2.6.1 was used for calculating the errors associated with the carbon flows.

Chapter 6. Results and discussions

This section presents the results and discussions on the carbon mass balance for all eight mills investigated. The section concludes by considering the effect of producing one type of pulp over the other and the effect of using different types of raw materials.

6.1 Material flow analysis results-Mondi Richards Bay Mill

Mondi Richards Bay mill has two main fibre lines. One produces softwood pulp with batch digesters while the other produces hardwood pulp via continuous digesters. Softwoods are debarked on site, while hardwoods are debarked in the forest. The black liquor from each of the fibre lines are mixed together and stored prior to evaporation and subsequently incinerated in a recovery boiler (refer to Figure 6.1).

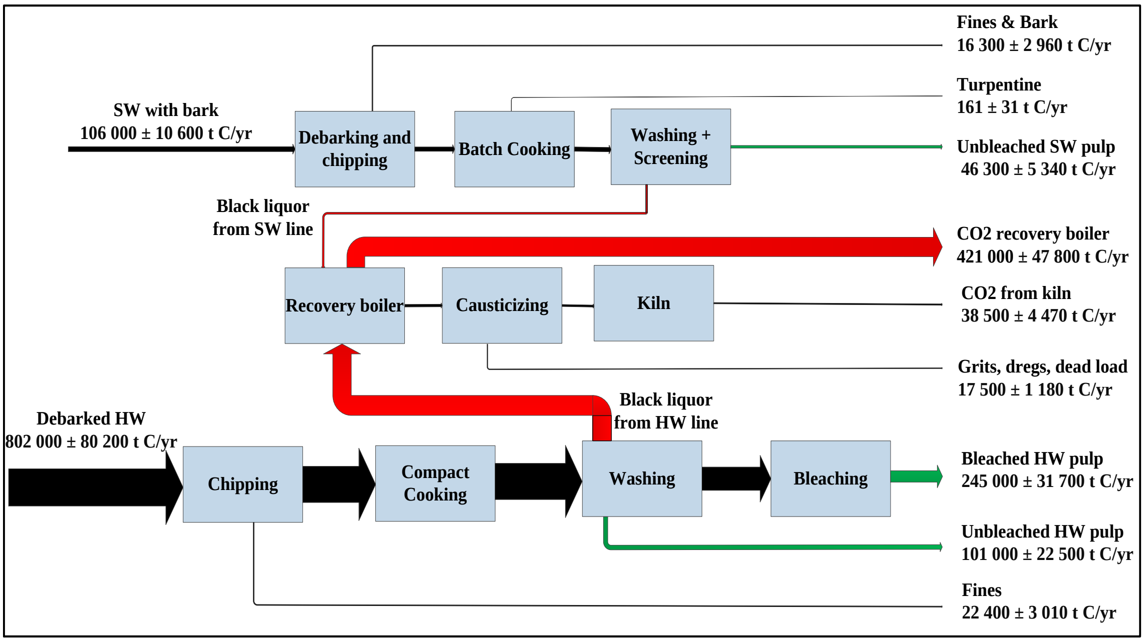

Figure 6.1: Carbon flows with actual values and associated errors-Mondi Richards Bay Mill

The yield for the softwood and hardwood lines where 56% and 52% respectively. The yield for the hardwood line was lower because the pulp was bleached to a very low kappa number, making it suitable for making white paper. It is often not possible to pulp softwoods to very low kappa numbers without degrading much of the carbohydrates, and thus causing a significant drop in the yield. In contrast, hardwoods can be pulped to a lower kappa number while still maintaining high yields. This could make some sense if it is considered that hardwoods have lower lignin content than softwoods (refer to Figure 3.1 in Section 3.1.2). About eight times more hardwoods where processed than softwoods and if the lower yield associated with this fibre line were to be considered, it becomes clear that a greater proportion of the carbon leaving the recovery boiler actually came from the hardwoods. Mass balance calculations, an in depth rationale and the assumptions made can be found in Appendix 1.

Figure 6.2 gives a summary of the distribution of carbon at the Mondi Richards Bay Mill. The analysis of the carbon flows from Figure 6.2 reveals that a significant fraction of the carbon in the woods processed is locked up in the final pulp product (i.e. 43%). This value is 5% less than the value reported by Manning and Tran (2010) (see Section 4.5.1) who conducted carbon balances over a kraft mill. They found that 48% of wood carbon ended up in the pulp.

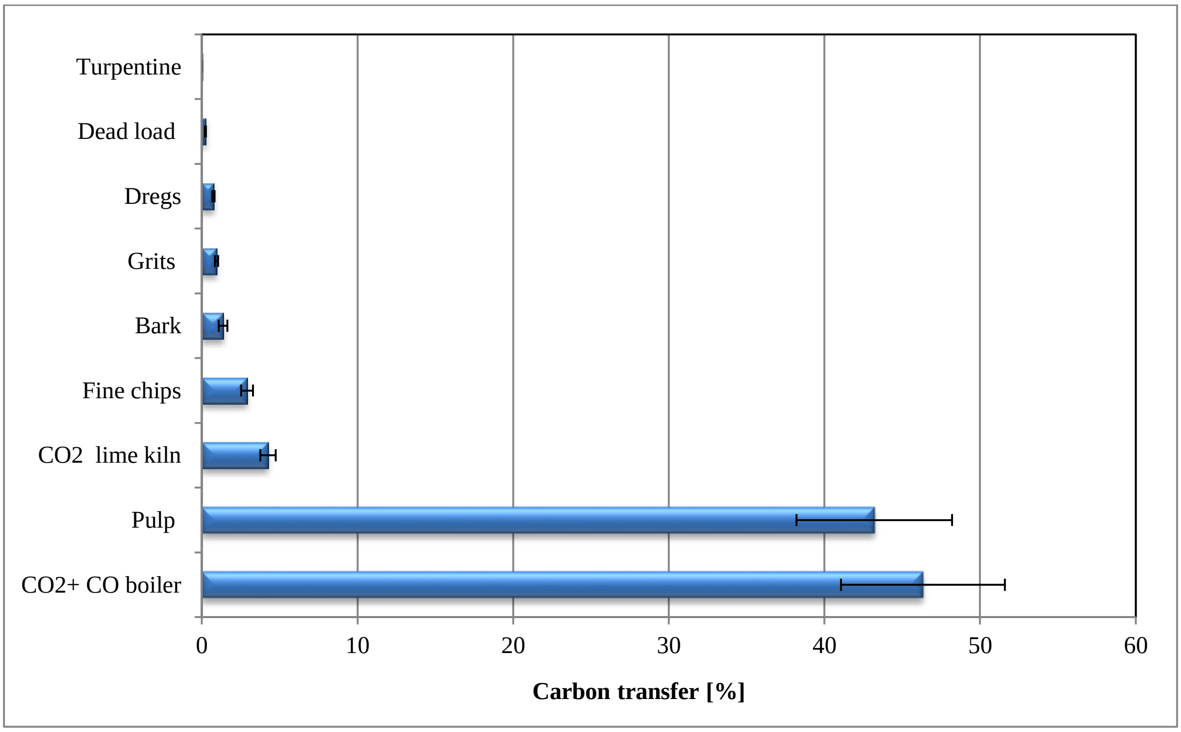

Figure 6.2: Summary of carbon flows at Mondi Richards Bay Mill

An equally significant amount (46%) is released as carbon-dioxide as a result of burning black liquor, bark, fines, turpentine and calcium carbonate. A comparatively small amount of carbon is lost to grits and dregs (~2%) which are sent to landfill. The carbon in the grits and dregs are locked up in unreacted sodium carbonate; calcium carbonate, potassium carbonate and unburned carbon, all of which are categorised as solid by-products, which amount to less than 1% of the total carbon from wood.

6.2 Material flow analysis results-Sappi Tugela Mill

Sappi Tugela Mill has two main fibre lines. The first line produces kraft pulp with softwood while the second line makes semi-chemical pulp (i.e. NSSC) using hardwood. This kraft pulp is bleached while the NSSC pulp is not bleached. Before 2011, the spent liquor from the NSSC line was burnt in a Copeland reactor while the liquor from the kraft line was burnt in a recovery boiler. However, in 2011, the spent liquors from both lines where combined and subsequently incinerated in a recovery boiler as can be observed in Figure 6.3.

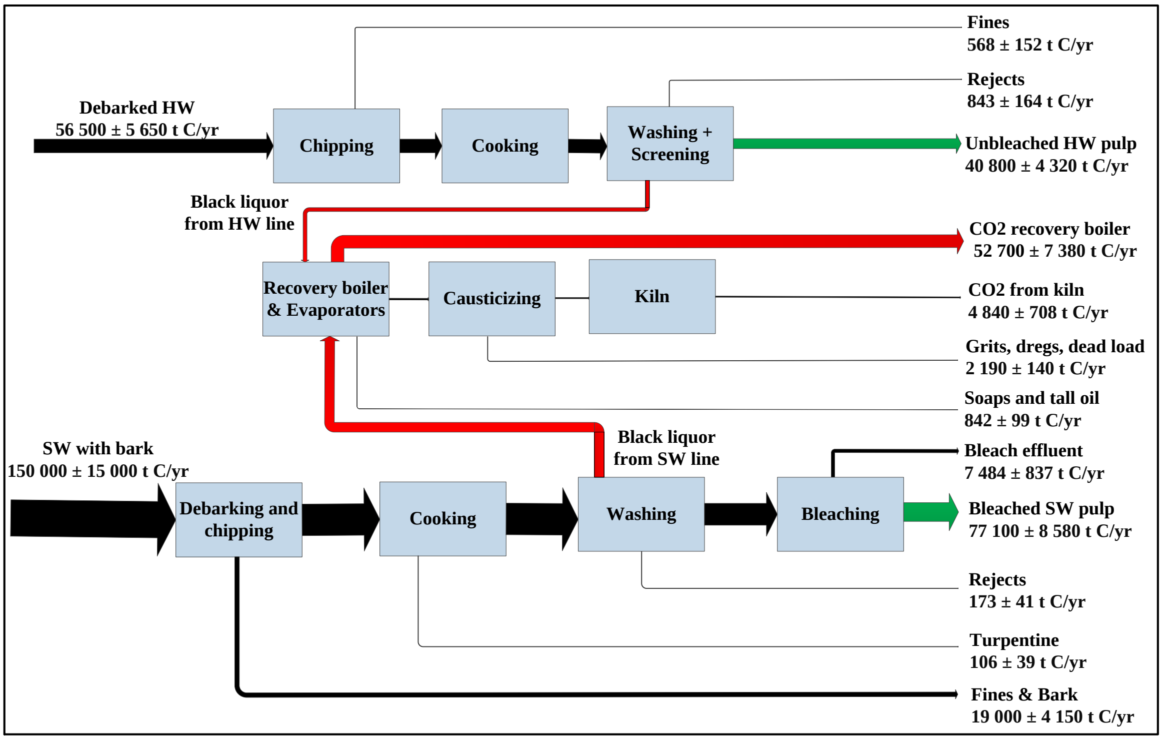

Figure 6.3: Carbon flows with actual values and associated errors-Sappi Tugela Mill

A sample calculation for this mill has not been provided because the method and assumptions followed are quite similar to those of a typical kraft mill as conducted for the Mondi Richards Bay Mill (see Appendix 1).

A 65% pulp yield was achieved on the kraft line prior to bleaching, while the bleached pulp yield was calculated as 54%. On the other hand, the pulp yield for the NSSC line was 74%. For the softwood fibre line, 51% of the carbon reported to the pulp while 31% ended up in the black liquor stream. Furthermore, for the hardwood fibre line (NSSC), 72% of the carbon ended up in the pulp while 25% was lost to the black liquor stream. The higher carbon transfer for the NSSC was expected as a result of the higher pulp yield.

Figure 6.4 is a graph showing the distribution of carbon at the Sappi Tugela Mill. In this graph, there is no distinction between the separate fibre lines as they have been combined as one. Overall, the significant numbers on the carbon transfer are once again observed for the pulp and the flue gas from the recovery boiler which are at 57% and 26% respectively.

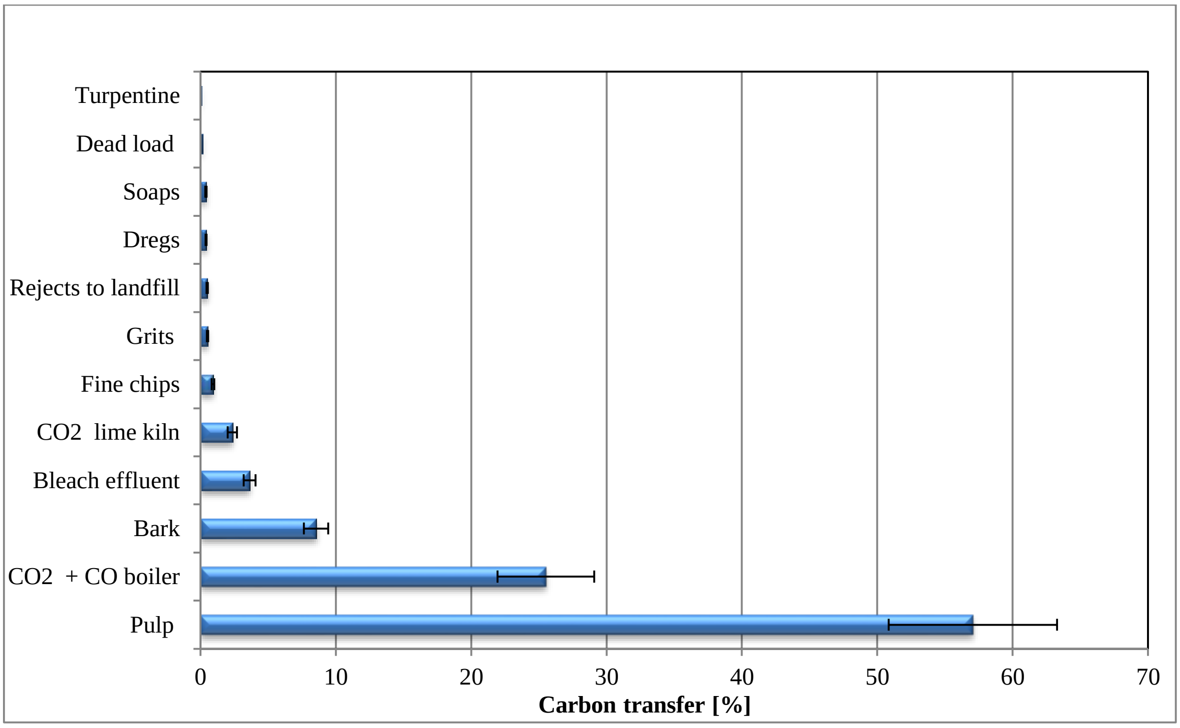

Figure 6.4: Distribution of carbon flows at Sappi Tugela Mill

The carbon in the bark (8.5%) was much higher simply because nearly three times more softwood were processed than hardwood. And it is worth noting that the carbon in the bark referred here originates from softwood since hardwood is debarked in the forest. This bark was used for composting and sometimes as a bio-fuel. About 4% was transferred to the organics in the bleach effluent, 2% was accounted for by the carbon-dioxide from the lime kiln, while the remaining fractions where all less than 1%.

6.3 Material flow analysis results-Sappi Ngodwana Mill

Sappi Ngodwana Mill has three main fibre lines. The first line employs mechanical pulping to produce newsprint, while the second and third fibre lines are used for pulping softwoods and hardwoods via the kraft processes to produce both unbleached and bleached pulps. The spent liquor from the second and third fibre lines are mixed, stored and thereafter sent for evaporation, then incineration in a recovery boiler.

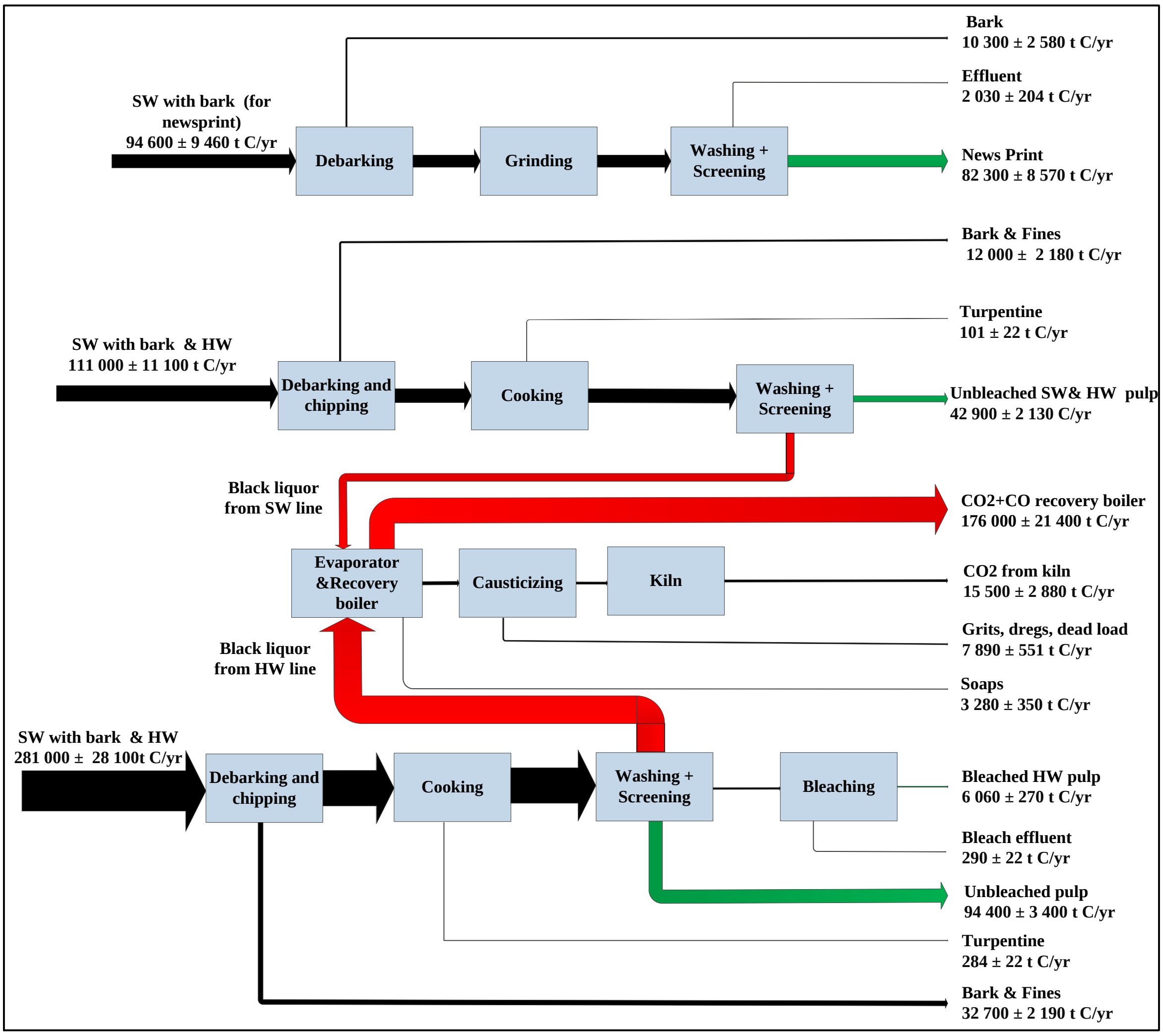

Figure 6.5: Carbon flows with actual values and associated errors-Sappi Ngodwana Mill

Figure 6.5 illustrates the material flow of carbon through the Sappi Ngodwana Mill. 2.39 tonnes of wood at 61% moisture content was required for every tonne of air dry groundwood pulp. This translated to a pulp yield of 97%. The high yield suggested that a significant portion of the dry wood material ended up in the pulp. Biermann (1996) has reported pulp yields for groundwood pulps in the range of 93 to 98%. Thus, the calculated yield was in the expected range. It turns out that the fraction of carbon in wood that reported to the pulp was 87%, 11% was lost to bark while the remaining 2% was lost to liquid effluent (See Appendix 4 for sample calculations).

For kraft line 1, the carbon transferred to the pulp and black liquor stream were 38% and 49% respectively when softwood was processed; while 42% and 55% carbon was transferred to the pulp and black liquor stream respectively when hardwood was processed.

For kraft line 2, the carbon transferred to the pulp and black liquor stream were 35% and 51% respectively when softwood was processed; while 40% and 59% carbon was transferred to the pulp and black liquor stream respectively when hardwood was processed.

Irrespective of the type of wood used, there was a higher transfer of carbon to the black liquor stream than to the pulp, and this is mainly due to the relatively low pulp yield of 48%. On the other hand, there was a much higher carbon transfer to both the pulp and the black liquor stream when hardwood was processed. This can be explained by the fact that hardwood was debarked in the forest while softwood was debarked at the pulp mill. The carbon in the bark that remained at the forest was outside the boundaries of the study and was therefore not counted.

