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**Multidisciplinary use of LCA and empirical data to improve  
the environmental sustainability and industrial viability of  
Kraft pulp mill**

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**A Thesis Submitted for the Degree of Doctor of  
Philosophy**

**Heriot-Watt University  
Institute of Mechanics, Process and Energy  
Engineering, School of Engineering and Physical  
Sciences**

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## ABSTRACT

About 4% of the world energy is used to produce paper and it takes 300 -2600 m<sup>3</sup> of water to produce 1 tonne of A4 sheet (Van Oel and Hoekstra 2012). Hence, the key aim of this research is to use a multi-disciplinary approach involving life cycle assessment (LCA) and empirical methodology to improve the environmental sustainability and industrial viability of the conventional Kraft pulp mill. The life cycle assessment methodology (LCA) used to study the Kraft pulp mill identified energy as the elementary flow with most impact closely followed by water. The chemical recovery unit was identified as the process unit of highest concern followed by the washing and screening process unit. The LCA study suggested that using smaller wood particle size during cooking would reduce energy consumption and emission to the air. Furthermore, the use of a re-usable liquid as part of the washing process could reduce water consumption and enable the recovery of extractable chemicals in the form of a green crude. The empirical data showed that reducing the particle size from 8mm currently used in the conventional Kraft process to < 2mm could save up to 20% energy during pulp production. Replacing part of the water during washing with recoverable hexane could reduce water consumption during the pulp washing close to 37%. In addition, using hexane as a replacement for water enabled approximately 19% green crude recovery from particle size <2mm cooked in 30mins based on initial dry wood weight. The recovery of green crude could transform the Kraft pulp mill into a potential biorefinery. The LCA outcome indicated that the impact of energy generation on climatic change is equivalent to about 713 kgCO<sub>2</sub>eq for a conventional Kraft mill and this was reduced by 20% to about 570 kgCO<sub>2</sub>eq for the proposed Kraft biorefinery. In conclusion, the combination of LCA and empirical methodology showed how a Kraft pulp mill could be transferred into a more sustainable and industrially viable biorefinery resulting in lower environmental impact and producing green chemicals from wood.

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## **DEDICATION**

This work is dedicated to my beloved wife Dr Ezinne Franklin-kalu and my children Princess Chinecherem Michelle Franklin-kalu and Prince Chinemerem William Franklin-kalu.

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## **ACKNOWLEDGEMENTS**

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## NOMENCLATURE (optional)

MJ	Mega Joule
LCA	Life Cycle Assessment
COD	Chemical oxygen demand
BOD	Biological Oxygen demand
TRS	Total reduce sulphur
TSP	Total suspended solid
NoP	Number of potassium
LCIA	Life cycle impact assessment
LCI	Life cycle inventory
BAT	Best available technique/technology
EJ/yr.	Energy Joule/year
CO <sub>2</sub>	Carbon (II) Oxide
NO <sub>x</sub>	Oxides of Nitrogen
SO <sub>x</sub>	Oxide of sulphur
NH <sub>4</sub>	Ammonia
Kg	Kilogram
AoPs	Area of protection
R&D	Research and development
LCA	Life cycle assessment
TGA	Thermogravimetric analysis
GC/MS	Gas chromatography
TSS	Total suspended solid
Total P	Total Potassium
AOX	Adsorbable Organic Halides
Total N	Total Nitrogen
SO <sub>x</sub>	Sulphur oxide
NO <sub>x</sub>	Nitrogen oxide
NaS	Sodium sulphide
KWh	Kilowatt hour
ECF	Elemental chlorine free
TCF	Total chlorine free
MWh	Megawatt/hour
GJ	Giga Joules
ADt	Air dry tonne
ISO	International standard organisation
O <sub>2</sub>	Oxygen
NaClO <sub>3</sub>	Sodium trioxochloride
HCL	Hydrogen chloride
W <sub>EV</sub>	Weight of empty vial
H <sub>AE</sub>	Hexane after extraction
BL <sub>AE</sub>	Black liquor after extraction
P, A, N	Paraffin, Naphthene, Aromatic
I.S	Impact score
C.F	Characterisation factor
FF	Fate factor
EF	Effect factor
XF	Exposure factor
NaOH	Sodium hydroxide

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## Chapter 2– Introduction and General overview

### 2.1 Introduction

Biomass as feedstock for biorefineries can be used to produce bioenergy, fuel and bio crude (Menon and Rao 2012). Therefore, the LCA will be applied to give background information on biomass conversion using a biorefinery (Ahlgren et al. 2015). Biorefinery is defined as a cluster of bio-based refining facilities where the biomass feedstock is separated into different components using variety of integrated bio-based technologies to sustainably produce biocrude, biofuel and energy (Diep et al. 2012). Biorefineries are categorized into six types, namely green biorefineries, whole crop biorefineries, forest and lignocellulose biorefineries, algae biorefineries, integrated biorefineries and thermochemical biorefineries (Diep et al. 2012, Sonnenberg et al. 2007). However, the green biorefineries, whole crop biorefineries, algae biorefineries, integrated biorefineries and thermochemical biorefineries are not commercially viable, since they are either still in their laboratory stage, R&D stage, or pilot scale stage (Chandel et al. 2018, Zollmann et al. 2019). The only biorefinery that has the potential for proper utilization of raw material and excellent processing of by-product is Forest and lignocellulose biorefineries (FitzPatrick et al. 2010). Forest and Lignocellulose biorefinery is in its industrial stage and have been in existence for a very long time (Menon and Rao 2012). It is the only biorefinery option, which have abundance of unutilized feedstock that do not have impact on the use of land for food production and fibre crops (Menon and Rao 2012, Sims et al. 2010), An example of Forest and Lignocellulose biorefinery is Conventional Kraft pulping mill (Hassan et al. 2019). The conventional Kraft pulp paper mill accounts for 9 out of 10 of the global chemical pulping process plants and 75% of the global produced pulp (Bajpai 2015). This is so because of its relative simplicity, speediness, ability to tolerate varying condition of wood and pertinent to all kinds of wood types (Kleppe 1970). The challenge with the conventional Kraft pulping mill is that it is paper focused, making it economically unsustainable. The innovation of visual media has brought about a great reduction in the demand for newspapers, magazine, and paper related products. The pulp and paper industry have been seriously affected by the visual media innovation, especially the Conventional Kraft pulp mills since it is the most popular chemical pulping process use all over the globe. To make the conventional Kraft pulp mill business attractive to investors again, the conventional Kraft pulping mill have constantly upgraded with the

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use of best available techniques and technology (Suhr et al. 2015). Hence, there is need to still improve the conventional Kraft pulp mill.

## **2.2 Aim**

The aim of this research is to use a multi-disciplinary approach involving life cycle assessment (LCA) methodology and empirical data to improve the environmental sustainability and the industrial viability of the conventional Kraft pulp mill under study.

## **2.3 Objectives**

This work has the following research objectives:

- Firstly, identify the two key elementary flow of concern and the process units affected most by the mentioned elementary flows. Also, identify the most significant environmental problem generated during Kraft pulp production.
- Secondly, prove that reducing the particle size from 8mm currently used in the conventional Kraft process to < 2mm and replacing half of the water used during washing with recoverable hexane, can generate value added organic compound, reduce energy use, water consumption and environmental problem during Kraft pulp production.
- Thirdly, apply the outcome of the empirical methodology to the new conventional Kraft pulp mill called Kraft biorefinery and measure the difference in energy consumption, water consumption and the environmental problems generated during Kraft pulp production using LCA methodology.
- Finally, compare the conventional Kraft pulp mill and the proposed Kraft biorefinery to determine which is more environmentally sustainable and industrially viable.
- Summarize of the conclusions and future works.

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## 2.4 Structure of the Thesis

Each chapter of the thesis will be structured in the following way:

- Chapter 1 presents a general introduction, the aim, and objectives of the research.
- Chapter 2 discussed biomass, Biorefinery and the different types, wood and its chemical composition, pulping, types of pulping, Best Available Techniques/technology in Kraft process, life cycle assessment, the four different phases of LCA, the uses of LCA and its limitations.
- Chapter 3 described the methods used to achieve the aim and objectives listed in chapter 1. The LCA methodology and experimental methods including Particle size analysis, TGA, GC/MS and liquid- to-liquid extraction were discussed in chapter 3.
- Chapter 4 discussed the LCA of a conventional Kraft pulp mill. During the LCA analysis, energy was identified as the key elementary flow with the most impact on the selected process unit closely followed by water. The chemical recovery unit, washing and screening process unit were affected most by the mentioned elementary flows. Also, Climatic change is the most significant environmental problem generated during Kraft pulp production.
- Chapter 5 is the outcome of the experimental methodology. The outcome of the experimental methodology proves that reducing the particle size (thickness) from 8mm currently used in the conventional Kraft process to < 2mm and replacing part of the water during washing with recoverable hexane reduced energy consumption, water consumption and generated value-added organic compound.
- Chapter 6 is the LCA of the proposed Kraft biorefinery. In chapter 6, the use of particle size < 2mm and a re-usable organic compound as part of a washing liquid was applied to the conventional Kraft pulp mill and re-examined using an LCA. The LCA outcome indicated that the impact of energy generation on climatic change was reduced by 20%. In addition, energy consumption and water consumption were reduced while a value-added product called the green crude generated.

- 
- Chapter 7 is where the energy consumption, water consumption and the quantity of product from the conventional Kraft pulp mill and the proposed Kraft biorefinery were compared to know which is more environmentally sustainable and industrially viable.
  
  - Chapter 8 is Summary of the conclusions and recommendation for future work.

## Chapter 3 – Literature Review

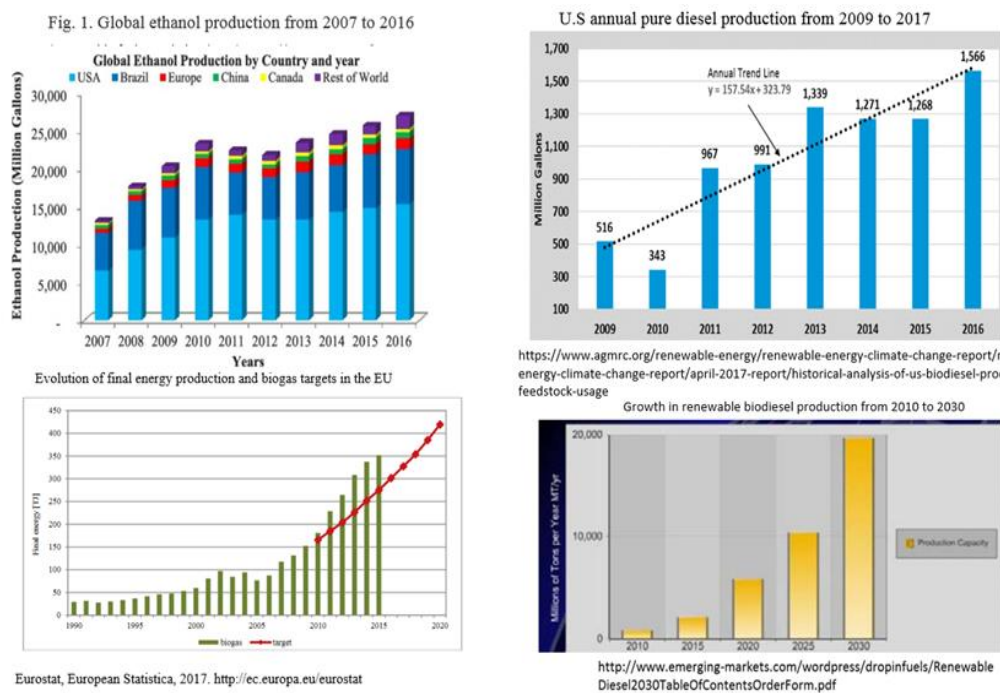
### 3.1 Biomass

They are various forms of renewable energy e.g. (sun, wind, hydro, geothermal etc.) but the only form of renewable energy that have the capacity to replace fossil resources used to produce transportation fuel, chemicals, electricity and heat is biomass (Lucia 2008). Biomass has been accepted globally that it can replace a large portion of fossil resources as feedstock refined into chemicals and fuels (de Jong et al. 2012). Biomass feedstocks like wood, agricultural residue, food waste, are widely available (Li et al. 2004). Biomass is the third largest main energy resources in the world, where 40% - 50% of biomass energy from agriculture is consumed in developing countries (Gani and Naruse 2007). Biomass is a source of bioenergy and provides about 10% of annual global energy from a variety of biomass resource (Popp 2013). Bioenergy produced from biomass is needed to reduce carbon emission going into the atmosphere as a result of fossil fuel use, which contribute up to 64.1% of the world greenhouse gas emission by estimate (Valentine et al. 2012, Baumert et al. 2005). Therefore, the use of renewable energy is one of the alternatives to stabilizing atmospheric CO<sub>2</sub> (Pacala and Socolow 2004). However, energy storing devices are required to store other kinds of renewable energy due to their intermittent nature (Barton and Infield 2004). The only viable energy forms that can replace Petro-chemicals through biorefineries are biomass (Valentine et al. 2012). Secondly, biomass can replace most fossil fuels such a coal, gas and heavy oil, as a contribution to energy security by reducing dependence on fossil fuel (Valentine et al. 2012). Thirdly, biomass will encourage urban and rural economic growth by creating jobs up the supply chain for part time farmers mostly in develop countries like Europe (Thornley et al. 2008), in addition biomass will bring opportunities for income generation in an emerging economy such as Africa through the sales of biofuel feedstock (Licht and Isebrands 2005, da Silva et al. 2018). Furthermore, there would be employment opportunities through Argo industries and improvement in the standard of living (Openshaw 2010). Finally, biomass is important because it will help to decrease the reliance of large-scale agriculture on non-renewable fuels and increase the production of bioenergy that will replace fossil energy (Lemm et al. 2020). Biomass are used to produce bioenergy through biofuel e.g. biodiesel, bioethanol and biogas) (Akia et al. 2014).

The first attempt to produce biofuels, which was called first generation biofuel, was using food crops, like maize and wheat (Havlík et al. 2011). However, Tyner WE,1981 suggest



that this would lead to increase in food price resulting to starvation, hunger, and death (Tyner 1981). Also, an LCA study by (M. Rocha, et al, 2014) suggest that the first-generation biofuel requires more energy during its conversion than the actual energy they produce. Therefore, there was a strong demand for an alternative to the first-generation biofuel. Researchers then came up with another alternative, which was called second-generation biofuels, produced from crop residues of mostly annual crop, example maize, oat, sorghum etc (Havlík et al. 2011). This could not still hold grounds due to competition with the availability of animal feed, soil nutrients and was not sustainable enough due to the cost involved in processing the feedstock (Sims et al. 2010). The third option was the use of dedicated lignocellulose, perennial crops that grow between 15 to 30 years with no extra maintenance (Valentine et al. 2012). Wood and shrubs form 80% of this feedstock while the remaining are from agriculture (Menon and Rao 2012). The introduction of lignocellulose biomass as a third-generation biofuel has brought about a breakthrough in the energy and transportation industry but most of these production plants are now closed due to market condition and need to be upgraded with new techniques and modern facilities. Biomass can be converted to biogas to produce synthetic hydrocarbon and alcohols by gasification (Rauch et al. 2014). In addition, bio oil used for powering turbines, boilers, diesel engine and stationary engine are produced by a conversion process called fast pyrolysis (Bridgwater et al. 1999).



**Figure 3-1:** The world growth in bioenergy (biofuel, bio-oil and biogas).

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Biomass is also used in the production of biochemical like sugar solution which are produced through mild acid hydrolysis (Kumar et al. 2008), phenolic compounds produced by partial depolymerisation of biomass, are used in the pharmaceutical and other related industry (Long et al. 2014). Other products such as terpenoids, waxes, resins, sterols, and alkaloids are example of products generated from biomass (Gallezot 2012). Also, biomass can generate bio-crude which is used as drop-in fuels (Koley et al. 2018, Agblevor et al. 2012). Finally, biomass can be used to generate electricity and heat. Biomass can be converted to energy through thermochemical and biological process (Saxena et al. 2009). Direct combustion of feedstock like wood pellet, pulp rejects etc is one of the ways biomass can be used directly for energy generation (Jenkins et al. 1998). However, energy can also be produced through anaerobic digestion of biomass in landfill (Chynoweth and Isaacson 1987).

The big challenge facing biomass conversion is that it is not environmentally sustainable and economical attractive, because the cost involved in developing the right technologies is exorbitant making the processing cost of the biomass in commercial quantity enormous (Carriquiry et al. 2011). Therefore, conversions of the by-product generated from processing the biomass into value-add products using biorefineries will help reduce the investment cost, thereby making the process a less capital-intensive project.

### **3.2 Biorefinery**

Biorefinery can be defined as a cluster of bio-based refining facility where the biomass feedstock is separated into different components using variety of integrated bio-based technologies to sustainably produce biochemical, biofuel and bioenergy (Diep et al. 2012). Biorefineries are categorized into six types namely Green Biorefineries, whole crop biorefineries, Algae biorefineries, integrated biorefineries, thermochemical biorefineries, forest and lignocellulose biorefineries. Among all the mentioned biorefinery in table 2.1, forest and lignocellulose biorefinery is the most preferred biorefinery because it has been existing for a very long time (Menon and Rao 2012). It is the only biorefinery option, which have abundance of unutilized feedstock that do not have impact on the use of land for food and fibre crops production (Menon and Rao 2012, Sims et al. 2010).

*Table 3-1: Types of biorefinery*

<b>Type of biorefinery</b>	<b>Type of feedstock</b>	<b>Technologies used</b>	<b>Challenge</b>	<b>Development stage</b>	<b>Reference</b>
<b>Green biorefineries</b>	Wet biomass feedstock. Such as green grass and green crops	Pre-treatment, pressing, fractionation, separation and digestion.	Feedstocks compete with feed for livestock,	Pilot stage	(Thornton 2010)
<b>Whole crop biorefinery</b>	Whole crop such as maize, wheat, millet and their straws.	The predominant technologies used are milling and biochemical conversion	It competes with food production due to land use.	Pilot	(Valentine et al. 2012)
<b>Algae or marine biorefinery</b>	Seaweed	Cell disruption, product extraction and the separation of the extract	The technical and economic feasibility are barriers prohibiting the commercial growth of this process	Pilot stage	(Pienkos and Darzins 2009)
<b>Integrated biorefinery</b>	All types of biomass as feedstock	Thermochemical and biochemical	It is not proved commercial feasible.	Pilot scale	(Diep et al. 2012)
<b>Thermochemical biorefineries</b>	All kinds of biomass feedstock	Pyrolysis, gasification, catalytic synthesis, direct combustion, product separation or	Lack of advance technologies for proper use of process by-product.	Pilot scale	(Diep et al. 2012)

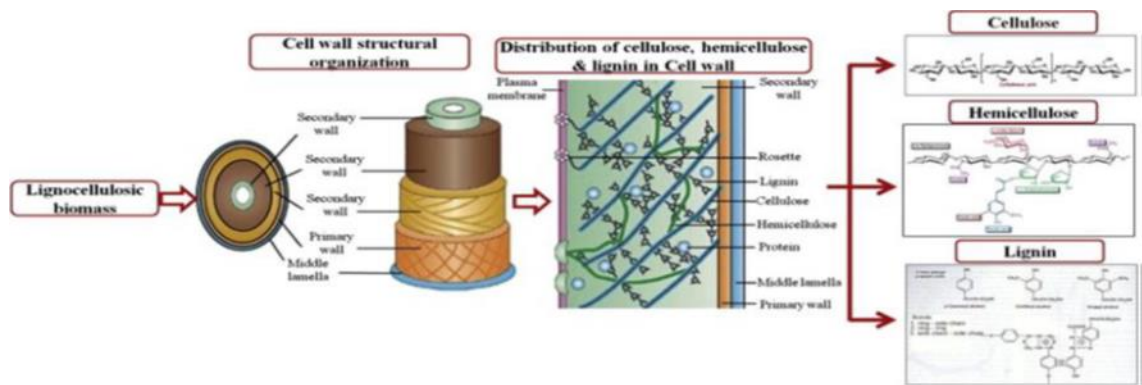
		thermochemical conversion			
<b>The forest and lignocellulose biorefineries</b>	Forest residue, wood waste, miscanthus and wood	Chemical pre-treatment method, biological pre-treatment method, mechanical process, fermentation, hydrolysis and separation.	environmentally unsustainable and industrially not viable	Commercial and is well established all over the world	(Peron et al. 2011)  (Menon and Rao 2012),(Sims et al. 2010)  (Lu and Ralph 1997)

The technologies used in forest and lignocellulose biorefinery are well established and its development stage is above the development stage of any other biorefinery listed in table 2.1. Forest and lignocellulose biorefinery can be sub-divide into two, namely woody and non-woody biorefinery. The thesis will focus on the woody forest and lignocellulose biorefinery, how to make it environmentally sustainable and industrially viable. In the next sections we will discuss wood as a major raw material for lignocellulose biorefinery, its chemical composition and pulping as one of the wood conversion process.

### 3.3 Wood

Wood is an essential resource used almost in every aspect of everyday life. It is used for construction of houses, roofs, bridges, papermaking, kitchen utensils, textiles, poles etc. It can also be used as a source of fuel and organic chemicals (Lebo et al. 2000). However, most of the wood is pulped to produce paper.

The figure 2.2 below is a diagrammatic representation of a woody lignocellulose biomass showing the cross-sectional areas.



**Figure 3-2:** Schematic framework of woody lignocellulose (Menon and Rao 2012).

The above illustration is used to explain the plant cell wall structure and composition of the woody lignocellulose (Menon and Rao 2012). For effective use of a woody lignocellulose (potential energy crop), there are two important things to consider. First, a knowledge of its anatomical structure e.g. resistance to penetration of water and chemical, resistance to decay, pulp quality and chemical reaction (Wilson and White 1986). The second is the composition of the lignocellulose e.g., the quantity of lignin, carbohydrate (cellulose and hemicellulose), extractives and ash. In the next sections, the following qualities of woody lignocellulose mentioned above will be discussed.

### 3.3.1 Cellulose

Cellulose is an unlimited polymeric raw material that is abundant in most plants (Poletto et al. 2014). Cellulose are made up of long chains of glucose unit formed by algae, bacteria, fungi and protozoan (French et al. 2000). Cotton fibres have 94% cellulose in its cell wall while other plants like wood; have cellulose trapped in 36% lignin (French et al. 2000). Cellulose is use in textile industry, food industry, pharmaceutical industry, automobile industry, paper industry and plastic industry (Gupta et al. 2019). Alfred D French and his colleague discovered that cellulose are insoluble in common environment due to the presence of van der Waal forces and hydrogen bond, but they are degraded by enzymes called cellulase which are existent in fungi, bacteria and protozoan in the soil and intestine of ruminants (Kovalenko 2010). Sources of cellulose can be wood through industrial conversion, seeds such as cotton, milkweed, on leaves such as agave leaf, banana leaf and pineapple leaf (Lavanya et al. 2011). In addition, cellulose can be found in algae and bacteria (Brown Jr 1989). Cellulose is a tasteless and odourless hydrophilic substance which breakdown by treating the cellulose with an acid that is concentrated at

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a high temperature (Sasaki et al. 1998). Cellulose can be extracted by chlorine free multiple step procedure (Rosa et al. 2012). The cellulose-contained material is cooked with alkaline to remove the hemicellulose and lignin (Sun et al. 2004). The cellulose produced after cooking lignocellulose material is treated with hydrogen peroxide/acidified sodium chlorite to brighten the cellulose (Qasim et al. 2020). Furthermore, crude cellulose is treated with a mixture of acetic and nitric acids, for additional removal of lignin and hemicellulose from the crude cellulose (Sun et al. 2004). During the Kraft pulping process, most of the cellulose in the pulp used for making paper, textile, and other paper related products account for up to 30.35% of the wood.

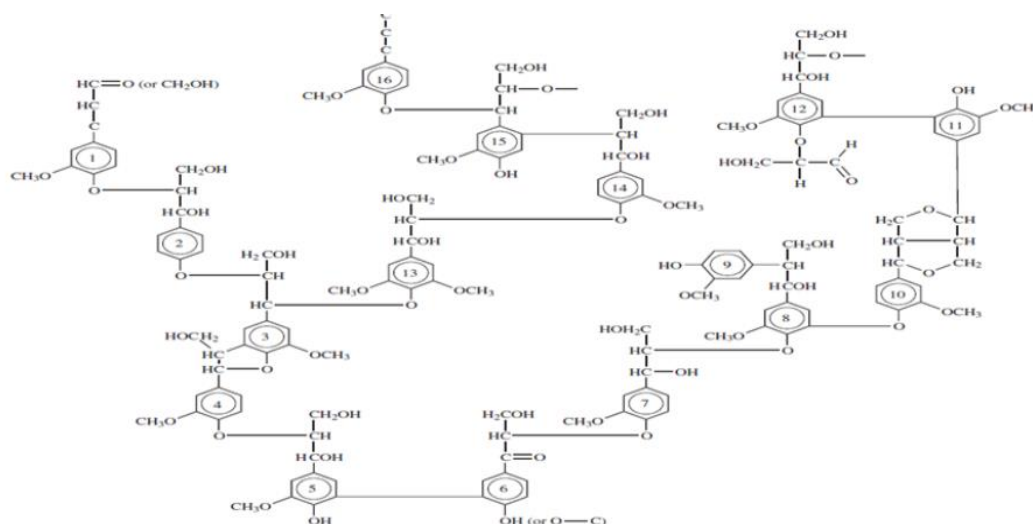
### **3.3.2 Hemicellulose**

Hemicellulose is known as polyose and is a non cellulose polysaccharide found in cell wall of plants (Scheller and Ulvskov 2010). Hemicellulose, unlike cellulose, is made up of short chains derived from mannose, galactose, rhamnose arabinose, xylose and glucose (Gibson 2012). It has low degree of polymerisation. Hemicellulose can exist in different forms as Xylans, Galactomannans, Galatians, Glucans, Xyloglucan, peptic substances, Arabian, Arabinogalactans, and Glucuronomananans (Thompson 2000). Synthesis of hemicelluloses is done by glucosyltransferases, which is in the Golgi membranes (Scheller and Ulvskov 2010). A bone-dry mass of wood about to be pulped contain between 23-32% of hemicellulose (Vakkilainen 2000). During the pulping process most of the hemicellulose are found in the spent liquor where they are burnt to generate steam used in turbines for electricity generation (Vakkilainen 2000). Hemicellulose can be extracted through auto-hydrolysis, acid hydrolysis and alkaline hydrolysis (Rydholm 1965, Hashimoto and Hashimoto 1975, Carvalho et al. 2003). Hemicellulose can also be extracted through fractionation, hot water extraction, ammonia fibre explosion, steam pre-treatment with addition of catalyst (Kenealy et al. 2007, Jørgensen et al. 2007, Menon and Rao 2012). Near-neutral is one of the recent method used for extracting hemicellulose (Mao et al. 2007). During the pulping process, some of the generated hemicellulose are extracted to produce biochemicals while the rest are scorched in the recovery boiler to produce energy which is utilized by pulp mill (Hamaguchi et al. 2013).