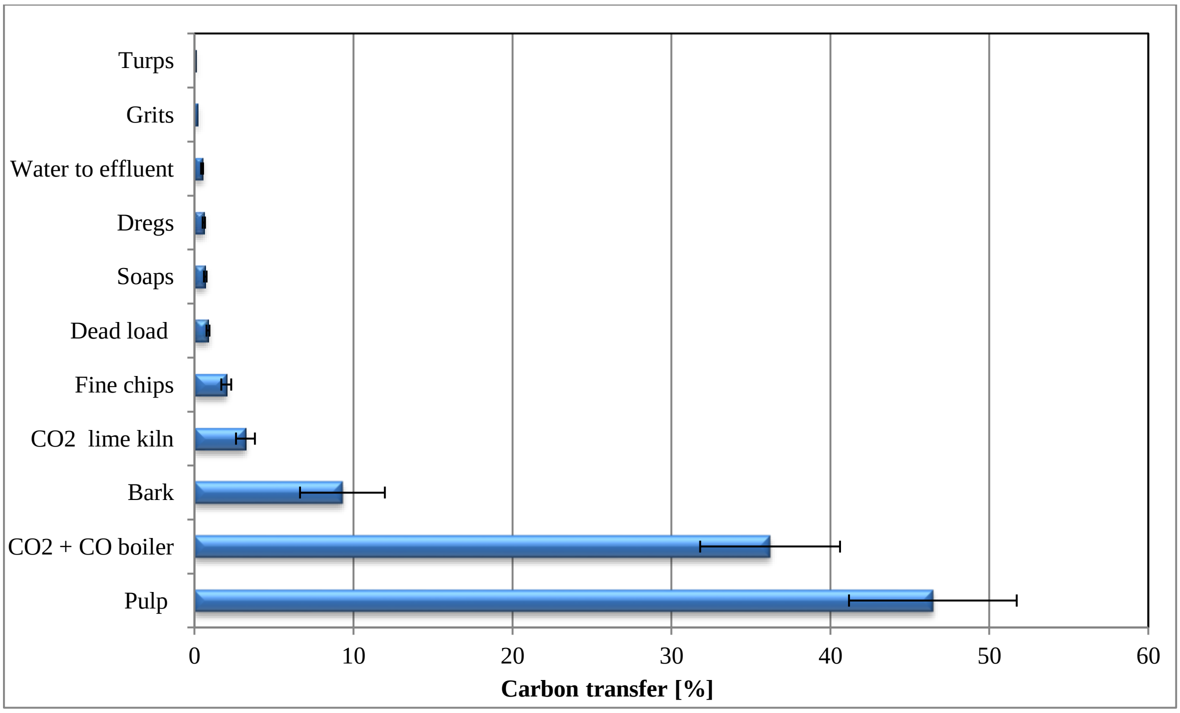

Figure 6.6: Distribution of carbon flows at Sappi Ngodwana Mill

Figure 6.6 is a graph showing the distribution of carbon at the Sappi Ngodwana Mill. Of the total carbon input from all three main fibre lines, 46% of the carbon ended up in the pulp, 36% was lost to air as a result of burning black liquor, while 9% was lost to bark. As for the remaining fractions, they were all less than 5%. The mill minimizes pulp mill rejects by recycling them back to the digester. Some of the rejects were sent to landfill (10 tonne) but they were ignored because they were very small compared to the major carbon flows.

6.4 Material flow analysis results-Mpact Piet Retief Mill

Mpact Piet Retief Mill produces NSSC pulp which is used in making linerboard. The mill uses a mixture of softwood and hardwood for manufacturing pulp. It is important to note that while this practice may enhance the mechanical properties of the pulp (Mokebe, 2007), this is not a normal practice in the pulp sector. Softwoods and hardwoods are almost exclusively pulped separately and if desired, the different pulps may be combined to achieve a particular grade of paper after pulping.

Figure 6.7 shows the flow of carbon through the Piet Retief Mill.

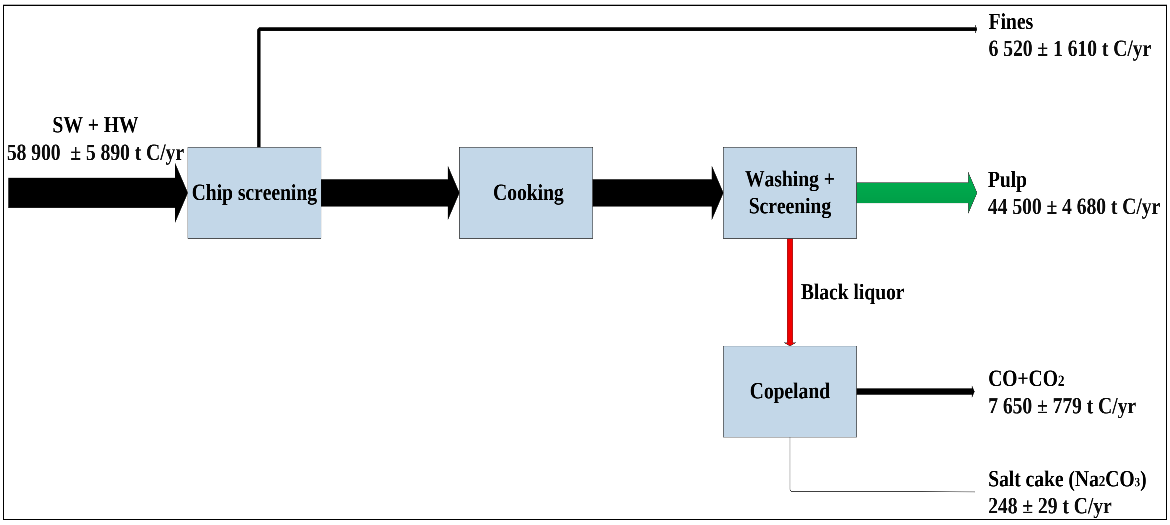

Figure 6.7: Carbon flows with actual values and associated errors-Mpact Piet Retief Mill

The pulp yield reported by the mill ranges between 63% and 76%. This equates to 70% on average which is fairly reasonable for a semi-mechanical pulp mill (i.e. NSSC) because the yield ranges from 65 to 80% (refer to Table 3.5 in Section 3.3). The data acquired from the mill suggested that 0.11 tonne of salt cake was produced per tonne of pulp, this finding was consistent with the work of Mokebe (2007) who conducted a life cycle assessment over the Piet Retief Mill. He reported 0.1tonne of salt cake per tonne of pulp. Figure 6.8 is a graph showing the distribution of carbon at the Mpact Piet Retief Mill. As a result of the high yield, a greater portion (76%) of the carbon ended up in the pulp. Much of the organic fraction of the wood reported to the pulp which caused a decrease in the carbon transfer to the black liquor stream. As a result, 13% of the carbon ended up in the flue gas from the Copeland reactor.

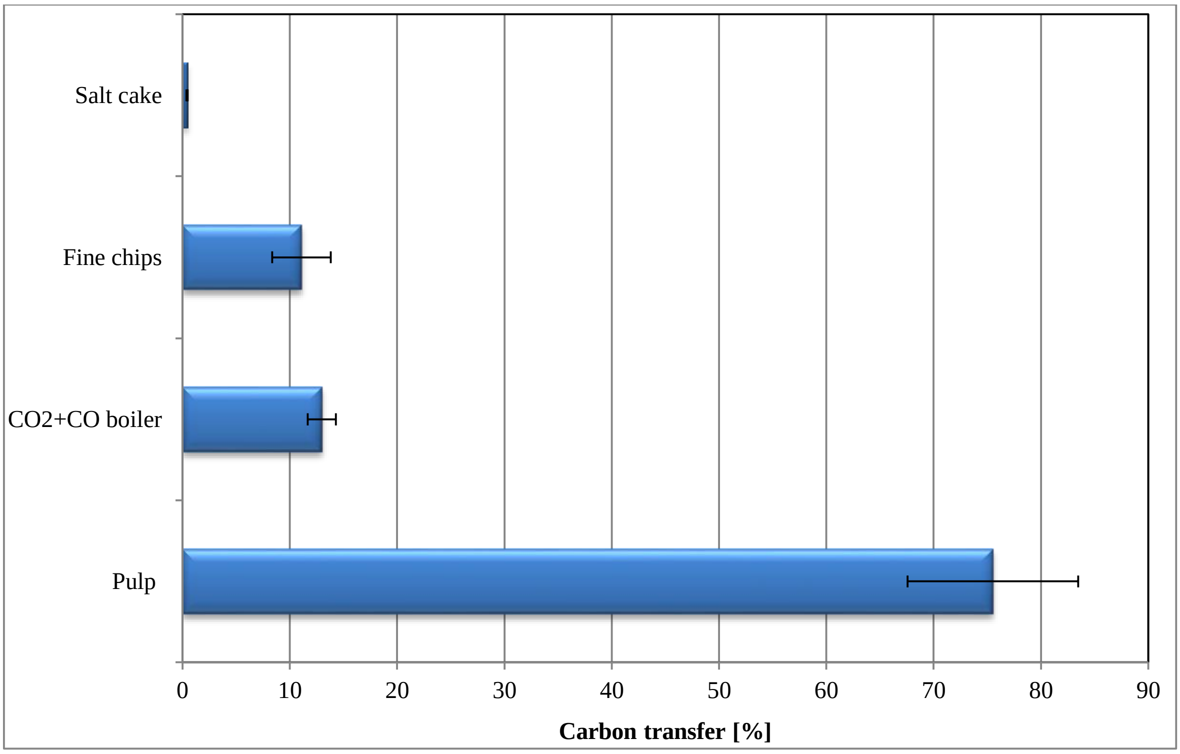

Figure 6.8: Distribution of carbon flows at Mpact Piet Retief Mill

The fines had 11% carbon transfer. This was due to the chipping efficiency (85%). This meant that for every tonne of wood fed, 0.15 tonnes was lost as fines (i.e. 15% loss). The only reason why the carbon transferred to fines was less than 15% was because the mill purchased chips in addition to the wood chipped onsite. The fines were sold off to other companies. The carbon in the salt cake (which includes sodium carbonate) formed was less than 1%. The salt cake was sold off to other companies, but if there was no market for it, they were kept in storage due to their hazardous nature.

6.5 Material flow analysis results-Mondi Merebank Mill

Mondi Merebank produces thermomechanical pulp which is the most important type of mechanical pulp due to its high strength. The softwood is received with bark which is debarked onsite and thereafter sent for chipping. The chips are then pre-steamed to encourage fibre liberation and then sent for refining. Pulp rejects are minimized by continuously recycling fibres back into the process.

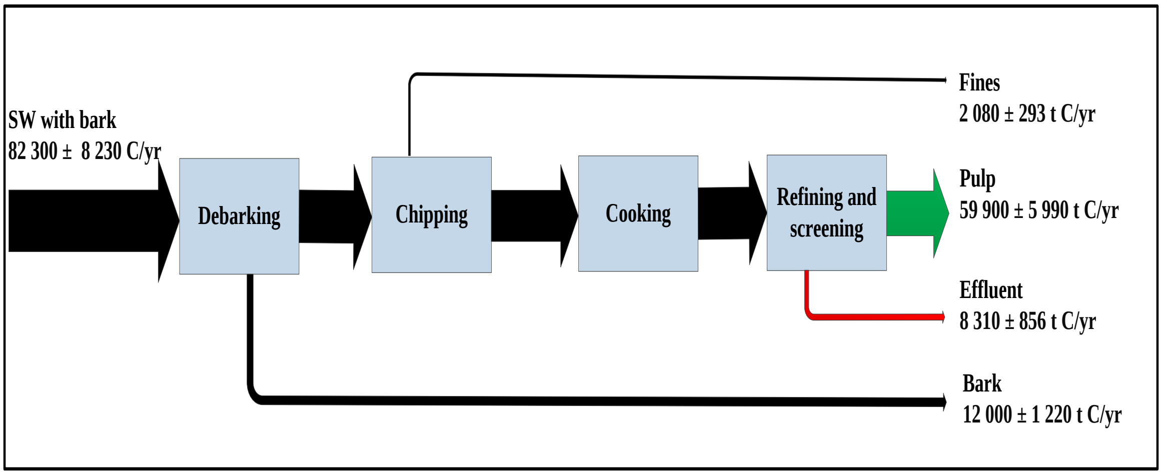

Figure 6.9: Carbon flows with actual values and associated errors-Mondi Merebank Mill

Figure 6.9 illustrates the flow of carbon through the Mondi Merebank Mill. The pulp yield was calculated as 82%, but this yield turns out to be much lower than what would have been expected for a typical thermomechanical pulp mill, that is between 91 to 95% (Biermann, 1996). This could mean that either the pulp production was under reported, or the softwood used was over reported.

There is a possible scenario where off gasses could have been vented while chips are pre-steamed. These gases could contain volatile organics, however, it was assumed that the carbon fraction would be extremely small compared to other major flows, thus, they were ignored. The errors were also calculated with Gauss's law of error propagation. Details of the calculations on the mass balance can be found in Appendix 2.

Figure 6.10 gives a summary of the carbon flows at the Mondi Merebank Mill. From Figure 6.10, it can be observed that a greater proportion of the carbon reported to the pulp (i.e. 73%). This is consistent with mechanical pulp mills. A possible explanation for the increased carbon content could be that mechanical pulp mills operate at very high yields, which suggests that most of the wood material, especially lignin, ends up in the pulp. Lignin has higher carbon content (67%) than cellulose (44%) and hemicellulose (40%), this increases the carbon content because a drop in yield can be attributed mainly to losses in cellulose and hemicelluloses. It also makes sense for most of the lignin to bind with the fibres because unlike kraft or sulphite pulping, mechanical pulping does not usually make use of chemical action to degrade lignin, it only uses mechanical action to separate the fibres.

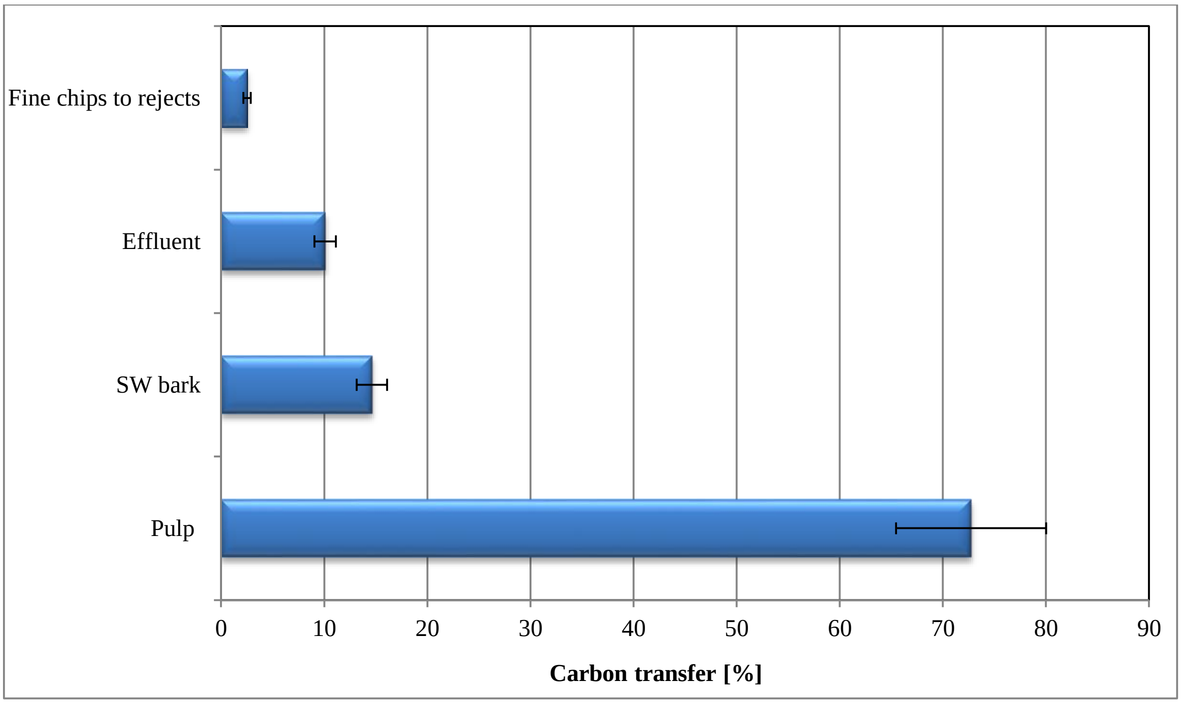

Figure 6.10: Summary of carbon flows at Mondi Merebank Mill

About 15% of the carbon ended up the bark. Of this 15%, 60% was burnt for energy while the remaining 40% was sent for composting. 10% of the carbon reported to the waste water stream which was sent for treatment while the residual 2% reported to fines, which were taken to the boiler.

6.6 Material flow analysis results-Sappi Saiccor Mill

Sappi Saiccor is the largest producer of dissolving (or cellulose) pulp in South Africa. The dissolving pulp is produced using the sulphite process, either with a calcium or magnesium base as described in Section 3.3.1.3. A portion of the spent liquor from the calcium bisulphite process is piped to sea while the remaining portion is used for making lignosulphonate which finds commercial use as an admixture for cement and for dust suppression at mines.

Lignosulphonate is produced by LignoTech SA (LTSA). Sappi has a 50% stake in this company; Borregaard Lignotech (a Norwegian company) holds the other 50%. Using magnesium as a base allows for the recovery of magnesium oxide from the recovery boiler.

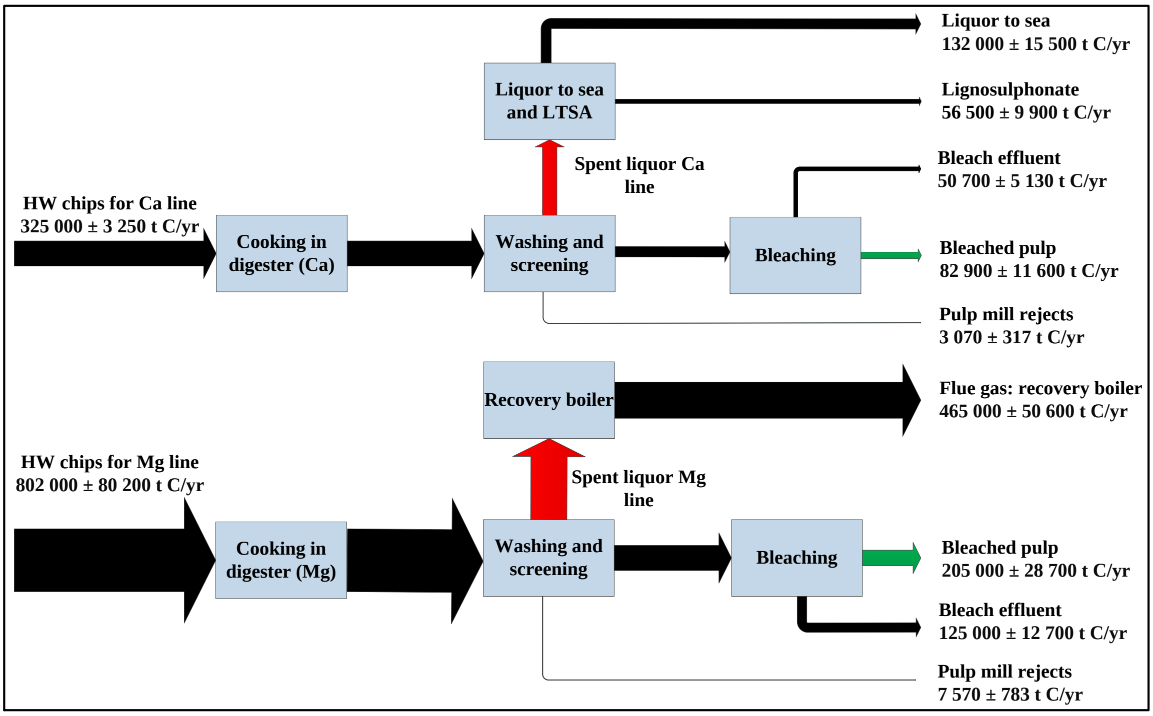

Figure 6.11: Carbon flows with actual values and associated errors-Sappi Saiccor

Figure 6.11 illustrates the material flow of carbon through the Sappi Saiccor Mill. The details of the calculations, the data used and the assumptions made in achieving the results above can be found in Appendix 3.

The pulp yield was 47% before bleaching but dropped sharply to 29% after bleaching for both the calcium and magnesium fibre lines. The loss in pulp yield after bleaching was 18% and the fibre recovery rate was 61%. The tremendous drop in the pulp yield after bleaching was imperative in order to ensure that the final dissolving pulp product was low in lignin and extremely high in cellulose. But on the other hand, this increased the flow of carbon to the bleach effluent and reduced the carbon that reported to the pulp. For both the calcium and magnesium fibre lines, 26% of the carbon from the wood processed on each of those lines ended up in the pulp produced.

Figure 6.12 is a graph showing the distribution of carbon at the Sappi Saiccor Mill. From Figure 6.12, it can be observed that a greater proportion of the carbon (41%) was transferred to the air as a result of burning spent liquor from the magnesium line as well as rejects. It is also observed that 26% of the carbon ended up in the pulp. This percentage was much lower than the expected value of about 50% for a typical kraft mill. However, the low pulp yield associated with the acid pulping process is the cause of the low carbon transfer. This acid pulping process is characteristic of a rigorous pulping process that results in high degradation of hemicelluloses.

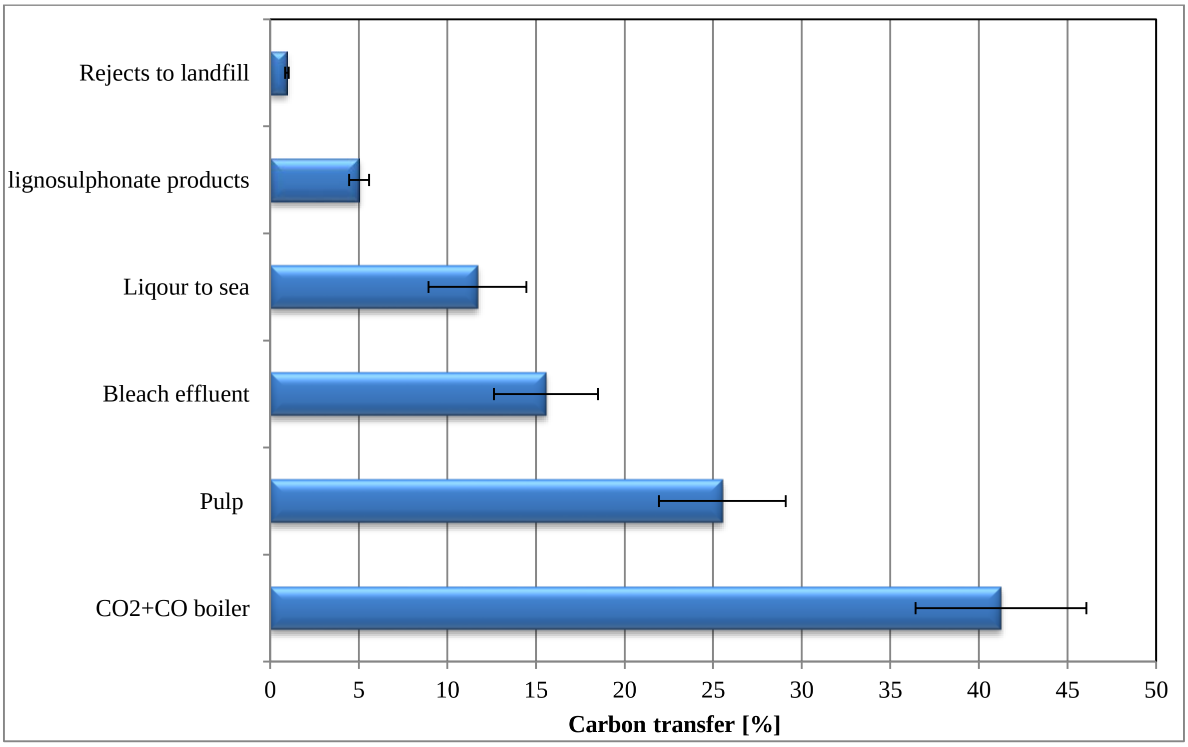

Figure 6.12: Distribution of carbon flows at Sappi Saiccor Mill

Additionally, because the pulp was bleached, this resulted in a reduction in lignin content and thus a drop in carbon content. Furthermore, a combined 27% of the carbon was lost to waterway through the bleach effluent and spent liquor to sea, while 6% of the carbon losses were accounted for by the pulp mill rejects and lignosulphonate products from Lignotech.

6.7 Material flow analysis results-Sappi Stanger Mill

Sappi Stanger uses bagasse as the main source of fibre for making pulp. This bagasse is obtained from the Gledhow Sugar mill which is located next to the pulp mill. The bagasse contains pith, and before the bagasse can be pulped, it is desirable to remove as much of this pith as possible. This is because the pulp is produced using the soda process and the pith contributes to excessive consumption of caustic (sodium hydroxide) during pulping. The pith also deteriorates the quality of the pulp. Thus, the pulp mill has a depithing plant onsite where pith is removed.

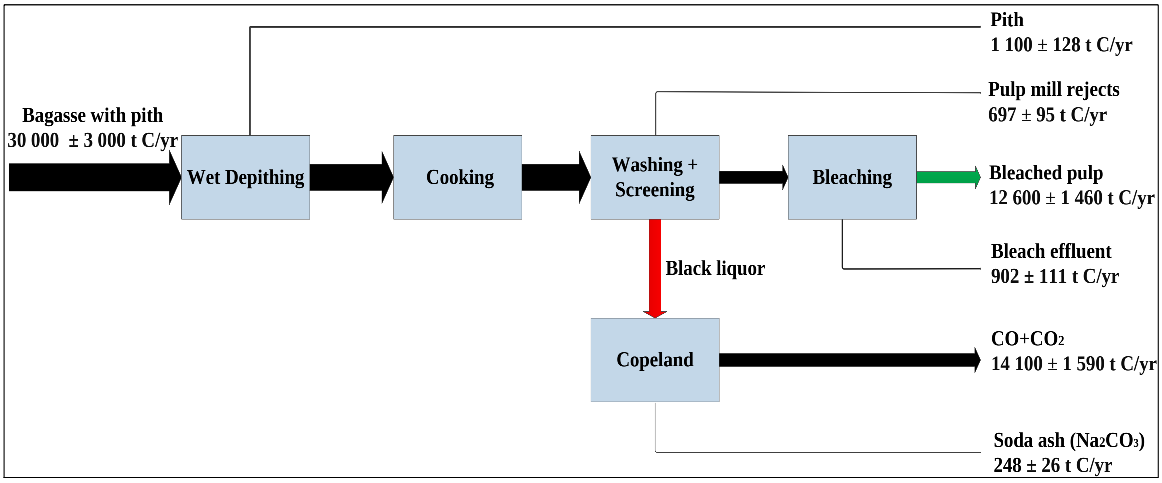

Figure 6.13: Carbon flows with actual values and associated errors-Sappi Stanger Mill

Figure 6.13 illustrates the material flow of carbon through the Sappi Stanger Mill. For every 1 tonne of bleached pulp produced, 2.1 tonnes of dry bagasse was fed to the digester, this equated to a pulp yield of 48%. The bleached pulp was assumed to be lignin free, meaning that all the lignin in the unbleached pulp was lost to bleach effluent because the bleached pulp contains less than 0.1% lignin.

It was acknowledged that some of the soda ash would be lost as dust into the air but this quantity was assumed to be negligible. There was a 6% fibre loss over the bleach plant which constitutes a 3% overall carbon yield loss over the bleaching process.

Figure 6.14 is a graph showing the distribution of carbon at the Sappi Stanger Mill. From this figure, it can be seen that a vast proportion of the carbon (54%) was lost to the air from burning spent liquor in the Copeland reactor while 35% of the carbon reported to the pulp. The low pulp yield associated with this pulping process causes a significant portion of the carbon to end up in the black liquor stream.

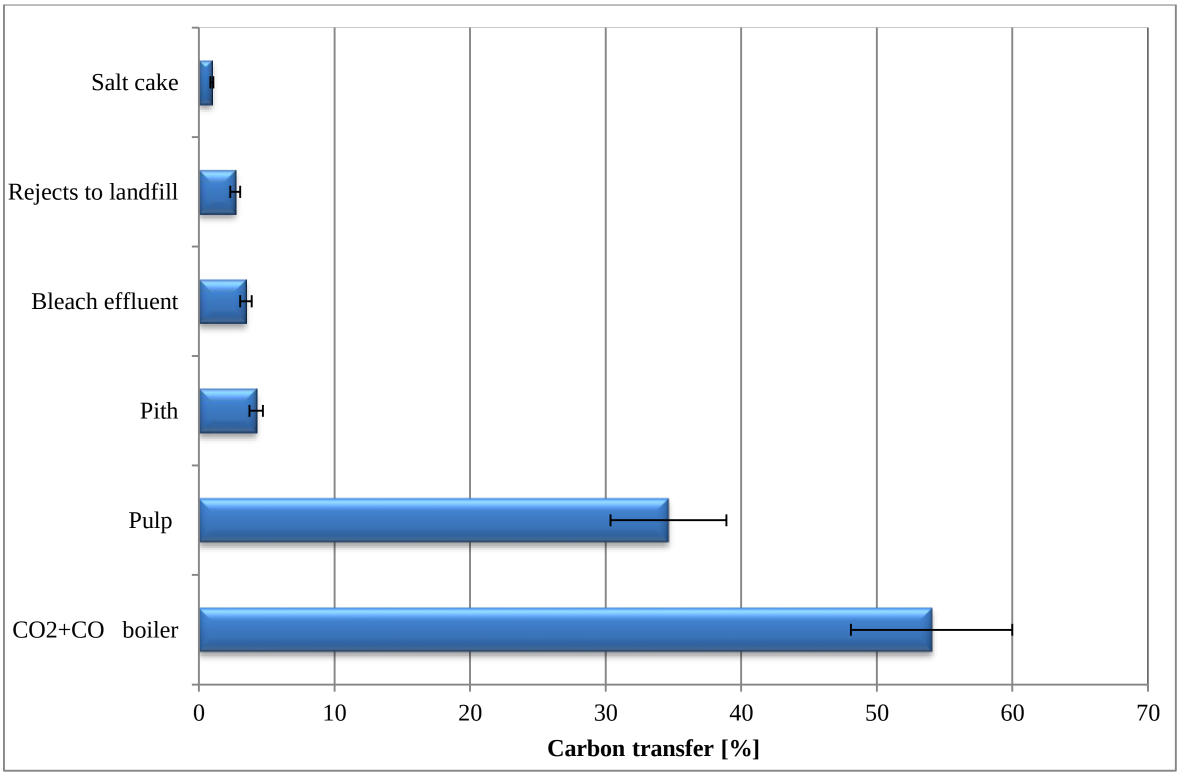

Figure 6.14: Distribution of carbon flows at Sappi Stanger Mill

About 4% was lost to pith and the bleach effluent. This effluent is first treated before being sent to a waterway. Moreover, the solid waste and by-products generated constituted about 7% of the original carbon from the bagasse processed. These solid waste and by-products included pith, pulp mill rejects and soda ash. The pith was used for compositing and agricultural purposes while the rejects were sent to landfill.

6.8 Material flow analysis results-Mpact Felixton Mill

Finally, the Mpact Felixton Mill like the Sappi Stanger Mill also uses bagasse for making pulp. However, the bagasse pulp is mixed with recycled paper to make a fluting paper. At present, the mill is exploring the possibility of replacing bagasse with recycled fibre as the only fibre source. Because the objective of this project was focused primarily on tracking the carbon flow directly from extracted resources, the carbon in the recycled paper was not considered.

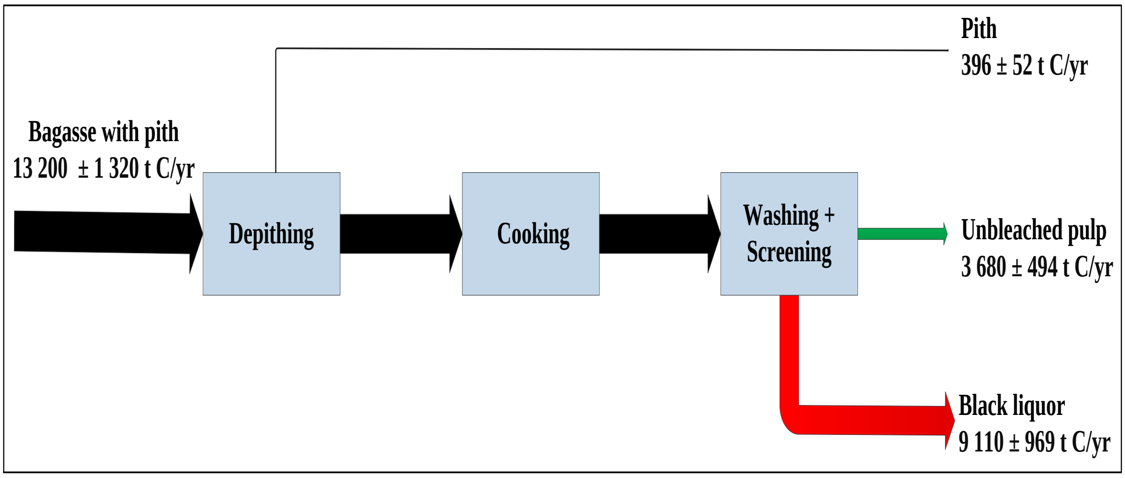

Figure 6.15: Carbon flows with actual values and associated errors-Mpact Felixton Mill

Figure 6.15 illustrates the material flow of carbon through the Mpact Felixton Mill. Mass balance calculations and the assumptions made can be found in Appendix 5.

Figure 6.16 is a graph showing the distribution of carbon at the Mpact Felixton Mill. The pulp yield achieved for this mill was 43% (as reported by the technical manager at the mil). This meant that the remaining 57% of the material from the bagasse ended up in the black liquor and as pith. The substantial loss in yield is unacceptable because the expected yield for the soda process is between 50 to 55% (see Table 3.5 in Section 3.3) and also because the pulp was not bleached, thus the yield should have been higher. In terms of carbon, 69% of the carbon ended up in the black liquor, 28% was transferred to the pulp while 3% was lost to pith. The pith was used for compositing.

Because the mill uses the conventional soda process, the caustic soda was not recovered from the liquor, thus, it was discharged into nearby rivers after treatment. It is important to note that the significant fraction of carbon reporting to the black liquor stream makes a tremendous difference when comparing the Felixton mill to other mills in the pulp sector; this will be observed in subsequent discussions to follow. The treatment of the liquor involved the reduction of the suspended solids content by means of a clarifier and thereafter discharged to nearby rivers.

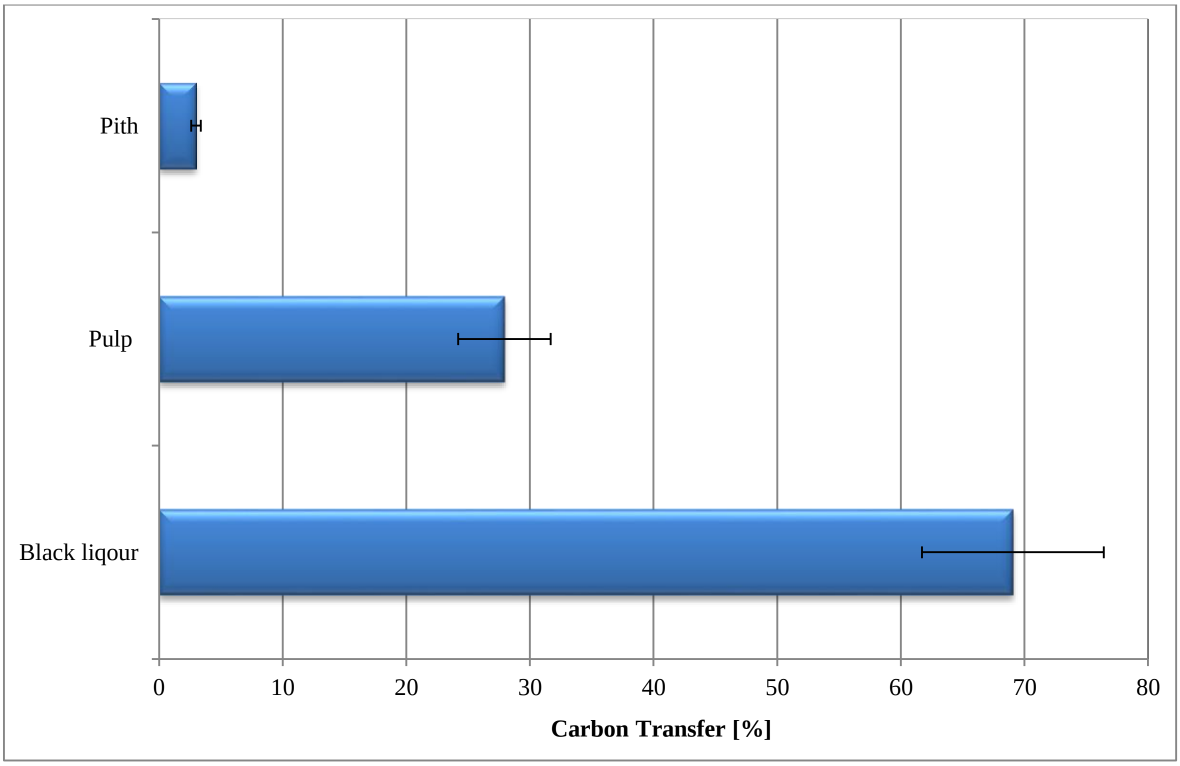

Figure 6.16: Distribution of carbon flows at Mpact Felixton Mill

Table 6.1 is a summary of the yields, kappa, hypo and k numbers of the pulp produced from each of the mills prior to bleaching.

Table 6.1: Summary of yields, kappa, hypo and K numbers for each mill

Mill	Process	Yield	Kappa no	Hypo no	K no
Mondi Richards Bay	SW Kraft	56	60	-	-
	HW Kraft	52	16	-	-
Mondi Merebank	Thermomechanical	82	-	-	-
Sappi Saiccor	Sulphite	41.3	-	-	3
Sappi Stanger	Soda	48	10	-	-
Sappi Ngodwana	Mechanical	97	-	-	-
	SW Kraft	47.5	50	-	-
	HW Kraft	48	20	-	-
Sappi Tugela	NSSC	67	-	-	-
	SW Kraft	65	80	-	-
Mpact Piet Retief	NSSC	70	-	175-190	-
Mpact Felixton	Soda	43	-	-	-

6.9 Summary of carbon flows from all the pulp mills

A summary of the overall carbon flows will be provided in this section.

6.9.1 Effect of pulp product on carbon transfer

Figure 6.17 gives a measure of the carbon transferred as direct emissions to the air, liquid and solid effluents for each of the major pulp mills in the South African pulp sector. The direct emissions refer to the burning of black liquor, fines, bark and gaseous discharge from lime kiln. The liquid effluents are classified as either spent liquor sent for treatment and bleach effluent. Solid effluents and by-products include: pulp mill rejects, grits and dregs sent to landfill as well as pith and bark sent for composting.

By considering the type of pulp produced, it can be observed from Figure 6.18 that sulphite pulp had the highest carbon transfer on aggregate (.i.e. 74%). The driving force for this excessive dissipation of carbon is a result of the low pulp yield associated with the rigorous acid and magnesium bisulphite pulping process employed. This was required in order to degrade a significant portion of the hemicellulose and lignin so that the final product was high in cellulose. In contrast, mechanical pulps had the least carbon transfer to air, liquid and solid effluents (i.e. 20%). This was due to the high yields experienced for groundwood (97%) and thermomechanical pulping (82%). It is interesting to note that mechanical pulps in general, are made from softwoods which have higher lignin content than hardwoods. The lignin is also much richer in carbon (67%) than cellulose (44%) and hemicellulose (40%). Mechanical pulps retain most of the lignin; this is why they are rich in carbon.

Dissolving pulp and soda pulp mills had the highest transfer of carbon to solid by-products and waste at 5.5% and 6% respectively. In the case of dissolving pulp, the lignosulphonate product constituted the bulk of the solid by-products while the pith was the main waste in the soda process. Kraft and semi-chemical pulp mills had the least transfer of carbon to solid by-products and waste at 2.1% and 1.4% respectively.

Furthermore, soda and dissolving pulp mills also had the highest transfer of carbon to liquid effluents at 26% and 27% respectively. The Felixton mill (see Figure 6.17) was responsible for the significant transfer of carbon to liquid effluent for the soda mills simply because all the spent liquor was sent to sea. As for the dissolving pulp, a portion of the spent liquor (41% of the carbon in the wood processed) from the calcium line at the Saiccor mill was piped out to sea.

With regard to carbon emitted to the air, the kraft and dissolving pulp mills had the greatest carbon transfer at 55% and 42% respectively. This can be explained by the fact that both types of pulp mills operated at low yields which meant that most of the organic portion of the wood reported to the spent liquor stream which was incinerated in a recovery boiler.

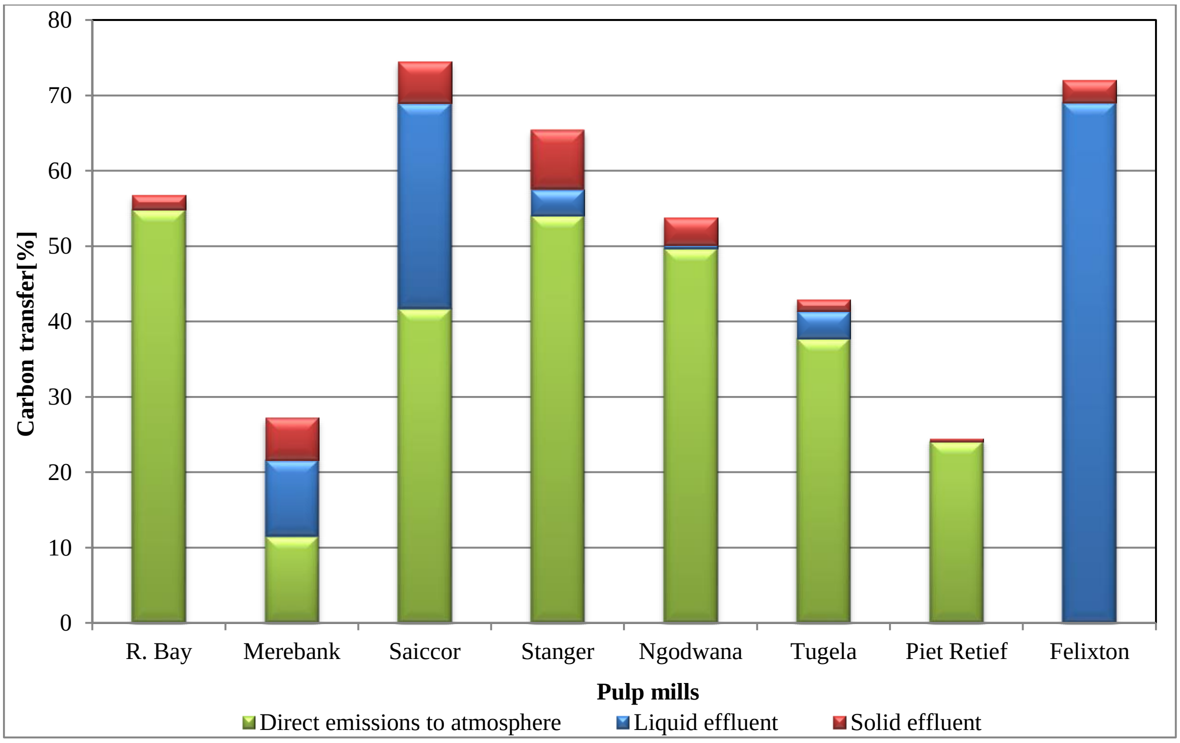

Figure 6.17: Carbon transfer from each mill to air, liquid and solid effluents

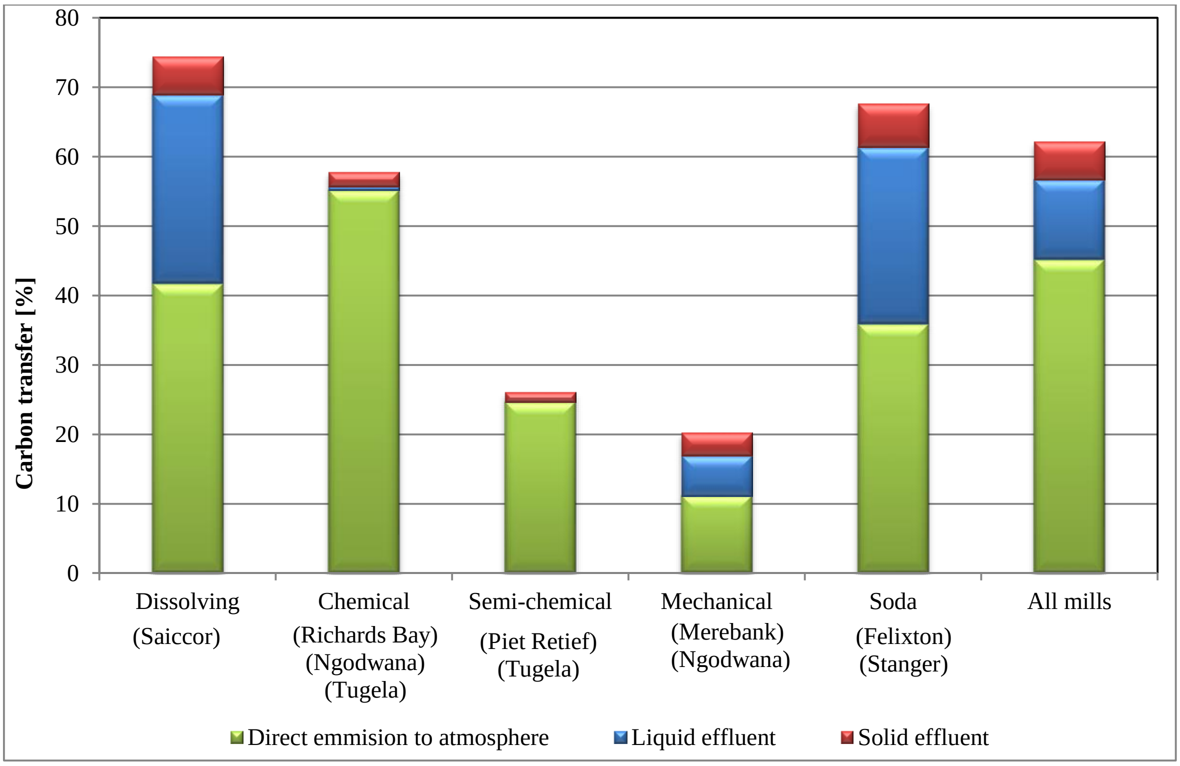

Figure 6.18: Effect of pulp product on carbon transfer to air, liquid and solid effluents

6.9.2 Effect of raw material type on carbon transfer

Figure 6.19 shows how the type of raw material used (.i.e. wood or bagasse) affects the carbon transferred to the air, liquid or solid effluents.