### **3.3.3 Lignin**

Lignin is a shapeless polyphenolic substance generated from enzymatic dehydrogenative polymerisation of sinapyl, p-coumaryl and coniferyl alcohol (Lebo et al. 2000). Lignin

help in plant biological process example transportation of nutrient, water and waste product in plant (Lebo et al. 2000). Apart from cellulose, lignin is one of the most available raw materials on earth (Tejado et al. 2007). But only 2% of lignin produced by pulp and paper industries annually are utilised due to the rigorous process involved in converting this by-product to value added product (Gargulak and Lebo 2000). In addition, the commercial aspect of the by-product is negligible because the pulp and paper industries prefer lignin as fuel to generate heat and electricity (Tomani et al. 2011). Also, lignin promotion and valorisation procedures are suggestively less-developed (Azadi et al. 2013). Therefore, introducing newly developed cluster of integrated bio-based techniques and facilities called biorefinery changed the fate of lignin. These integrated bio-based techniques and facilities will assist in the extraction and conversion of lignin to value added product like liquid fuels, valuable aromatic monomers and bio-crude which on the other hand will make lignin economically viable (De Wild et al. 2014, Renders et al. 2017). 90% of the spent liquor produced in the Kraft pulp mill produce steam, used to generate electricity and smelt, used to produce the cooking liquor know as white liquor (Jin et al. 2013). The heat load on the recovery boiler is a major challenge in the Kraft pulp and paper industry. Extraction of lignin from black liquor is a wonderful technique which can be applied to reduce the heat load on the recovery boiler (Vakkilainen and Välimäki 2009). Lignin is connected to each other via carbon-carbon and ether bond given rise to a network as shown in Figure 2.3



**Figure 3-3:** A model structure of a softwood lignin (Adler 1977).

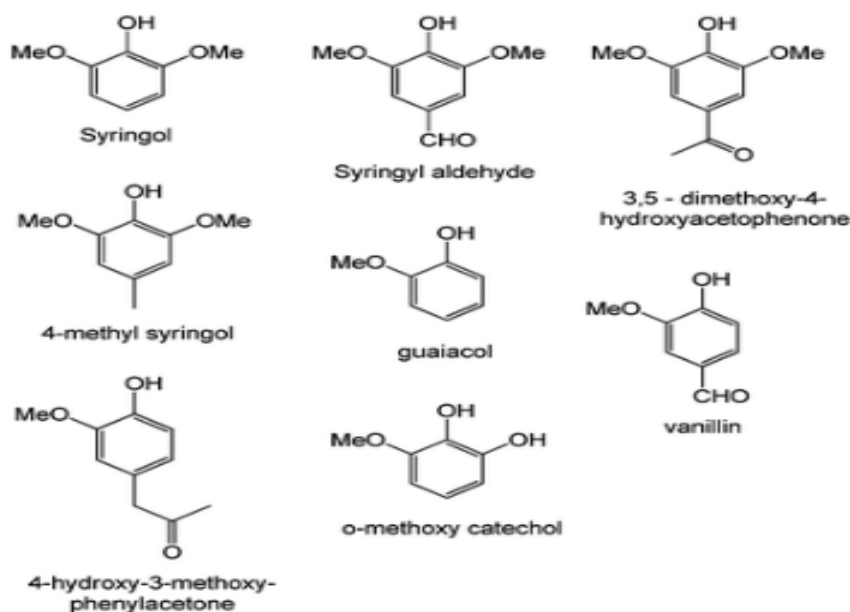
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Due to the strong interlinked bonds existing in lignin, it is difficult to breakdown lignin without disintegrating the carbon-carbon and ether bond binding them together (Braun et al. 2005). Therefore, solvolysis of the ether can make the breakdown of lignin easier (Lebo et al. 2000). This method will help in breaking of the phenolic hydroxyl, benzylic hydroxyl and carbonyl groups which are responsible for a characteristic chemical reaction that contribute to lignin binding force (Lebo et al. 2000). A reaction that will break the carbon – carbon bonds between the aromatic ring could be used to produce valuable monomer from lignin (Wang et al. 2019). According to (Xu et al. 2014) complex organic compound like biphenols with strong carbon – carbon bond can be disintegrated by chemical and thermal depolymerisation. Therefore, part of this study will look at how to use the thermochemical depolymerisation plus solvent extraction method to convert the Kraft lignin in black liquor to value added monomers.

#### ***3.3.4 An overview of Kraft lignin***

Kraft lignin can be formed by thermochemical depolymerization when a homogenous acid /base-catalyst react with black liquor at temperature between 160<sup>0</sup>C – 170<sup>0</sup>C (Echresh et al. 2019). The homogenous base depolymerization is achieved by using a strong base like sodium hydroxide to fragment and separate different monomer from the black liquor at high temperatures in the range of 240–340 °C (Xu et al. 2014). Homogenous base depolymerization has a huge advantage because the strong base does not allow the separated monomer's to polymerise (Chaudhary and Dhepe 2017). Homogenous acid depolymerization is achieved by using an acid catalyst in conjugate with an alcohol at high temperatures (Chandel et al. 2012). Dilute hydrochloric acid in a neutral organic solvent, at room temperature can be used to extract Kraft lignin from the Black liquor (Chandel et al. 2012). Kraft lignin usually contain few impurities after isolation (Lange et al. 2013).





**Figure 3-4:** Different products generated after a homogenous base depolymerisation of Kraft Lignin from black liquor (Xu et al. 2014).

### 3.3.5 Other types of lignin

**Cellulolytic enzyme lignin:** This lignin is developed by treating the mill wood lignin (MWL) with enzymes that degrade polysaccharide down to the level they can be separated from the product. They have a monomer molecular weight of 187(Da) and polydispersity ranging between 5.7 and 6.7 (Lapierre et al. 1985, Zoia et al. 2011).

**Sulfite lignin:** This lignin is produced from sulfite pulping of wood (Lebo et al. 2000). During the pulping process, sulfonation is used to isolate the lignin from the wood. Sulfite lignin which is alternatively called liginosulfonate can be produced from softwood with a monomer molecular weight of range 215 to 254(Da) and polydispersity between 4-9 or from hardwood with a monomer molecular weight 188 (Da) and polydispersity between 4-9 (Söderbaum et al. 2005).

**Organosolv lignin:** organosolv lignin, are produced when pulping chips from hardwood are pulped with an aqueous ethanol or methanol (Diebold et al. 1978). After pulping the organosolv lignin is separated from the organic black liquid called Black liquor via precipitation, followed by distillation (Lange et al. 2013). The organosolv lignin does not dissolve in acid or neutral solvent like water but dissolves in weak alkali solutions (Lebo

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et al. 2000). An example of an organosolv pulping process is Allcel process (Diebold et al. 1978).

**Pyrolysis lignin:** this lignin is produced through thermal decomposition of wood when oxygen is not present. The product of this process is lignin steam used in biorefineries (Lange et al. 2013) while the by-product is char and flue gas. The downside of this process is that large amount of carbohydrate is consumed in the process. In addition, lignin produced by this process has low molecular weight due to an increase in the degree of polymerisation (Lange et al. 2013).

### **3.3.6 Depolymerisation and Extraction of lignin**

Depolymerisation is the efficient removal of lignin using one of the depolymerisation method to break the recalcitrant lignin layer from other structural polysaccharides (Ma et al. 2021). Before the depolymerisation of Lignin, there are two important things to be noted 1) Lignin repolymerise under setting conditions or undergoes self-condensation during the formation of radical and carbon-carbon bond. 2) The catalyst used must be stable in the reaction condition (Xu et al. 2014). The different depolymerisation methods are chemical depolymerisation, oxidative depolymerisation, Ionic-liquid catalysed depolymerisation, heterogeneously catalysed depolymerisation, enzymatic depolymerisation strategies and thermal deconstruction (Tarrsini et al. 2021, Mazar et al. 2021). After depolymerisation, the extraction technique is used to separate the solute from the solution. Examples of extraction solvent used are; toxic aluminium potassium sulfate dodecahydrate (Lopez-Camas et al. 2020), toluene and ethyl acetate (Radoykova et al. 2013), chloroform or dichloromethane and ethanol (Whalen 1975). Furthermore, it has been demonstrated that Lignin can also be efficiently extracted from black liquor using membrane-assisted electrochemical approach (Jin et al. 2013) and CO<sub>2</sub> precipitation (Velez and Thies 2013).

**Table 3-2: The different between cellulose, hemicellulose and lignin**

Cellulose	Hemicellulose	Lignin
Macromolecules from C6 sugars	Macromolecules from C5 sugars	Complex polymer synthesized from phenylpropanoid (c)
45% of the dry weight of wood (a,b).	25–30% of total wood dry weigh (a, b)	10–40 wt.% of the plant material (a, b)
Cellulose is produced by the polymerization of exclusively $\beta$ -glucose monomers (a)	hemicellulose is made by depolymerisation of cellulose to form several monomers example xylose, galactose, mannose, rhamnose, and arabinose (a)	Lignin is a complex polymer generated by enzymatic dehydrogenative polymerisation (c)
cellulose is a straight-chain polymer. It appears in crystalline or amorphous form (d)	hemicellulose is a cross-linked polymer do not form aggregates (e)	lignin is an amorphous heteropolymer (c)
not easily hydrolysable (d)	easily hydrolysable (c)	non-water soluble and optically inactive (c)
In the presence of oxygen, cellulose breakdown to release CO <sub>2</sub> and water(a)	Hemicellulose breakdown in the presence of enzymes to produce monomeric sugar and acetic acid. (e)	Lignin breakdown in the presence of NaS and NaoH to form monomers which are extracted using extraction solvents(a)

a) (Pérez et al. 2002) b) (Stefanidis et al. 2014) c) (Lebo et al. 2001) d) (Poletto et al. 2014) e) (Scheller and Ulvskov 2010).

### 3.4 Commercial wood

Wood is commercially classified into hardwood and soft wood (Kretschmann et al. 2000).

Examples of hardwood are aspen, birch, eucalyptus, and cottonwood while example of softwood are long leaf pine and Douglas fir. Birch and pine are the two wood samples for this study. The table below shows the difference between the two wood species used in this study.

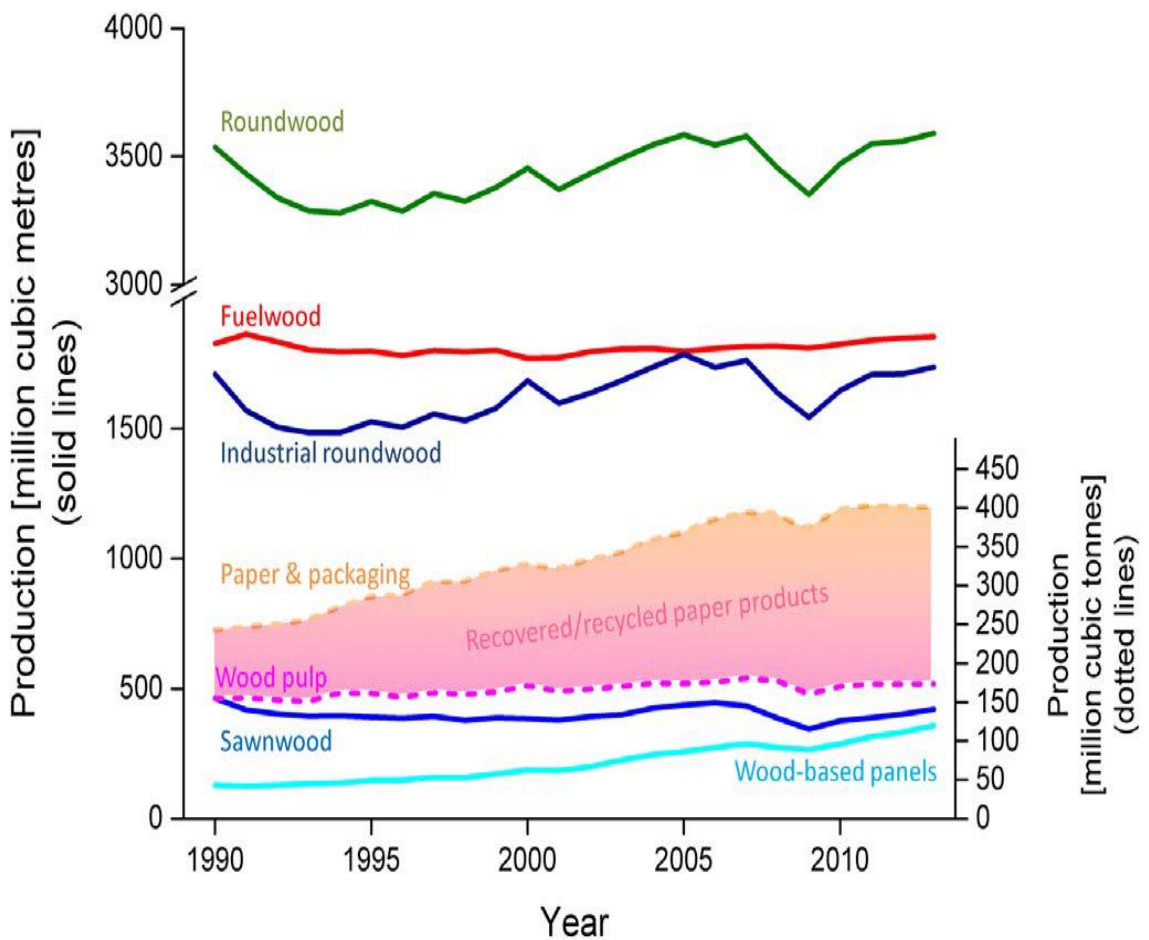
**Table 3-3: The different between Birch and Pine**

Wood species	Type of wood	Pulp quality	Primary Chemical component	reference
Birch	Hardwood	High	Cellulose (44%), Hemicellulose (29%) Lignin (20%) Ash (4%)	(Lachowicz et al. 2019)
Pine	Softwood	Medium	Cellulose (41%), Hemicellulose (22%) Lignin (30%) Ash (5%)	(Pereira et al. 2013, Räisänen and Athanassiadis 2013)

Wood like every other lignocellulose biomass is chemically made up of lignin and carbohydrate (hemicellulose and cellulose) (Hagglund 1951). There are some organic chemical and inorganic minerals which do not contribute to the wood structure but contribute to the wood's chemical composition (Kretschmann et al. 2000). Therefore, the application of a biorefinery concept on the woody biomass is aimed at extracting those chemical compositions like lignin and hemicellulose from the black liquor which is a by-product generated from processing wood. The fibre (cellulose) obtained after processing wood is used across wide varieties of industries starting from the textile industry, food industry, pharmaceutical industry, automobile industry, paper industry, plastic industry and cellophane company (Blanco et al. 2018, Sundarraj and Ranganathan 2018). The hemicellulose in the spent liquor can be extracted to produce biochemicals while the rest burnt in the recovery boiler to generate energy used in the pulp mill (Vakkilainen 2000). Finally, the biorefinery will assist in the extraction and conversion of lignin to value added product like liquid fuels, aromatic monomers, and bio-crude which on the other hand will make lignin economically viable.

The figure below shows that wood is still the preferred biomass and best choice for a lignocellulose biorefinery due to the abundance of opportunity that comes with it. Figure 2.5 are trends in global Roundwood harvest and wood-products produced from 1990 to 2017. We can see that the amount of wood produced out ways the use. The Y-axis labelled solid line show that less than 3500+ million cubic tonnes are produced annually while the

Y-axis labelled dotted line show that 450 million cubic tonnes are only used to produce Pulp, paper, packaging etc. This means that we have 3550 million tonnes of unused wood.



**Figure 3-5:** FAO. FAOSTAT dataset. Food and Agriculture Organization of the United Nations; 2013

### 3.5 Pulping

Pulping is the process of breaking the bonds binding the wood structure to produce a fibrous substance called pulp. Pulps are utilized in paper making, paperboards and absorbents (Kadla and Dai 2000).

#### 3.5.1 Type of pulping

The most popularly type of commercial Pulping are mechanical pulping and chemical (sulphite and sulphate) pulping method. In this study, we are going to focus more on chemical pulping methods.

**Table 3-4: Properties of the selected pulping process (Bajpai 2018)**

<b>Process</b>	<b>Species</b>	<b>Pulp properties</b>	<b>Yield</b>	<b>Global production</b>
Mechanical pulping	Hard and non-resinous softwood	High opacity, low strength and brightness	92% – 96% yield	21%
Sulphite pulping	Hard and soft wood	Medium pulp strength easily brightened. Very high yield	48% -51% for bleachable pulp. 46% -48% after bleaching	2%
Kraft or sulphate pulping	All kinds of wood	High strength and bright when bleached. Brown when unbleached.	65%-70% for brown paper, 47%-50% for bleached pulp.	77%

**Mechanical pulping method:** This method of pulping is used to isolate the fibrous substance through the application of mechanical force which torn out the wood fibre from the wood (DaGue 1992, Northey 1992). Ground wood process is a commonly used mechanical pulping process. In this process, the log of wood is pressed against the rotating grinding Stone, which converts the wood into pulp. The pulp is cooked in order to be soft and ready for use (Bajpai 1996). There are also other types of mechanical pulping process like the refiner mechanical pulping process (RMPP). The (RMPP) process involves the use of a refiner (machine used for shredding wood chips into fibres), use of steam (thermomechanical pulping) or chemicals + steam (chemithermomechanical pulping) processes, which helps to reduce the chips hardness and enhance the pulp quality (Bajpai 2012, Kadla and Dai 2000). Mechanical pulp is 50% cheaper to produce and has its yield efficiency ranging between 85%-95% (Bajpai 1996). On the contrary, chemical pulps are stronger than mechanical pulps.

**Chemical pulping method:** According to (Miller et al. 2005) chemical pulping is the commonest pulping process used in the pulp and paper industry. Chemical pulp is a kind of pulping process that uses chemical and heat to isolate lignin and hemicellulose, leaving behind the pulp (cellulose) (Chandra 2004). The most popular type of chemical pulping methods are sulphite and Kraft pulping.

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***Sulphite pulping:*** Sulphite pulping was made patent in 1867 (Bajpai 1996). In 1874 the process was used in a Sweden mill for the first time by a Swedish chemist by name C.D. Eckman (Biermann 1996). The negative impact on the environment is one of the major disadvantage's sulphite pulping (JRC 2000). On the other hand, sulphite pulping produces brighter pulp however less bleaching is required. Pulp produced through this process are less porous, easy to refine and are of higher yield (Biermann 1996). Sulphite pulping is almost equivalent to Kraft pulping except that the chemical composition of the cooking liquor and the pH range of both processes are not the same (Smook 1992). Furthermore, the use of sulphite pulping gives room to produce different pulp varieties for wide range of application (Bajpai 2012). Sulphite pulping can be classified into different types with respect to their pH.

The following are different types of sulphite pulping; acid sulphite pulping, Bisulphite pulping, neutral sulphite pulping and alkaline sulphite (Smook 1992). Each of the pulping types has advantages as well as disadvantages. Sulphite pulping is a process, which involves various acidic sulphite and their acid to separate lignin from woodchips via hydrolysis and saponification reaction without effecting the properties of the fibrous substance (Wiley-Blackwell 1999), (N.I.Nikitin 1966). The targeted pulp determines the specie of acid sulphite to be used (Wiley-Blackwell 1999).

***Kraft pulping:*** in this method, the woodchip reaction with sodium hydroxide and sodium sulphide, known as white liquor, to break off lignin from the wood (Miller et al. 2005). The amount of temperature and how long the pulp is cooked depends on the amount of pulp brighten needed (Colodette et al. 2002). Kraft pulping is a complex process that involves several steps, which include debarking of the wood, cooking to enable delignification, washing of brown stocks, and further delignification by oxygen, bleaching, cooking liquor recovery process and different primary and biological treatments (Biermann 1996). The first knowledge of Kraft process was first discovered in 1879 when Dahl, a German chemist, produced  $\text{Na}_2\text{S}$ , which was a faster delignifying agent aiding cooking time reduction, and less degradation of carbohydrates. Kraft pulping takes place at a PH above 12, and temperature between 160-180<sup>0</sup>C (Biermann 1996). Kraft cooking is done between 0.5-3 hrs to give more room for delignification (Yoon and Van Heiningen 2008, Latham et al. 2021). Pulp produced from Kraft process are stronger and degrade less cellulose than acidic sulphite process (Biermann 1996). Kraft pulping process is widely adapted due to its relative simplicity, speediness, ability to tolerate varying wood condition and applicability to all kinds of wood species (Macleod 2007,

Tomani 2010). The essence of Kraft process is to extract the fibres which is the raw material for pulp and paper industries and spent liquor or black liquor (by-product) which goes to the recovery boiler where it is used to generate energy for steam turbines used for powering the mill (Darmawan et al. 2017). The deposits (molten smelt) at the bottom of the boiler after evaporation is recycled using chemical process to generate white liquor which is re-used in the pressure cooker (digester) (Naqvi et al. 2010). Kraft pulping involves so many processes starting from the wood handling, cooking of the woodchip, washing, screening, oxygen delignification, bleaching, chemical recovery process, pulp drying up to the point where the pulp is transported either as market pulp, pulp for the paper mill or pulp stored in pulp storage devices.

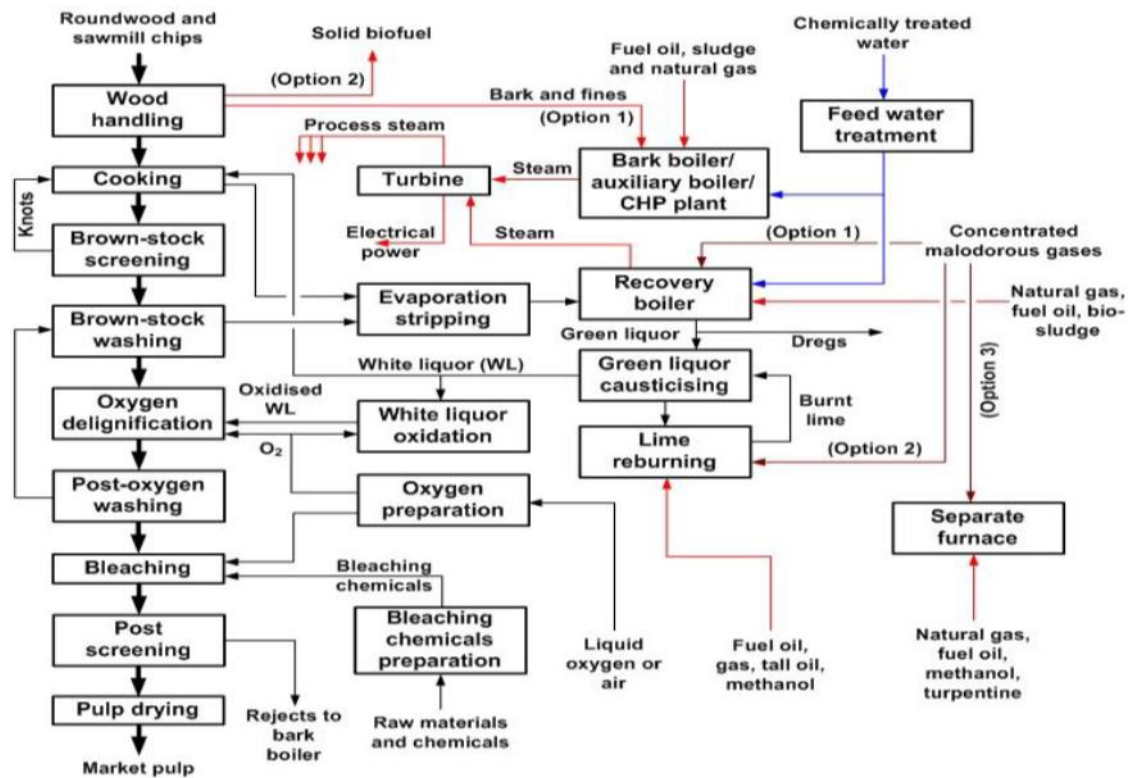


Figure 3-6: Major unit operations in Kraft pulping mill (JRC 2000)

### 3.5.2 Description of major unit operations in Kraft pulping mill

The major operations in Kraft pulping process as mentioned in (Suhr et al. 2015) are as follows; wood handling, cooking, screening & washing (pre-washing and post-washing), oxygen delignification, Pulp drying, Chemical recovery process, Auxiliary boiler, Wastewater treatment process unit, bleaching and Bleaching chemical preparation



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### **3.5.2.1 Wood handling (WH)**

Wood handling can be defined as the systematic process involved in wood conversion from timber to woodchips (Spinelli et al. 2020, Spinelli et al. 2011). These conversions are carried by different kinds of machines such as canter head chipper, drum chipper and disc chipper. The equipment used during the wood handling determines the kind of product expected, the amount of energy involved in the process and the overall impact the system have on the environment (Buonocore et al. 2014, Spinelli et al. 2020). To minimize cost and maximizes profits, selection of machine that will optimize the use of the raw material is important. Among the three-chipping machine listed above, disc chipper is the preferred because disc chipper produces conical chips. It also reduces logs to chips with good pulping properties and produce woodchip with high packing density (Huntley et al. 2004).

### **3.5.2.2 The effect of particle size on pulp production**

According to (MacLeod 2007, Carvalho et al. 2003, Colodette et al. 2002, Akhtaruzzaman and Virkola 1979) the initial affective alkali concentration, H-factor, pulp viscosity, fibre length, paper strength, kappa number and yield are determined by chip geometry (chip length, width and thickness). Furthermore, Akhtaruzzaman and Virkola speculated that the thicker chips are harder to cook since they are denser, reducing the rate at which the cooking liquor diffuse into the woodchips. Several studies have found that particle geometry (chip length, width and thickness) have significant effect on Kraft pulping process (Dang and Nguyen 2008, Cáceres et al. 2015). Chip thickness is an important dimension that effect the rate at which the cooking liquor penetrate the capillary structure of the woodchips (Malkov et al. 2001, Malkov et al. 2003). When the woodchip thickness is more than 3mm the rate at which the cooking liquor diffuse into the chip is reduced making the woodchip undercooked. As a result, plenty of rejects and non-uniform pulp are produced. In addition, huge quantity of raw materials (water, chemical, energy etc.) are used. According to (Hatton 1979) the thickness of a woodchips should not exceed 3-4mm in other to achieve a bleachable grade kappa number. Kappa number is a measure of the lignin content of the pulp (Bajpai 2018). However, it has been established that there is reduced delignification and increase in screening time when the thickness of the chips exceed 3mm (Hartler and Onisko 1962). Furthermore, when the chip thickness is more than 8 mm there is a reduction in pulp yield and an increase in rejects (Un-pulp wood) (MacLeod et al. 2005). The thickness of a chip effect the chip

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pre-steaming, the rate at which the cooking liquor diffuse into the woodchips and the degree of delignification (MacLeod et al. 2005). The study on ``the Influence of chip dimensions in Kraft pulping'' reveals that pulp properties and the quality of paper produced depends on chips thickness, chip length, initial effective alkaline concentration and H-factor (Akhtaruzzaman and Virkola 1979). H-factor is a cooking variable that combines both temperature and time into a single variable meant to determine the rate of the cooking reaction (Bajpai 2018). Therefore particle size is the first parameter to be considered when analysing a traditional Kraft pulping mill (Dang and Nguyen 2008).

### **3.5.2.3 Particle reduction process and energy consumed**

This study was used to find out the impact of particle size reduction on the amount of energy used during wood handling. The amount of energy required during grinding of biomass depends on the size of the screen and moisture content (Mani et al. 2004). Therefore, smaller particle size will require higher energy while bigger particle size will require smaller energy. During grinding experiment, 3.2, 1.6 and 0.8mm screen size was used to reduce biomass with geometric mean chop size 20.52mm (Mani et al. 2004). When the hammer mill was operating with 0,8mm screen, the average specific energy consumed was 53kwh/t. When the screen was changed to 1.6mm the energy consumed changed to 38KWh/t. Finally, when the screen was change to 3.2mm the average energy consumed changed to 14KWh/t. In addition, (Cadoche and López 1989) showed the relationship between energy and particle size using a 10hp Knife mill and a 15hp hammer mill. The outcome of the size reduction depicts that 130KWh/t, 50KWh/t and 25KWh/t was consumed to achieve particle size 1.6mm, 3.2mm and 6.35mm. We can confirm that smaller particles size uses higher energy than bigger particle size. Furthermore, we used the outcome of these research work to assume the amount of energy particle size 0-2mm, 2-4mm and 4-8mm will consume during their reduction.

### **3.5.2.4 Kraft Cooking (C)**

Wood cooking is carried out in a digester. Digesters are container where woodchips are cooked together with the cooking liquor (sodium hydroxide and sodium sulphide) at a given temperature and pressure to produce pulp and a by-product called black liquor. Digesters are expensive but are necessary in the pulp yield and paper production (Doyle III and Kayihan 1999). The two main kinds of digester synonymous with paper and pulp

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industry are batch and continuous digester (MacLeod 2007). Batch and continuous process are the main factors responsible for 25% reduction of tear-tensile strength in the production of bleachable softwood pulp (MacLeod et al. 2005). 40% of Kraft pulp produced globally use batch digester (Lee and Bennington 2010). Therefore, a lot of effort has been made to enhance the uniformity of pulp produced using batch process. The depth of penetration depends on physical properties of the wood sample like (thickness, specific gravity, moisture content and thermal properties), cooking condition like (the amount of active alkali present in the reaction, effective alkali, the sulfidity of the reaction, liquor vs wood quantity, maximum temperature, pressure of cooking the chips, max cooking time, mini cooking time, H-factor etc), and digester equipment (MacLeod et al. 1995). Mills adjust their screening equipment to have an upper limit of 8mm in order to prevent thick chips that reduces diffusivity of cooking liquor. Theoretically woodchips for Kraft process are usually 4mm thick, 25mm long and 25mm wide (MacLeod et al. 2005). Chip thickness is one of the major factors that affect the impregnation and the rate that the cooking chemicals diffuse into the woodchips. When the woodchip is >3mm diffusion of the cooking liquor is slow, bringing about poor cooking of the woodchips and result in an increase in rejection (Dang and Nguyen 2008). The resultant speed at which the woodchips react with the cooking liquor depends on their heterogeneity. Furthermore, it is also assumed that the speed at which the reactions take place is a function of power and time (Wardrop and Davies 1961).

### **3.5.2.5 Kraft chemical recovery process (CRP)**

Chemical recovery process is an important part of Kraft process (Biermann 1996). It is used by more than 80% of paper and pulp industry in the US (Miller et al. 2005). The economic success of a kraft pulp mill is dependent on the efficiency of its chemical recovery facilities (Brewster 2007b). The recovery boiler is one of the most expensive facilities in a pulp mill (Brewster 2007a). The chemical recovery process helps to reduce: the amount of cooking liquor (white liquor) purchased by the pulp industry by enabling the chemical recycle process of the spent liquor, reducing the amount of waste to be treated. Finally, it helps to produce energy which can be utilized for the mill activities. In order to optimize Kraft process, there is a need to enhance its chemical recovery processes (Miller et al. 2005). The five steps involved in the chemical recovery processes as discussed by (Miller et al. 2005) is as follows

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1) Concentrating the black liquor by evaporation.

The evaporator concentrates the black liquor from 20% to 75% solids (Gullichsen et al. 1992). The evaporators are the major user of steam in a Kraft mill, accounting for about 25% of entire pulping process steam used in the mill (Suhr et al. 2015). Removing the excess water from the back liquor requires so much energy therefore using a re-usable liquid as part of the washing liquid as mentioned in the washing stage will cutdown the amount of water that needs to be evaporate from the spent liquor, reduce the amount of energy and the number of evaporators use.

2) Generation of molten smelt and steam for energy production via black liquor combustion in the recovery boiler.

The spent liquor is discharged into the recovery boiler to solidify the black liquor and burn off the organic solids. The heat of combustion from burning the organics is captured in the form of high-pressure steam while the inorganic compounds are recovered as smelt (Suhr et al. 2015).

3) Reproduction of white liquor from green liquor (the smelt) through recausticizing.

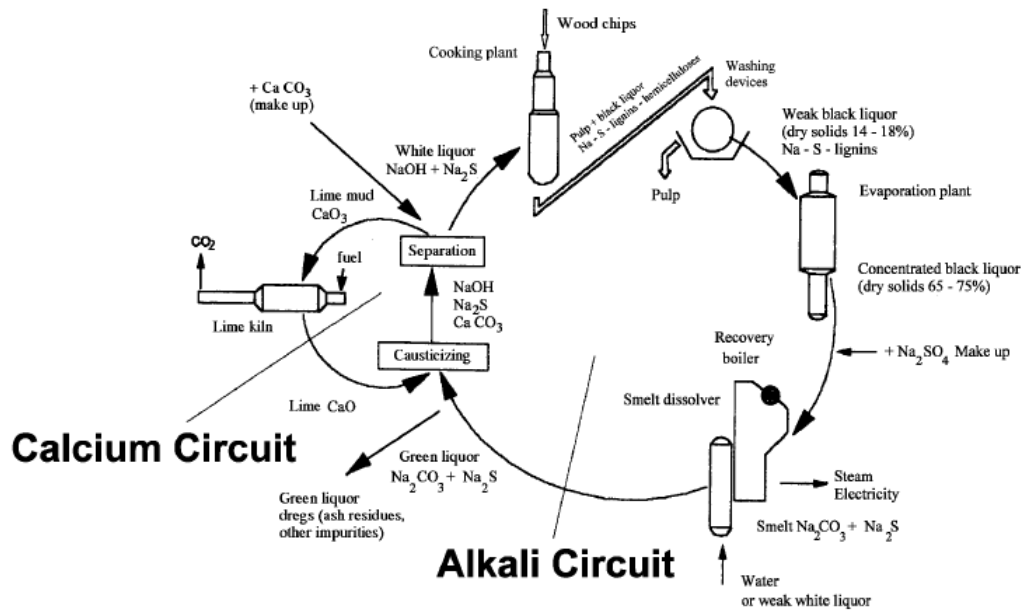
The process begins by the preparation of the green liquor. The smelt from the recovery boiler is dissolved in weak wash water from dregs and lime mud washing operations to for green liquor. The green liquor reacts with lime to form white liquor and lime mud.

The retrieved white liquor is re-introduced into the pulp digester where it is used to continue cooking the pulp.

4) The lime used in the recausticizing process is recovered through calcining process.

During the calcining process, the lime mud is washed, dried, and reheated to recover the lime and carbon dioxide. The lime is washed and screened to recover the lime which is used during the recausticizing process while the CO<sub>2</sub> is burnt in the lime kiln.

65 – 85% of the emission release into the air from the recovery boiler during pulp production contains NO<sub>x</sub> emissions (Suhr et al. 2015). The black liquor contains nitrogen which affects NO<sub>x</sub> development in the recovery boiler. Mill tests according to (Suhr et al. 2015) shows a relationship between NO<sub>x</sub> emissions and the nitrogen input in black liquor solids (BLS).



**Figure 2.7** Overview of Kraft chemical recovery process (JRC 2000).

### 3.5.2.6 Washing & Screening (WAS)

After pulping, the fibre coming out of the digester contains black liquor. The fibre is washed, and the weak black liquor is transferred to the recovery boiler where 99% of the chemical applied in the digester is recovered (JRC 2000). Pulps from batch digester are washed with drum washer while pulp from continuous digester are washed with either diffuser or drum washer. In modern times, pulp washing start in the digester by replacing hot spent liquor with cold wash liquid (Rahman et al. 2019). When the pulp is washed well, the quantity of chemicals consumed during oxygen delignification and bleaching is reduced. The quality of pulp produced after washing depends on the efficacy of the washing equipment used, the outlet stability of the pulp and the amount of liquid used to wash the pulp (JRC 2000). However, the quantity of water used during washing will determine the amount of energy required by the evaporator to concentrate the dilute black liquor. Using a re-useable liquid will help reduce the amount of water consumed during washing and aid in the extraction of value chemicals from the pulp spent liquor.

Screening is an important process, which involves the passage of the pulped fibre through a perforated plate, leaving behind the knot, shives and other debris (Gooding 1986). Pulp is screened with series of vibrating equipment and centrifugal separators that separates the fibre from other particles (reject). During screening the coarse reject are separated from the main pulp by vibrating perforated plates furthermore the hammer mill is used to reduce the coarseness of the reject after which the reject and coarse shivers are further

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filtered through a pressure screen which retains shives above setting size depending on the type of paper to be produced. Finally, the centrifugal separator is used to separate the fibre from other particle after which the final reject generated are discharged as solid waste while the fibres are returned to the fibre line (JRC 2000). After Screening, the pulp is transferred to the oxygen delignification process unit while the by-product (black liquor) collected after cooking goes to the chemical recovery process unit.

#### **3.5.2.7 Oxygen delignification (OD)**

Oxygen delignification is one of the processes involved in pulp bleaching. During the process up to 50% of the residue lignin is removed from the pulp (Miller et al. 2005). The oxygen delignification alternatively called brown stock oxygen bleaching are controlled by environmental, economic and energy related concern (McDonough 1996). The advantage of oxygen bleaching over other method of bleaching especially the chlorine method is that it is environmentally friendly. The by-product generated from oxygen delignification can be redirected into the recovery boiler where it can be used as a source of energy unlike those produced from chlorination that are polluted due to the presence of chlorine (Fu et al. 2004). In terms of cost, the quantity of lignin in the unbleached pulp determines the amount of bleaching chemical used. After oxygen delignification the quantity of bleaching chemical used is reduced because 50% of the residue lignin have already been removed.

#### **3.5.2.8 Bleaching (B)**

Bleaching is a chemical process used to brighten pulps produced by mechanical and chemical process. Pulp bleaching is important because it helps to remove extractives, chromophoric group, conjugate double bonds, complex metal ion and contaminants (Kadla and Dai 2000). Residue lignin in alkaline pulp are hard to bleach however, lignin degrading bleaching or lignin preserving bleaching can be used to remove the residue lignin and make the pulp reach the desire brightness (Kadla and Dai 2000). Lignin degrading bleaching involve using oxygen or chlorine chemicals to breakdown the Lignin Structure while lignin-preserving bleaching is the use of hydrogen peroxide and/or sodium dithionate in the brightening of the pulp.

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#### **3.5.2.9 Pulp drying (PD)**

This process involves the removal of moisture from pulp using a pulp dryer. Pulp drying involves two main operations, namely heating air in a steam coil and removing moisture away from the pulp sheet (JRC 2000). The former involves heating up the air in the steam coil to increase its ability to absorb water from the pulp sheet. The two important parameters, which enable the success of this operation, is the change in temperature and solubility of water in air (Suhr et al. 2015). However, change in temperature is directly proportional to solubility of water in air, so for every increase in temperature, there is a commensurate increase in the quantity of water in the air in the surrounding can hold (Muzaffar and Kumar 2015). The hot air in steam coil of the pulp-drying machine supplies heat to dry the pulp sheet and removes water vapour from the pulp sheet. The input require for the drying process are heated air, steam, electricity while the output is dried pulp, water vapour and heat.

#### **3.5.2.10 Auxiliary boiler (AB)**

This vessel produce super-heated steam when the fluid inside the vessel is heated until it starts vapouring (Rayaprolu 2009). The vaporized fluid is used for various purpose e.g. cooking, heating, cleaning, and electricity generation. Auxiliary boilers are manufacture with materials like steel and wrought iron. Steel containing chromium and nickel are not good for designing the interior of boiler because it can undergo stress corrosion cracking (Boiler and Code 2010). Heat energy is produced in the boiler by burning the fuel, which could be either renewable (bark, wood waste and wood reject produced after wood handling process) and non-renewable (coal, natural gas and fossil fuel).

#### **3.5.2.11 Bleaching chemical preparation (BCP)**

Bleaching sequences for chemical pulps are divided into two main stages (i) delignification stage (ii) brightness stage (Kadla and Dai 2000). During oxygen delignification up to 50% of the residue lignin is removed from the pulp (Miller et al. 2005). However, the follow bleaching agent (chlorine, hypochlorite's, NaOH, CLO<sub>2</sub>, peroxide and Ozone) carries out the brightening. Bleaching of chemical pulp involve several stages which are separated by washing, to remove the residue chemical and degraded lignin in the treated pulp. These beaching chemicals will release chlorine compound, which are toxic to the environment (Stringer and Johnston 2001).

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### ***3.5.3 Example of major modifications in Kraft pulp mills that encouraged environmental sustainability and industrial viability.***

Researchers have been working to develop best techniques and operational methods to improve the conventional Kraft pulping mill (Stankiewicz and Moulijn 2000). So far, many techniques have been developed over the years. However, majority of these techniques have commercially been used in Kraft pulp mill across Europe and over the world. The lists of best available techniques mentioned below are considered for both integrated and non-integrated Kraft pulp mill. However, this list is not considered exhaustive according to (JRC 2000). The list is always subject to updates. The following list below are measures towards improving Kraft mill sustainability (1) training, educating and motivating the staff on way to reduce discharge of harmful substances from the Kraft mill. (2) Process control optimisation. (3) Maintaining the technical unit of the pulp mill. (4) Enhancing the environmental management system (Suhr et al. 2015, JRC 2000). When the above measures are completed, the mill can then proceed to ways of reducing emission to the water, emission to the air, Solid waste and energy consumption.

#### ***3.5.3.1 Water pollution mitigation***

The following list of BATs(best available according to (JRC 2000) will reduce emission to the water during pulp production, The BATs are Dry debarking of wood, Modified cooking by either batch or continuous digesting system, Highly efficient brown stock washing and close cycle brown stock screening, Oxygen delignification, ECF or TCF final bleaching, process water recycling in the bleaching plant, Purification and re-use of condensates, Effective spill monitoring, recovery system for bleach plant effluents. Primary treatment of wastewater, External biological wastewater treatment, gathering clean cooling water and making sure it is use again. Installing enough black liquor evaporation plant and recovery boiler to cope with the additional liquor and dry solids loads due to collection of spills.

Finally, the use of all this available technology and techniques listed above will help in reducing the amount of emission released into the water body around Kraft pulp mills (Suhr et al. 2015). Table 2.5 shows the emissions reduced due to the application of best available technology and techniques. The abbreviations in table 2.5 is explained in page xix.



**Table 2.5:** examples of achieved emission levels to the water after applying the mentioned technologies and technique above to an existing pulp mills in Europe (JRC 2000)

<b>parameter</b>	<b>Unit</b>	<b>Bleached Kraft</b>
COD	Kg/ADt	8.0 - 25
BOD	Kg/ADt	0.3 – 1.5
TSS	Kg/ADt	0.6 – 1.5
Total P	Kg/ADt	0.01 – 0.03
AOX	Kg/ADt	0.0 – 0.25
Total N	Kg/ADt	0.1 – 0.2

### 3.5.3.2 Air pollution mitigation

According to (JRC 2000), the following Best Available Technique were applied to reduce emission to the air from the Kraft pulp mill. The first technique applied was the incineration of concentrated or dilute Malodorous gases from the fibre line, (Suhr et al. 2015). Secondly, TRS emission from the recovery boiler are controlled by high-tech combustion and surplus oxygen control while the remaining soluble sodium in the lime mud is fed to the kiln (Bajpai 2015). To reduce emission of SO<sub>x</sub> from the recovery boiler a black liquor of high dry solid content is fed to the recovery boiler (JRC 2000). The emission of NO<sub>x</sub> from the recovery boilers and limekiln were controlled by monitoring the firing condition, ensuring correct mixing, and partitioning of air in the recovery boiler. NO<sub>x</sub> emission is regulated in the auxiliary boiler by monitoring the boiler firing condition and fitting the right NO<sub>x</sub> control designs (Suhr et al. 2015). Furthermore, SO<sub>x</sub> from the auxiliary boilers is regulated by using renewable fuels from the Kraft mill, low sulphur oil and coal. In addition, cleaning the recovery boiler, limekiln and auxiliary boiler with electrostatic precipitator to alleviate dust emission is another novel technology which reduce air pollution (Onarheim et al. 2017). Finally, the use of all this available technique and technology listed above has help in reducing the amount of emission released into the air surroundings of the Kraft pulp mills. Table 2.6 shows the emissions released due to the application of best available technology and techniques. The abbreviations in table 2.6 is explained in page xix.

**Table 3-5:** Emission level to the air associated with the use of BATs mentioned above in a Kraft pulp mill (JRC 2000)

<b>Parameters</b>	<b>Units</b>	<b>Bleached and unbleached Kraft pulp mills</b>
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<i>TSP</i>	<i>Kg/Adt</i>	<i>0.2 - 0.5</i>
<i>SO<sub>2</sub> as S</i>	<i>Kg/Adt</i>	<i>0.2 – 0.4</i>
<i>NO<sub>x</sub> as NO<sub>2</sub></i>	<i>Kg/Adt</i>	<i>1.0 – 1.5</i>
<i>TRS as S</i>	<i>Kg/Adt</i>	<i>0.1 – 0.2</i>

Emissions from the auxiliary boiler are excluded from table 2.6 because these depend mostly on the type of fuel used. However, emission levels linked with BAT from an auxiliary boiler using the mills own biofuel (barks, wood waste and reject) and different fossil fuels are shown in the table below.

**Table 3-6:** Emission level linked with the use of BAT from different fuels (JRC 2000)

Release substance	coal	Heavy fuel oil	Gas oil	Gas	Biofuel
mg S/MJ fuel input	100 - 200	100 - 200	25 - 50	< 5	< 15
Mg NO <sub>x</sub> / MJ fuel input	80 - 110	80 - 110	45 - 60	30 - 60	60 - 100
Mg dust/Nm <sup>3</sup>	10 – 30 at 6% O <sub>2</sub>	10 – 40 at 6% O <sub>2</sub>	10 – 30 3% O <sub>2</sub>	< 5 3% O <sub>2</sub>	10 – 30 at 6% O <sub>2</sub>

### 3.5.3.3 Solid waste reduction

Solid waste generated in Kraft pulp mill can be reduced by using the best available techniques and technologies to increase the re-use, re-cycle and recovery of solid waste materials generated in Kraft pulp mill (Brown 1956), The BATs are also used to Incinerate all non –hazardous solid waste in the auxiliary boiler (Monte et al. 2009). Also, solid waste can be reduced by appropriate handling and intermediate storage of solid waste fraction from Kraft pulp mill (JRC 2000). Finally, the use of all this available technique and technology listed above will help in reducing the amount of solid waste release into the Kraft pulp mill environment.

### 3.5.3.4 Measures to save energy

To curtail the amount of energy (electricity and heat) consumed in a Kraft mill and increase the amount of energy internally generated, the following measures listed in table 2.8 are used. The measures are a) installing measure to enhance high heat recovery and low heat consumption (Kramer et al. 2009). b) Reduction in the amount of electrical power consume (JRC 2000). c) initiating technology and introducing techniques that enhance the generation of high electrical power in the Kraft mill (Kong et al. 2020).

Therefore, the following are ways to achieve each of the following measured listed above is listed in the table 2.8 below:

**Table 3-7: Energy saving measure-using BAT (JRC 2000)**

<b>Measures for high heat recovery and low heat consumption</b>	Using a black liquor with a high dry solid content.
	Using steam boiler with high efficiency
	Preventing linkage by closing the water system.
	Properly closing the bleaching plant.
	Making the pulp very concentrated
	Pre-dry the lime
	Heat the building with secondary heating
	Establish good process control
<b>Measures use to reduce the amount of electrical power consumption</b>	Reducing the speed of the large motors used in pulp mill.
	Use vacuum pump that are very efficient
	Use proper sizes of pump, pipes and fans
<b>Measures used for generating high electrical power in the Kraft mill</b>	Use boilers with high pressure.
	Using turbines with high efficiency.
	Preheating of fuel or air charged to the boiler
	Channelling excess produce seam to the turbine for energy generation

After applying the following measures listed in table 2.9, there was a reduction in energy consumption. Therefore, table 2.9 displays the outcome of using the BATs for energy reduction as mentioned in table 2.8.

**Table 3-8: Energy consumption linked with the use of BAT (JRC 2000)**

<b>Type of mill</b>	<b>Process heat consumption (net) in GJ/ADt</b>	<b>Power consumption (net) in MWh/ADt</b>	<b>Remarks</b>
Non-integrated bleached Kraft pulp	10-14 GJ/ADt about 2-2.5GJ/ADt can be used for power generation giving a heat surplus of 0.5 -1.0 GJ/ADt.	0.6-0.8 MWh/ADt modern pulp mills are power self-sufficient.	An integrated mill reported 10GJ/ADt heat consumption in the pulp mill

The entire mentioned BATs are already established and used commercially in the pulp and paper industry. However, they are still emerging techniques like gasification of black liquor (Naqvi et al. 2010), use of SNCR on the recovery boiler (Świeboda et al. 2020), removal of chelating agent by modest alkaline biological treatment or the use of Kidney (JRC 2000), increased system closure combined with the use of Kidney and organosolv pulping which are still on pilot and laboratory stage.