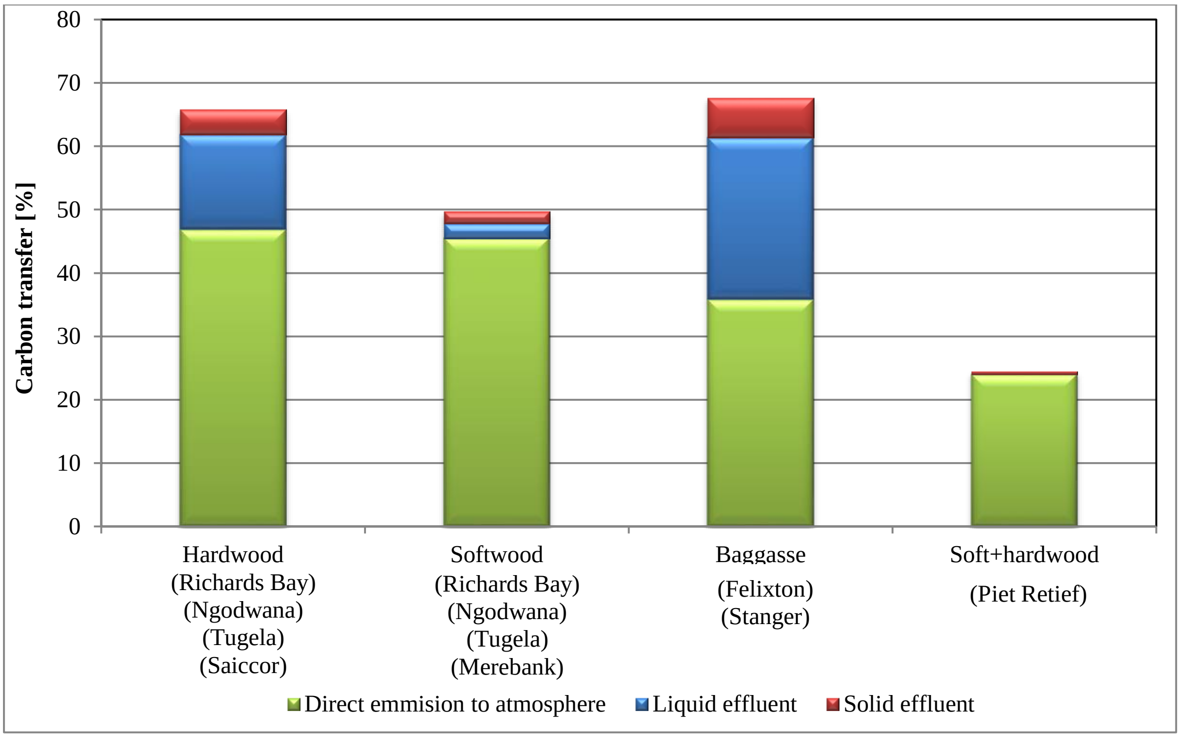

Figure 6.19: Effect of raw material type on carbon transfer to air, liquid and solid effluents

The types of raw materials used in the industry have been classified into four main groups. Some mills pulp only bagasse, or hardwoods and softwoods on separate fibre lines, while one mill pulps a mixture of softwoods and hardwoods together. By combining the mills that used a particular type of raw material, it was important that mass balance closure was achieved for each type of raw material. This task was accomplished but with some level of difficulty especially where raw materials from the bigger mills have been combined.

Mills that pulp bagasse and hardwoods had the highest carbon transfer at a combined total of 68% and 66% respectively. This was a direct consequence of the low yield achieved during pulping. Hardwood pulps are often bleached, thus, they are pulped to low kappa numbers (therefor low yield) in order to avoid putting too much pressure on the bleaching processes. Mills that used a mixture of softwoods and hardwoods had the least carbon transfer (24%) overall.

Additionally, bagasse and hardwood pulps exhibited the highest transfer of carbon to liquid effluent at 26% and 15% respectively. This can be explained by similar reasons as described previously. Also, hardwood and softwood pulps had the highest carbon transfer to the air at 47% and 45% respectively.

In most instances, the mills processing these woods had a recovery boiler in place where the spent liquor was burnt and carbon-dioxide was generated.

6.9.3 Overall carbon flows

Figure 6.20 shows the overall distribution of carbon for all the major pulp mills. Korhonen *et al*. (2001) reported that about 48% of the carbon in harvested wood ends up as CO_2 in the atmosphere as a result of combusting wood based fuel from the pulp and paper industry (see Figure 4.3 in Section 4.5.1). From Figure 6.20, 39% of the carbon ended up as CO_2 from the combustion of black liquor. It should however be noted that this value would be greater if the CO_2 from burning bark, fines as wells as CO_2 from the lime kiln are take into account. In fact, the carbon lost to the air in this regard is 45% (see Figure 6.18) which is 3% lower than the value reported by Korhonen *et al.* (2001).

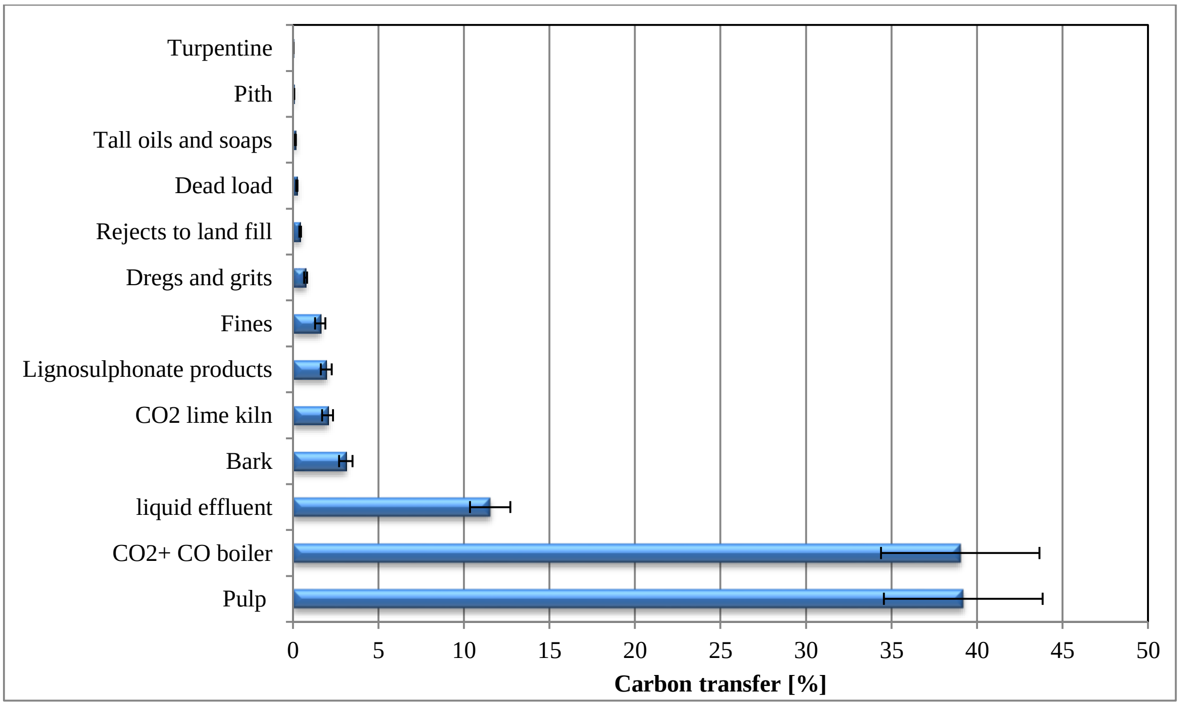

Figure 6.20: Distribution of carbon flows from wood and bagasse for all the major pulp mills

39% of the carbon ended up in the pulp, 11.5% was lost to liquid effluent, while the remaining fractions where all less than 5%.

Chapter 7. Conclusions and recommendations

This section will endeavour to provide the reader with the conclusions drawn from the results presented in the preceding section and how these results relate to the proposal of the study.

In this dissertation, a Material Flow Analysis with respect to carbon (from wood and bagasse) was conducted with the aim of tracking and quantifying the carbon flows. Overall, the results reveal that about 39% (.i.e. 1.15 Mt C) of the carbon originating from the natural resources eventually ends up in the pulp. This in itself reveals that pulp, as a product from either wood or bagasse, is a huge reservoir of organic carbon. Strictly speaking, there are other smaller reservoirs of the organic carbon such as: the lignosulphonate product, liquid effluents streams, grits, dreg, pulp mill rejects as well as bark and pith.

The lignosulphonate is commonly used for dust suppression and as an admixture for cement, which would see the carbon in this product locked away for decades if not centuries. The lignin in the effluents discharged to rivers and seas is not very susceptible to microbial degradation. Also, the grits, dregs and rejects sent to landfill will at some point decay, but this decay is slow and prone to occur over long periods of time. In fact, some of the carbon deposited into landfills will be locked away decades.

The pulp yield, which also depends on the type of raw material used and the pulping process employed, had a great effect on the carbon that ends up especially in the pulp. This meant that at high yields, the transfer of carbon to pulp was also high.

In 2011, South Africa’s greenhouse gas emissions were reported to be 433 Mt of CO_{2eq}. By considering the population (51 million) at the time, the emissions equated to 2.32 t C/capita. The carbon stored in the pulp was 0.09 t C/capita which is nearly 1% of the total carbon emissions.

If the larger mills like Mondi Richards Bay and Sappi Ngodwana increased the pulp yield on the Kraft processes by 5%, this would increase the overall carbon that reports to the pulp from 39% to 41%. This 2% increase also equates to a 2% increment in the fraction of carbon stored in pulp per capita. It is important to note that while the Saiccor mill is one of the biggest mills, it is not reasonable to increase the yield at this mill due to the sulphite process employed. This is because the desired product is pure cellulose which inevitably means that the lignin and hemicellulose that surround the cellulose must be degraded to a great extent to expose the cellulose fibres, this therefore results in lower pulp yield.

While some mills may produce one or two different types of pulps and also make use of one or two different types of raw materials, the carbon that flows either to the air, to liquid effluents or solid effluents varies greatly. This is can be observed in Figure 6.17, Figure 6.18, Figure 6.19, which ties up with the proposal that the carbon flows in the pulp mills in South Africa are affected by the type of raw materials used and the pulping processes employed. To sum up, mechanical pulp mills had the lowest carbon transfer to air, liquid and solids effluents (see Figure 6.18), while the use of a mixture of softwoods and hardwoods as a raw material for brown grade pulps resulted in the lowest carbon transfer (see Figure 6.18).

In the context of the carbon taxes that are scheduled to be implemented by the national treasury from July 2016, one could argue that the production of mechanical pulps would lead to lower carbon taxes because they contribute minimally to direct CO_2 emissions. This is correct, however, in the long run when taxes are implemented for indirect CO_2 sources from energy (from electricity) consumption, the possible taxes to be incurred for mechanical pulps would have to be examined closely due to the tremendous amount of electricity consumed by mechanical pulp mills.

Having conducted a carbon flow analysis over all pulp mills in South Africa, the following could also be investigated:

- Further studies involving carbon assessments in the forests products industry as a whole should take into account all other sources of carbon such as coal, gas, oil and electricity. This will give a much more accurate reflection of the industry’s ability to absorb or emit carbon (i.e. whether it is carbon positive or carbon negative).
- Additionally, the social and economic implications of the carbon flows should be tackled in future studies to provide a holistic account on the sustainability of the industry with respect to carbon. In fact, Statistical Entropy Analysis, which is an evaluation tool for Material Flow Analysis studies, has been hailed as a robust and powerful tool for measuring the sustainability of industrial processes. It is founded on concepts from the field of information theory and statistical mechanics and can actually be used to measure the industry’s ability to concentrate or dilute carbon.
- A farfetched idea would be to drop the conventional pulping processes entirely and adopt the use of Deep Eutectic Solvents (DES), which have the ability to separate the different constituents in wood (i.e. cellulose, hemicellulos, and lignin) into their individual entities. This technology is at a developmental stage and should be investigated further because it has the potential to cut back on carbon emissions coupled with high energy savings (see Appendix 8).

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Appendix 1

Calculations on the Mondi Richards Bay Mill

This section will endeavour to provide the reader with a detailed and chronological algorithm on how the carbon mass balance was conducted for five of the mills investigated in the study. The sample calculations presented in this section have been done for Kraft (Mondi Richards Bay), Soda (Mpact Felixton), Sulphite (Sappi Saiccor) and Mechanical (Mondi Merebank) pulping processes. A sample calculation has not been done for a Semi-mechanical pulping process because it is quite similar to the kraft. The data used in the calculations together with a rationale for the mass balance will also be presented. Furthermore, the premises on which a given set of data was rejected will be validated with evidence from the literature.

The Mondi Richards Bay mill has two fibre lines, one for softwoods (mainly *P. patula*) that produces pulp via batch kraft, while the other fibre line produces pulp from hardwoods (mainly *E. grandis*) via continuous kraft. Spent liquor from each fibre line is mixed and stored before being transferred to the liquor recovery circuit. Table A1.1 is a list of the data used for the mass balance.

Table A1.1: List of data for mass balances-Richards Bay Mill

	Value	**Source**
Mass of pulp produced	116 377 ADt/yr	PAMSA
Unbleached Yield (SW)	56%	Mill
Unbleached Yield (HW)	52%	Mill
% Bark in wood	11.8%	(Wright, 1994)
% Carbon in wood	50%	(Biermann, 1996)
Debarking efficiency	98%	(Kerr, 2013)
% Carbon in bark	50.6%	(Gavrilescu, 2008)
Turpentine density	850 kg/m^3	(Mirov, 1961)
Turpentine volume	17.9m^3/month	From Mill

Figure A1.1 is a block flow diagram showing the flow of carbon from wood through the softwood line.

A1.1 Mass balance – Softwood line

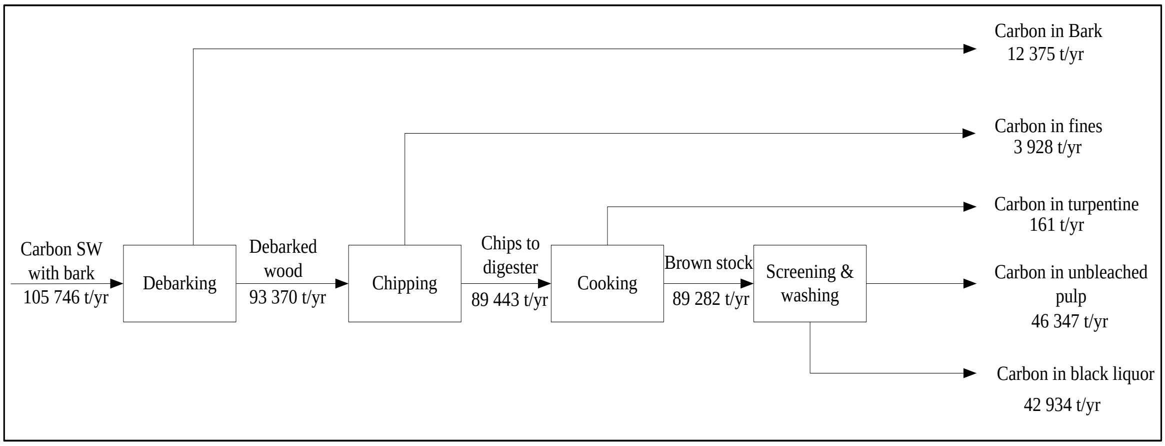


Figure A1.1: Block flow diagram of carbon flow through softwood line

<u>Mass balance rational</u>

Using the unbleached pulp yield, it was possible to calculate the mass of debarked softwood. The next step was to calculate the mass of dry softwood with bark. This was not trivial because while a significant portion of the bark was removed (i.e. 98%); there was a small portion that remained with the wood sent for chipping. Nonetheless, through some derivations, it was possible to determine the mass of dry wood with bark. This will be shown next.

$$\text{Let B} = \text{Mass of bark}$$

$$\text{WB} = \text{Mass of dry wood with bark}$$

$$\text{DW} = \text{Mass of debarked wood}$$

$$\%\text{B} = \text{Mass fraction of bark in wood}$$

$$\%\text{Ef} = \text{Debarking efficiency}$$

$$\text{Now,} \qquad \text{B} = \text{WB} \times \%\text{B} \times \%\text{Ef}$$

$$\text{And,} \qquad \text{WB} = \text{B} + \text{DW}$$

$$\text{So,} \qquad \text{WB} = (\text{WB} \times \%\text{B} \times \%\text{Ef}) + \text{DW}$$

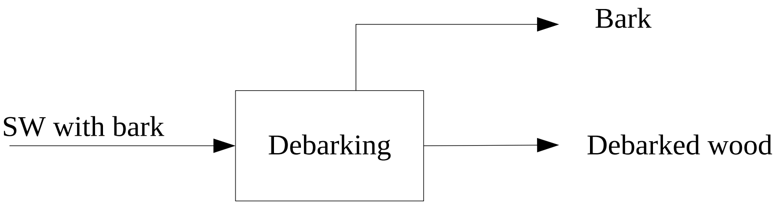
$$\text{Thus,} \qquad \text{WB}\big(1 - (\%\text{B} \times \%\text{Ef})\big) = \text{DW}$$

$$\Rightarrow \text{WB} = \frac{\text{DW}}{1 - (\%\text{B} \times \%\text{Ef})}$$

Since the mass of debarked wood was calculated from the yield, and because all other parameters are given, the mass of wood with bark can be determined. It should be noted that it was important to conduct this exercise because the carbon in the incoming wood could be determined once the total dry wood mass was known.

Debarking

Of the softwoods processed, 11.8% is bark based on the dry weight of wood. According to Ashton and Cassidy (2007), wood biomass and bark has a calorific value of 19.8 MJ/kg and 19.6 MJ/kg respectively. Because the calorific value depends on the relative proportion of carbon, hydrogen and oxygen in wood; and since wood and bark has similar caloric values, it was expected that the elemental composition of bark would be similar to that of dry wood; thus taking 50% carbon content for bark was used as a first estimate. The validity of this assumption was later confirmed by the work of Gavrilescu (2008) who reported the composition of pulp wood bark to be 50.6% on a dry basis.