Conventional Kraft pulp mill is a Kraft mill with all the modifications mentioned above. In other words, the system under study is a Kraft pulp mill fitted with all the best available technique for pollution control and prevention. However, the modifications are not exhaustive. Any new idea, or technique which will improve the Kraft pulping mill, is highly welcomed into the BAT list. So far, the need to further improve the Kraft pulp mill have led to studying the impact of using different particle thickness and an organic reusable liquid as part of the washing liquid on the Kraft pulp mill. The question one should ask is “can change in input parameter such as woodchip thickness and the use of a reusable liquid, improve the environmental sustainability and industrial viability of conventional Kraft pulp mills?” This brings us to the purpose of the study which is to use a multi-disciplinary approach involving life cycle assessment (LCA) and empirical methodology to identify areas where a conventional Kraft pulp paper mill can be improved. To achieve this purpose, we must identify the two key elementary flows of concern to the selected process units under the system boundary and the process units affected most by the mentioned elementary flows. Also, identify the most significant

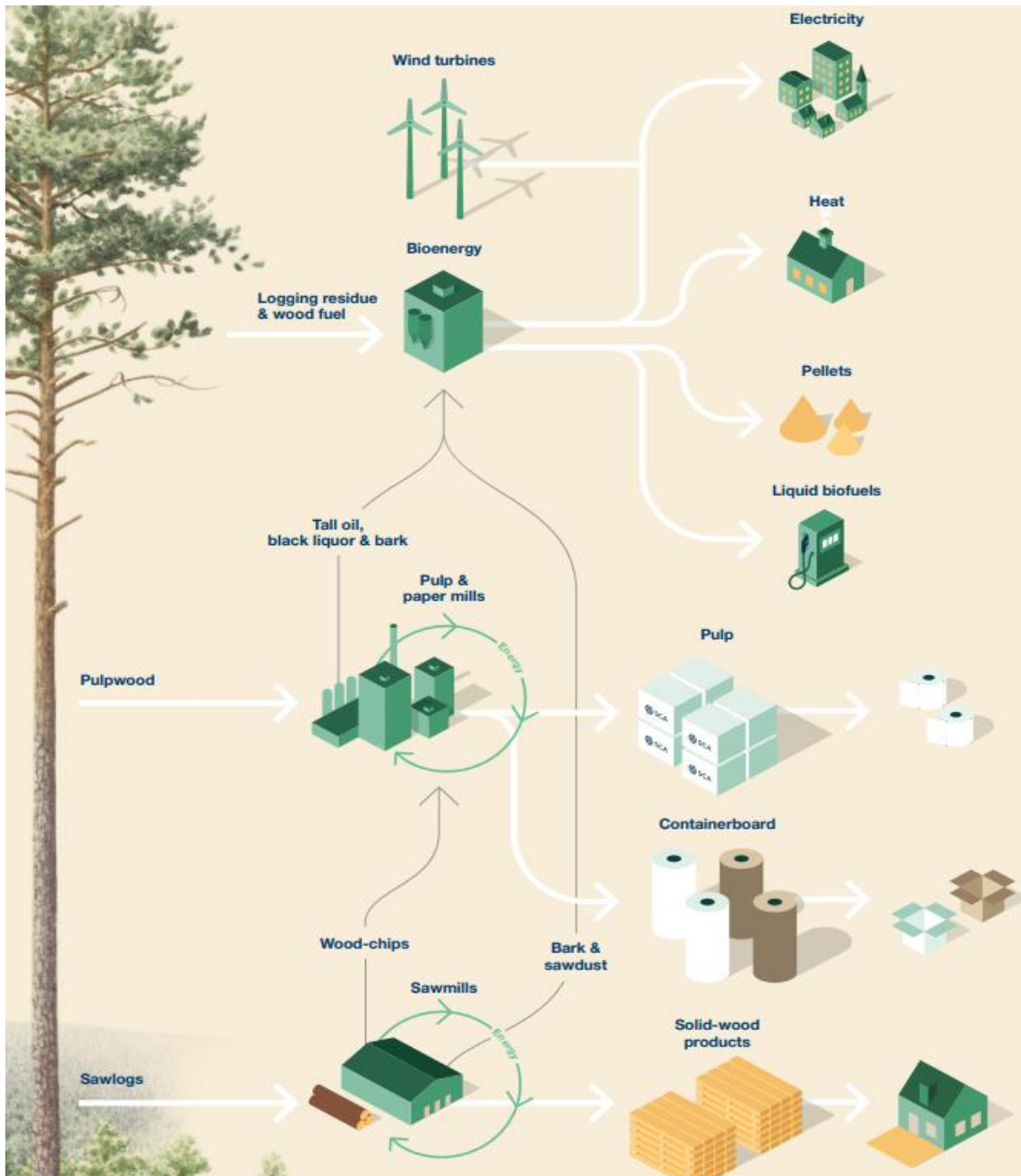
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environmental problem generated during Kraft pulp production. Secondly, we must prove that reducing the particle size from 8mm currently used in the conventional Kraft process to < 2mm and replacing half of the water used during washing with recoverable hexane can make Kraft mill sustainable by generating extractable organic chemical, reduce energy use, water consumption and release of emission in the air. Thirdly, apply the outcome of the empirical methodology to the new conventional Kraft pulp mill called Kraft biorefinery and measure the difference in energy consumption, water consumption and the environmental problems generated during Kraft pulp production using LCA methodology. Finally, compare the conventional Kraft pulp mill and the proposed Kraft biorefinery to determine which is more environmentally sustainable and industrially viable.

**Evidence of Kraft pulp mill and efforts to increase the environmental sustainability and industrial viability.**

Svenska Cellulosa pulp mill: According to Environmental information 2021, SCA Pulp Svenska Cellulosa pulp mill is a Swedish pulp with the largest private forest in Europe. This pulp mill is a world leading energy and resource efficient pulp mill. Svenska Cellulosa pulp mill has a 50% reduction in carbon footprint with an annual pulp production capacity of 1 million tonnes. Resource proficiency is a significant part of her sustainability effort. Water pollution mitigation through dry debarking of wood, modified cooking by either batch or continuous digesting system, ECF or TCF final bleaching, efficient brown stock washing and close cycle brown stock screening are technologies they use to mitigate the amount of pollution release in the water from the mill. Svenska Cellulosa pulp mill also reduce emission to the air by incinerating concentrated or dilute Malodorous gases from the fibre line, cooking plant. Evaporation plant, recovery boiler and limekiln. In the mill, solid waste is reduce by re-use, re-cycle and recovery of waste materials generated in the pulp mill. To curtail the amount of energy (electricity and heat) consumed in Svenska Cellulosa pulp mill, steam boiler with high efficiency are used. In addition, the speed of the large motors used in the pulp mill are reduced. Finally, Svenska Cellulosa pulp mill also generate high electrical power by channelling excess produce seam to the turbine. The application of those sustainable measures has improved the viability of not only Svenska Cellulosa pulp mill but also the grow of other world renowned pulp mills like other UPM-Kymmene Oyj (UPM), Stora Enso and Nippon

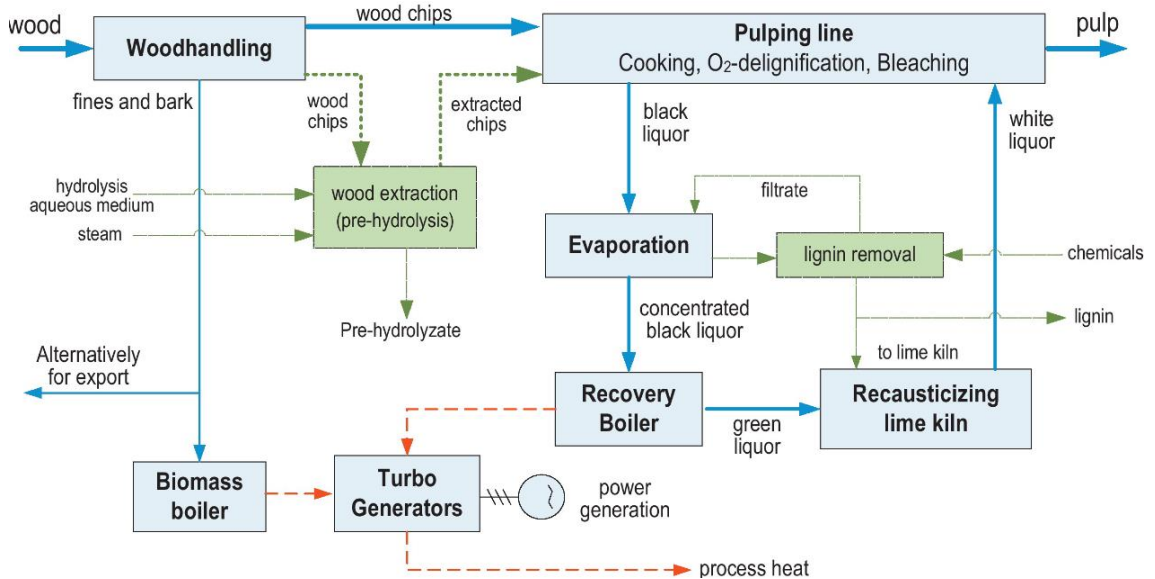
Unipac Holding (Nippon Paper Industries) who apply modifications like External biological wastewater treatment as a measure for water pollution mitigation. Also, air pollution was mitigated by using renewable fuels, monitoring the firing condition, ensuring correct mixing of fuel and partitioning of air in the recovery boiler. Energy can also be conserved in the mill by using vacuum pump that are very efficient.



**Figure 2.8** A schematic demonstration of how Svenska Cellulosa pulp mill sustainably use wood resources (Environmental information 2021)

### 3.6 Kraft Biorefinery

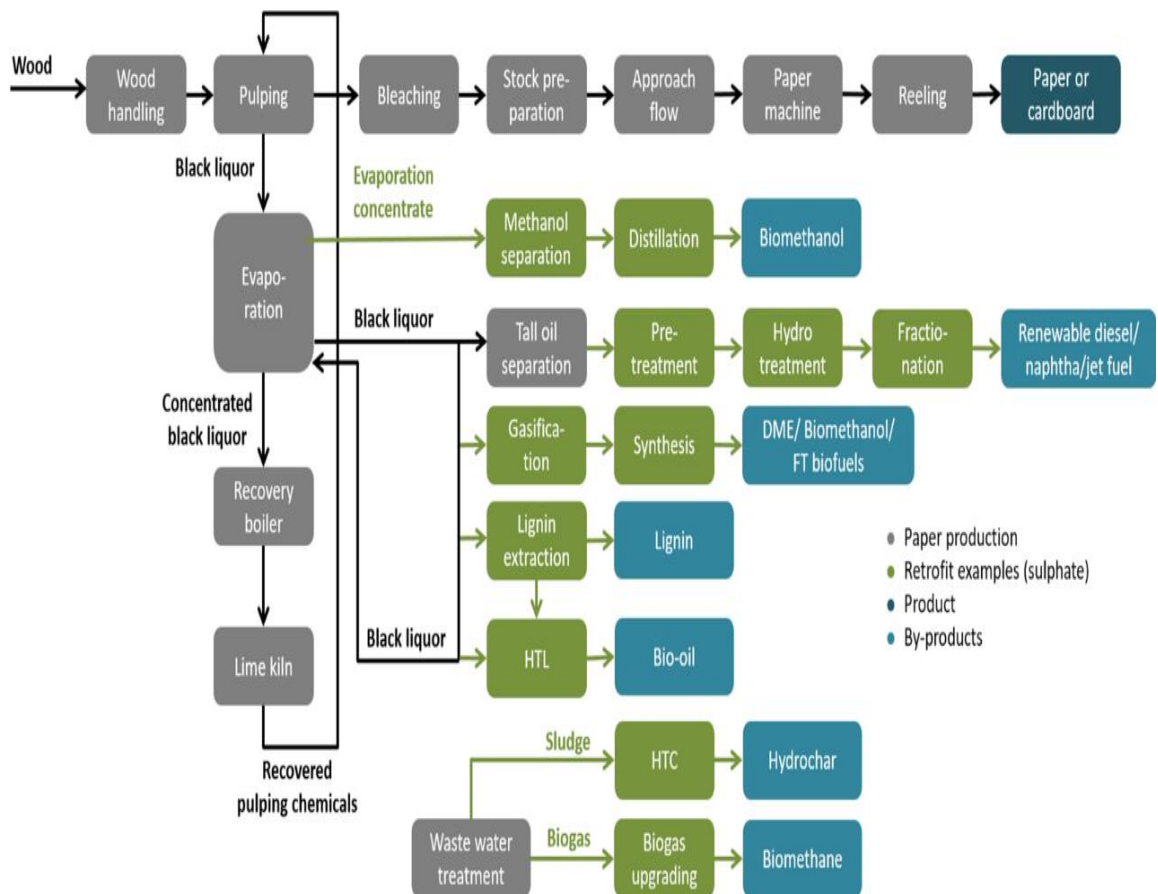
Kraft Biorefinery is a combination of the Conventional Kraft pulp mill with bio-based refining facility where biomass feedstock is separated into different components using variety of integrated bio-based technologies to sustainably produce biochemical, biofuel bioenergy and pulp (Demuner et al. 2019). The idea of a Kraft biorefinery was demonstrated by (Hamaguchi et al. 2013) in their study titled “Effects of hemicellulose extraction on the Kraft pulp mill operation and energy use.



**Figure 2.9:** Example of lignin removal and hemicellulose extraction integrated into a Kraft pulp mill. (Hamaguchi et al. 2013).

The study indicated that integrating biorefinery with Kraft pulp mill increased revenue generation however there will be need to carry out a feasibility study on hemicellulose extraction as to understand the impact of the integrated process.

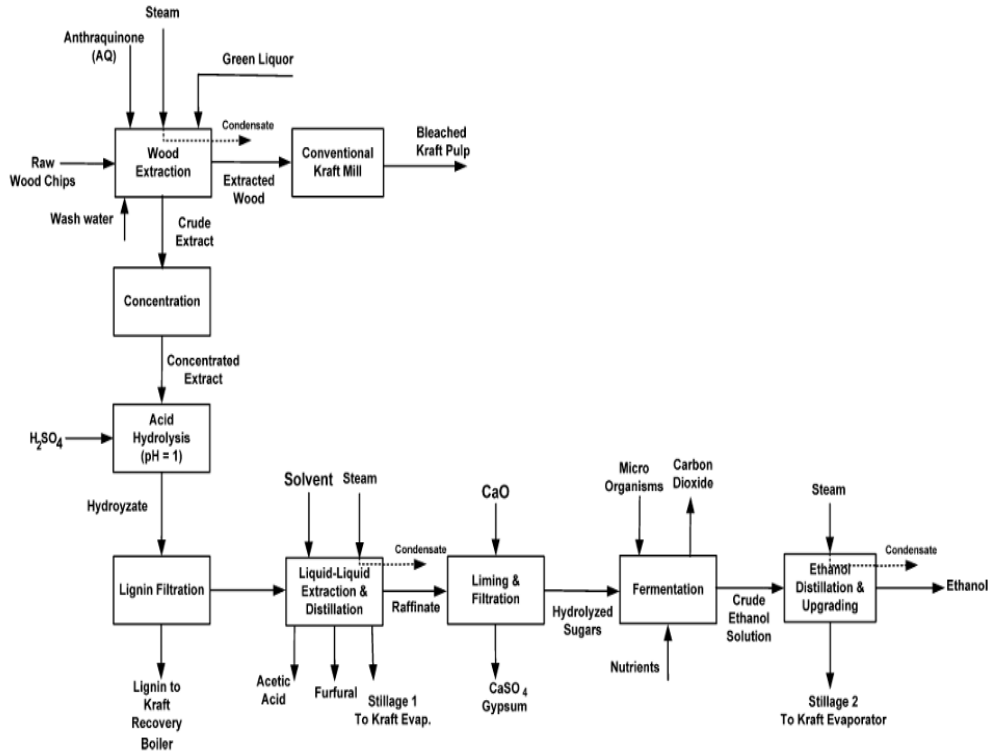
A study done by (Mäki, E et al, 2021) confirms that retrofitting the Kraft pulp mill with Biorefinery as demonstrated in figure 2.10 below will further decreasing the CO<sub>2</sub> emissions originating from the sector, generate alternative fuels and energy for renewable transport and the pulp mill operations. Mäki, E et al, further pointed out that integrating biorefinery with Kraft pulp mill will diversified renewable product portfolios of the existing mills.



**Figure 2.10** Kraft pulp mill retrofitted with biorefinery features

A study carried out by Walton, et al 2010 demonstrated the extraction of hemicellulose from a Kraft pulp mill using near-neutral hemicellulose extraction process as biorefinery technique. According to Walton, et al 2010 the innovated technique has the potential to remove hemicellulose selectively without degrading the cellulose fibre. The extra generated product will add value and revenue to the Kraft pulp mill.





**Figure 2-11** Schematic of proposed near-neutral hemicellulose extraction process (Walton, et al 2010)

However, selecting a suitable biorefinery to combine with the conventional Kraft pulp mill can be very challenging. According to a study conducted by (Johnson and Hart 2016), titled "Integrating a Biorefinery into an Operating Kraft Mill", few issues with selecting an appropriate biorefinery strategy was addressed during their SWOT analysis. The issues are 1) the environmental burdening of Kraft biorefinery may exceed what the site can handle at a pulp mill. 2) Wood sugar and lignin which are value added product are still at pilot scale and have no high market margin therefore investment will not be justify. 3) Potential alternative supply chain from other energy crop which can be used to generate the same product may emerge. Finally, Van Heiningen concluded by saying integrated forest biorefinery (IFBR) presents the Chemical pulp and paper industry a unique opportunity to produce not only pulp but also new structural products and diesel fuel which will make Kraft pulp mill economically sustainable and industrially viable. When different biorefinery platform like (thermochemical, biochemical, and material platforms) is incorporated with the conventional Kraft pulp mill, the mill does not only produce novel profitable by-product but improves the process output economically. The properties listed in table 2-9 are the Kraft pulp mill characteristics which allows the mill to be converted to biorefinery.

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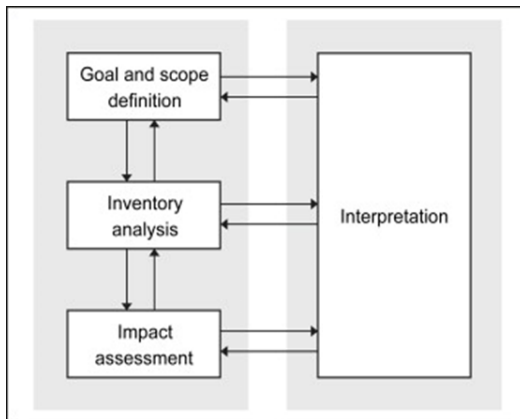
**Table 3-9 : the opportunities that make Kraft mill fit to be converted to a biorefinery**

1) The relative simplicity of the Kraft pulping process
2) Its speediness
3) The ability to tolerate varying wood condition
4) Kraft applicability to all kinds of wood species
5) Ability to blend with different biorefinery platform

However, the proposed Kraft biorefinery will be looking at how change in input parameter like woodchip thickness and black liquor extraction using hexane affects resource consumption, energy generation and consumption, the different types of products and by-products with the level of environmental burden reduced by proposed Kraft biorefinery. Finally, Life Cycle Assessment as an environmental tool will be used to compare the conventional Kraft pulp mill and Kraft biorefinery.

### **3.7 Life Cycle Assessment (LCA)**

LCA is not just a tool that provides solution but rather a technique that helps in understanding a problem and its possible solutions (Hellweg and i Canals 2014). Life cycle assessment is a tool to evaluate the impact of a product, activity or service on the environment starting from the beginning to the end of the product, activity, and service lifetime (Das and Houtman 2004). LCA is product oriented, integrative, scientific, and quantitative (UNEP 1996). Life-cycle assessment can also be defined as a tool that estimate the impact of commodity goods and their production process on the environment throughout the product lifetime (Roy et al. 2009). LCA involves four phases, which include (i) The goal and scope definition (ii) inventory analysis (iii) the impact assessment (iv) improvement and/or interpretation of results.



**Figure 3-7:** The four phases of the LCA and the interaction between each phase (standardization(ISO) 1997).

LCA standards are revised by ISO technical committees and presented to the member bodies for voting (ISO, 1997). The developed international standard will be published when 75% of the member bodies are in support of the report (ISO 2006). Developing an ISO manual for the preparation of life cycle assessment is a vital step to achieving a more accurate LCA ISO manual which will help to find out the impact of both manufactured and consumed product on the environment (Finkbeiner et al. 2006).

The four most popular approaches to LCA are:

**Cradle-to-grave approach:** This is the whole Life Cycle Assessment of a product starting from the extraction 'cradle', handling of raw materials, manufacturing, transporting, and distribution of manufactured products, usage phase, recycling phase until the disposal phase 'grave' (Singh et al. 2010).

**Cradle-to-cradle approach:** This is an LCA where the end of life / disposal phase of a product is a reutilizing/recycled process (Yam and Lee 2012). According to Yam and Lee Sustainable packaging is a cradle-to-cradle flow of packaging materials in which resources can be used repeatedly without exhausting resources.

**Cradle-to-gate approach:** This is a type of life cycle assessment that start from the extraction 'cradle' to any stage or phase of the product life cycle. The cradle-to-gate LCA approach evaluate the impact of product, activity or service from the extraction phase (cradle) to either handling of raw materials, manufacturing, transportation, distribution or usage phase on the area of concentration. The Cradle-to-gate methodology was used for the investigation of mycoprotein and key Quorn retail products (Lippolis et al. 2019).

**Gate-to-gate approach:** this is a type of LCA use to study the impact of a product or system starting from any phase of the product or system under study. This is the approach we will be using in this report to compare the production phase of a conventional Kraft

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pulp mill and Kraft biorefinery. Gate-to-gate modules of a product life cycle may likewise be linked to the product appropriate production chain to form a complete cradle-to-gate evaluation (Jiménez-González et al. 2000).

### ***3.7.1 Goal and scope definition***

According to (ISO 2006), goal and scope definition is a very crucial part of the LCA because the goal of the LCA elaborates the reason for the study, the anticipated audience and meant application. While the scope of the LCA covers the system under study, the system functional unit (SFU), the system boundary (SB), allocation procedure, Data quality requirement and assumption (Finnveden et al. 2009).

#### ***3.7.1.1 System description and study boundary***

According to (ISO 2006) System description is a detail description of the functions, components, and application of the system under study while the system boundary is a theoretical line that separate part of a system you want to study from the entire. According to (ISO 2000) the criteria used for selecting the system boundary should align with the goal of the study. It is important to show the relationship between the entire system under study and the selected process units within the system boundary using a flowchart (Finkbeiner et al. 2006). Example of the process units in the system boundary are wood handling process unit, Kraft cooking process unit, washing & screening washing process unit, oxygen delignification process unit, chemical recovery process units, pulp drying process unit, bleaching process unit, axillary boiler, bleaching chemical preparation process unit and wastewater treatment unit. The impact of the process units listed above were analysed using the gate-to-gate LCA. In Fig 2.8, the summary of the system boundary showing the energy use, material input and output, emission to the air, emissions to the land, emission to the water, by-product, solid waste and products of the conventional Kraft pulp mill is shown below

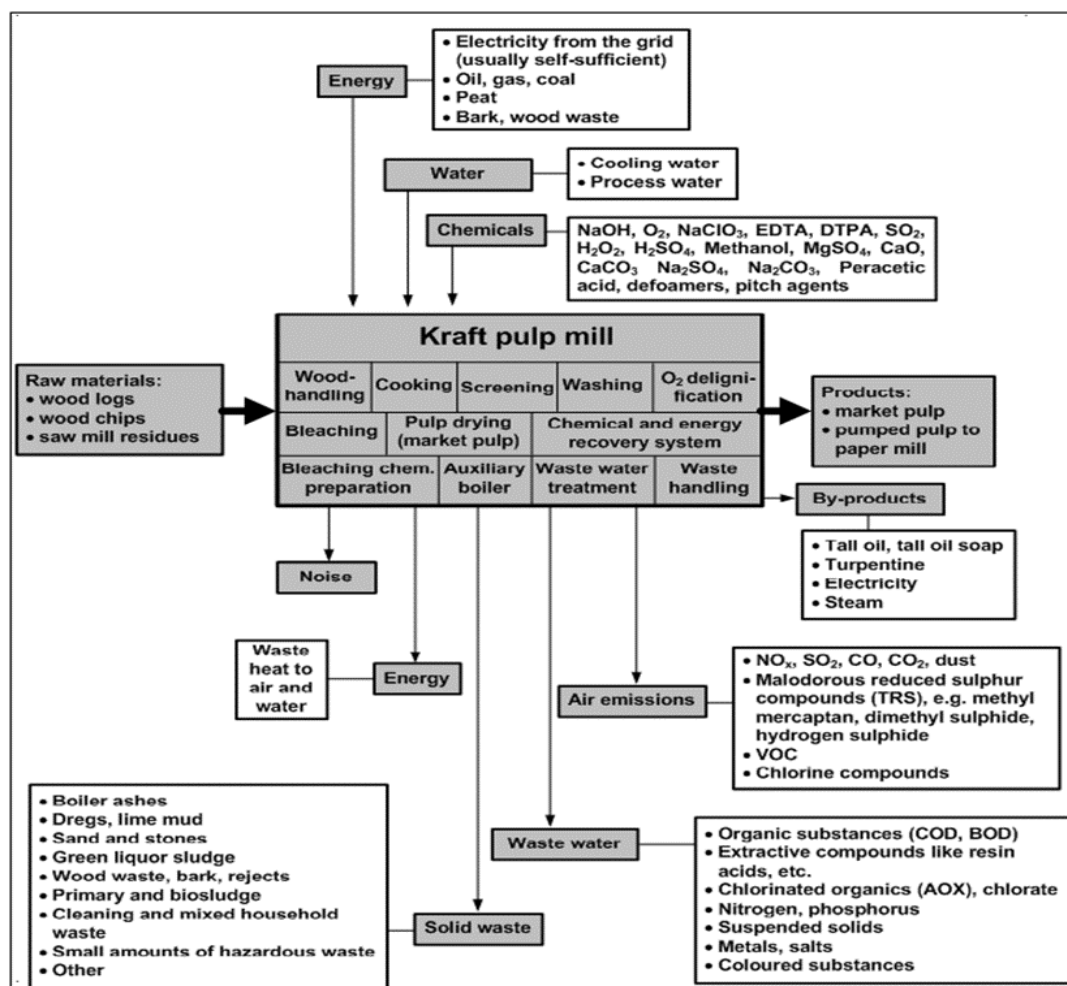


Figure 2.8 Overview of the system boundary (Suhr et al. 2015)

### 3.7.1.2 Functional unit

The purpose of a functional unit is to produce a reference unit, which can be used to normalize the inventory data (ISO 2006, Guinée and Lindeijer 2002). The functional unit should be very clear and measurable. In this study the functional unit is defined as a tonne of pulp produced by the conventional Kraft pulping mill.