The mass of debarked wood was calculated from the yield. This was because the original mass of the wood reported by PAMSA together with the moisture content, led to a much higher yield than what the mill was reporting. To overcome this inconsistency, it was decided to work backwards by using the pulp produced and the pulp yield to calculate the feed of debarked wood. The mass of unbleached pulp was reported as air-dry tonnes (10%). This means that it contains 10% moisture content, while the remaining 90% is the fraction containing lignin, cellulose and hemicellulose.

$$\text{Mass of debarked wood} = \frac{\text{Mass of Unbleached pulp}}{\text{Unbleached Yield (SW)}}$$

$$\text{Mass of debarked wood} = \frac{116\ 377\frac{\text{ADt}}{\text{yr}} \times \frac{90}{100}}{\frac{56}{100}} = 187\ 034\frac{\text{t}}{\text{yr}}$$

Now applying the formula derived previously:

$$\text{WB} = \frac{\text{DW}}{1 - (\%\text{B} \times \%\text{Ef})}$$

$$\text{Mass of dry wood with bark} = \frac{187\ 034\frac{\text{t}}{\text{yr}}}{1 - \left(\frac{11.8}{100} \times \frac{98}{100}\right)} = 211\ 491\frac{\text{t}}{\text{yr}}$$

$$\text{Mass of bark removed} = \text{Mass of dry wood with bark} \times \%\text{Bark in wood} \times \text{Debarking efficiency}$$

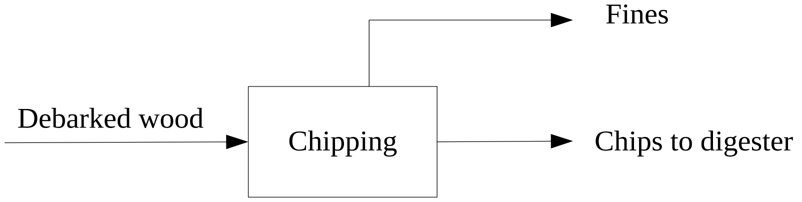
$$\text{Mass of bark removed} = 211\ 491\frac{\text{t}}{\text{yr}} \times 0.118 \times 0.98 = 24\ 457\frac{\text{t}}{\text{yr}}$$

Wood and bark have about the same carbon content (i.e. 50%).

$$\text{C}_{\text{Debarked wood}} = \text{C}_{\text{SW with bark}} - \text{C}_{\text{bark}}$$

$$C_{\text{Debarked wood}} = \left(0.5 \times 211\,491\frac{\text{t}}{\text{yr}}\right) - \left(0.506 \times 24\,457\frac{\text{t}}{\text{yr}}\right) = 93\,370\frac{\text{t}}{\text{yr}}$$

Chipping



According to Gavrilescu (2008), the mass of fines generated from chip screening ranges from 50-100kg/ t of pulp which amounts to 75kg/ t of pulp on average. The carbon content of fines is also assumed to be 50%. Thus, the mass of chips to fines was calculated as follows:

$$\text{Mass of fines} = \frac{75}{1000} \times \left(116\,377\frac{\text{ADt}}{\text{yr}} \times \frac{90}{100}\right) = 7\,855\frac{\text{t}}{\text{yr}}$$

$$\text{Mass of chips to digester} = \text{Mass of debarked wood} - \text{Mass of fines}$$

$$\text{Mass of chips to digester} = 187\,034\frac{\text{t}}{\text{yr}} - 7\,855\frac{\text{t}}{\text{yr}} = 179\,179\frac{\text{t}}{\text{yr}}$$

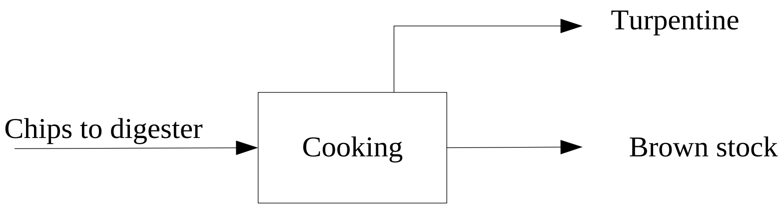
$$C_{\text{chips to digester}} = C_{\text{debarked wood}} - C_{\text{fines}}$$

$$C_{\text{chips to digester}} = 93\,370\frac{\text{t}}{\text{yr}} - \left(0.5 \times 7\,855\frac{\text{t}}{\text{yr}}\right) = 89\,443\frac{\text{t}}{\text{yr}}$$

Digester

Turpentine was recovered only on the softwood fibre line; perhaps due to a higher content of extractives in softwoods compared to hardwoods. It was then stored temporarily in a 25m^3 storage tank from which the turpentine was pumped when the tank level reached just about 80%. The amount of turpentine recovered was calculated based on the difference between the volume of turpentine in the tank between two time intervals before and after the tank was emptied. The calculations revealed that 1.57 kg of turpentine was recovered per tonne of pulp produced. This value was comparatively low because the expected value falls in the range of 5-10 kg/t of pulp as reported by Sixta *et al.* (2006). Since the extractives in wood stimulate the production of turpentine (an organic compound) it is quite possible that the small recovery of crude turpentine could be attributed to a lower proportion of extractives in the softwoods.

Fibre in the pulp mill rejects are continuously recycled to the digesters and the amount discarded as rejects were far too small compared to the amount of wood processed and would therefore have an insignificant effect on the overall carbon flow; for this reason, they were ignored in the calculations.



The volumetric flow rate of turpentine was estimated by considering the volume of turpentine in the storage tank between two time intervals and was found to be 17.9m^3/month. The monoterpenes in turpentine have the formula ($C_{10}H_{16}$) and thus have a carbon content of 88% by mass.

$$\text{Mass of turpentine} = \text{Tupentine density } \times \text{Turpentine volumetric flow rate}$$

$$\text{Mass of turpentine} = 850\frac{\text{kg}}{\text{m}^3} \times 17.9\frac{\text{m}^3}{\text{month}} \times \frac{1\text{t}}{1000\text{kg}} \times \frac{12\text{months}}{1\text{yr}} = 183\frac{\text{t}}{\text{yr}}$$

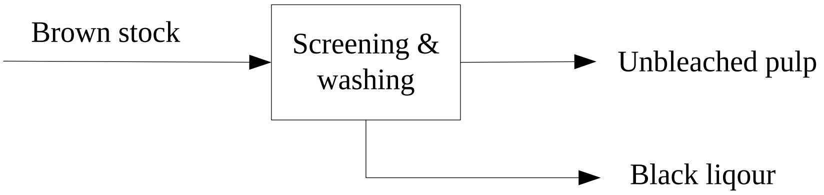
$$\text{Mass of brownstock with liqour} = \text{Mass of chips to digester} - \text{Mass of turpentine}$$

$$\text{Mass of brownstock with liqour} = 179\ 179\frac{\text{t}}{\text{yr}} - 183\frac{\text{t}}{\text{yr}} = 178\ 996\frac{\text{t}}{\text{yr}}$$

$$\text{Therefore, } C_{\text{Brown stock}} = C_{\text{Chips to digester}} - C_{\text{turpentine}}$$

$$C_{\text{Brownstock}} = 89\ 443\frac{\text{t}}{\text{yr}} - \left(0.88 \times 183\frac{\text{t}}{\text{yr}}\right) = 89\ 282\frac{\text{t}}{\text{yr}}$$

<u>Screening and washing</u>



To determine the mass of organics from wood that ends up in the black liquor from the SW fibre line, the mass of unbleached pulp was subtracted from the mass of brown stock with liquor solids. The mas of unbleached pulp was 116 377 ADt/yr.

$$\text{Mass of organics to recovery} = \text{Mass of Brownstock} - \text{Un bleached pulp}$$

$$\text{Mass of organics to recovery} = 178\ 996\frac{\text{t}}{\text{yr}} - \left(116\ 377\frac{\text{t}}{\text{yr}} \times \frac{90}{100}\right) = 74\ 257\frac{\text{t}}{\text{yr}}$$

The challenge was to determine the carbon that ends up in the black liquor. This was achieved by first estimating the carbon in the unbleached pulp. Since the wood was pulped to 60 kappa, it was possible to determine the fraction of lignin in the pulp. Lignin contains about 67% carbon. The remaining portion of the pulp was assumed to be equal parts of cellulose (44% carbon) and hemicellulose (40% carbon) with an average carbon content of 42%. This assumption would be somewhat inaccurate because there was a greater fraction of cellulose in softwoods and also because the hemicellulose surrounds the cellulose and as such, it would be more susceptible to chemical degradation, hence its fraction would have been reduced.

$$\text{lignin [\%]} = 0.15 \times \text{kappa number}$$

$$\text{lignin [\%]} = 0.15 \times 60 = 9\%$$

$$\text{Mass of lignin in pulp} = \text{lignin [\%]} \times \text{Mass of unbleached pulp}$$

$$\text{Mass of lignin in pulp} = \frac{9}{100} \times \left(116\,377 \frac{\text{ADt}}{\text{yr}} \times \frac{90}{100}\right) = 9\,427 \frac{\text{t}}{\text{yr}}$$

$$\text{C}_{\text{unbleached pulp}} = \text{C}_{\text{lignin}} + \text{C}_{\text{cellulose\&hemicellulose}}$$

$$\text{C}_{\text{unbleached pulp}} = \left(0.67 \times 9\,427 \frac{\text{t}}{\text{yr}}\right) + 0.42 \times \left(\left(116\,377 \frac{\text{ADt}}{\text{yr}} \times \frac{90}{100}\right) - 9\,427 \frac{\text{t}}{\text{yr}}\right) = 46\,347 \frac{\text{t}}{\text{yr}}$$

$$\text{C}_{\text{black liquor}} = \text{C}_{\text{brown stock}} - \text{C}_{\text{unbleached pulp}}$$

$$\text{C}_{\text{black liquor}} = 89\,282 \frac{\text{t}}{\text{yr}} - 46\,347 \frac{\text{t}}{\text{yr}} = 42\,934 \frac{\text{t}}{\text{yr}}$$

A1.2 Mass balance – Hardwood line

Figure A1.2 shows a block flow diagram of carbon flows throw the hardwood line.

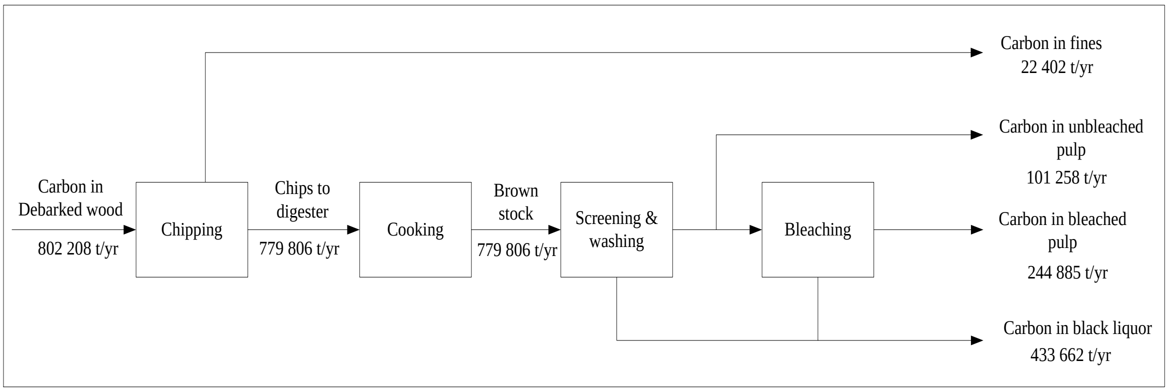


Figure A1.2: Block flow diagram of carbon flow through hardwood line

The mass balance for the hardwood line was similar to that of the softwood line. One difference being that there was no wood debarking since it is done at the forest. Secondly, hardwoods have a very small amount of extractives, thus, no turpentine was recovered on the hardwood line. Another difference was that most of the pulp is bleached to a very low kappa number (~0) which suggests that the lignin content of the pulp is very low. Thus, the carbon content of the pulp was taken as the average of that of cellulose and hemicellulose, which is 42%.

A1.3 Mass balance – Liquor recovery cycle

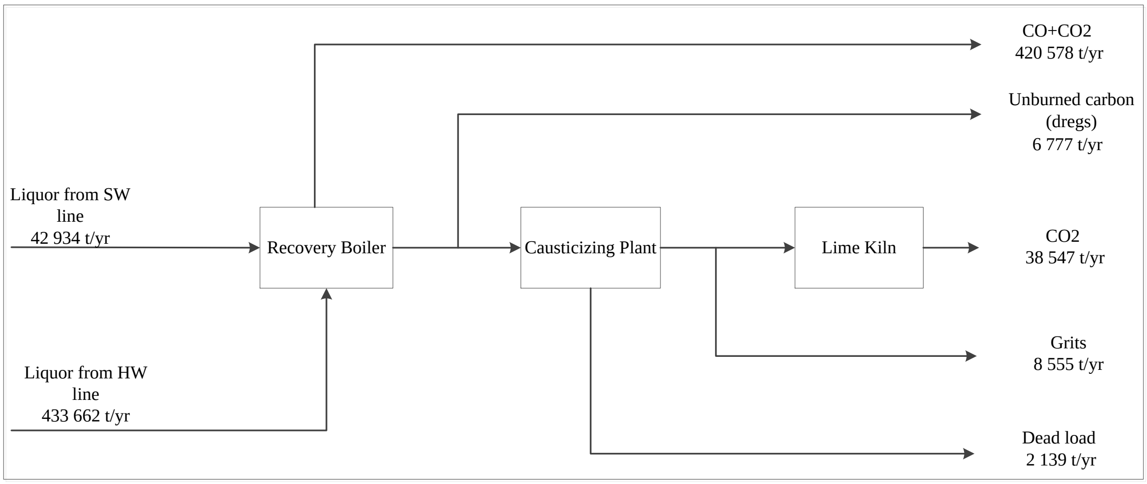


Figure A1.3: Block flow diagram of carbon flows in the liquor recovery cycle

The liquor from both the soft and hardwood lines are mixed (see Figure A1.3) to give a combine total carbon flow of 476 596 t/yr. It was assumed that liquor from the two lines exhibit similar chemical characteristic (e.g. composition) thus upon mixing, these properties are maintained.

Recovery boiler

For simplicity, the detailed mass balance conducted over the recovery boiler has been omitted (refer to Section 5.1.3. for details). Nonetheless, the carbon balance generated is shown in Table A1.2. Furthermore, it was assumed that the unburned carbon is filtered off.

Table A1.2: Results of carbon balance over recovery boiler

	Flow rate [t/yr]
In: C in HBL	476 596
Out: C CO in flue gas	10
Out: C CO_2 in flue gas	420 568
Out: C in Na_2CO_3 in smelt	46 443
Out: C in K_2CO_3 in smelt	2 798
Out: C unburned carbon in smelt	6 777

Recaustisizer

Using a causticizing efficiency (CE) of 83%, it was possible to determine the amount of calcium carbonate formed from the causticizing reaction, as well as the sodium carbonate that remained unreacted. The analogy employed was that sufficient amount of slaked lime (i.e. calcium hydroxide) was present to force an 83% conversion rate of sodium carbonate to calcium carbonate and sodium hydroxide.

$$\mathrm{CaCO_3\ formed = Na_2CO_3forned \times CE \times \frac{M_r(CaCO_3)}{M_r(Na_2CO_3)}}$$

$$\mathrm{Na_2CO_3\ formed = C_{Na_2CO_3} \times \frac{M_r(Na_2CO_3)}{M_r(C)}}$$

$$\mathrm{Na_2CO_3\ formed} = 46\,443\frac{\mathrm{t}}{\mathrm{yr}} \times \frac{106}{12} = 410\,244\frac{\mathrm{t}}{\mathrm{yr}}$$

$$\text{Therefore, } \mathrm{CaCO_3\ formed} = 410\,244\tfrac{\mathrm{t}}{\mathrm{yr}} \times 0.83 \times \tfrac{100}{106} = 321\,228\tfrac{\mathrm{t}}{\mathrm{yr}}$$

$$\mathrm{Unreacted\ Na_2CO_3 = Na_2CO_3formed \times (1 - CE)}$$

$$\mathrm{Unreacted\ Na_2CO_3} = 410\,244\frac{\mathrm{t}}{\mathrm{yr}} \times (1 - 0.83) = 69\,741\frac{\mathrm{t}}{\mathrm{yr}}$$

80% of the unreacted sodium carbonate, calcium carbonate formed and potassium carbonate were assumed to be purged while the remaining 20% was assumed to circulate as dead load (refer to Section 5.1.3.6). This calculation has not been shown because it is trivial.

Kiln

It was assumed that all the calcium carbonate (which originated from wood carbon) was converted to carbon-dioxide and calcium oxide. This assumption was important because some of the carbon in the make-up calcium carbonate added would also end up as carbon-dioxide, and perhaps some would not be converted. It therefore becomes problematic to determine unreacted calcium carbonate that originated from wood carbon.

$$\mathrm{CO_2\ formed = CaCO_3\ burned\ \times \frac{M_r(CO_2\,)}{M_r(CaCO_3)}}$$

$$\mathrm{CO_2\ formed} = 321\,228\frac{\mathrm{t}}{\mathrm{yr}} \times \frac{44}{100} = 141\,341\frac{\mathrm{t}}{\mathrm{yr}}$$

Appendix 2

Calculations on the Mondi Merebank Mill

The list of data used for the carbon flow calculations for the Mondi Merebank Mill is shown in Table A2.1.

Table A2.1: List of data for mass balance at Mondi Merebank Mill

	Value	**Source**
Mass of wood	348 175 t/yr	From mill
Moisture content of wood/bark	60%	From mill
Mass of bark (wet)	60 196 t/yr	From mill
Mass of purchased chips (dry)	25 344 t/yr	From mill
Mass of unbleached pulp	115 594 t/yr	From mill
Chips to rejects (wet)	10 405 t/yr	From mill

Figure A2.1 is a schematic showing the flow of carbon at Mondi Merebank Mill.

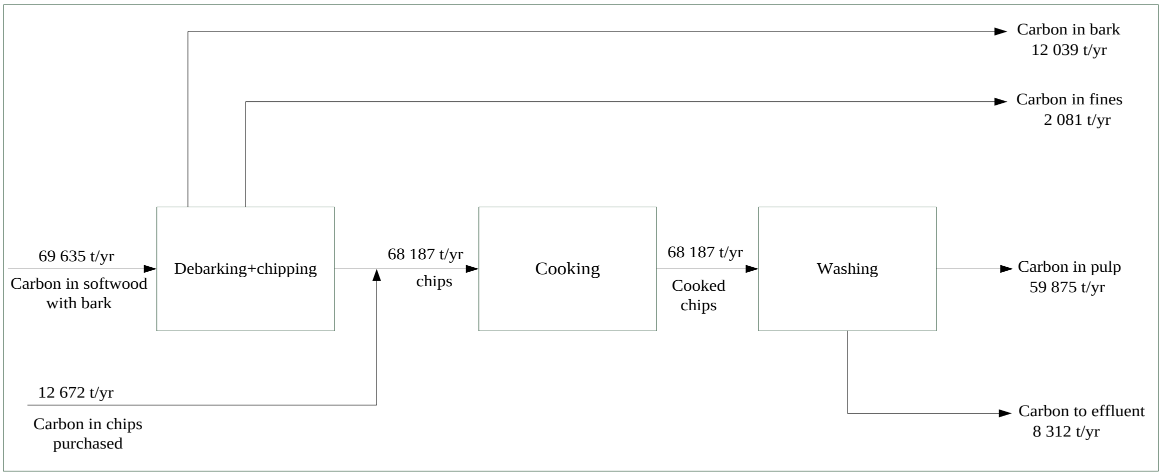


Figure A2.1: Block flow diagram of main fibre line at Mondi Merebank Mill

Debarking

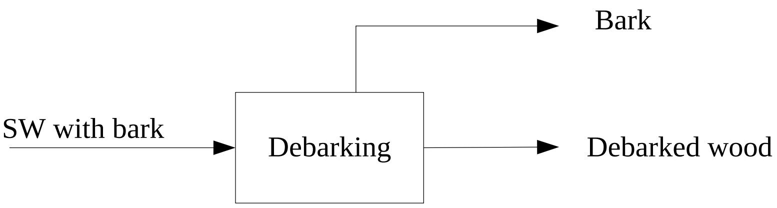
The softwood contains 60% moisture. This moisture content is assumed to be the same for bark. The mass of bark measured was 24 078 t/yr. After subtracting the moisture content and the bark removed wood, this yields the dry weight of wood sent for chipping.

$$\text{Mass of dry debarked wood} = \text{Mass of dry wood wth bark} - \text{Mass of bark (dry)}$$

$$\text{Mass of dry debarked wood} = (348\ 175 \times 0.4) - (60\ 196 \times 0.4) = 115\ 192\,\frac{\text{t}}{\text{yr}}$$

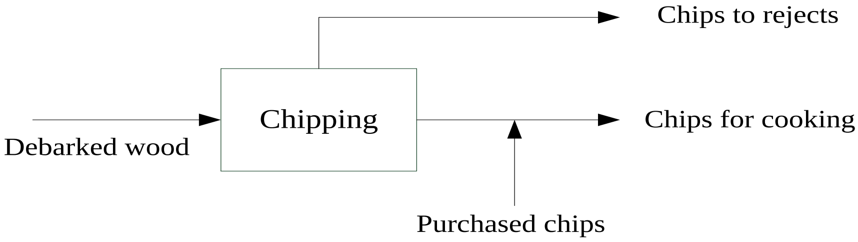
$$\text{C}_{\text{debarked wood}} = \text{C}_{\text{SW with bark}} - \text{C}_{\text{Bark}}$$

$$\text{C}_{\text{debarked wood}} = (0.5 \times 139\ 270) - (0.5 \times 24\ 078) = 57\ 596\,\frac{\text{t}}{\text{yr}}$$



Chipping

Fine chips to rejects were measured as 10 405 t/yr (on a wet basis). The mass of chips sent for cooking was calculated as the sum of chips purchased and the chips from debarked wood.



$$\text{Mass of chips to digester} = \text{Mass of chips from debarked wood} + \text{Mass of chips purchased}$$

$$\text{Mass of chips from debarked wood} = \text{Mass of debarked wood} - \text{Mass of chips to rejects}$$

$$\text{Mass of chips from debarked wood} = 115\ 192 - (0.4 \times 10\ 405) = 111\ 030 \frac{\text{t}}{\text{yr}}$$

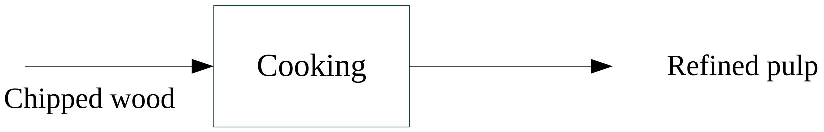
$$\text{Mass of chips to digester} = 111\ 030 + 25\ 344 = 136\ 374 \frac{\text{t}}{\text{yr}}$$

$$\text{C}_{\text{chips to digester}} = \text{C}_{\text{debarked wood}} + \text{C}_{\text{purchased chips}} - \text{C}_{\text{fines}}$$

$$\text{C}_{\text{chips to digester}} = 57\ 596 + (0.5 \times 25\ 344) - (0.5 \times 0.4 \times 10\ 405) = 68\ 187 \frac{\text{t}}{\text{yr}}$$

Cooking

The mass of chips cooked is equal to the mass of pulp produced. This also holds for the carbon balance.



$$\text{Mass of refined pulp} = \text{Mass of chips to digester} = 136\ 374 \frac{\text{t}}{\text{yr}}$$

$$C_{\text{refined pulp}} = \text{C}_{\text{chips to digester}} = 68\ 187 \frac{\text{t}}{\text{yr}}$$

Washing and screening

Because the mass of pulp was known, it was easy to estimate the amount of pulp material that ended up in the effluent. It was thus assumes that the degraded fraction that reported to the effluent is degraded hemicellulose with a carbon content of 40%. However, the problem lied in estimating the amount of carbon in the screened pulp and the carbon that reported to the effluent. Because mechanical pulps often retain much of the lignin derived from wood, it was expected that their carbon content would be higher compared to other kinds of pulp. As such, as a simplifying assumption, all the lignin was assumed to reside in the pulp, while the yield loss was attributed to hemicellulose degradation. The yield was calculated as 82%.

$$\text{Mass of pulp to effluent} = \text{Mass of refined pulp} - \text{Mass of screened pulp}$$

$$\text{Mass of pulp to effluent} = 136\,374 - 115\,594 = 20\,780\,\frac{\text{t}}{\text{yr}}$$

$$\text{C}_{\text{screened pulp}} = \text{C}_{\text{refined pulp}} - \text{C}_{\text{pulp to efluent}}$$

$$\text{C}_{\text{screened pulp}} = 68\,187 - (0.4 \times 20\,780) = 59\,875\,\frac{\text{t}}{\text{yr}}$$

Appendix 3

Calculations on the Sappi Saiccor Mill

Table A3.1 contains the list of data used in the carbon calculations for the Sappi Saiccor Mill

Table A3.1: List of data for Sappi Saiccor Mill

	Value	**Data Source**
Bleached pulp produced MgO1 line	233 729 ADt	From Mill
Bleached pulp produced MgO2 line	283 233 ADt	From Mill
Bleached pulp produced Ca line	209 485 ADt	From Mill
Yield (unbleached)	0.472 BDt pulp/BDT wood	From Mill
Yield (bleached)	0.875 BDt bleached pulp/ BDt unbleached pulp	From Mill
Moisture content	39%	From Mill
Rejects	2-3% of unbleached pulp, 50% to landfill, 50% to boiler.	From Mill
Total dry wood processed	1 680 445 BDt/yr	From Mill
K number of pulp before bleaching	3	From Mill
Density of spent liquor Ca line	1050 kg/m^3	From Mill
Flow rate of liquor to sea	2800 m^3/day	From Mill
Flow rate of liquor to LTSA	4000 m^3/day	From Mill
Solids content of liquor	12.5%	From Mill
Carbon content of liquor	37.9%	Calculated

A3.1 Mass balance - Calcium line

Figure A3.1 is a simplified block flow diagram that traces the flow of material and hence carbon through the calcium line at the Sappi Saiccor mill.

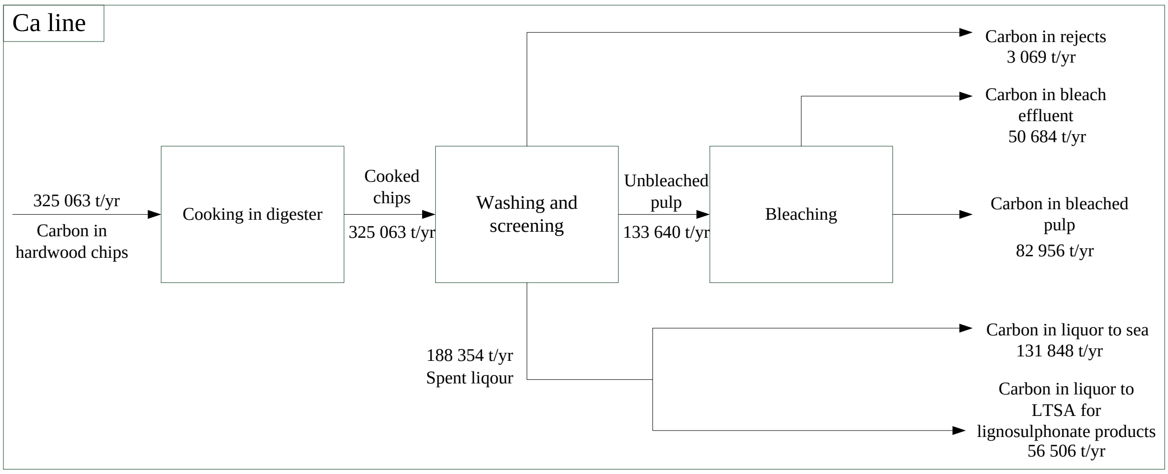
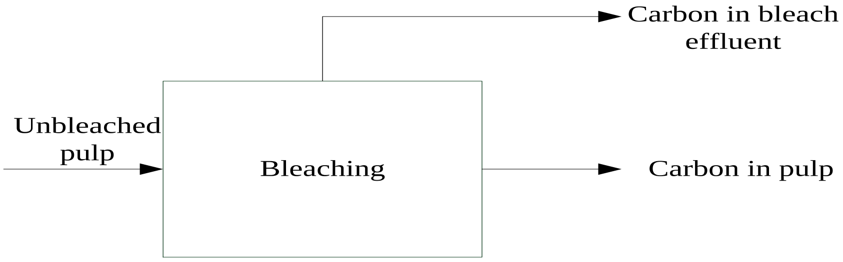


Figure A3.1: Block flow diagram of calcium line at Sappi Saiccor Mill

<u>Rationale for mass balance</u>

The mass of wood processed on the calcium line was not given; however, the total wood processed over all three fibre lines was given together with the yield before bleaching and after bleaching. With this information, it was possible to calculate the feed in various ways. But one way was to start at the bleach plant, and then using the data on pulp produced and the yields provided in Table A3.1, the mass of unbleached pulp could be calculated (see Appendix 6, Section A6.2 for derivation) and hence the feed.

Balance over bleach plant



The mass of unbleached pulp was calculated as follows:

$$\text{Unbleached pulp} = \text{Bleached pulp} \times \left(\frac{\text{Yield(unbleached)}}{\text{Yield(bleached)}}\right)$$

$$\text{Unbleached pulp} = \left(209\ 485\frac{\text{ADt}}{\text{yr}} \times 0.9\right) \times \left(\frac{0.472}{0.29}\right) = 306\ 859\frac{\text{BDt}}{\text{yr}}$$

Knowing the yield loss over the bleach plant, it was actually possible to determine the fraction of unbleached pulp lost to bleach effluent.

$$\text{Loss to bleach effluent} = \text{Unbleached pulp} - \text{Bleached pulp}$$

$$\text{Loss to bleach effluent} = 306\ 859\frac{\text{BDt}}{\text{yr}} - \left(209\ 485\frac{\text{ADt}}{\text{yr}} \times 0.9\right) = 118\ 323\frac{\text{BDt}}{\text{yr}}$$

The material lost to the bleach effluent will comprise of cellulose, hemicellulose, lignin and some extractives. The extractives in hardwoods are very low therefore they are ignored. The difficulties hear lies in determining the relative proportions of lignin, cellulose and hemicellulose lost to the effluent, which was almost impossible to determine since the study relied on historical data. In some studies, such as the work of Côté *et al*. (2002), they assumed that all losses to bleach effluent was completely lignin. This unforgiving assumption immediately overestimates the carbon lost to effluent simply because lignin has higher carbon content (67%) than both cellulose (44%) and hemicellulose (40%).

The strategy adopted in this study was to calculate the mass of lignin lost to effluent so that the remainder of the material lost to effluent would be assumed to be a combination of cellulose and hemicellulose with an average carbon content of 42%.

The residual lignin in the bleached pulp was much less than 0.1%, therefore as a simplifying assumption, all the lignin in the unbleached pulp was assumed to be removed in the bleaching stage. The lignin removed would end up in the bleach effluent. To determine the lignin in the unbleached pulp, the permanganate number (or K number) of the pulp was used. There is no direct correlation between the K number and the lignin content; however, with the understanding that the kappa number is directly related to the lignin content of the pulp, it was useful to find a correlation that relates the K number to kappa number. One such correlation has been reported by Biermann (1996), nonetheless, this correlation holds for K numbers measured with 40ml of permanganate (for low yield pulps) as in Equation (A3.1).

$$\log(\text{kappa no.}) = 0.837 + 0.0323 \times\ (40\text{ ml K no.}) \tag{A3.1}$$

For pulps produced using hardwoods either via kraft or sulphite processes, the following relationship between kappa number and lignin content has also been reported by Biermann (1996) given by Equation (A3.2).

$$\text{lignin [\%]} = 0.15 \times \text{kappa number} \tag{A3.2}$$

$$\text{therefore,}\ \ \text{lignin [\%]} = 0.15 \times 10^{0.837+0.0323\times\ (40\text{ ml K no.})}$$

$$\text{lignin [\%] in unbleached pulp} = 0.15 \times\ 10^{0.837+0.0323\times\ (3)} = 1.288\%$$

$$\text{Mass lignin in unbleached pulp} = \frac{1.288}{100} \times 306\ 859 \frac{\text{BDt}}{\text{yr}} = 3\ 953 \frac{\text{t}}{\text{yr}}$$

$$\text{C}_{\text{bleach effluent}} = \text{C}_{\text{lignin}} + \text{C}_{\text{cellulose\&hemicellulose}}$$

$$\text{C}_{\text{bleach effluent}} = (0.67 \times 3\ 953) + 0.42 \times (118\ 323 - 3\ 953) =\ 50\ 684 \frac{\text{t}}{\text{yr}}$$

The cellulose pulp was assumed to contain pure cellulose with no lignin in it. All the lignin was assumed to be lost through the bleach effluent.

$$\text{C}_{\text{bleached pulp}} = 0.44 \times \left(209\ 485 \frac{\text{ADt}}{\text{yr}} \times 0.9\right) = 82\ 956\ \frac{\text{t}}{\text{yr}}$$

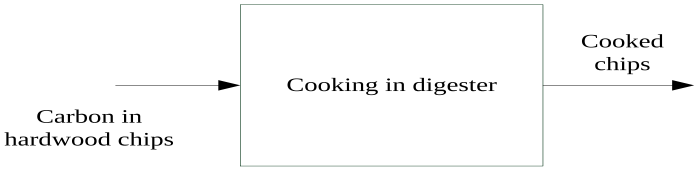
The carbon in the unbleached pulp was calculated as the sum of the carbon that ends up in the pulp and the carbon that reports to the bleach effluent.

$$\text{C}_{\text{unbleached pulp}} = \text{C}_{\text{bleach effluent}} + \text{C}_{\text{bleached pulp}}$$

$$\text{C}_{\text{unbleached pulp}} = 50\ 684 + 82\ 956\ \ = 133\ 640 \frac{\text{t}}{\text{yr}}$$

This completes the mass balance over the bleach plant.

Balance over digester



Using either the bleached or unbleached pulp yield, it was possible to determine the mass of wood processed as mentioned earlier.

$$\text{Mass of wood chips} = \frac{\text{bleached pulp}}{\text{Yield (bleached)}}$$

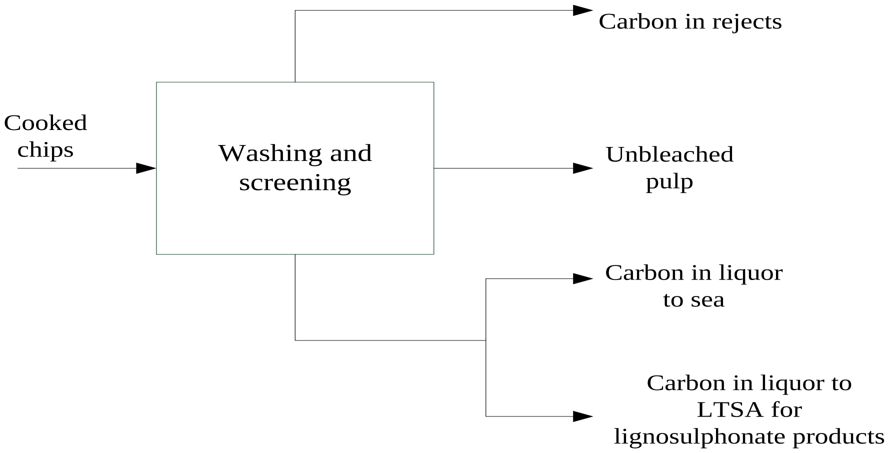
$$\text{Mass of wood chips} = \text{Mass of cooked chips} = \frac{188\ 537\,\frac{\text{BDt}}{\text{yr}}}{0.29} = 650\ 126\,\frac{\text{BDt}}{\text{yr}}$$

Wood contains on average about 50% carbon on a dry basis. This value has been reported by various authors (Biermann, 1996, Pettersen, 1984, Pingoud *et al*., 2006).

$$\text{Carbon in wood chips} = \text{carbon in cooked chips} = 50\% \times \text{Mass of chips (on dry basis)}$$

$$\text{Carbon in wood chips} = 0.5 \times 650\ 126\,\frac{\text{BDt}}{\text{yr}} = 325\ 063\,\frac{\text{t}}{\text{yr}}$$

Balance over washing and screening



The material that reports to the spent black liquor stream contains wood solids, lignin and inorganic chemicals from the puling process. This quantity of wood solids and lignin (not including inorganics) was calculated by subtracting the unbleached pulp and pulp mill rejects from the mass of cooked chips from the digester.

$$\text{Spent liquor (Wood solids + lignin)} = \text{Cooked chips} - \text{Unbleached pulp} - \text{Pulp mill rejects}$$

$$\text{Spent liquor(without inorganics)} = 650\ 126\,\frac{\text{BDt}}{\text{yr}} - 306\ 859\,\frac{\text{BDt}}{\text{yr}} - \left(0.025 \times 306\ 859\,\frac{\text{BDt}}{\text{yr}}\right) = 335\ 595\,\frac{\text{BDt}}{\text{yr}}$$

The rejects are 2.5% of unbleached pulp and are assumed to be mainly degraded hemicelluloses with a carbon content of 40%. With this assumption, it was possible to calculate the amount of carbon that ends up in the spent liquor since all other inputs and outputs are now known.

$$\mathrm{C}_{\text{spent liquor}} = \mathrm{C}_{\text{cooked chips}} - \mathrm{C}_{\text{unbleached pulp}} - \mathrm{C}_{\text{pulp mill rejects}}$$

$$\mathrm{C}_{\text{spent liquor}} = 325\,063\,\frac{\mathrm{t}}{\mathrm{yr}} - 133\,640\,\frac{\mathrm{t}}{\mathrm{yr}} - 0.4 \times (0.025 \times 306\,859)\,\frac{\mathrm{t}}{\mathrm{yr}} = \ 188\,354\,\frac{\mathrm{t}}{\mathrm{yr}}$$

It is worth noting that although the flow rate of the spent liquor (4000 m^3/day), density (1050 kg/m^3) and solids content (12.5%) was given, using these values led to inconsistent results in the mass balance, this will be shown next.

The composition of spent sulphite liquor in the case where hardwoods are used for pulping has been reported by Lin and Lebo (2001) as shown in Table A3.2.

Table A3.2: Composition of spent sulphite liquor

	% of total solids (Lin and Lebo, 2001)	**% C content**	**Mass of carbon per 100 kg of solids**
Lignosulphonate	42	47	19.7
Hexose sugars ($C_6H_{12}O_6$)	5	40	2
Pentose sugars ($C_5H_{10}O_5$)	20	40	8
Non-cellulosic carbohydrates	11	40	4.4
Acetic and formic acid	9	33	2.97
Resins and extractives	1	83	0.83
Ash	10	0	0
Total			37.9

The chemical formula for lignosulphonate isolated from softwoods and hardwoods has been reported to be $C_9H_{8.5}O_{2.5}(OCH_3)_{0.85}(SO_3H)_{0.4}$ and $C_9H_{7.5}O_{2.5}(OCH_3)_{1.39}(SO_3H)_{0.8}$ (Lin and Lebo, 2001). This chemical formula was used to compute the percentage of carbon in the lignosulphonate. Acetic (CH_2O_2) and formic acid ($C_2H_4O_2$) on average contain 33% carbon. On aggregate, the spent sulphite liquor has 37.9% carbon. It should be noted that this 37.9% carbon content represents the carbon in the liquor solids which obviously contains inorganics from the pulping process. Using the data given (i.e. 4000 m^3/day) the mass of liquor solids is calculated as:

$$\text{Mass of liquor solids (with inorganics)} = \text{liquor flow rate } \times \text{density} \times \text{solids content}$$

$$\text{Mass of liquor solids(with inorganics)} = 4000\,\frac{\mathrm{m}^3}{\mathrm{day}} \times 360\,\frac{\mathrm{days}}{\mathrm{year}} \times 1050\,\frac{\mathrm{kg}}{\mathrm{m}^3} \times \frac{1\mathrm{t}}{1000\mathrm{kg}} \times 0.125 = 189\,000\,\frac{\mathrm{t}}{\mathrm{yr}}$$

The plant was assumed to operate for 360 days in a year, because it has to stop for maintenance from time to time.

Immediately, it can be noted that $189\ 000\frac{\mathrm{t}}{\mathrm{yr}} < 335\ 595\frac{\mathrm{t}}{\mathrm{yr}}$ which is unacceptable because if the density, the flow rate of the liquor, and the solids content are assumed to be correct, then the mass of solids (with inorganics, i.e. 189 000 t/yr) would be expected to be much greater than the mass of solids (without inorganics, i.e. 335 595 t/yr). Therefore, the data on the liquor flow rates were rejected because the presence of inorganics from the sulphite pulping process would have increased the mass of liquor solids with lignin, meaning that the mass of liquor solids would be greater than 335 595 t/yr.

Moreover, using 189 000 t/yr of liquor solids and assuming 37.9% carbon content leads to 71 631 t/yr of carbon which underestimates the carbon in the liquor by 62% from 188 354 t/yr.

Using carbon content of 188 354 t/yr in the spent liquor, the flow rate of the liquor was calculated as:

$$\text{Liquor flow rate(calculated)} = 188\ 354\ \frac{\mathrm{t}}{\mathrm{yr}} \times \frac{1}{0.379 \times 0.125} \times \frac{1000\mathrm{kg}}{1\mathrm{t}} \times \frac{1\mathrm{yr}}{360\mathrm{days}} \times \frac{1\mathrm{m}^3}{1050\mathrm{kg}} = 10\ 518\frac{m^3}{\mathrm{day}}$$

The calculated flow rate is more than double the 4000 m^3/day sent to Lignotech.

Also, the percentage of inorganics in the liquor was found as follows:

$$\%\text{inorganics} = \frac{\text{Mass of inorganics}}{\text{Mass of liquor solids(with inorganics)}}$$

$$\text{Mass of inorganics} = \text{Mass of solids with inorganics} - \text{Mass of solids without inorganics}$$

$$\text{Mass of liquor solids(with inorganics)} = \frac{\text{Carbon content of liquor solids}}{\text{Carbon fraction of liquor}}$$

$$\text{Therefore, } \%\text{inorganics} = \frac{\frac{188\ 354}{0.379} - 335\ 595\frac{\mathrm{t}}{\mathrm{yr}}}{\frac{188\ 454\frac{\mathrm{t}}{\mathrm{yr}}}{0.379}} = 32.5\%$$

Black liquor solids comprises of 30 to 40% inorganics and 60 to 70% organics (Brajpai, 2014). The percentage of inorganics (32%) is fairly acceptable because it falls within the expected range; this shows that the mass balance can be regarded as being consistent. It should also be noted that the percentage of inorganics would have been higher provided the inorganics in wood were accounted for. Nonetheless, the increase would not be much because inorganics in wood are very small.

A3.2 Mass balance - Magnesium line

Figure A3.2 shows the two magnesium lines combined as one line, the reasons are given in the mass balance rational to follow.

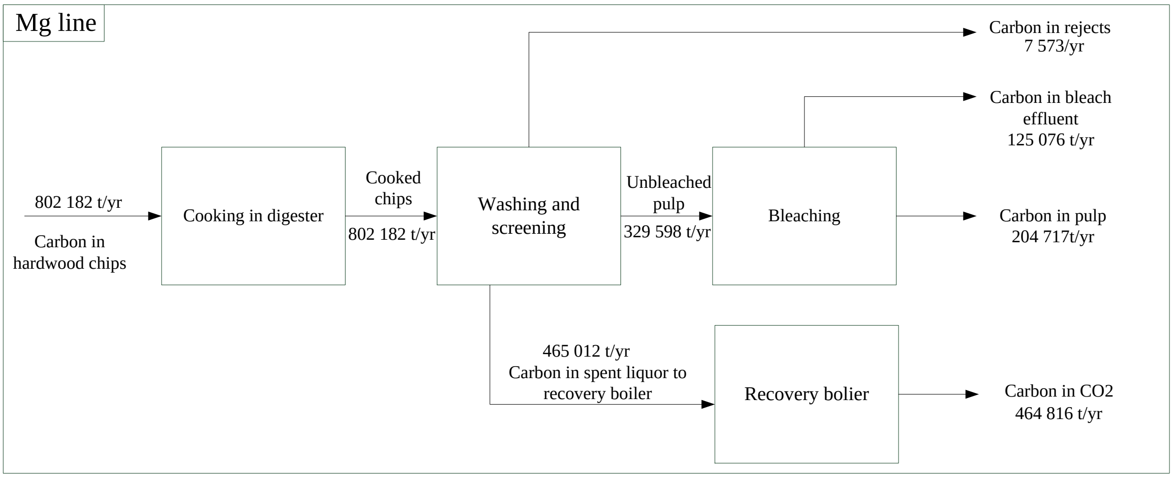


Figure A3.2: Block flow diagram of magnesium line at Sappi Saiccor Mill

Rationale for mass balance for the Magnesium line

It is worth emphasizing that Material Flow Analysis studies aim at simplifying the material flow system as much as possible (Brunner and Rechberger, 2004) while still being able to extract sufficient information from the system to make a judgment. With this in mind, the two magnesium lines were combined into one line as in Figure A3.2.

Similar to the calculations on the calcium line, the yield was used to determine the dry weight of wood processed on both of the two magnesium lines. Therefore, the mass balance could now start from the digester, then washing and screening through to bleaching. This was carried out in the exact same way as with the calcium line using the same assumptions. A step by step calculation has not been provided in order to avoid repetition of the exercise conducted in the case of the calcium line.

In the case of the spent liquor, it was assumed that all the carbon was combusted to carbon-dioxide and exited through the flue gas. It was easy to make this assumption since the recovery boiler had no smelt stream. There could however have been some unburned carbon in the magnesium oxide ash from the boiler but it was assumed that this quantity was very small.