### 3.7.1.3 Allocation

Allocation means to assign environmental impacts to all the outputs that have been studied (ISO 1997). The three main points about allocation as recommended by ISO manual are a) Allocation could be avoided by system boundaries expansion and unit process division. b) If it is necessary that allocation must be done, the system input and output must be arranged to physically have a relationship with each other. c) If the second does not work the input and output should be assigned to the product and function in a way that other connections, they have among them can be reflected.

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#### 3.7.1.4 *Data quality requirement*

The type of data an LCA require depends on the goal and scope of the Life Cycle Assessment (ISO,14044). Data connected with the system boundary could be collected directly from the production site or obtained using mixture of measurements, data calculating and estimating devices like software and digital or analogue calculating devices. In addition, when selecting the required data for the study, precautions are taken to make sure the data meet up data quality requirement (Bicalho et al. 2017).

**Data source:** The source of data used during the LCA process must be reported. Data used during an LCA can be obtained from a primary or secondary source. When the data used is from the production site or result from an experiment in the laboratory, it is called primary data source and when the data is from a publication or an external database like government websites and company websites, it is called secondary data source. When majority of the data used in carrying out the LCA are from secondary source, the LCA level of accuracy is affected because the conditions the data was generated is unknown. This is why we further conduct consistency check, completeness check and sensitivity check to increase the data competency levels (Björklund 2002).

**Data accuracy:** This is a measure of precision, completeness and consistency of data used for the LCA study. If the data used for an LCA study is not free from error the outcome of the LCA will not be free from error. Therefore, data accuracy is a very important data quality requirement (ISO 1997).

**Data age:** This is the amount of time data used to conduct an LCA study have existed. Whether primary or secondary data, the age of data used have a direct or indirect impact on the outcome of the LCA. When the age of data used in conducting the LCA is inconsistent, the result of the LCA becomes inconsistent as well.

**Time-related coverage:** This allows for a correlation between the age of all the data used for the LCA and the least duration of time each data was collected. Time relation coverage is an important data requirement because it allows the LCA practitioner to understand the duration of time which the LCA data should be collected (ISO 1997).

**Technology coverage:** This identifies the type of technology/technologies used to generate both the primary and secondary data used for the LCA study. It is very important to know the technologies used to generate the data used to carry out the LCA, most especially when the LCA is a comparative study (Finkbeiner et al. 2006).

**Geographical coverage:** This is the geographical area which the data used for the LCA study covers. It is an important data requirement because it helps the LCA Practitioner to

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know where data for the LCA study should be collected from to satisfy the goal of the study. Therefore, if all the data used for the LCA study were obtained from Europe, the geographical coverage of the data used for the study becomes Europe.

#### **3.7.1.5 Inventory steps and data source overview**

The data obtained are reviewed to get the most efficient information adequate to meet the aim and objectives of the study. The data for the Life cycle inventory are obtained by collecting data from the primary source or reviewing literature to discover available secondary data and their source. Secondly, process flowchart with detail of the inputs and outputs of the system under study are developed. Thirdly, a base case analysis to determine significant input and output results are developed. Finally, data accuracy and fact required to achieve the goal and scope of the LCA is achieved through sensitivity, completeness, and consistency check.

#### **3.7.2 Life cycle inventory analysis**

This is a collection and calculation of data to show input and output that are relevant to the system. The collected data could be measured, calculated, or estimated bearing in mind the goal and scope of the LCA. Example of data compiled can be categorised under the following heading: energy input, raw material inputs, products, co-product, waste, release to air, release to water and soil. The data compiled undergo validation before relating them to unit process and functional unit. Data collected must be precise, complete and consistent (Finkbeiner et al. 2006).

##### **3.7.2.1 Type of inventory**

According to (UNEP 1996) the inventory of a system is classified into economic and environmental inventory.

**Economic inventory** is the compilation of any input and output that effect the cash flow of the system under study. Example of economic inventory are raw materials, services, energy inputs, final or semi-final products, by-products and waste (Tersine and Barman 1991).

**Environmental inventory** is the compilation of any input and out coming from the environment or going into the environment. Example of environmental inventory are plant material, water, emissions to air and water such as CO<sub>2</sub>, BOD and solid waste dumped (Chester 2008).

After compiling the inventory, the inventory data used for the study are further classified into different categories. Example of some of categories include energy input, raw

material input, emission release to the air, water, solid waste, product and by-products (ISO 14044:2006). The data collected for the inventory should be constantly validated, with respect to the unit process and functional unit. Below are some of the inventory categories and their definitions.

**Energy input:** energy consumed in the conventional Kraft pulp mill is a combination of heat and electricity (JRC 2000). The heat energy used is the heat consumed when heating different fluids and evaporating water while the electrical energy used in the pulping mill are energy needed during pumping. Energy consumed by the different process unit depend on the configuration, process equipment and process control efficiency (JRC 2000). The data in the table below represents the energy consumption of a Swedish mill built in the 90`s.

**Table 3-10:** the quantity of electricity and heat consumed by the different process unit of a conventional Kraft pulp mill (JRC 2000)

Department	Process heat (MJ/ADt)	Electric power (KWh/ADt)
Wood handling	150	55
cooking	2050	65
Washing and screening	0	55
Oxygen delignification	400	45
Bleaching	500	83
Chemical recovery unit	6210	120
Wastewater treatment plant	0	20
Auxiliary boiler	0	30
Pulp drying	2850	105

**Raw material input:** this is feedstock or unprocessed materials used during the production of Kraft pulp such as wood, input chemical and water.

**Wood:** Wood is a vital natural resource that is used in the production of pulp used for paper making. Wood is commercially classified into hardwood and soft wood (Kretschmann et al. 2000). Examples of hardwood are aspen, birch, eucalyptus and cottonwood while softwood are long leaf pine and Douglas fir.

**Water:** water is another important raw used in pulp production. Some of the water consumed in the pulp and paper industry is during Kraft cooking, bleaching, washing and screening process unit. Nearly 85% of the water utilized in the pulp mill is used only for



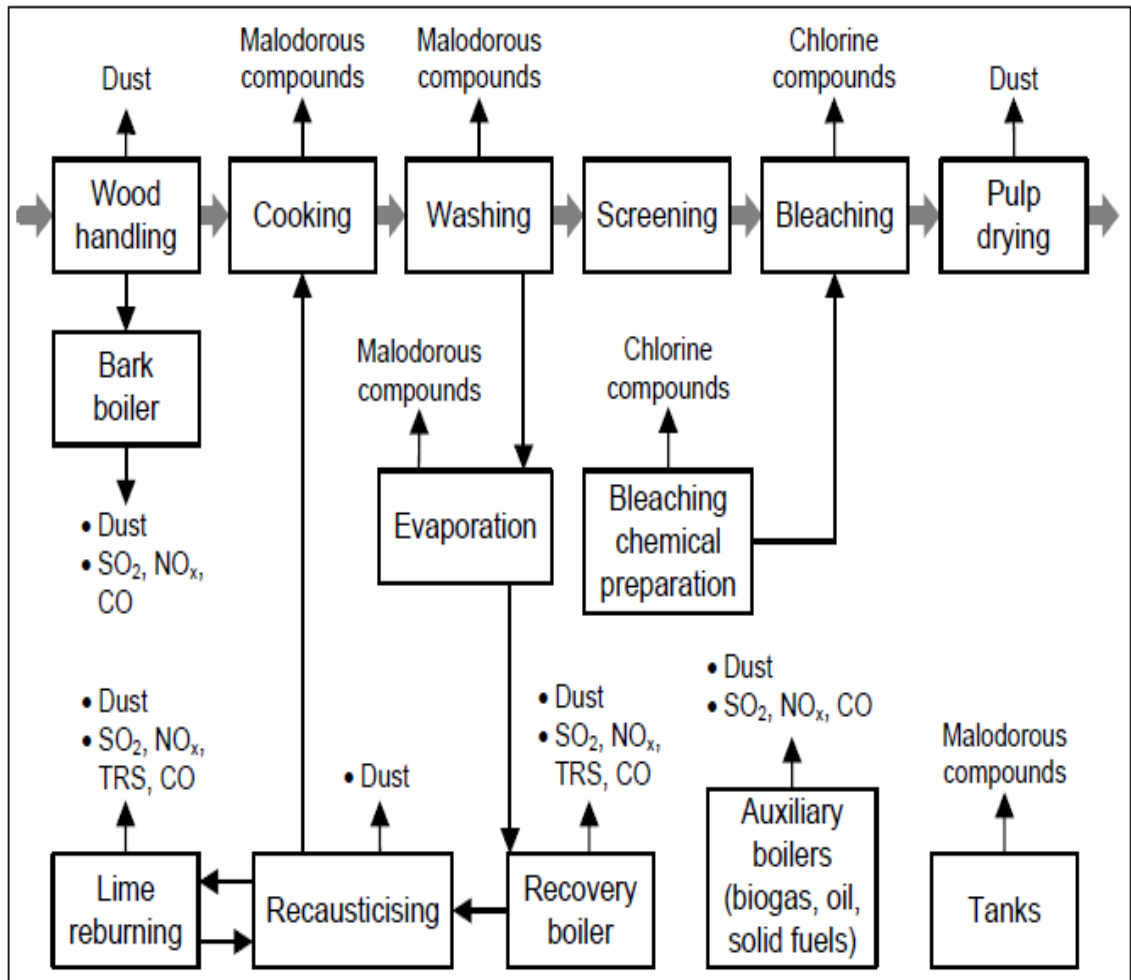
processing (JRC 2000). Processing a tonne of Kraft pulp needs between 15 to 100 metric tonnes of water (Suhr et al. 2015). Recycling wastewater is one of the ways wastewaters can be recovered. However, re-use of treated wastewater can be a big challenge for the Pulp and paper industry, because most times they recycled water contain substance that harm equipment and degrade product quality.

*Input Chemicals:* These are chemicals required to produce Kraft pulp. Examples of these chemical are NaOH, O<sub>2</sub>, NaClO<sub>3</sub>, EDTA, SO<sub>2</sub>, H<sub>2</sub>O<sub>2</sub>, O<sub>2</sub>, MgSO<sub>4</sub> and CaO (JRC 2000). NaOH is one of the cooking chemicals used to breakdown the natural binding material holding the components of the wood (JRC 2000), MgSO<sub>4</sub> is used to preserve the strength of the pulp during oxygen delignification (JRC 2000).

**Table 3-11:** Consumption of main chemicals in kg/t ADP for Kraft pulp production (JRC 2000, CEPI 1997): All chemical consumption is expressed as 100% effective chemical.

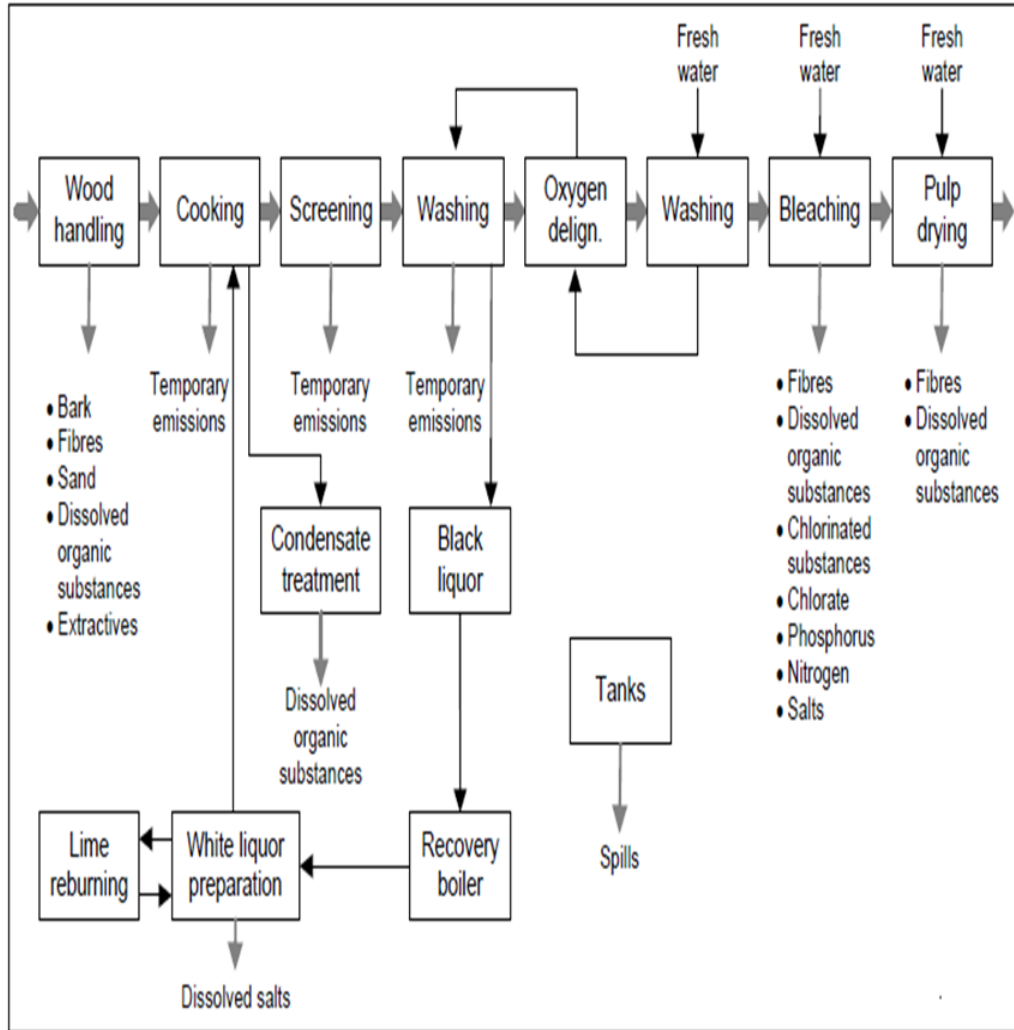
Substance	Consumption for unbleached Kraft pulp (Kg/ton)	Consumption for bleached Kraft Pulp (Kg/ton)
NaOH	10-20	25-50
O <sub>2</sub>	-	5-25
NaClO <sub>3</sub>	-	20-50
EDTA	-	0-4
SO <sub>2</sub>	-	2-10
H <sub>2</sub> O <sub>2</sub>	-	2-30
O <sub>3</sub>	-	0-5
MgSO <sub>4</sub>	-	0-3
CaO	5-10	5-10

**Release to the air:** Emission to the atmosphere from the conventional Kraft pulp mill is released during wood handling, Kraft cooking, pulp washing, bleaching process, bleaching chemical preparation, chemical recovery, evaporation, burning in the bark furnace, recovery boiler, white liquor preparation, lime kiln and pulp drying stage. Examples of emission released into the air are SO<sub>x</sub>, CO<sub>2</sub>, TRS, VOC, NO<sub>x</sub> and Particulate (Suhr et al. 2015). Figure 2.11 contains the major air emissions released by the conventional Kraft pulp mill.



**Figure 3-9:** Emissions to the air from the conventional Kraft pulping mill (Suhr et al. 2015).

**Emission to the water:** Majority of the emission to the water are mostly organic compound consuming oxygen (JRC 2000). These organic compounds are called COD (chemical oxygen demand) and BOD (Biological oxygen demand). Other examples of emission to the water are AOX (organic bound chlorine compound), nitrogen and phosphorous nutrients (Lopes et al. 2003). Figure 2.11 contains the major emissions release to the water from the conventional Kraft pulp mill.



**Figure 3-10:** Emission to the water from a Conventional Kraft pulp mill (Suhr et al. 2015).

**Solid waste:** Solid waste are waste generated from the chemical recovery process unit, wood handling unit, effluent treatment unit, boilers and furnace (Bajpai 2015). Examples of solid wastes generated from the conventional Kraft mill after using best available techniques/technology are represented in the table below.

**Table 3-12: Solid waste from the conventional Kraft pulp mill (JRC and policy report, 2015)**

Type of Waste	Kg dry solid/ADt of pulp
Wastewater treatment sludge	10
Wood ash	9
Other ashes	14
fibre	5
Wood waste	6
Dregs, grits and green liquor sludge	10-20
Lime enriched with non-process element	10-20
Hazardous waste	0-2
Total	60-80

**Product:** According to (ISO 14040, 2006) product is defined as any service or goods that can be offered to the market and sold to satisfy consumers need. In the pulp production mill, the main product is the manufactured pulp which is conveyed to the pulp dryer where the pulp is dried before transporting them to either the pulp storage units, paper mill or pulp markets.

**By-product:** These are secondary products generated from the Kraft pulp production process. Example of the by-product generated during Kraft pulp production are Tall-oil, crude sulfate turpentine and extractives.

### 3.7.3 Life cycle impact Assessment

The impact assessment is the third phase of the LCA (ISO 14040). It helps in identifying the potential environmental impact using the outcome of the inventory analysis by associating it with specific environmental impacts (Brentrup et al. 2004). The environmental impact assessment involves classification (this is assigning inventory data to impact categories), characterisation (this models the inventory data to fit in the impact category in a way that the goals and scope of the study is achieved) weighting (in this element of the LCIA, indicator result of different impact are converted using numerical factors) and Normalization (the results with selected weighting factor or results across impact category are normalized) (ISO 1997).

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Furthermore, the ISO 14040 explained the 5 steps towards achieving a life cycle impact assessment. The first three steps are called the mandatory steps while the last two steps are called optional steps. The Mandatory steps are:

**Step 1** - selection of impact categories, category indicator and characterisation model (Selection).

**Step 2** - assigning LCI result to the selected impact categories (Classification).

**Step 3** - Calculation of category indicator results (Characterisation).

The optional steps are:

**Step 4** - Calculating the magnitude of category indicator results relative to reference information (normalisation).

**Step 5** - Converting indicator results of different impact categories by using numerical factors based on value-choices (weighting).

For the sake of this study, only mandatory steps (step 1-3) will be discussed.

**Step 1- selection of impact categories, category indicator and characterisation model (Selection)**

#### ***3.7.3.1 Impact categories***

These are environmental problems of concern to which Life cycle inventory study results may be allocated. The following are the things that needed to be considered during the selection of an impact category (ISO 14044, 2006):

- The impact categories must be globally recognized.
- The impact categories should represent the total impacts of inputs and outputs of the product system on the category endpoints through the category indicator.
- The impact category should avoid double counting unless required by the goal and scope definition.

One might ask ``How do someone know the exact impact categories to select? `` According to (Hauschild and Huijbregts 2015), ISO guide did not provide clear guidance on how to select impact categories. Therefore, the following impact categories defined below were selected based on the relationship between the elementary flows and the environment.

***Climatic change***: this is a greenhouse effect triggered by human emission which increase radiative forces triggering the increase in the earth's surface temperature. This impact category affects the ecosystem health, human health, and material welfare. The characterisation factor of climatic change can be measured as global

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warming potential for a 100-year time horizon (GWP100) for each greenhouse gas emission to the air (in kg carbon dioxide equivalent/kg emission) (Ramanathan and Carmichael 2008).

***Renewable and Non-renewable energy generation:*** Non-renewable energy is the type of energy that cannot be replenished after use (Adams et al. 2018) whereas, renewable energy is energy from a source that is not depleted when used. Examples of non-renewable energy include coal, kerosene, fossil fuel and natural gas and renewable energy are wind, hydro, tidal and solar power. The goal of the 2000-watt society is to increase the proportion of renewable energies to 2000 watts per person. With 1500 of that, energy generated from renewable sources (Müller and Rutherford, Bundesrat 2002). According to Eco-Factors 2006, the characterisation factor of the Renewable and Non-renewable energy is expressed in MJ-eq/MJ. However, the characterisation factor is 1 MJ-eq. /MJ for non-renewable energy and  $\frac{1}{3}$  MJ-eq. /MJ for renewable energy (Bundesrat 2002).

***Freshwater Depletion:*** this is defined as the amount of water loss from the ground water reservoirs (Ramakrishna and Babu 1999). Water can be short in some places while plentiful in other places. Unlike other resources, there is no universal market that guarantees a universal supply. Extraction of water in arid areas can bring about major harm to ecosystems and human health, but models for expressing damage at the endpoint level are not yet available. However, it is advisable to use an intermediate indicator that simply represents the total amount of water consumed. The midpoint indicator for this impact category is water depletion (WD). The characterisation factor represented as water depletion potential (WDP) is measured in  $\text{m}^3/\text{m}^3$  (Brauman et al. 2016).

***Acidification:*** Acidification is caused by a deposition of inorganic substance (oxides of nitrogen and sulphur) in the surroundings (Rodhe and Herrera 1988). These deposited materials react with water molecules in the atmosphere to produce acidic rain, which is dangerous to both dwelling and inanimate things. Acidification is divided into 2 categories. Terrestrial acidification - this can be the sort of acidification, that effects the terrestrial system (Roy et al. 2012). Aquatic acidification - this can be the sort of acidification affecting the aquatic system. During

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this study, we are going to discuss terrestrial acidification. For example, SO<sub>x</sub> from the conventional Kraft pulp mill released into the atmosphere react with water vapour in the atmosphere to form sulphurous acid. Sulphurous acid is hazardous to equally living and non-living components of the environment. Terrestrial Acidification has its midpoint indicator represented as (TA) and measured in kg (SO<sub>2</sub> to air). The characterisation factor of Terrestrial Acidification is represented as terrestrial acidification potential (TAP) measured in kg SO<sub>2</sub> equivalents /kg emission (Roy et al. 2012).

**Toxicity:** These are the effect of chemicals deposited in air, water and the land around the conventional Kraft mill. These chemicals once inhaled, eaten or exposed to humans, damage organs, tissues and cells (Paget and Barnes 1964, Sleeswijk and Heijungs 2010). The midpoint indicator used for this impact category is human toxicity (HT). Human toxicity is measured in kg (14DCB to urban air). The characterisation factor of human toxicity is represented as HTP (Human toxicity potential) measured in kg/kg (McKone and Hertwich 2001).

**Malodourous Air:** This is the amount of bad odour present in an environment (Hasselaar et al. 2003). Odour becomes a problem once it exceeds a setting threshold making the atmosphere unpleasant (Pennington et al. 2004). Malodourous air (MA) has a category indicator represented as the amount of air measured in m<sup>3</sup> per odour threshold measured in kg. The characterisation factor of Malodourous air is represented as reciprocal of odour threshold value (1/OTV, in m<sup>3</sup>/kg) (Pennington et al. 2004).

**Respiratory Inorganics:** According to (Hunkeler 2014) these are primary and secondary particles that cause damage on the respiratory system. The result of breeding in the particulate will cause illness and death. The characterisation factor with respect to consequence on human health is measured in kg PM<sub>2.5</sub>- equivalent (Hong and Li 2012).

**Eutrophication:** this is described as nutrient and organic matter emission in water resulting in decrease of oxygen levels in water (Finnveden and Potting 1999). The nutrient within the water renders the surface water undesirable as a supply of

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drinkable water. Hence, the quantity of oxygen needed by the microbe to disintegrate the biomass released in the water throughout the milling process is called biological oxygen demand (BOD) (Hauschild and Huijbregts 2015). The level of BOD in water is used as a gauge to know the efficacy of the wastewater treatment plant in the pulp mill. The characterisation factor is represented as eutrophication potential (EP) for each emission to air, water, soil, and are measured in kgPO<sub>4</sub> equivalents/kg emission (Hauschild and Huijbregts 2015).

### **3.7.3.2 Category indicator**

The category indicator of an impact category can be defined as the measurable description of an impact category (ISO 14042, 2000). Furthermore, the concept of category indicator must be based on an environmental mechanism (Owens 1996). The following requirements applied during the selection of category indicator:

- The category indicator must be reliable with the goal and scope of the LCA study.
- The category indicator has to be internationally accepted.
- The category indicator must be environmentally relevant.
- Double counting should be avoided when finding the category indicator, unless required by the goal and scope definitions.



**Table 3-13: Impact category and category indicator**

Impact category	Abrev	Category indicator	reference
Climatic change	CC	infra-red radiative forcing	(Goedkoop et al. 2009)
Terrestrial acidification	TA	base saturation	(Roy et al. 2012)
Toxicity	HTP	hazard-weighted dose	(Sleeswijk and Heijungs 2010)
Freshwater water depletion	WD	amount of water	(Brauman et al. 2016).
Eutrophication	EE	phosphorus and Nitrogen concentration	(Hauschild and Huijbregts 2015)
Respiratory Inorganics	IR	PM2.5 intake	(Hong and Li 2012)
Malodourous Air	MA	Volume of air per odour threshold value	(Guinée and Lindeijer 2002)
Renewable and Non-renewable energy	NREG & REG	2000 watts per person	(Bundesrat 2002)

### 3.7.3.3 Characterisation model

The characterization model is a harmonious approach to modeling principles and choices, but provides outcomes at both intermediate and endpoint levels. (Huijbregts et al. 2017, Goedkoop et al. 2009). Furthermore, Characterisation model is a method that reflects all the ecological processes related to impact characterization by explaining the relationship between life cycle inventory results and category indicators (ISO 14044, 2006). In addition, the characterization model is used to derive the characterization factors. The following recommendations apply to the selection of characterization models. Firstly, characterization models should be internationally accepted. Secondly, assumptions made during the selection of characterization models must be reduced. Thirdly, the characterization model for every category indicator should be scientifically and technically acceptable and based on clearly

identifiable environmental mechanisms and reproducible empirical observations. (Hauschild and Huijbregts 2015). Finally, examples of characterisation model are CML2002, Eco-indicator 99, EDIP97 – EDIP2003, EPS 2000, Impact 2002+, LIME, LUCAS, Recipe, Swiss Eco scarcity 07, TRACI and MEEuP.

*Table 3-14: The characterisation model used for the impact category*

<b>Impact Category</b>	<b>unit</b>	<b>Characterisation factor</b>	<b>Characterisation Model</b>
Climatic change	kg (CO2 to air)	global warming potential	(IPCC) model
Renewable energy	MJ-eq/MJ	Amount of energy consumed	The Ecological Scarcity Method
(Non-renewable Fossil) Energy	MJ-eq/MJ	Amount of energy consumed	The Ecological Scarcity Method
Water Depletion	m <sup>3</sup> (water)	water depletion potential	ReCiPe 2008 or ILCD method
Acidification	kg (SO2 to air)	terrestrial acidification potential	RAINS10 model,
Toxicity	kg (14DCB to urban air)	human toxicity potential	USES-LCA model.
Malodourous Air	m <sup>3</sup> /kg	reciprocal of odour threshold value	CML 2002 model
Respiratory Inorganics	kg (PM10 to air)	particulate matter formation potential	Eco-indicator 99 model
Eutrophication	kg (P to freshwater)	freshwater eutrophication potential	LIME Method

***Step 2 - assigning LCI result to the selected impact categories (Classification)***

According to (ISO 14042, 2000) assignment of Life Cycle Inventory results to impact categories must take into consideration the following, except otherwise needed by the goal and scope:

- Assignment of Life Cycle Inventory results that are limited to one impact category (Hauschild and Huijbregts 2015)
- Identifying LCI results related to multiple impact categories. This includes the distinction between parallel mechanisms (eg, SO<sub>2</sub> is divided into human health and acidification impact categories) and continuous mechanisms (eg, classifying NO<sub>x</sub> and contributing to both surface levels). increase. Ozone formation and acidification) (Ling-Chin et al. 2016).

### **Step 3 - Calculation of category indicator results (Characterisation)**

Characterization as the third step of the LCIA, involves multiplying the elementary flow assigned to impact categories with the characterization factor. However, characterization factor qualitatively indicates an elementary flow for a particular impact category. Therefore, the indicator score obtained from the characterization is expressed in a unit common to all other elementary flows contributing to that impact category (Dreyer et al. 2010). For instance, a Kg of NO<sub>x</sub>, SO<sub>x</sub> or NH<sub>4</sub> emission release during the production of 1Kg of pulp are all measured in Kg.SO<sub>2</sub> eq, which is a unit common to NO<sub>x</sub>, SO<sub>x</sub> and NH<sub>4</sub>. Finally, the indicator scores for all elementary flow contributing to a particular impact category is added up to arrive at a particle impact score for that impact category (Van Zelm et al. 2009).

### **Midpoint verse Endpoint Indicators**

Characterisation is a pathway directing the elemental flow from the inventory in an order; both for impacts that are casually related to the areas of protection (AoPs) (Hauschild 2005). The area of protection are those sensitive areas effected directly or indirectly by the elementary flow. The LCA through its third phase will show the degree of harm the environmental problem caused by the system under study can cause the area of protection (AoPs).

#### **3.7.3.4 Characterization principle**

Characterization principle is expressed as a product of fate factor (FF), an exposure factor (XF) and an effect factor (EF) (Udo et al (2002).

Therefore,  $CF = (FF) * (XF) * (EF) \dots \dots \dots \text{eq (1.1)}$

Characterisation factors are expressed per unit of elementary flow.

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### ***Impact/indicator Scores***

Impact score is calculated by the following formula

$$IS = Q \cdot CF \dots \text{eq (1.2)} \text{ ((Hunkeler 2014)}$$

IS is an impact score produced by an input or output that is obtained at a site or released into the site's environmental compartments (air, water and soil).

Q is the amount of input or output going in or out of the system under study.

CF is the characterisation factor.

Equation (1.2) demonstrates that characterization centres on important characteristic of elementary flow (input or output) generated from a given location. Secondly, the impact score is clearly related to the quantity of elementary flow consumed or released in the system.

Finally, the indicator scores for all elementary flow contributing to a particular impact category is added up to arrive at a particle impact score for that impact category.

$$IS = \Sigma IS \dots \text{eq (1.3)} \text{ (Hauschild and Huijbregts 2015)}$$

Where IS is the impact score of the impact categories achieved from adding up all elementary flows contributing to the impact category

Where  $\Sigma IS$  are the sum of the indicator score that contribute to the specific impact category (environmental problem).

### **Step 4 – Normalization**

The intention of normalization is to apprehend the relative importance of every indicator result (Andreas et al. 2020). Normalization is an elective element that help in testing for irregularities, delivering and conveying knowledge on the relative significance of the indicator outcomes, planning for grouping and life cycle interpretation (Cucurachi et al. 2017). Normalization converts an indicator result by dividing it by the total inputs or outputs obtained either global, regional, national or local (Hauschild and Huijbregts 2015).

### **Step 5 - weighting**

Weighting is an optional element. It can be obtain by dividing the indicator results by normalized results with selected weighting factors, Weighting are centred on the value obtained during the weighting calculation and not on any scientifically evidence (Bengtsson and Steen 2000).

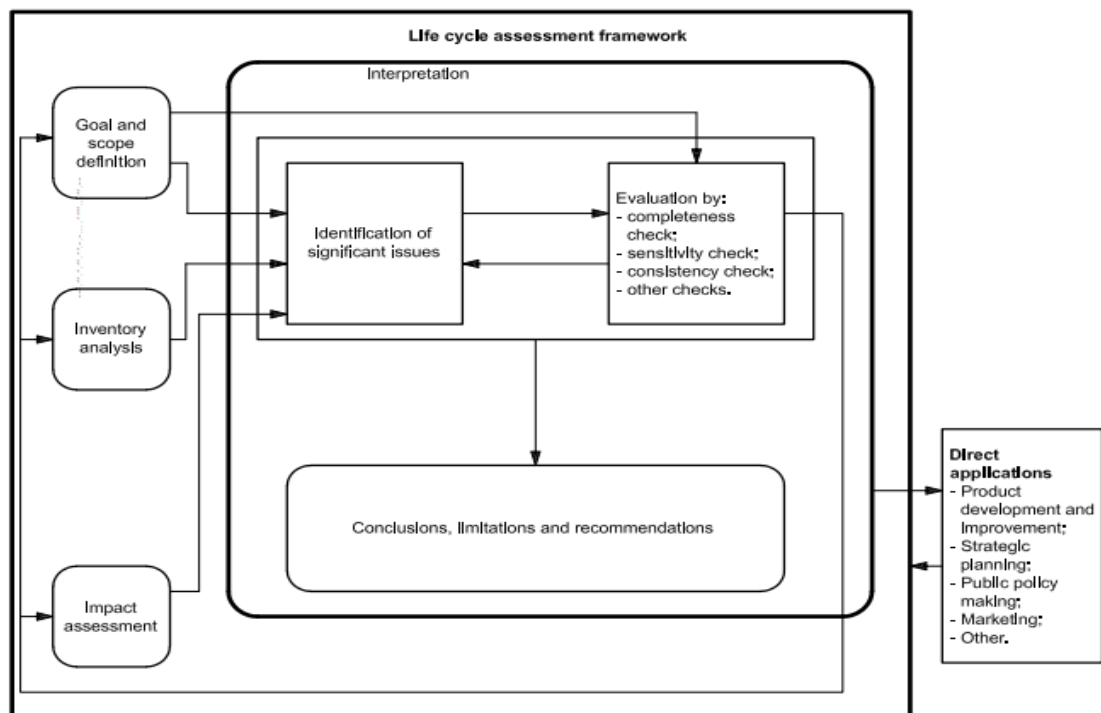
### 3.7.4 Life cycle interpretation

Result interpretation is the assembly of the goal and scope, life cycle inventory and life cycle impact assessment to achieve the goal of the study (Laurent et al. 2020). The observation made during result interpretation is subjected to completeness check, sensitivity check and consistency check (Hauschild et al. 2018). Interpretation helps in discovering the implications of methodology used and assumption made.

The life cycle interpretation phase of an LCA according to (ISO, 14040) comprise of several elements as follows:

- Identification of the problems of the system under study based on the outcomes of the LCI and LCIA phases of LCA.
- Evaluating the outcome of the first element through completeness, sensitivity and consistency checks.
- Conclusions, limitations, and recommendations.

The relationship between the interpretation phase and other phases of LCA is shown in the Figure below.



**Figure 3-11:** Relationships between elements within the interpretation phase with the other phases of LCA (ISO 14044,2006)

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During the interpretation phase factors like system function, functional unit, system boundary limitations, data quality assessment and sensitivity analysis should be considered with respect to the goal and scope definition. The first element of the interpretation phase is the identification of the significant issues based on the results of the LCI and LCIA of the LCA (ISO 14044). Example of significant issues that can arise when carrying out the LCA are not limited to the following: amount of energy used, the amount of emission released, the quantity of waste and the amount of discharge released into the environment. Environmental problems like acidification, climatic change, eutrophication and Human toxicity. Therefore, to carry out an LCA interpretation phase efficiently, the following is needed as recommended by (ISO 14044,2006):

- the outcome of the LCI and LCIA phases of the Life Cycle Assessment.
- All the methodological choices used for both the LCI and LCIA phases of the Life Cycle Assessment.
- The goal and scope definition with the interest of the parties involved should be known.

When the result of the proceeding phases has be found to meet the requirement of the goal and scope definition then the important issued are determined.

The second element of the interpretation phase is evaluation. Evaluation includes completeness, sensitivity, and consistency checks (ISO 14044,2006). The purpose of the evaluation element is to launch and improve confidence and trustworthiness in the result of the LCA (ISO 14044,2006). In other words, the evaluation element helps to give the interest party a strong and comprehensible opinion of the result of the study. In addition, the evaluation should be done with respect to the goal and scope of the study.

The three-technique used when carrying out the second element of the interpretation phase are completeness check, sensitivity check and consistency check (Skone 2000).

- Completeness check ensures that all related evidence and data required for the interpretation are obtainable and complete.
- Sensitivity check ensures how reliable the results and decision are affected by uncertainties in the data and calculation of category indicator results.
- Consistency check ensures that the assumptions, approaches, and information are consistent.

The third element of the interpretation phase is the conclusions, limitations, and recommendations (ISO 14044,2006). The focus of this element is to put together conclusions, recognise limitation and make commendations.

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### 3.7.5 *Uses of LCA*

LCA as an evaluation tool have been used across different sectors. LCA methodology was used to discover the impact production, distribution, processing, and pattern of consumption of food products have on the environment, food security and food sustainability. The outcome of the LCA study suggested alternative food product cycle to enhance food security, food sustainability and international trade (Roy et al. 2009). LCA was used by ENVIRON International Corporation to assess the comparative impacts of deinked pulp produced from wastepaper against the impacts of virgin pulp produced from virgin wood sources that would be replaced using the deinked pulp. The outcome of the LCA as illustrated in the multiple sensitivity analyses demonstrated that deinked pulp was better for the environment when it displaces 50% Kraft and 50% mechanical pulp. LCA was used to determine the sustainability of the printing and writing paper production in Portugal, the results of inventory analysis and impact assessment show consumption of paper in Portugal led to a decrease in the environmental burdens of the paper distribution stage, but to an increase in the environmental burdens of the final disposal stage, when compared with the consumption of paper in Germany (Lopes et al. 2003). As earlier discussed LCA help discover the environmental aspect and potential impact of a product starting from purchase of material to the waste disposal however it assist decision makers in the industry, governmental and non-governmental organisation to detect chances to make a product environmentally friendly through process intensification, strategic planning and priority setting. Furthermore, LCA assist in identifying relevant indicators of environmental performance including techniques to measure them. LCA have made it possible for the establishment of an elaborate scheme that make environmental claims on products, possible and implementable. Furthermore, LCA was used to find out the difference in the environmental impact of using heavy fuel oil and natural gas in a Kraft pulping mill located in Portuguese, while the outcome of that finding showed that using natural gas is more sustainable (Lopes et al. 2003). Also, Environ used the LCA methodology to compare the impact of virgin pulp and deinked pulp for the production of magazine (Environ 2012).finally the use of LCA in the analysis of the conventional Kraft mill and Kraft biorefinery will help determine the difference in the energy use, water use, emission released and amount of value added products generated. However, valorisation of lignocellulose feedstock (wood) and process by-product through the

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modification of Kraft pulping mill will lead to the production of high quality cellulose for textile fibre, spin textile fibre, fine paper and speciality cellulose but would produce hemi-cellulose/sugars for yeast, bio-ethanol, acetic acid and lignin which are suitable for catalytic conversion into high value monomers (Wu et al. 2019).

### **3.7.6 LCA limitations**

LCA has several limitations according to (Curran, 2014). One of the limitations is the lack of inventory data. Gathering inventory data is time and resource consuming. In addition, most of the data used for carrying out LCA whether from primary or secondary source are either held private by LCA practitioners in software which are not reliable because the assumptions and decisions which the software designed are based are not revealed (Speck et al. 2016). Furthermore, public data are also difficult to use because they are collected from different source, facilities, and geographical locations. Another thing is the unit of data collected. The data collected, have different units of measurements difficult to convert and compare (Hunkeler 2014). However, introduction of a system that will encourage active sharing of data between the LCA practitioner, producers, suppliers and consumers will make inventory data collection simple and easy to collect (Curran 2014). Scarcity of impact data and models to carry out life cycle impact assessment is another limitation of LCA. Additional information to support the relationship between important inventory results and the environment are missing therefore LCA modelers and practitioners have no option but to ignore some of the important inventories listed in the life cycle inventory phase of the LCA. This on the other hand affects the transparency of the LCA outcome. However, this limitation can also be address by encouraging research. Research will help in the development of easy impact pathway for impact categories connecting elementary flows from the inventory to the areas of protection (Hauschild and Huijbregts 2015).The level of inevitable uncertainty with the life cycle inventory and the life cycle impact assessment is another huge LCA limitation (Ekvall 2002). Uncertainty in LCA makes it difficult sometimes to use the result in decision making because the process use in obtaining some of the result are not based on the principals of natural science (Curran 2014). This does not imply that decision makers cannot use LCA to make decision, it simply means that LCA results should be supplemented by tools like risk assessment, site-specific environmental assessment, cost assessment and technoeconomic impact assessment during comprehensive decision making. Uncertainty in LCA can be



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categorised into parameter uncertainty, model uncertainty and uncertainty from value choices (Huijbregts 1998). This type of uncertainty arises when there is an error in the parameters used in either the life cycle impact assessment models or life cycle inventory as a result of error in measurement, simulations from probability, limited sample size and Statistical uncertainty is called parameter uncertainty. Model uncertainty arises because of assumption made when designing LCA model. Finally, uncertainty from value choices are determined by individual opinions and ideals that replicate what they care about (McKone and Hertwich 2001). Hofstetter 1998 and Hofstetter et al. 2000 used cultural theory to show how the view of the stakeholders and decision makers can be influenced during the LCA (Hofstetter et al. 2000). The three different perspective use during the Life cycle impact assessment are the individualist, the hierarchist, and the egalitarian perspective. Each of this perspective will affect the views or decision of a decision maker on the society or nature (Goedkoop et al. 2009). They are need to establish guidelines for practitioner on how to manage, communicate and interpret uncertainties in both LCI and LCIA (Margni and Curran 2012). Despite the limitation of LCA, it is still a strong environmental tool to consider when discussing how to achieve sustainability.

Finally, the three major ways to overcome the LCA limitations as suggested by (Curran 2014) are a) continuously studying and developing the LCA tool. b) Constantly educating and training LCA users on how to appropriately apply LCA tools. c) Developing guidance and globally agreed approach by LCA practitioners and modelers. With these three suggestions implemented, decision makers can increase confidence in LCA result.

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## Chapter 4- **Material and method**

### **4.1 Introduction**

Life Cycle Assessment is the main methodology used in this work to provide background information needed to improve the environmental sustainability and industrial viability of the conventional Kraft pulp paper mill while the experimental methodology will demonstrate how the change in input parameters like wood particle thickness and the use of a re-usable liquid as part of the washing process reduce water consumption, energy use, emission released in the air and enable the recovery of extractable value-added compounds.

### **4.2 Life cycle assessment methodology**

The framework use for this study is the LCA framework developed by international standard organisation (ISO), recommended by (ISO, 1997). Life Cycle Assessment is divided into four phases (goal and scope definition, inventory analysis, impact assessment and interpretation of results)(ISO 2006). The four phases of the LCA methodology would be used to provide background information needed to improve the environmental sustainability and industrial viability of the conventional Kraft pulp paper mill. This chapter will explain how the four phases of the LCA methodology was carried out, starting from the goal & scope definition phase.

#### ***4.2.1 Goal of the LCA study***

The goal of the study was determined by finding out the motives for organising the LCA. In addition, it was important to find out the intended application of the LCA result and the targeted audience. The intended application was realised by revisiting the aim of the study. The targeted audience will be discussed in chapter 4.

#### ***4.2.2 Scope of the LCA study***

The scope of this study covers the system boundary of the conventional Kraft pulp and paper mill, the functional unit, quality of data required and the cut-off criteria.

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### **4.2.3 System boundary**

According to (ISO 14040, 1997) LCA practitioners select system boundary based on different criteria. For this LCA the criteria use to select the boundary applied is based on the goal of the gate-to-gate LCA. The boundary choose for this Life Cycle Assessment were categorized into ten process units as mentioned below: Wood handling (WH), cooking(C), Oxygen delignification (OD), Chemical recovery process (CRP), Bleaching (B), Pulp drying (PD), Auxiliary boiler (AB), Wastewater treatment (WWT), Washing and screening (WAS) and bleaching chemical preparation (BCP).

The cut-off criteria of the conventional Kraft pulp mill were based on the goal of the LCA while the cut-off criteria for input and output entering or leaving the system boundary was based on the contribution of each elementary flow moving in and out of the system boundary.

### **4.2.4 Functional unit**

The functional unit was established as 1 Adt of pulp from the Kraft pulp mill for papermaking. 1 Adt of pulp was used as a reference unit which the inputs and outputs were related. This reference is essential to confirm comparability of the LCA result.

### **4.2.5 Inventory data compilation**

During the data collection, serious cautions were taken to avoid gaps and double counting by giving a detail description of each unit process and its functions as discussed in chapter 2 and 4. The inventory compilation phase was conducted by designing process flow charts showing all the unit process modelled and their interactions. In addition, we also documented the calculation used in converting the data including assumptions and their explanation for both the conventional Kraft pulp mill and the proposed Kraft biorefinery. Secondly, references of the data sources were recorded. Thirdly, the inventory data of both the conventional Kraft pulp mill and the proposed Kraft Biorefinery were compiled under the following headings: energy input, raw material inputs, products, by-product, solid waste and emission release to air. The source of all secondary data was carefully referenced. Few calculation procedures were adapted to convert the acquired data into a unified inventory result. Any assumption made was clearly specified and defensible. Every anomaly was replaced with another data value. Furthermore, every elementary

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flow was related to the functional unit with exception of a few. In addition, the elementary flows of the process unit were normalized to the functional unit. Precaution was taken to make sure data categories with similar environmental impact are aggregate together. Relevant inventories were identified by ranking and prioritization (Finkbeiner et al. 2006) of input and output contributing to the selected process units. Ranking and prioritization was also used to determine the elementary flow of significant influence with respect to the goal of the study. The system boundary of the product under study was constantly under check in accordance with the cut-off criteria established in the scope of this study.

### **4.3 Inventory analysis**

The inventory analysis conducted to achieve the goal of this LCA was carried out according to ISO 14041. The inventory analysis was conducted in three steps: 1) identification and structuring of elementary flows. 2) contribution analysis. 3) ranking and prioritization of input and output contribution to the selected process units to determine the elementary flow of significant influence with respect to the goal of the study. After the inventory analysis, an impact assessment was carried based on ISO 14042 guideline.

#### ***4.3.1 Identification and structuring***

During identification and structuring the relationship between the elementary flow and the selected process unit is established. Secondly, the exact amount of each elementary flow generated or consumed by each process unit within the system boundary is structured and presented as a two-dimensional matrix in which, for example, the elementary flow forms the rows while the selected process unit in the system boundary forms the Column as represented in appendix A. Identical elementary flow generated at different units of the life cycle stage were summed-up together to prevent double counting.

#### ***4.3.2 Contribution analysis***

The contribution of the elementary flow towards the selected process unit is analysed to determine the two key elementary flow of concern. During the contribution analysis the relationship between each elementary flow and the selected process unit is represented with an X with the assumption that each X is equivalent to 10%. The letter “X” marks the

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interception between the rows and columns. Therefore, the two-element flow with the highest number of X was identified as the two key elementary flow of concern.

### ***4.3.3 Ranking and prioritization***

The ranking and prioritization demonstrated in the inventory phase of the LCA is based on the degree of influence each elementary flow have on the process units. The two elementary flows with the highest number of X after the contribution analysis were ranked and prioritized as the most impactful elementary flows.

## **4.4 Impact assessment**

Impact assessment phase was conducted according to ISO 14040. The Impact assessment comprise of 5 steps, 3 mandatory steps and 2 optional steps. The 3 mandatory steps listed below are steps used for the LCA. According to ISO 14042, the mandatory elements are:

- Selection of the impact categories, category indicators and characterisation models.
- Assignment of LCA results to the selected impact categories (classification)
- Calculation of the category indicator result (characterisation)

The first mandatory element is the selection of impact category, category indicator and characterisation model. Table 3.1 shows the impact category, category indicator and the characterisation model used to conduct the life cycle impact assessment stage of chapter 4 and 6.

**Table 4-1:** *The impact category, category indicator and characterisation model used in chapter 4 & 6*

<b>Impact category</b>	<b>Abbreviation</b>	<b>units</b>	<b>Category indicator</b>	<b>Characterisation model</b>
<b>Acidification</b>	AP	kg (SO <sub>2</sub> to air)	Acidification potential	Recipe 2008
<b>respiratory inorganic</b>	RI	kg (PM <sub>10</sub> to air)	Disability Adjusted Life Years (DALY).	Eco-indicator 99
<b>Human toxicity</b>	HT	kg (14DCB to urban air)	Human toxicity potential (HTP).	USES-LCA model
<b>Climatic change</b>	CC	kg (CO <sub>2</sub> to air)	Global-warming potential	Recipe 2008
<b>Water Depletion</b>	WD	M <sup>3</sup> (water)	amount of water consumed	ReCiPe 2008

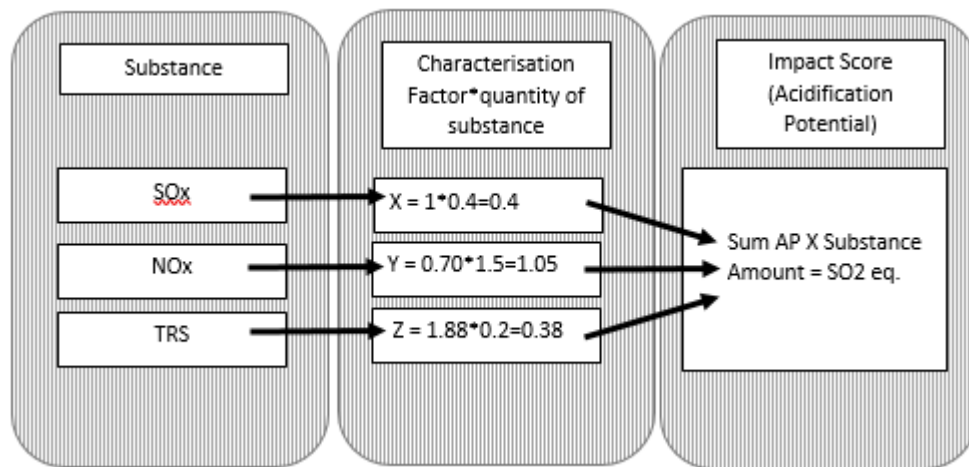
The second mandatory element is classification. During classification, elementary flows (input and output) are assigned to different impact categories as shown in the table 3.2. For better explanations, we looked at table 3.2 as an excel sheet with rows and columns. Each elementary flow (input and output) was assigned to an impact category (environmental problem) created by the elementary flow. Where the rows intercept with the columns, create a cell. Each cell contains an elementary flow matched with the impact categories (environmental problem) created by the elementary flow. Examples of elementary flows are NO<sub>x</sub>, SO<sub>x</sub>, CO<sub>2</sub>, TRS while examples of impact categories are Acidification, Respiratory inorganic, Climatic change and Human toxicity.