Appendix 4

Calculations on the Sappi Ngodwana Mill

Table A4.1 contains the list of data used in the carbon calculations for the Sappi Ngodwana Mill

Table A4.1: List of data for Sappi Ngodwana Mill

Mechanical pulp fibre line		
	Value	**Data Source**
Mechanical pulp	163 684 BDt	From Mill
Pulp yield	97 %	From Mill
Flow rate of effluent	0.28 MLpd	From Mill
Solids in effluent	0.6 %	From Mill
Density of effluent	1000 kg/m^3	Assumed
Kraft line 1		
	Value	**Data Source**
Softwood pulp	68 826 BDt	From Mill
Hardwood pulp	28 087 BDt	From Mill
Yield (SW & HW)	48%	From Mill
Turpentine production	1.5 kg/ADt pulp	From Mill
Softwood Kappa	50	From Mill
Hardwood Kappa	20	From Mill
Debarking efficiency	92 %	From Mill
Fines	3 %	From Mill
Kraft line 2		
	Value	**Data Source**
Softwood pulp	192 802 BDt	From Mill
Hardwood pulp	38 773 BDt	From Mill
Yield (SW)	45 %	From Mill
Yield (HW)	48 %	From Mill
Softwood Kappa	26 - 27	From Mill
Hardwood Kappa (before bleaching)	20	From Mill
Hardwood Kappa (after bleaching)	2 - 3	From Mill
Yield loss over bleach plant	4 - 5 %	From Mill
Fraction of pulp not bleached	40 %	From Mill

A4.1 Mass balance - Mechanical pulp fibre line

Using the mass of mechanical pulp produced (163 684 BDt) together with the pulp yield of 97%, it was possible to calculate the required amount of wood on a dry basis. Figure A4.1 is a diagram showing the flow of carbon through the mechanical pulp fibre line.

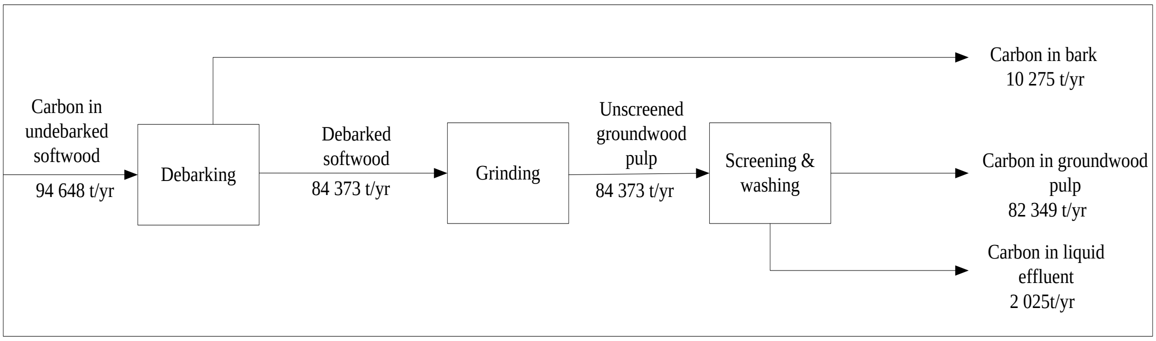
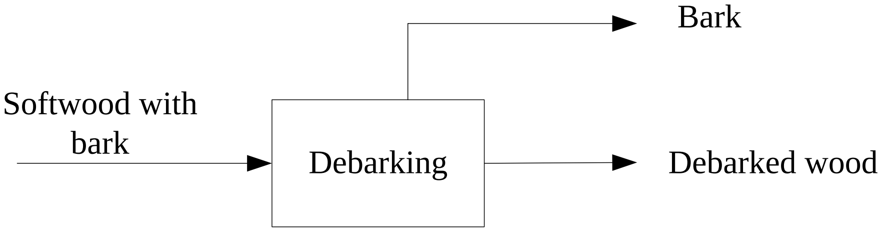


Figure A4.1: Block flow diagram of mechanical pulp fibre line at Sappi Ngodwana Mill

Balance over debarker



$$\text{Mass of dry debarked SW} = \frac{\text{Mass of groundwood pulp}}{\text{Yield}}$$

$$\text{Mass of dry debarked SW} = \frac{163\ 684\ \frac{\text{BDt}}{\text{yr}}}{0.97} = 168\ 746\ \frac{\text{BDt}}{\text{yr}}$$

Softwood contains about 11.8% bark. This value was used to estimate the mass of undebarked wood and hence the bark content.

$$\text{Mass of dry undebarked SW} = \frac{\text{Mass of dry debarked SW}}{\text{fraction of debarked wood}}$$

$$\text{fraction of debarked wood} = 1 - \%\ \text{Bark} \times \%\text{Debarking efficiency}$$

$$\text{Mass of dry undebarked SW} = \frac{168\ 746\ \frac{\text{BDt}}{\text{yr}}}{1 - \frac{11.8}{100} \times \frac{92}{100}} = 189\ 296\ \frac{\text{BDt}}{\text{yr}}$$

$$\text{Mass of Bark} = \frac{11.8}{100} \times \frac{92}{100} \times 189\ 296\ = 20\ 550\ \frac{\text{BDt}}{\text{yr}}$$

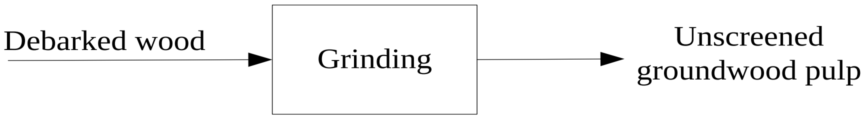
Wood contains about 50% carbon; the same applies to the bark.

$$\text{C}_{\text{Debarked wood}} = \text{C}_{\text{undebarked wood}} - \text{C}_{\text{bark}}$$

$$\text{C}_{\text{Debarked wood}} = (0.5 \times 189\ 296\ ) - (0.5 \times 20\ 550\ \ ) = 84\ 373 \frac{\text{BDt}}{\text{yr}}$$

This completes the mass balance over the debarking operation. Next, wood grinding is considered.

Balance over grinder

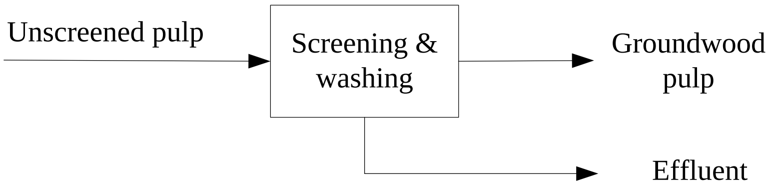


The carbon entering and leaving the grinder is the same. There are no carbon losses. Thus,

$$\mathrm{C_{Unscreend\ groundwood\ pulp}} = \mathrm{C_{Debarked\ wood}} = 84\ 373\,\frac{\mathrm{BDt}}{\mathrm{yr}}$$

Balance over washers and screeners

Knowing the mass of unscreened pulp and groundwood pulp, it was possible to calculate the mass of solids that reported to the effluent, which were assumed to be hemicellulose with 40% carbon content.



$$\text{Mass of Solids to effluent} = \text{Mass of unscreened pulp} - \text{Mass of groundwood pulp}$$

$$\text{Mass of Solids to effluent} = 168\ 746 - 163\ 684 = 5\ 062\,\frac{\mathrm{t}}{\mathrm{yr}}$$

$$\mathrm{C_{groundwood\ pulp}} = \mathrm{C_{Unscreened\ pulp}} - \mathrm{C_{Effluent}}$$

$$\mathrm{C_{groundwood\ pulp}} = 85\ 276 - (0.4 \times 5\ 062) = 83\ 251\,\frac{\mathrm{t}}{\mathrm{yr}}$$

A4.2 Mass balance - Kraft line 1: Softwood and hardwood pulp

Figure A4.2 is a diagram showing the flow of carbon through the mechanical pulp fibre line kraft line 2.

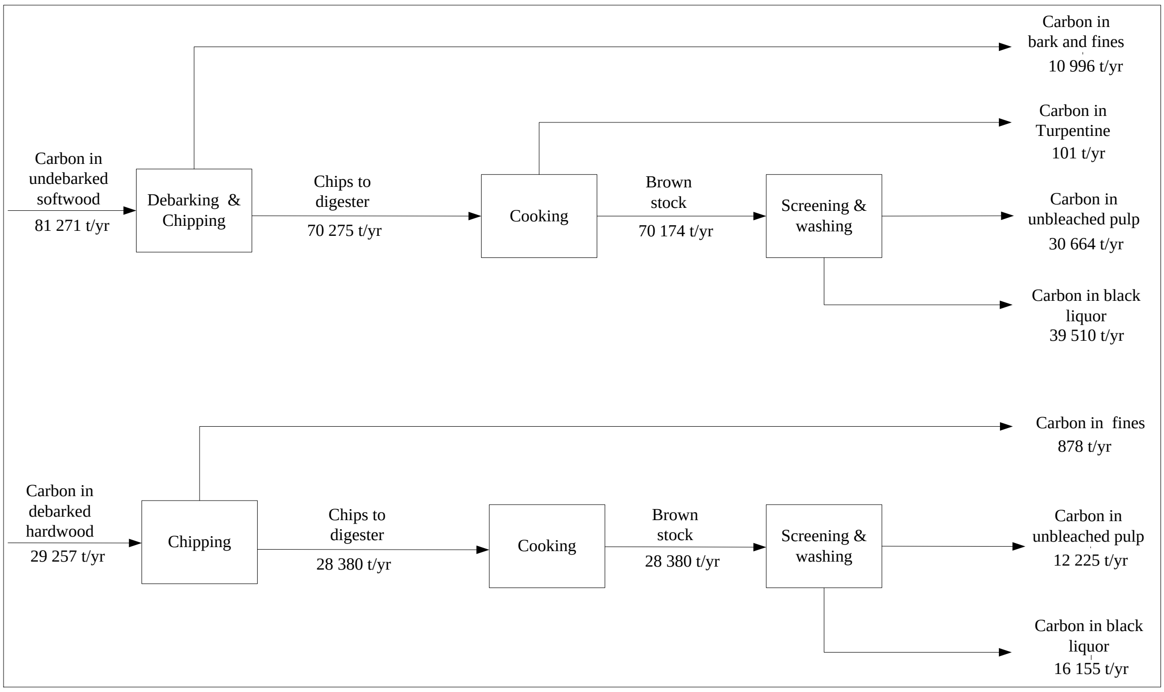
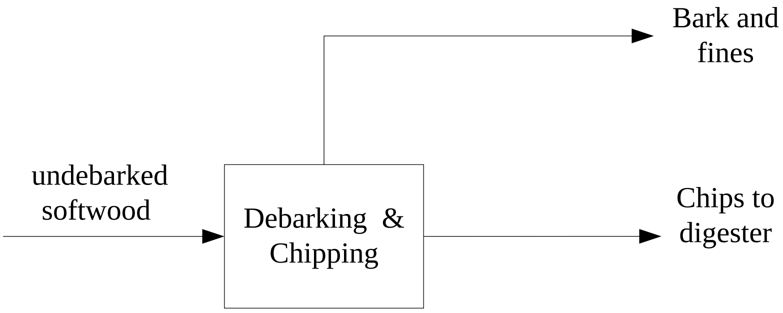


Figure A4.2: Block flow diagram of kraft fibre line 1 at Sappi Ngodwana Mill

<u>Balance over debarking and chipping</u>

The pulp yield for this fibre line was 47.5%. Using this yield, together with the mass of softwood pulp produced on this fibre line, the mass of softwood before debarking was calculated just as it was done for the mechanical pulp line.



$$\text{Mass of dry debarked SW} = \frac{\text{Mass of softwood pulp}}{\text{Yield}}$$

$$\text{Mass of dry debarked SW} = \frac{68\,826\,\frac{\text{BDt}}{\text{yr}}}{0.475} = 144\,897\,\frac{\text{t}}{\text{yr}}$$

$$\text{Mass of dry undebarked SW} = \frac{144\,897\,\frac{\text{t}}{\text{yr}}}{1 - \frac{11.8}{100} \times \frac{92}{100}} = 162\,542\,\frac{\text{BDt}}{\text{yr}}$$

$$\text{Mass of bark} = \frac{11.8}{100} \times 162\,542\,\frac{\text{BDt}}{\text{yr}} \times 0.92 = 17\,646\,\frac{\text{t}}{\text{yr}}$$

3% of the chips end up as fines, thus,

$$\text{Mass of fines} = \frac{3}{100} \times \text{Mass of dry debarked SW}$$

$$\text{Mass of fines} = \frac{3}{100} \times 144\,897\,\frac{\text{t}}{\text{yr}} = 4\,347\,\frac{\text{t}}{\text{yr}}$$

$$\text{Mass of chips to digester} = \text{Mass of dry debarked SW} - \text{Mass of fines}$$

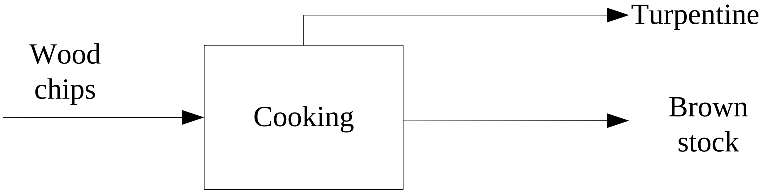
$$\text{Mass of chips to digester} = 144\,897 - 4\,347 = 140\,550\,\frac{\text{t}}{\text{yr}}$$

At this point, all material inputs and outputs into the debarking and chipping operations have not been chemically altered, and are therefore assumed to have the same carbon composition as wood, that is 50%, thus,

$$\text{C}_{\text{chips to digester}} = \text{C}_{\text{undebarked SW}} - \text{C}_{\text{bark}} - \text{C}_{\text{fines}}$$

$$\text{C}_{\text{chips to digester}} = (0.5 \times 162\,542) - (0.5 \times 17\,646) - (0.5 \times 4\,347) = 70\,275\,\frac{\text{t}}{\text{yr}}$$

Balance over digester



Turpentine production for softwoods was 1.5 kg / ADt. Turpentine ($C_{10}H_{16}$) contains 88% carbon. In order to obtain the mass of turpentine produced, the mass of pulp was first converted to air-dry basis by dividing by 90% since 10% of the air-dry pulp is moisture.

$$\text{Air} - \text{dry pulp} = \frac{\text{Bone} - \text{dry pulp}}{90\%}$$

$$\text{Air} - \text{dry pulp} = \frac{68\,826\,\frac{\text{BDt}}{\text{yr}}}{\frac{90}{100}} = 76\,473\,\frac{\text{Adt}}{\text{yr}}$$

$$\text{Mass turpentine} = \frac{1.5\text{kg}}{\text{Adt}} \times 76\,473\,\frac{\text{Adt}}{\text{yr}} \times \frac{1\text{t}}{1000\text{kg}} = 115\,\frac{\text{t}}{\text{yr}}$$

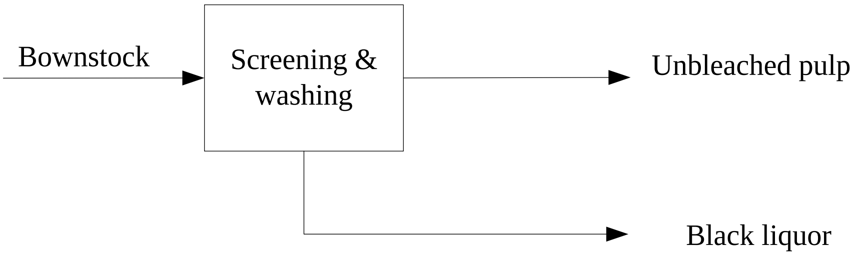
$$\text{Mass brown stock} = \text{Mass of wood chips} - \text{Mass of turpentine}$$

$$\text{Mass brown stock} = 140\ 550 - 115 = 140\ 435\frac{\text{t}}{\text{yr}}$$

$$\text{C}_{\text{brown stock}} = \text{C}_{\text{chips to digester}} - \text{C}_{\text{turpentine}}$$

$$\text{C}_{\text{brown stock}} = 70\ 275 - (115 \times 0.88) = 70\ 174\frac{\text{t}}{\text{yr}}$$

Balance over screening and washing



Because the mass of unbleached pulp and the brown stock have been calculated, it is possible to determine the mass of wood solids that end up in the black liquor. These solids essentially make up the organic portion of black liquor.

$$\text{Mass of wood solids in black liqour} = \text{Mass of brown stock} - \text{Mass of unbleached pulp}$$

$$\text{Mass of wood solids in black liqour} = 140\ 435 - 68\ 826 = 71\ 609\frac{\text{t}}{\text{yr}}$$

The difficulty at this juncture, is in determining the mass of carbon that reports to the unbleached pulp and the black liquor respectively. The rationale adopted hear was that unbleached pulp comprises mainly of cellulose, hemicellulose and lignin and thus if these fractions can be determined, so can their carbon content.

$$\text{Mass of lignin} = \text{lignin}[\%] \times \text{Mass of SW pulp}$$

$$\text{Mass of lignin} = \frac{7.5}{100} \times 68\ 826 = 5\ 162\frac{\text{t}}{\text{yr}}$$

Sharkford (2003) has reported the following composition for pulp produced from pine as shown in Table A4.2.

Table A4.2: Composition of softwood pulp

	% of dry weight of wood (Sharkford, 2003)	% of bone dry weight of wood	% of bone dry weight of wood (calculated)
Cellulose	35	73	73.2
Glucomannan	5	10	9.15
Xylan	5	10	9.15
Lignin	2.5	5	7.5
Extraneous compounds	0.25	1	1
Total	48	100	100

The extraneous compounds refer to the extractives which are obviously very low, thus, they have not been taken into account in the carbon balance. The glucomannan and xylan make up the hemicellulose fraction of the pulp and they amount to 10% of the dry weight of wood. As a coincidence, the yield for the pulp with the composition reported in Table A4.2 is also 48%, however; the softwood pulp was pulped to kappa numbers between 24 and 28, which immediately suggests that the pulp will have much lower lignin content than pulp with kappa at 50. In fact, at 50 kappa, the fraction of lignin in the pulp is 7.5% compared to 5% in Table A4.2.

$$\text{lignin}[\%] = 0.15 \times \text{Kappa number}$$

$$\text{lignin}[\%] = 0.15 \times 50 = 7.5\%$$

Also, from Table A4.2 the cellulose fraction in the pulp is about 4 times more than the hemicellulose fraction. If the extractives content are assumed to be the same at 7.5% (i.e. 1%) then the cellulose and hemicellulose fractions can be adjusted accordingly (using 1:5 ratio) to 73.2% and 18.3% respectively. The carbon in the pulp was calculated as follows:

$$\mathrm{C}_{\text{SW pulp}} = \mathrm{C}_{\text{cellulose}} + \mathrm{C}_{\text{hemicellulose}} + \mathrm{C}_{\text{lignin}}$$

$$\mathrm{C}_{\text{SW pulp}} = (0.44 \times 0.732 \times 68\,826) + (0.4 \times 0.183 \times 68\,826) + (0.67 \times 0.075 \times 68\,826) = 30\,664\,\frac{\text{t}}{\text{yr}}$$

$$\mathrm{C}_{\text{Black liqour}} = \mathrm{C}_{\text{Brown stock}} - \mathrm{C}_{\text{SW pulp}}$$

$$\mathrm{C}_{\text{Black liqour}} = 70\,174 - 30\,664 = 39\,510\,\frac{\text{t}}{\text{yr}}$$

Note that the carbon in the cellulose, hemicellulose and lignin are 44%, 40% and 67% respectively.

A4.3 Mass balance - Kraft line 1: Hardwood pulp

The calculations for this line were carried out in the exact same way as the softwood line. However, it was assumed that no turpentine was produced when hardwoods were processed; this was based on the knowledge that hardwoods have very low extractives content.

A4.4 Mass balance - Kraft line 2: Softwood and hardwood pulps

Figure A4.3 is a schematic showing the carbon flows through kraft line 2.

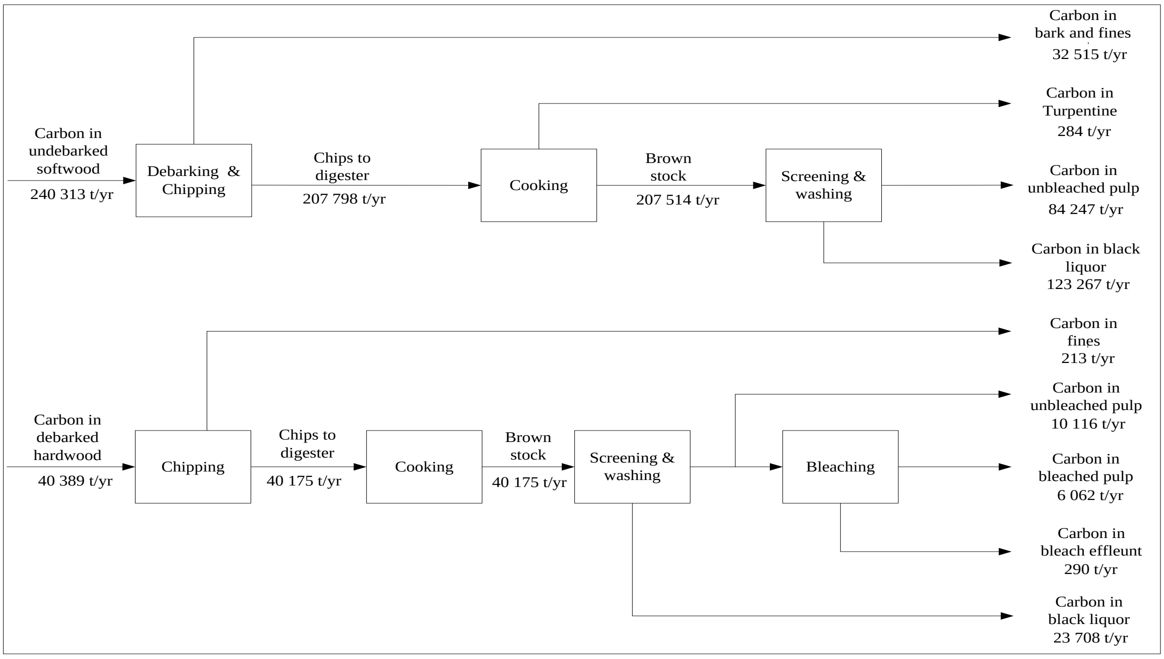


Figure A4.3: Block flow diagram of kraft fibre line 1 at Sappi Ngodwana Mill

Similar calculations as conducted for kraft line 1 was performed for kraft line 2. Because 60% of the hardwood pulp was bleached, the kappa number before and after bleaching was used to determine the lignin that reported to the bleach effluent. Also, the 4% weight loss over the bleach plant was used to determine the fractions of cellulose and hemicellulose that reported to the effluent.