**Table 4-2: Classification (The process of assigning elementary flows to impact categories)**

		<b>Impact Categories</b>		
		(column) <sub>1</sub>	(column) <sub>2</sub>	(column) <sub>3</sub>
		Acidification (AP) ↓	Climatic change (CC) ↓	Human toxicity (HT) ↓
Elementary flow	(Row) <sub>1</sub>	(Cell) <sub>1,1</sub>	(Cell) <sub>1,2</sub>	(Cell) <sub>1,3</sub>
	NO <sub>x</sub> →	(NO <sub>x</sub> , AP)	(NO <sub>x</sub> , CC)	
	(Row) <sub>2</sub>	(Cell) <sub>2,1</sub>	(Cell) <sub>2,2</sub>	(Cell) <sub>2,3</sub>
SO <sub>x</sub> →	(SO <sub>x</sub> , AP)		(SO <sub>x</sub> , HT)	
(Row) <sub>3</sub>	(Cell) <sub>3,1</sub>	(Cell) <sub>3,2</sub>	(Cell) <sub>3,3</sub>	
TRS →	(TRS, AP)			

The third mandatory element of the impact assessment phase is characterisation. During characterisation, the quantity of each elementary flow as represented in table 3.2 multiplies the characterisation factor of the impact category (environmental problem) created by the elementary flow to generate an impact score. A summation of all the impact scores from an impact category gives the characterisation of that impact category. In table 3.2 the quantity of NO<sub>x</sub> in kg multiplied the characterisation factor of Acidification potential in kg/kgSO<sub>2</sub> in (Cell)<sub>1,1</sub> to give X in kgSO<sub>2</sub> as represented in figure 3.1. We repeat the same calculation for (Cell)<sub>2,1</sub> and (Cell)<sub>3,1</sub> in table 3.2 to give Y and Z in kgSO<sub>2</sub> as represented in figure 3.1. Therefore, the characterisation of acidification potential is equal to X+Y+Z. NB, X, Y and Z are the values obtained after multiplying the elementary flows and the impact categories. The same pattern was used to achieve the characterisation of Climatic

Change, Freshwater Depletion and Human Toxicity. The figure below demonstrates characterisation of acidification potential.



**Figure 4-1** Principle of characterisation with modification (Environ international Corporation and National Geographical Washington DC, 2012)

#### 4.5 Interpretation of result

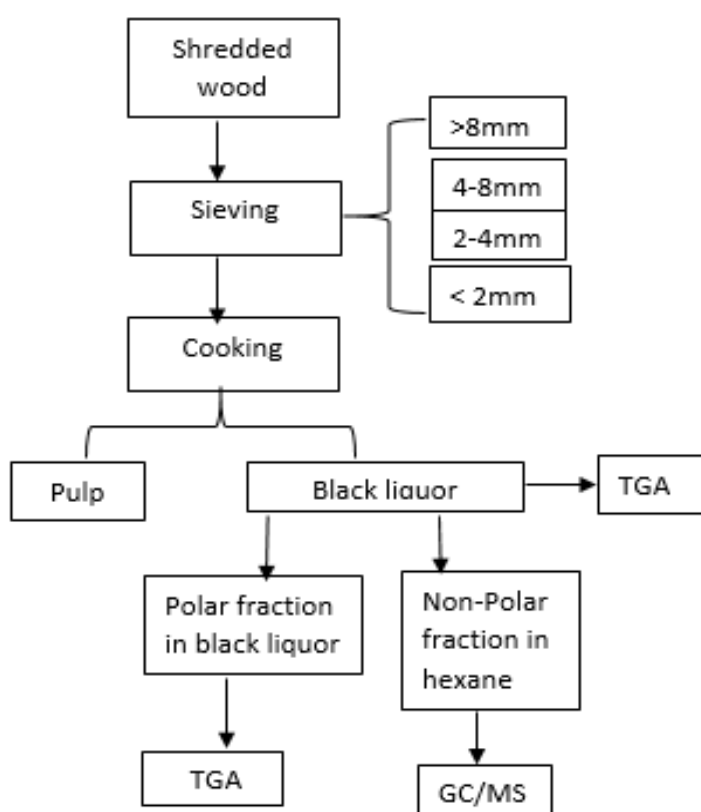
The Interpretation phase was the final stage of the LCA according to ISO 14043. At this stage of the LCA, the significant issues with the conventional Kraft pulp and paper mill as identified by the second and third phase of the LCA were documented, Secondly, the issues identified by the second and third phase of the LCA were evaluated, by a completeness, sensitivity and consistency check. The completeness check was to make sure that all relevant information about the issues identified by the second and third phase were complete. The sensitivity check was to determine the effect of assumption or decisions made during the LCA. Example, the effect of changing the particle sizes used during pulp production in the pulp mill from 8mm to <2mm and used 50% re-usable organic liquid at the washing stage. During the consistency check the assumptions, approaches and information used in the LCA were verified. Details of the completeness check, sensitivity check, and consistency check were explained in the baseline chapter (chapter 4). Finally, we summarised our findings, noted limitation experienced during the LCA and gave some recommendations.



## 4.6 Experimental methodology

### 4.6.1 Experimental flow

The experimental methodology will demonstrate how the change in input parameters like wood particle thickness and the use of a re-usable liquid as part of the washing process reduce water consumption, energy use, emission released in the air and recovery of extractable chemicals in the form of a green crude. Five main experimental steps were taken as demonstrated at figure 3.2 below. Firstly, the wood was shredded and separated into different Particle sizes using sieves of different aperture. The separated particles were cooked and washed. The black liquor from the digester was analysed using liquid – liquid extraction (LLE) method. The extract from the LLE was analysed using a gas chromatography / mass spectroscopy (GC/MS) while the raffinate from the extraction and black liquor before extraction was analysed with a Thermogravimetric analysis (TGA).



*Figure 4-2: Schematics diagram of the experimental methodology*

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#### 4.6.2 Shredded wood

The samples used for this study was an industrially processed white Birch and pine woodchips, purchased from Moyne Sawmill located in Glasgow Scotland on 11 July 2015.

Table 3.1 shows some of the characteristics of the birch and pine analysed on a dry weight basis.

**Table 4-3: Structural analysis of birch and pine wood (ECN, 2014; IEA, 2014)**

<b>Component</b>	<b>Composition of birch in (wt.% dry)</b>	<b>Composition of pine in (wt.% dry)</b>
Cellulose	39	44
Hemicellulose	29	25
Lignin	22	26
Ash content	0.5	0.7

The initial moisture content of the samples (white birch and pinewood) was 72% (wb). After drying over night at a temperature of 60°C using a carbonite oven (an oven for laboratory, manufactured by Carbolite Gero, United Kingdom) a dry solid content of approximately 92% was achieved. The wood samples were classified using a high-performance Endecott sieve shaker manufactured by air and vacuum technologies JHB, South Africa. The sieve was separated from each other in other to collect the different particle sizes, which were weighed using portable balance manufactured by Kern in Stuttgart – Balingen before packing the samples in different sample bags.

#### 4.6.3 Sieve Analysis

This analysis demonstrates the relationship between particle size and their mass percentages by allowing the particles pass through sieve of precise mesh sizes. An octagonal D200 digital Endecott sieve shaker was used to classify the wood sample containing different particle sizes. The octagonal D200 digital Endecott sieve shaker is a high-performance digital shake with perforated sieve aperture ranging from 1mm & 125mm (Williams et al. 2018). According to Endecott Brochure, the octagonal D200

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digital is set to maximum efficiency. However, the equipment is portable and compact. It also has a precise sieve clamp which put the sieve in position to separate the samples. It is also total operator control. Below is the picture of an octagonal D200 high performance digital Endecott sieve shaker and the controls.



**Figure 4-3:** An Octagonal D200 high performance digital Endecott sieve shaker (Endecott Brochure).

All samples were weighed and recorded. The test sieve with mesh apertures were stacked on each other with the finest opening (2mm) on the bottom of the stack. The different sieve sizes use to analyse the different particles were 2, 4 and 8mm mesh sizes. However, the stacking continued in ascending order until the last sieve (8mm) was place on top of the stacked sieves. 2kg of each wood sample was divided into 200 portions containing 10g each. This was done to avoid blinding the sieve as a result of overloading. Therefore, 10g of each wood sample was paced on the top sieve. After that, the stacked sieve was transferred into the sieve shaker with the cover on the top sieve. The test running time was set to be 5mins per 10g. The Shaker carryout the test operation through vibrational and oscillatory motion of around 150 blows/min by a weight of 2kg under the impact of gravitational force. At the end of the test, the stack sieve was removed from the shaker. Each sieve and the bottom pan were emptied into individual container while holding the sieve over each container. The sieve was brushed gently to remove all remaining particles. The content in the container was weighed and recorded. The same procedure was repeated for the rest of the particle sizes. Finally, the percentage mass of the particle size retain per mess for 10g of the nine samples were calculated and recorded per mess size.

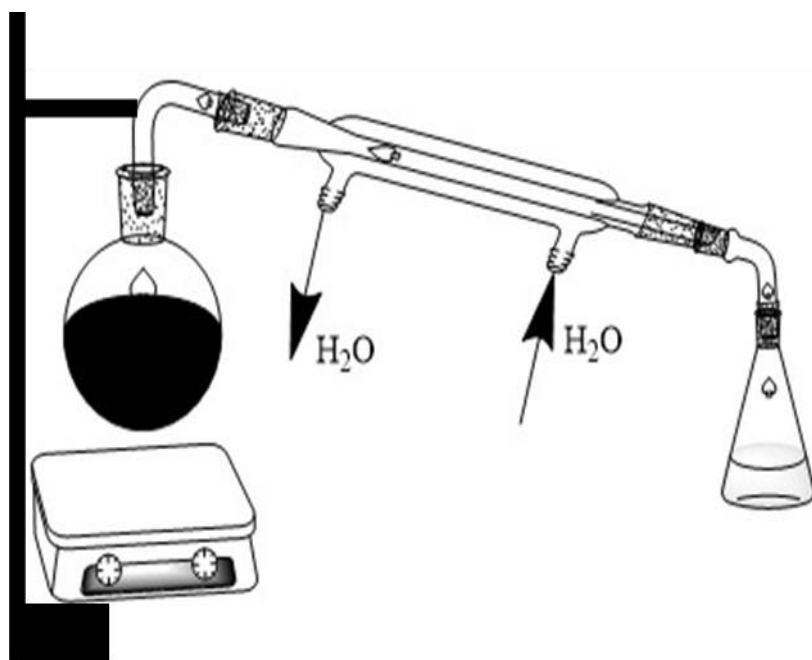
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#### 4.6.4 Kraft cooking

The classified particle sizes were cooked using Kraft cooking process. The procedure used in carrying out the Kraft cooking was adopted from (Brannvall 2014) with modification.

##### 4.6.4.1 Cooking equipment

A hot plate with stirrer and a round bottom flask with a capacity of 250ml was used for the cooking. The round bottom flask was heated by the hot plate and the sample (white liquor and the woodchip) inside the flask stirred by the magnetic stirrer. The thermometer attached to the column was used to measure the temperature of the cooked sample while the reflux technique was used for the condensation of vapour coming out of the system.



**Figure 3.4:** A schematic diagram of a Kraft cooking experiment.

##### 4.6.4.2 Cooking procedure

The cooking method was adapted from (Brannvall 2014) with modification such as using hot plate instead of an electrically heated oil bath with polyethylene glycol, a magnetic stirrer instead of slightly tilting the container to enable circulation of the liquor as they are rotated in the glycol bath. Batches of 10 g birch and pine wood chips were cooked in a round bottom flask containing Kraft cooking liquor. A hot plate with a magnetic stirrer was used to cook the samples. However, the Kraft cooking liquor was prepared from

NaOH ( $\geq 97\%$  purity) and a solution of Na<sub>2</sub>S from technical-grade scales of sodium sulphide-Y-hydrate ( $\geq 60\%$  purity from sigma Aldrich). However, 0.1M of Sodium chloride concentrate purchased from Sigma Aldrich was used to increase the ionic strength of the pulping liquors. The salt solution was introduced into the cooking flask using a pipette. To cook 10g of each woodchip sample, the white liquor was prepared from 94.75g of NaOH dissolved in 150mL of deionized water and 31.59g of Na<sub>2</sub>S dissolved in 150mL of deionized water. The NaOH and Na<sub>2</sub>S combine to for the white liquor have a concentration of 0.016mol/mL and 0.003mol/mL. The liquor-to-wood ratio is 1:10. The conditions for the Kraft cooking are represented in Table 3.4.

**Table 4-4:** *Cooking condition for birch and pine woodchips*

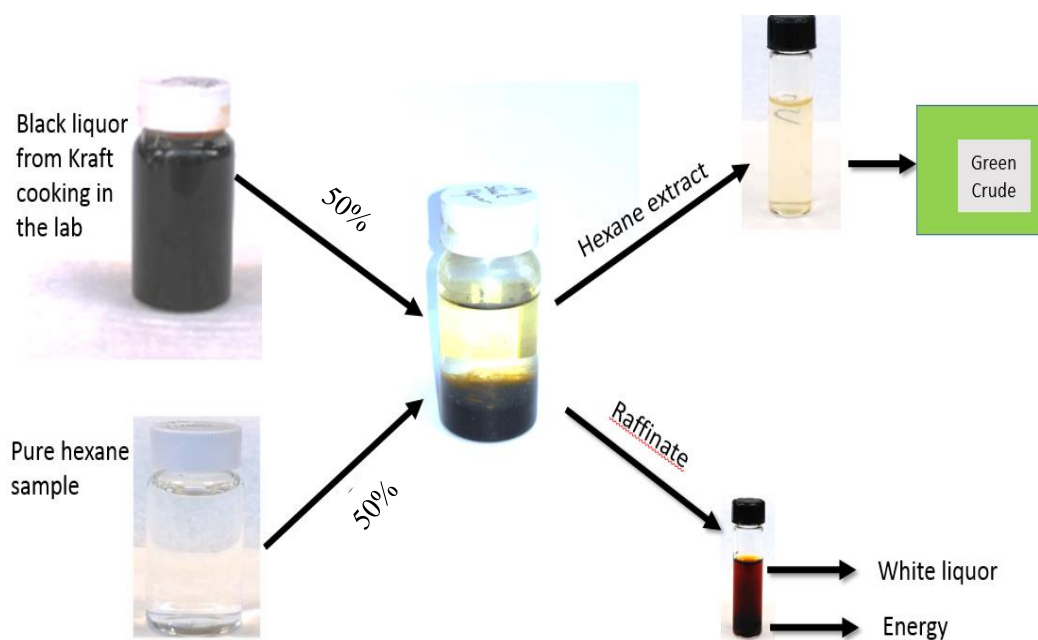
<b>Kraft Cooking method</b>	<b>Quantity</b>
Amount of birch or pine cooked	10g
Liquid to birch or pine woodchips ratio (L/W)	1:10
Particle size	< 2mm (0-2mm), 2-4mm, 4-8mm, < 8mm
Cooking temperature	165°C
Pulping time (mins)	30,60,120

The woodchips and the cooking liquor mixture was stirred every 5mins at a cooking temperature of up to 165°C. The different particle sizes ranging from < 2mm, 2-4mm and 4-8mm, were cooked at different cooking time starting from 30, 60 and 120mins. After cooking, the reaction was cooled down to room temperature before separating the pulp and black liquor. The pulp was separated from the black solvent using a filter paper, washed, and dried at a temperature of 105°C. The rate of delignification for each particle size range was determined by calculating the weight difference between the wood sample

before cooking and after cooking the woodchips. The strong Kraft spent liquor (SKSL) collected from the samples was submitted for liquid-liquid extraction (LLE).

#### 4.6.5 Liquid-liquid extraction

Nine strong Kraft spent liquor (SKSL) samples were obtained from cooking 10 grams of each different wood particle size range (<2 (0-2mm), 2-4 and 4-8mm). This was done by using different cooking times (30, 60 and 90mins) under the cooking conditions in table 3.4. After cooking, the pulp was washed with a mixture of water and hexane as the washing liquid. The hexane phase was separated from the water phase by using a pipette. Below is a simple laboratory illustration of the experiment that led to the discovery of the green crude explained in chapter 7.

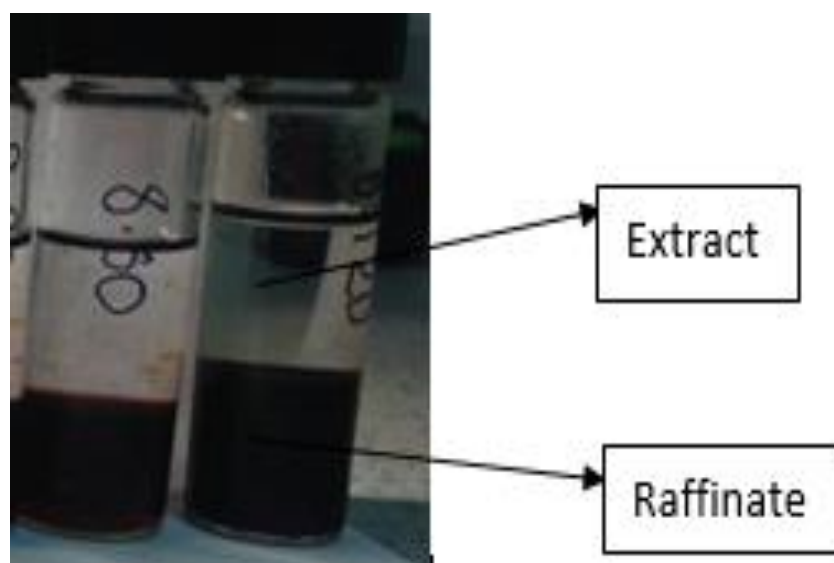


**Figure 4-5:** Simple laboratory illustration showing the Liquid-Liquid extraction

The liquid-liquid extraction was carried out on Strong Kraft spent liquor (SKSL). The SKSL with a pH of  $12 \pm 1$  was collected from cooking different woodchip sizes at different cooking time in the CICC laboratory, Heriot Watt University. Analytical grade Hexane (95% anhydrous, Sigma Aldrich) was used as the extraction solvent. Other equipment used during the experiment was pipette, 2mL vials, 7mL vials and a digital weighing balance. After separating the non-polar phase (hexane rich phase) from the

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aqueous phase (black liquor phase) using a Pasteur pipette, the Extract (E) was transferred into a 2mL GC vial, measured and recorded as WEV<sub>2</sub>+HAE. The Raffinate (R) was measured and recorded as WEV<sub>2</sub> + BLAE. The small remaining extraction solvent in the mixture, due to the surface tension that exists between the polar and non-polar phase was able to evaporate within 90mins. After the liquid-liquid extraction, the weight of the polar phase of the mixture before and after extraction was measured and recorded. Likewise, the raffinate as well.



**Figure 4-6:** *The extract and raffinate phase*

In order to determine qualitatively the different compounds in the Extract (E), the extracts were taken for a GC/MS analysis. In addition, the Raffinate (R) was quantitatively analysed using a TGA. Table 3.5 summarizes the parameters used during the liquid-liquid extraction.

#### **4.6.5.1** *Extraction procedure*

Adapting the Direct organic extraction method of the Batchwise single stage liquid – liquid extractions principal with modification according to (Müller et al. 2000), 2mL of each nine SKSL samples containing the inorganic compound, organic compound and water were agitated with 2mL of Hexane (95% anhydrous, Sigma Aldrich) in a 7mL vial at a Sample-to-solvent ratio of 1:1. The black liquor samples were properly agitated

before use in other to unify the solution. Each of the nine samples were vigorously mixed for 2 minutes, at room temperature (Faustino et al. 2010, Cruz et al. 2005).

**Table 4-5: Parameters used during the Liquid-liquid extraction.**

Parameter	
Extraction solvent	Hexane
Initial pH of the mixture.	7.0 (Original)
Settling time	From 10 to 90 min
Sample-to-solvent ratio	1.1(v/v)
Number of extraction stages	1

The quantity of extracted organic compound (EOC) was determined by subtracting weight of empty vial + black liquor after extraction (WEV + BLAE) in 90mins from weight of empty vial + black liquor before extraction (WEV + BLBE). Therefore, the percentage (%) value of the extracted organic compound (EOC) was calculated by multiplying the value of extracted organic compound (EOC) by the quantity of wood loss in percentage (%).

#### **4.6.6 Gas chromatography and mass spectroscopy (GC/MS)**

Adapting the GC/MS technique by (Chauhan et al. 2014) with modification different compounds in the non-polar phase extracted from the nine SKSL samples was identified using an Agilent 6850 Series II gas chromatograph. Figure 3.1 shows an Agilent 6850 Series II gas chromatograph (Wilmington, DE, USA) used to carry out the experiment. Accompanying the gas chromatograph was a split/spitless injector operated at 270 °C in split less mode for a time interval of 1min and an electron-capture detector (ECD) M1766. However, a DB-5MS fused silica capillary column (J&W Scientific, Folsom, CA, and USA) of 30m x 0.25mm I.D with (0.25m film thickness in mm) was used during the experiment. The initial temperature of the column oven was maintained at 50 °C for 1 min, after which it was increased to 220 °C via a ramp of 15 °C min<sup>-1</sup>, then to 280 °C via a ramp of 20 °C min<sup>-1</sup> and was seized at 280 °C via a ramp of 20 °C min<sup>-1</sup>. Helium



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was used as the carrier gas while nitrogen was used to make up for the remaining required gas. Furthermore, a gas purifier Hewlett-Packard containing molecular sieve 5A and an oxygen-adsorbing gas purifier (OxiClear), was used to further purify the carrier gases.



**Figure 4-7:** *Agilent 6850 GC Gas Chromatograph Series*

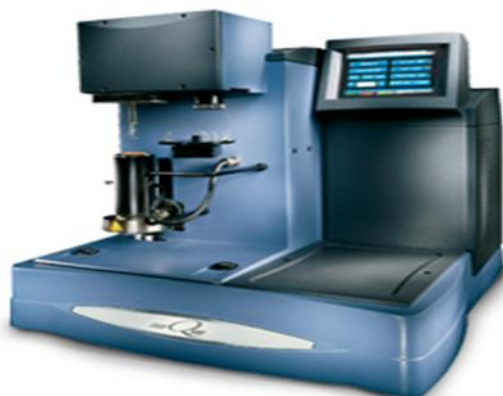
The extracts collected from the nine SKSL samples were analysed by an Agilent 6850 series II gas chromatograph coupled with split/spitless injector operated at 270 °C in pulse spitless mode for 1 min, an electron-capture detector (ECD) M1766 and a DB-5MS fused silica capillary column of 30m x 0.25mm was used during the experiment. This device was used in separating the different component in the sample as the temperature of the column oven gradually increases. The initial temperature of the column oven was maintained at 50 °C for 1 min, after which it was increased to 220 °C via a ramp of 15 °C min<sup>-1</sup>. The temperature of the column oven was further increase to 280 °C via a ramp of 20 °C min<sup>-1</sup> and was maintained at 280 °C via a ramp of 20 °C for 5 min. Each increase in temperature encouraged the separation of the components with low boiling point first followed by those with high boiling point. This is because temperature is one of the distinct forces that brings about selective attraction of component in the stationary phase. However, the carrier gas was helium with purity up to 99.9%; helium was further purified by passage through a helium gas purifier Agilent model RMSH-2. As the component leaves the column, they enter the detector, which created electronic signals whenever a compound was found. Therefore, these signals were translated into chromatographs. The selected ion monitoring (SIM) mode was used for determination of target compounds.

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**4.6.6.1** *The Normalized value of the Aromatics, naphthene and paraffin in the nine samples analysed during the GC/MS were calculated with the formula below:*

The total values of aromatic (A), naphthene (N) and paraffin (P) in the nine samples analysed by the GC/MS were normalized by summing up the total organic compound (T) = A+N+P for each particle size cooked at a given cooking time. However, the aromatic was normalized by  $A/T*100/1$ , likewise naphthene and paraffin which is calculated by  $N/T*100/1$  and  $P/T*100/1$ .

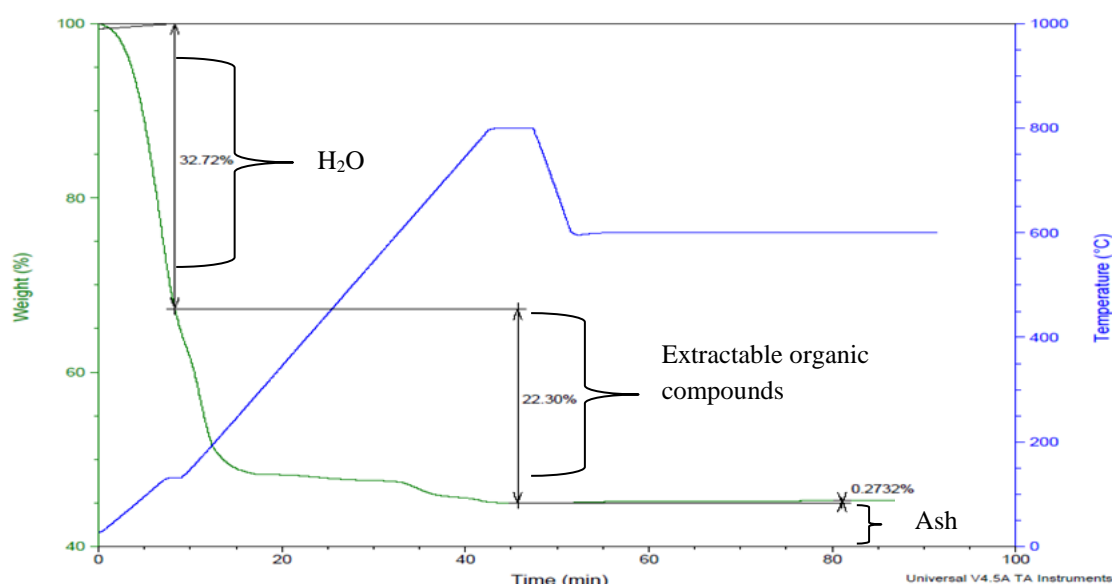
**4.6.7** *Thermogravimetric Analyser (TGA) meaning/principal/application*



**Figure 4-8:** *TGA Q500 with Auto sampler*

The Thermogravimetric Analyser (TGA) is an instrument that measures the rate of weight change in a material, either as a function of increase in temperature, or time, in a controlled atmosphere (TA Instruments 2001-2006). Figure 3.6 is the picture of the TGA Q500 with an auto sampler. The samples for the TGA analysis were taken from nine SKSL (strong Kraft spent liquor) before extraction and after extraction (R). The equipment used was a TGA Q500 with Auto sampler. Firstly, the pH of the samples was diluted from 14 to a range of 7-7.5 for both SKSL before and after extraction (R). Due to the corrosive nature of the samples, each of the sample was diluted with 0.1 M HCl and tested, using the pH paper to obtain a pH of  $7\pm 0.5$ . Since the platinum pans can only contain 50-100 $\mu$ L, a drop of each sample was dropped in the platinum pans and allowed to dry under room temperature overnight. Adapting the TGA technique used in (Prime et al. 2009), the TGA experiment was run in two

phases, the first phase was for the Strong Kraft Spent Liquor before the liquid to - liquid extraction. The second phase was for the Strong Kraft Spent Liquor after liquid-liquid extraction. As the TGA is meant to measure the amount and rate of weight change, precautions were taken to make sure the pan are placed properly on the Auto sample pan holder. Before using the TGA Analyser, the necessary gas lines were connected. Pan type and necessary material required for the experiment were selected. Proximate analysis was chosen as the test procedure before entering the experimental information through the TA instrument. The gas flowrate was adjusted before starting the experiment. The sample pans were selected and tared before loading and running the sample. At the end of the experiment, the pans were carefully unloaded and cleaned using water or Acetone.