A4.5 Mass balance - liquor recovery circuit

The calculations for this area of the plant were conducted in the exact same way as with the Richards Bay mill. Figure A4.4 is a schematic showing the carbon flow through the liquor recovery circuit.

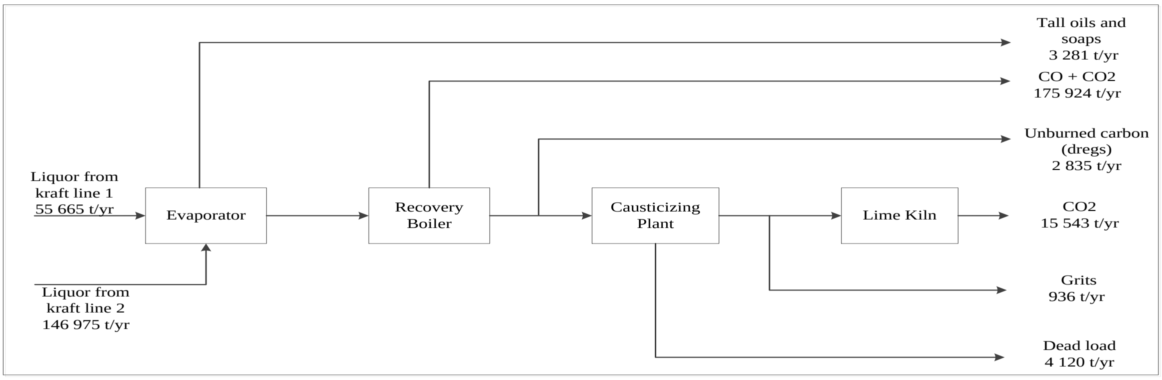


Figure A4.4: Block flow diagram for the liquor recovery circuit

Appendix 5

Calculations on the Mpact Felixton Mill

Table A5.1 contains the list of data used in the carbon calculations for the Mpact Felixton Mill.

Table A5.1: List of data for Mpact Felixton Mill

	Value	**Data Source**
Mass of bagasse (wet)	70 200 t/yr	From Mill
Moisture content of bagasse	55%	From Mill
% pith in bagasse	10-20%	From Mill
Pith removal efficiency	20%	From Mill
Pulp yield	43%	From Mill
% carbon in bagasse	48.33%	Calculated

Figure A5.1 is a block flow diagram showing the main bagasse fibre line.

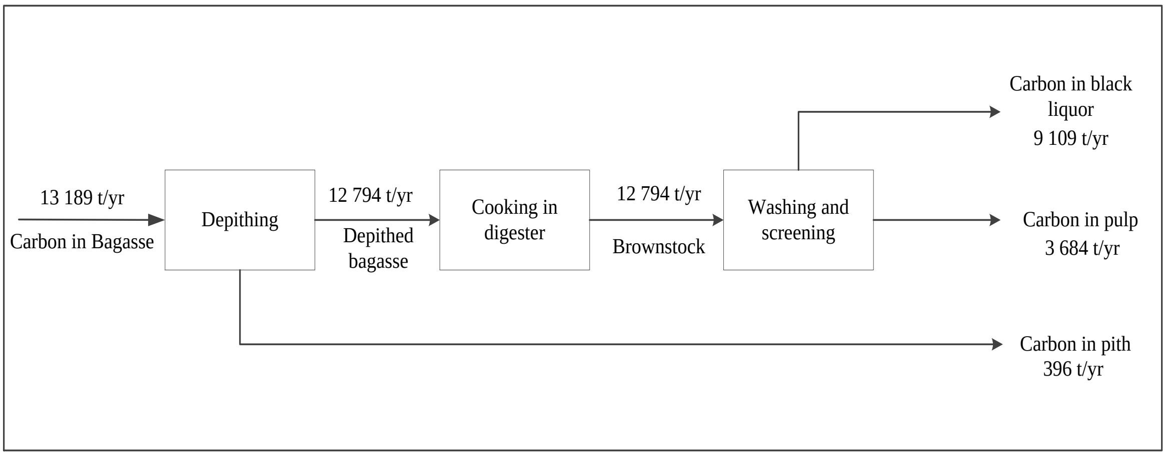
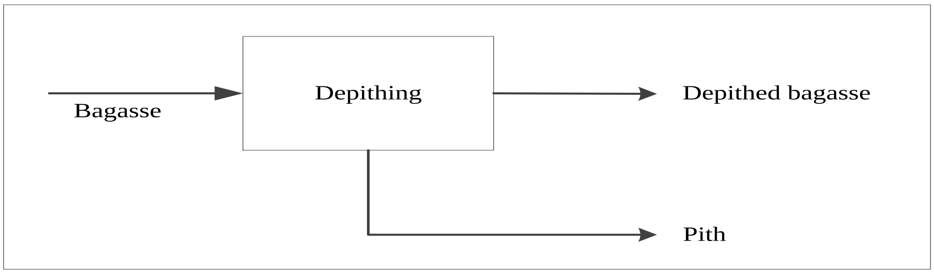


Figure A5.1: Block flow diagram of main bagasse fibre line at Mpact Felixton Mill

Rational for mass balance

Mpact Felixton produces fluting paper from a mixture of bagasse pulp and recycled fibre. Nonetheless, only the carbon in the bagasse was considered. To obtain the carbon content of bagasse, the composition in terms of the relative proportions of carbohydrates and lignin reported in the literature was used to estimate the carbon content. This carbon content was assumed to be the same for pith. The pulp produced was calculated from the yield. Similarly, the carbon content of the pulp was estimated from the composition.

Balance depithing process



It is imperative to remove as much of the pith from the bagasse as possible because the pith leads to high consumption of cooking chemical (caustic) and it also does not contribute to the fibrous mass (pulp). Pith content of bagasse ranges from 10 to 20% on a wet basis, while the pith removal efficiency was 20%.

$$\text{Mass of depithed bagasse (dry)} = \text{Mass of Bagasse(dry)} - \text{Mass of Pith removed(dry)}$$

$$\text{Mass of Bagasse (dry)} = (1 - 0.55) \times 70\ 200 = 31\ 590 \frac{\text{t}}{\text{yr}}$$

$$C_{\text{Bagasse}} = 0.4175 \times 31\ 590 = 13\ 189\ \frac{\text{t}}{\text{yr}}$$

$$\text{Mass of Pith removed (dry)} = (1 - 0.55) \times 0.15 \times 70\ 200 \times 0.2 = 948 \frac{\text{t}}{\text{yr}}$$

$$\text{C}_{\text{Pith}} = 0.4175 \times 947 = 396 \frac{\text{t}}{\text{yr}}$$

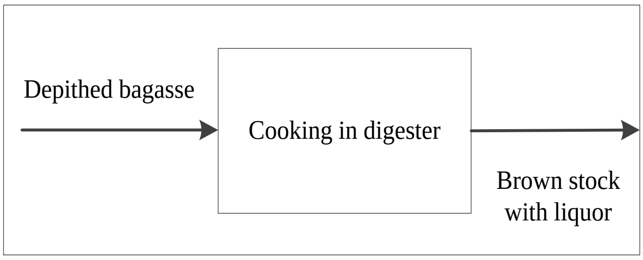
$$\text{Mass of depithed bagasse (dry)} = 31\ 590 - 948 = 30\ 642\ \frac{\text{t}}{\text{yr}}$$

$$\text{C}_{\text{Depithed bagasse}} = \text{C}_{\text{Bagasse}} - \text{C}_{\text{Pith}}$$

$$\text{C}_{\text{Depithed bagasse}} = 13\ 189 - 396 = 12\ 794 \frac{\text{t}}{\text{yr}}$$

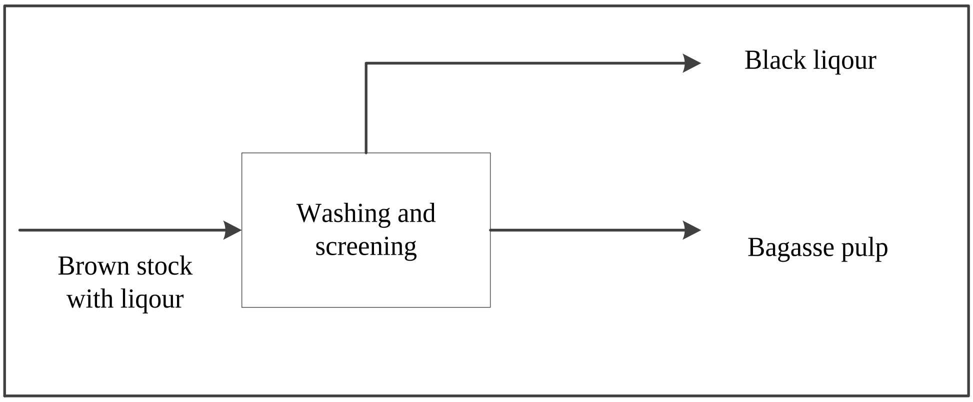
Balance over digester

The carbon in the depithed bagasse is the same as the carbon in the pulp and the spent liquor formed.



$$\text{C}_{\text{Depithed bagasse}} = \text{C}_{\text{Brown stock with liqour}} = 12\ 794 \frac{\text{t}}{\text{yr}}$$

Balance over washing and screening



The mass of dry pulp was calculated from the yield, making it easy to determine the organic portion of the bagasse that reports to the black liquor stream. It is important to reiterate that this organic fraction is the main carbon rich component of the liquor.

$$\text{Mass of pulp(dry)} = \text{Mass of depithed bagasse(dry)} \times \text{Yeild} = 30\ 642 \times 0.43 = 13\ 176\,\frac{\text{t}}{\text{yr}}$$

$$\text{Mass of liqour solids} = \text{Mass of brownstock with liqour} - \text{Mass of pulp(dry)}$$

$$\text{Mass of liqour solids (organic fraction)} = 30\ 642 - 13\ 176 = 17\ 466\,\frac{\text{t}}{\text{yr}}$$

It was difficult to determine the mass of carbon that reports to the pulp because neither the kappa number of the pulp nor the split between cellulose and hemicellulose in the pulp was known. Nonetheless, reports from the literature indicate that the organic fraction of black liquor is about 65% (Brajpai, 2014) of the black liquor solids mass, while the liquor solids contain about 33.9% carbon (Gonçalves *et al.*, 2004).

$$\text{C}_{\text{Pulp}} = \text{C}_{\text{Brown stock with liqour}} - \text{C}_{\text{Black liqour}}$$

$$\text{C}_{\text{Black liqour}} = \frac{\text{Mass of liqour solids (organic fraction)}}{\text{\% organics}} \times \text{\% carbon in liqour solids}$$

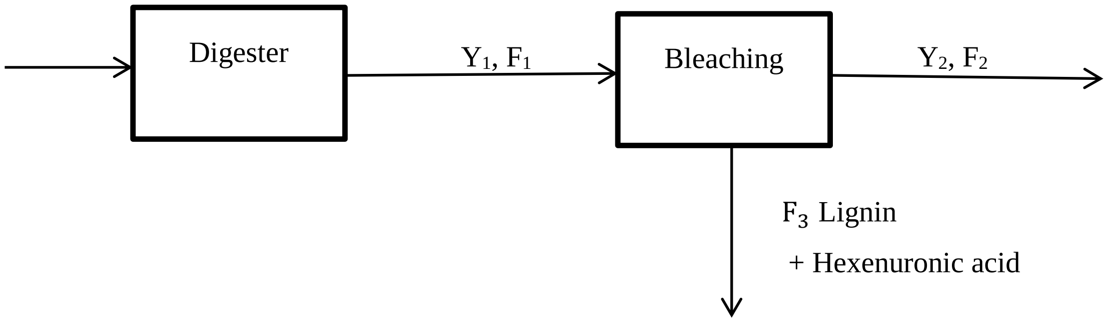
$$\text{C}_{\text{Black liqour}} = \frac{17\ 466}{\frac{65}{100}} \times \frac{33.9}{100} = 9\ 109\,\frac{\text{t}}{\text{yr}}$$

$$\text{C}_{\text{Pulp}} = 12\ 794 - 9\ 109 = 3\ 684\,\frac{\text{t}}{\text{yr}}$$

Appendix 6

Derivation of some formulae

A6.1 Percentage fibre loss expressed in terms of yield



Let Y_1 and Y_2 be the yields for unbleached and bleached pulps respectively, and F_1 and F_2 their respective flows.

Assuming a basis of 1tonne of digester feed means that:

$$\mathrm{F_1 = Y_1 \text{ and } F_2 = Y_2}$$

$$\text{Now,} \qquad \%\mathrm{loss} = \left(\frac{\mathrm{F_1 - F_2}}{\mathrm{F_1}}\right) \times 100\% = \left(\frac{\mathrm{Y_1 - Y_2}}{\mathrm{Y_1}}\right) \times 100\% = \left(1 - \frac{\mathrm{Y_2}}{\mathrm{Y_1}}\right) \times 100\%$$

A6.2 Mass of unbleached pulp expressed in terms of yield

Now, suppose Y_1 , Y_2 and F_2 are known, then F_1 can be calculated easily as follows:

$$\mathrm{F_1 = F_2 + F_3}$$

$$\text{But, } \mathrm{F_3 = F_1 \times \left(1 - \frac{Y_2}{Y_1}\right)}$$

$$\text{Thus, } \mathrm{F_1 = F_2 + F_1 \times \left(1 - \frac{Y_2}{Y_1}\right)}$$

$$\Rightarrow \mathrm{F_1 \left(1 - \left(1 - \frac{Y_2}{Y_1}\right)\right) = F_2}$$

$$\Rightarrow \mathrm{F_1 = F_2 \left(\frac{Y_1}{Y_2}\right)}$$

Appendix 7

Import and export data on pulp

Table A7.1 is a table of data on the values of exports and imports of pulp from 1998 to 2012. The data was acquired from Forestry South Africa and is the same data used in plotting Figure 1.3 in Chapter 1.

Table A7.1: Values of imports and exports of pulp from 1998 to 2012

Year	**Imports**	**Exports**	**Trade Balance**
		Rand Million	
1998	371.1	4 116.4	3 745.3
1999	396.5	4 570.1	4 173.6
2000	553.9	6 789.7	6 235.8
2001	404.7	4 896.6	4 491.9
2002	500.0	4 973.2	4 473.2
2003	378.7	4 596.3	4 217.6
2004	383.4	3 936.3	3 552.9
2005	376.0	4 035.8	3 659.8
2006	659.3	4 304.0	3 644.7
2007	573.2	4 852.8	4 279.6
2008	713.5	5 746.8	5 033.3
2009	458.6	4 964.5	4 505.9
2010	472.8	6 135.5	5 662.7
2011	500.3	7 459.5	6 959.2
2012	479.3	5 889.7	5 410.4

Appendix 8

Carbon reduction technologies

A8. 1: Deep Eutectic Solvents (DES)

The use of DES in pulping is a revolutionary technology that allows the production of pulp at low temperatures and at atmospheric pressure. Also, DES has the potential to breakdown biomass into its different constituents (i.e. lignin, cellulose and hemicellulose) at low energy consumption, minimal carbon emissions and residue formation. This ground-breaking technology, which is still at a developmental stage, has won the first place for the ‘Two team project’ initiated by the Confederation of European Paper Industry (CEPI). The ‘Two team project’ comprised of eight projects which were aimed at cutting back on the carbon footprint in the European pulp and paper industry.

A8. 2: Chemistry and properties of DES

DESs gained wide spread popularity after 2004, being labelled as ‘green solvents’ because they are biodegradable. DESs are ionic solvents that comprise of a hydrogen bond donor and a hydrogen bond acceptor. The individual constituents used in fabricating the DESs are readily available and in abundance in natural compounds such as fruits and vegetables. These components are also nontoxic, inexpensive and biodegradable. The DESs in themselves are also considered non-volatile, non-flammable and miscible in water.

The amazing aspect of the DES is that it has a much lower melting point than any of its individual components. The first documented DES came into light in 2002 when Abbott *et al.* (2003) published a paper on a eutectic mixture comprising of urea and choline chloride with melting points at 133°C and 302°C respectively, in a ratio of 2:1. The resulting mixture had a melting point of 12°C. Figure A8.1 is a graph showing the variation of the melting point of the binary chemical mixture comprising of urea and choline chloride as a function of their composition.

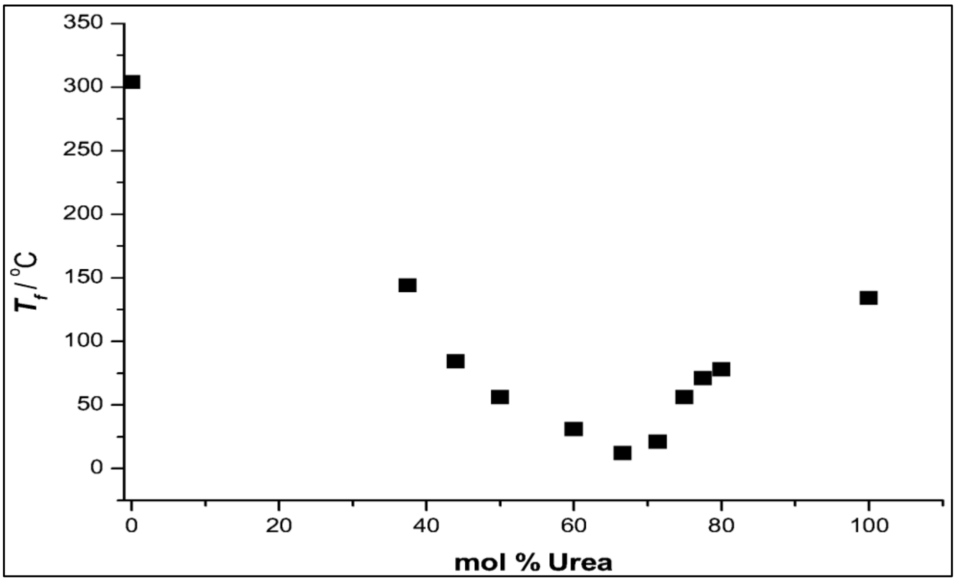


Figure A8.1: Eutectic mixture of urine and choline chloride (Abbott *et al*., 2003)

DESs normally have a higher density than water and are usually liquids at temperatures below 150°C. Nonetheless, it is quite rear to find DESs that exist as liquids at ambient temperatures (25°C). In fact, the melting points of different DESs are highly dependent on the starting materials and the ratios in which they are combined. Figure A8.2 shows the different starting materials that can be used in fabricating DESs. The compounds shown below are by no means exhaustive.

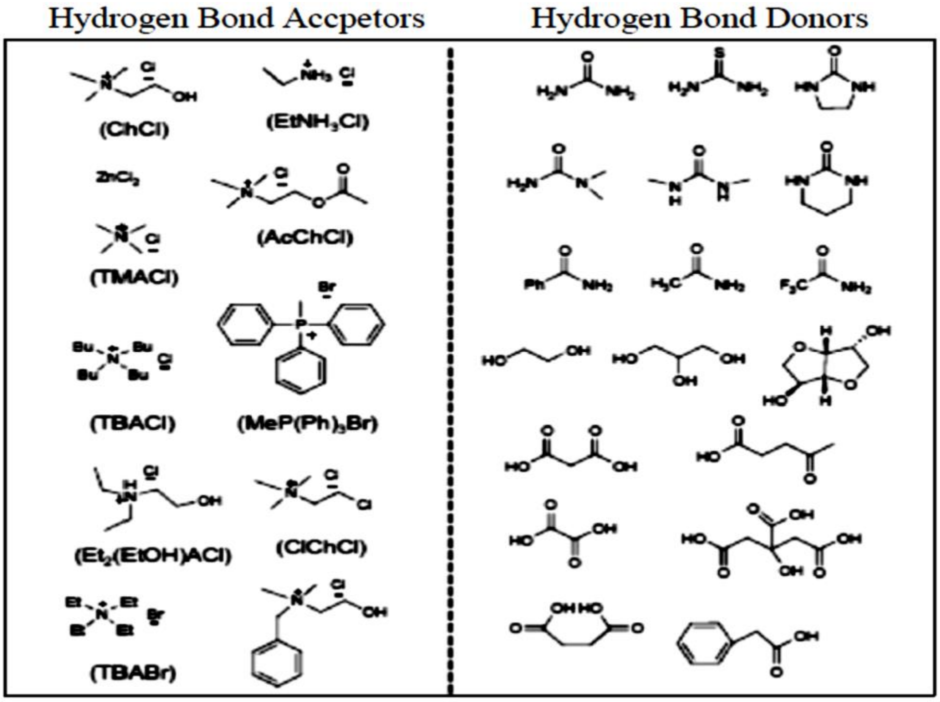


Figure A8.2: Starting compounds for synthesizing Deep Eutectic Solvents (Dios, 2013)

It is interesting to note that due to the existence of various combinations of hydrogen bond acceptors and donors for making DESs, it is quite possible to prepare DESs that can be used for a specific application.

A8. 3: Applications of DES to biomass processing

Due to the novelty of the DES, there is very little published work on the application of DESs to biomass processing. Francisco *et al*. (2012) developed different DESs, some of which were identified as solvents for lignin and cellulose. The study showed that lignin could be solubilised by the DES while cellulose had a poor and negligible solubility in the DES. Similar studies conducted by deDios (2013) who tested different DESs on pine wood and straw found that lignin had a high solubility in the DESs, while cellulose and hemicellulose had negligible solubility. It was concluded in the study that the most suitable DES to be deployed in separating biomass into its different constituents, depends on the nature of the biomass.

The results from the preceding studies were alluring because they showed that lignin could be extracted quite easily from biomass due to its high solubility in the DES over that of cellulose and hemicellulose. There is a lot of work that is required in this subject. For instance, it would be useful to tailor-make DESs that solubilise both lignin and hemicellulose but leaves the cellulose insolubilized. This opens the window of possibilities of developing DESs for specific applications.

It is speculated that the use of DESs for pulping will surely be deployed within the next 15 years provided the pulp industry embraces the concept and further research is conducted in this subject. The shift towards this new technology, which is mostly motivated by the anticipated energy savings and the drop in carbon emissions, makes it almost inevitable and thus compels the South African pulp sector to explore the potential use of DESs for making pulp.