**Figure 4-9:** A graphical representation of the TGA results obtained from the decomposition of the strong Kraft spent liquor.

Figure 3.8 show a weight change due to decomposition of the sample as the temperature of the furnaces during the TGA analysis increase. The red vertical in figure 3.7 represents weight of the sample in (%) while the blue vertical axis in figure 3.8 represents temperature in (<sup>o</sup>C). Furthermore, the x-axis represents the time in (mins). However, the result of any weight change in percentage was calculated and recorded in the graph. As temperature of the furnaces increase up to 105 OC at an isothermal of 2min, all the water in the sample evaporated. Therefore, the weight change due to the decomposition of the sample in percentage was recorded as 32.72%, after the temperature of the furnaces increase to 800 OC at an isothermal of 5mins the weight change due to decomposition of the volatile organic matter in percentage was recorded as 22.30%. Finally, when the

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temperature of the furnace went down to 600 °C at an isothermal of 40mins, the gas switched over from nitrogen to oxygen gas which supported the combustion of the inorganic compounds to form ash. The weight changes due to the decomposition of the inorganic compound to form ash were recorded as 0.2732%. After running the nine analysed samples, the result was transferred into software (universal analysis) which helps to interpret the data provided into information on the graph. However, the graph established the weight loss in the SKSL before and after extraction as a function of increased in temperature and time.

In summary, the LCA methodology will be used to provide background information need to make conventional Kraft pulp mill environmentally sustainable and industrially viable. while the five main experimental methodology will confirm whether change in woodchip size and the use of hexane as part of the washing liquid will help reduce energy consumption, water use and reduce environmental impact of emission released to the air during energy generation.

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## Chapter 5- Life Cycle Assessment of the conventional Kraft Pulping Mill

### 5.1 Introduction

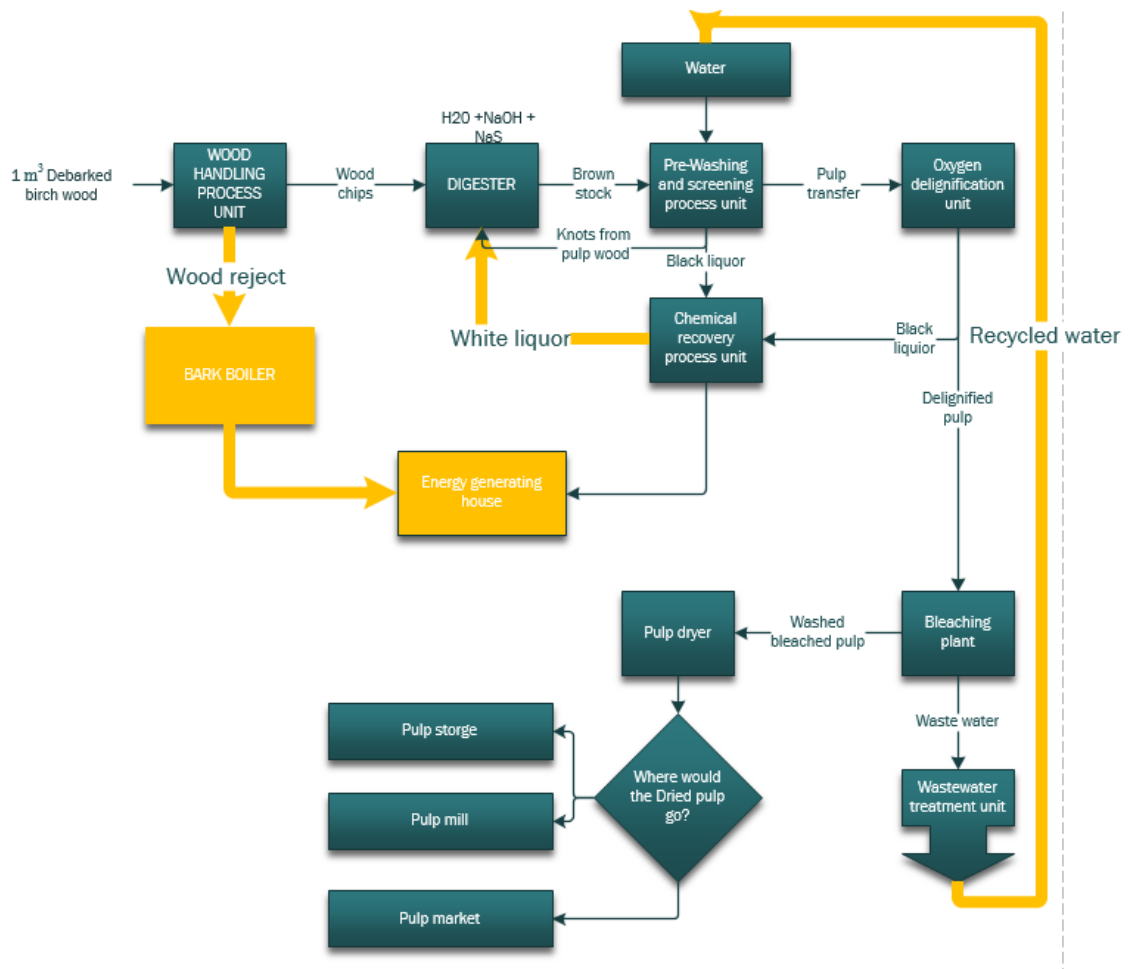
This chapter will discuss the four phases of the LCA including the goal and scope of the study, inventory analysis, environmental impact assessment and interpretation of results. In summary, the outcome of the four phases of the LCA will be used to provide background information needed to improve the environmental sustainability and industrial viability of the conventional Kraft pulp paper mill.

### 5.2 The goal and scope of the study

LCA as an environmental tool will help to identify the two key elementary flows of concern during Kraft pulping process and the selected process units affected most by the elementary flows. Secondly, the LCA will identify the most significant environmental problem generated during conventional Kraft pulp production. The targeted audience are the pulp and paper production industries globally and research institutes interested in pulp production. The scope of the study covers the Product System, functional unit, product system boundary, quality of data used, inventory analysis, environmental impact assessment and result interpretation.

#### 5.2.1 *Product system description for the conventional Kraft pulp mill under study*

The conventional Kraft pulp mill under study was taken from Suhr et al. 2015 with modification. The conventional Kraft pulping process started by converting the debarked wood into wood chips at the wood handling process unit. The generated woodchips are transported into the digester where they are cooked in a solution of sodium hydroxide and sodium sulphate at temperature between 155 °C – 175 °C depending on the rate of delignification required (Suhr et al. 2015). The brown stock from the digester is washed and screened before it is oxygen delignified. However, during the oxygen-delignified pulp undergoes post oxygen washing before it is transferred to the bleaching plant. The washed oxygen delignated pulp is bleached, re-washed and conveyed to the pulp dryer where the pulp is dried before transporting them to either the pulp storage units, paper mill or pulp markets.



**Figure 5-1:** A schematic overview of the conventional *Kraft pulp mill* under study according to Suhr et al. 2015 with modification

The knots generated after screening the digested pulp are conveyed back to the digester while the black solution, which contains organic and inorganic substance, is moved into the chemical recovery process unit. The chemical recovery process starts from the evaporator where the black liquor is concentrated before it is transferred to the recovery boiler. The black liquor is subjected to heat in the recovery boiler to produce steam used for onsite electricity generation and an inorganic compound called smelt (Bajpai 2015). The molten smelt is recovered to produce the pulp cooking liquor (white liquor) through a process called recausticizing (Tran and Vakkilainen 2008). Furthermore, the lime used during the recausticizing process is produced through Calcining process (JRC 2000). The bark boiler utilises any available reject from the wood handling unit as fuel to generate steam that powers the steam turbine. Therefore, the total renewable energy generated onsite comes from the steam produced by the bark boiler (auxiliary boiler) and the recovery boiler in the chemical recovery process unit. The wastewater from the mill is chemically and biological treated, recycled and reused by the bark boiler and recovery

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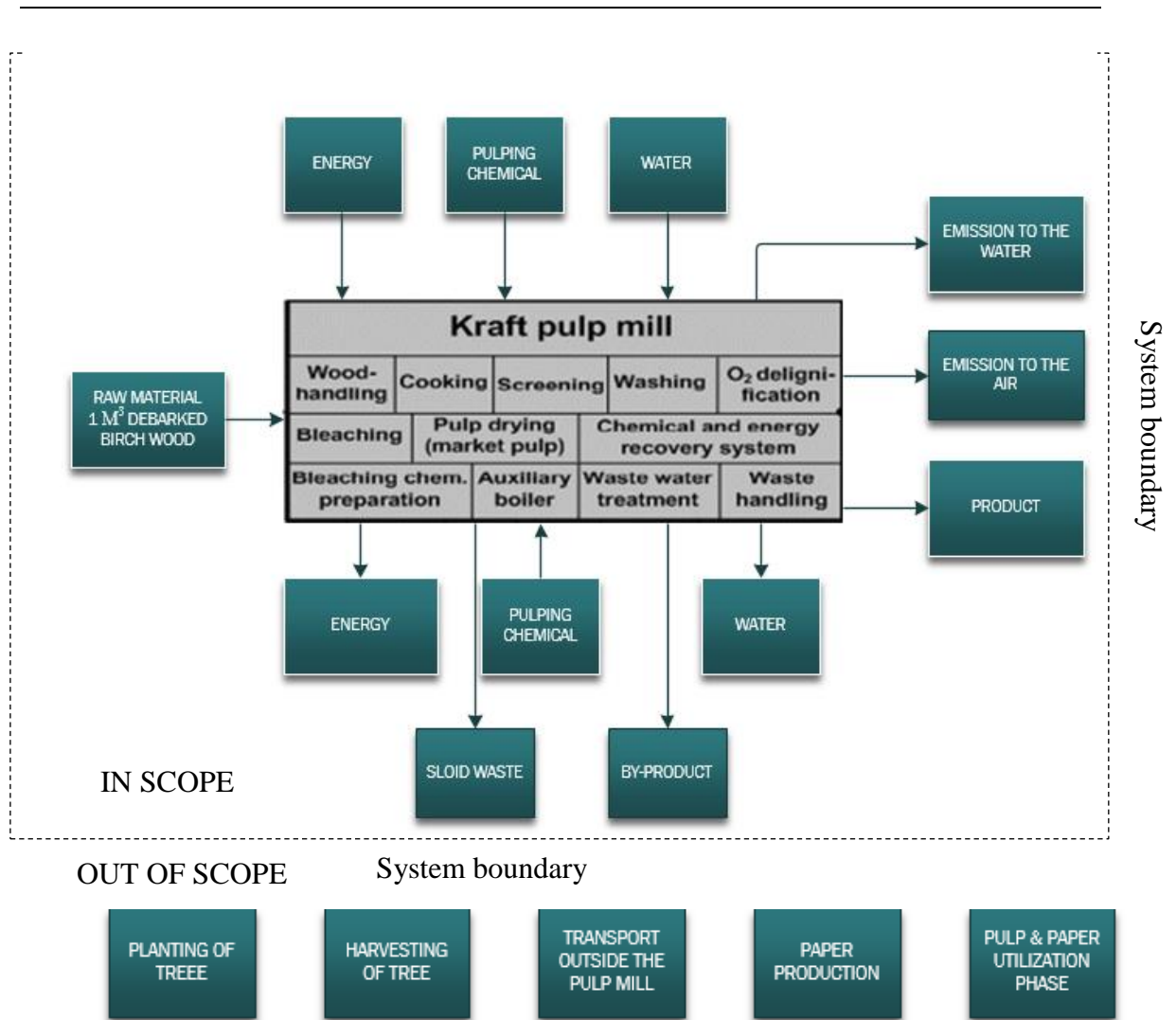
boiler while the solid wastes are treated and discharged into the landfills. The bleaching chemical used for pulp bleaching is produced in the bleaching plant while the oxygen used during the oxygen delignification is prepared in the oxygen plant. In summary, the conventional Kraft pulp mill under study is a mill that takes in debarked wood, water, chemicals and energy as input to generate pulp, energy, white liquor, tall oil and turpentine as products and by-product. Hence, an inventory analysis of each process unit listed in the schematic overview of the conventional Kraft pulp mill under study would help bring out the performance characteristics of the system under study in order to achieve the goal of the study. Note, the process in green are modifications due to the use of best available techniques and technology. While the process in red are the AS-IS process of the conventional Kraft pulp mill without modification.

### ***5.2.2 The functional unit***

The functional unit used in the LCA study is one air dry tonne of pulp for papermaking. This will be a reference unit, where the outcomes of the study will be compared to achieve a common result. Therefore, every elementary flow (EF) compiled for this study would be measured in EF unit per air dry tonne of pulp. However, other by-products like tall oil and turpentine generated during Kraft pulping was not measured and recorded because they were not within the goal and scope of the study.

### ***5.2.3 System boundary of the conventional Kraft pulp mill***

The system boundary used for this study was selected with respect to the goal of the study. The system boundary comprises of all the Input, output and process units mentioned in figure 4.2 below. Within the scope of the system boundary, we have the following elementary flow including the energy generated, energy consumed, material input and output, emission release to the air, emissions released to the land, emission release to the water, by-product, solid waste and products of the conventional Kraft pulp mill flowing in and out of the selected process units. Outside the scope of the system boundary, we have a list of activities excluded from the system under study because they are outside the goal and scope of the study. These activities include planting of trees, harvesting of trees, Transportation outside the pulp mill, paper production and utilization phase.



**Figure 4.2** Overview of the system boundary (Suhr et al. 2015)

#### 5.2.4 Quality of data used in the inventory.

The data used to carry out this LCA were secondary data source from external database (Government and Organisational reports) and academic resource. For this kind of data, it is difficult to assess precision, because many conversions were carried out. Data completeness for this study was achieved by conducting a completeness check in sub section 4.6.2. Representativeness was measured with the time, technology, and geographical coverage of the data, therefore the data use for this study is from year 2000 to present with few exceptions. The technologies used between the ranges of time the data was collected were best available technology. As of data location, data used for this study was obtained from Europe. For data, not available proxies from Canada, Africa, and United States were used.



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### **5.2.5 Summary of the goal and scope phase of the LCA**

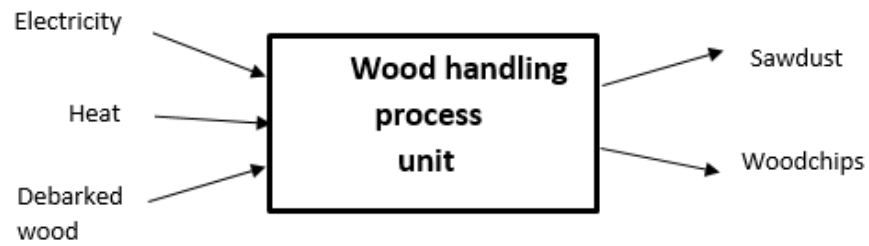
The goal and scope phase of this study helped us to understand that the LCA was conducted to identify the two key elementary flow of concern and the process units affected most by the mentioned elementary flows. Secondly, the LCA will identify the most significant environmental problem generated during Kraft pulp production. It also enables us to know that we are studying a conventional Kraft pulp mill with 1 air-dry tonne of pulp as the reference unit which every elementary flow compiled for this study would be measured. In the goal and scope phase, we also found out that the Kraft pulp mill under study have ten process units, which were selected, based on the goals of the study and cut-off criteria. System boundaries expansion and unit process division was used to avoid allocation. Finally, all the data selected for the LCA study was based on data quality requirements, however, we did not fail to state the limitation of the study.

## **5.3 Inventory compilation / analysis**

The inventory compilation begins with the flowchart of each process unit, the energy, material input and output as well as the environmental emissions and waste associated with the system under study.

### **5.3.1 Wood handling**

With reference to the study boundary, the conventional Kraft pulping mill discussed in this chapter begins with wood handling. Wood handling process is the process of converting debarked round wood into wood chips (Spinelli et al. 2011). In the conventional Kraft pulp mill the particle size used is particle between 2-8mm. In Figure 4.3, the flowchart shows input entering and output leaving the process unit.



**Figure 5-3:** A flow diagram showing the input and output of the wood handling process unit

Table 4.2 below represent raw input and output data entering and leaving the wood handling process unit and their units.

**Table 5-1:** Elementary flow of the wood handling process unit (Suhr et al. 2015, JRC 2000)

Input & output	Quantity	Range used for the LCA	Unit
Debarked wood	3.0 - 6.6	4.8	m <sup>3</sup> /Adt
Sawdust	8.0 - 10	5.0	KgDS/Adt
Woodchips	7.5– 16.5	12.0	m <sup>3</sup> /Adt
Heat	120 - 180	90.0	MJ/Adt
Electricity	45 - 65	55.0	Kwh/Adt

Adt = Air dry tonne of Pulp

After data acquisition for the wood handling process unit, Calculation used to convert the input and output inventory data with reference to the functional unit including assumption were documented.

### **Steps taken during Calculations and Assumptions made during the wood handling inventory compilation.**

The data for debarked wood was decided by considering information from two different source. Since the data for debarked wood range between 3 - 6.6 m<sup>3</sup>/ton of pulp, 4.8m<sup>3</sup>/Adt was used for the LCA.

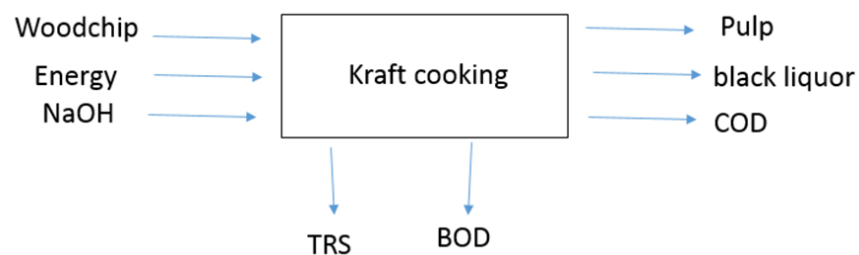
An air-dried Pulp contains 10% water. Therefore, the pulp produced by the conventional Kraft pulp mill is measured in Adt because it contains only 10% of water. Therefore, the functional unit is in Adt.

One must know the relationship between wood volume before and after chipping. This depends on chip geometry, degree of settling and compaction. According to the rural technology initiative, it is assumed that chips occupy 2.5 times the original solid wood volume. Therefore, the amount of woodchip generated is 12.0 metric tons, which is  $2.5 \times 4.8\text{m}^3/\text{Adt}$ .

The total energy use during wood handling was calculated by summing the heat and electrical energy used during the wood handling process. This was achieved by converting kWh to MJ. This was achieved by multiplying kWh by 3.6 then summing both the heat and electrical energy together to achieve the total energy consumed during the wood handling.

### 5.3.2 Kraft cooking

This is the second process unit in the system boundary. The woodchips generated by the wood handling process unit are transported into the digester where they are cooked at a given time in a solution of sodium hydroxide and sodium sulphate at a temperature depending on the rate of delignification required. The particle size transferred from the wood handling process unit to the Kraft cooking process unit are woodchip between 2-8mm. In Fig 4.4, the flowchart shows input entering and output leaving the process unit.



**Figure 5-4:** A flow diagram showing the input and output of the Kraft cooking process unit.

The table below represent raw input and output data entering and leaving the Kraft cooking process unit and their units. The inventory data used come from more than one source.

**Table 5-2: Elementary flow of the Kraft cooking process unit (Bonhivers and Stuart 2013, Suhr et al. 2015, JRC 2000)**

<b>Input &amp; output</b>	<b>Quantity</b>	<b>Range used for the LCA</b>	<b>unit</b>
NaOH	25-50	25	kg/Adt
electricity	50 - 65	57.5	KWh/Adt
Heat	1800-2050	1925	MJ/Adt
Black liquor	0.369-0.428	0.3985	t/Adt
Woodchip.	7.5–16.5	12	M <sup>3</sup> /Adt
TRS	1-2	1	Kg TRS/Adt
COD	20-30	25	KgCOD/Adt
BOD	7-10	8.5	KgBOD/Adt
pulp	1	1	Adt

**Steps taken during Calculations and Assumptions made during Kraft cooking inventory compilation.**

When obtaining data for the Kraft cooking process unit, sulphur compounds were categorised under total reduce sulphur (TRS).

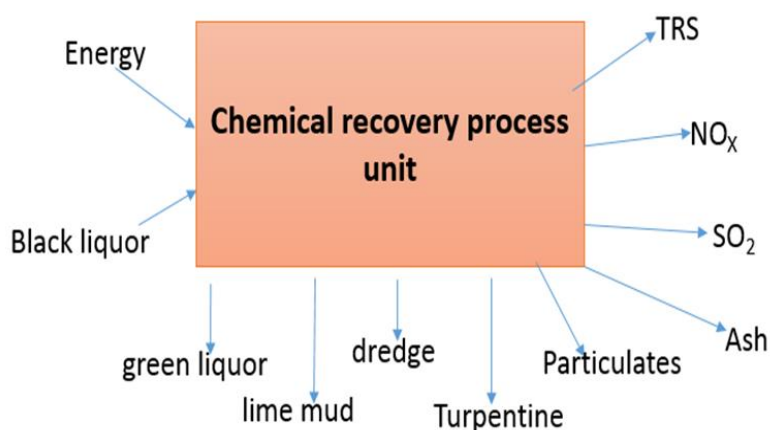
The quantity of NaOH consumed in the Kraft cooking process unit was not in their commercial form. It is 100% effective chemical with no water.

The total energy use during Kraft cooking was calculated by considering total energy consumed by adding up the total heat and electrical energy during Kraft cooking. This was achieved by converting KWh to MJ. This was achieved by multiplying kWh with 3.6.

The quantity of Black liquor from the evaporator at 65–80% dry solids content is between 1600 -1900 kg/Adt. Therefore, black liquor at 15–18% dry solid content is? Assuming black liquor at 80% dry solid content is equivalent to 1900kg therefore, 18% dry solid content will give 428 kg/Adt. Alternatively, if 65% dry solid content of black liquor is equivalent to 1600 kg/Adt, 15% dry solid content will be equal to  $0.15 * 1600 \text{ kg} / 0.65 = 369 \text{ kg/Adt}$  (Jean-Christophe Bonhivers & Paul.R. Stuart, in the Handbook of Process Integration (PI), 2013).

### 5.3.3 Chemical recovery process unit

The black liquor solution, which contains organic and inorganic substance, is transferred into the chemical recovery process unit. The chemical recovery process starts from the evaporator where the black liquor is concentrated before it is transferred to the recovery boiler. The black liquor is burnt in the recovery boiler to produce steam used for onsite electricity generation and an inorganic compound called smelt. The molten smelt is recovered to produce the pulp cooking liquor (white liquor) through a process called recausticizing. Furthermore, the lime used during the recausticizing process is reproduced through Calcining process.



**Figure 5-5:** A flow diagram showing the input and output of the chemical recovery process unit.

**Table 5-3:** Elementary flow of the chemical recovery process unit (JRC 2000, Bonhivers 2013)

Input & output	Quantity	Range used for the LCA	unit
Solid waste (green liquor sludge, lime mud, dredge)	70-60	60	kg/Adt
Heat	6500-5500	5500	MJ/Adt
Electricity	101	101	KWh/Adt
black liquor	1600 - 1900	1800	Kg/Adt

Turpentine	1-2	1.5	Kg/Adt
SO <sub>2</sub> from limekiln.	0.003- 0.002	0.0025	Kg/Adt
SO <sub>2</sub> from recovery boiler	0.5 - 0.4	0.4	Kg/Adt
NO <sub>x</sub> from recovery boiler	1.9 - 1.8	1.8	Kg/Adt
NO <sub>x</sub> from lime kiln	0.04 - 0.03	0.03	Kg/Adt
NO <sub>x</sub> , for evaporator	3-2	2	Kg/Adt
TRS from recover boiler	0.04±1	0.04	Kg/Adt
TRS from lime kiln	0.03±1	0.03	Kg/Adt
Particulates From a recovery boiler	0.1-1.8	1.6	Kg /Adt
Particulates from a limekiln	0.01-0.1	0.05	Kg /Adt

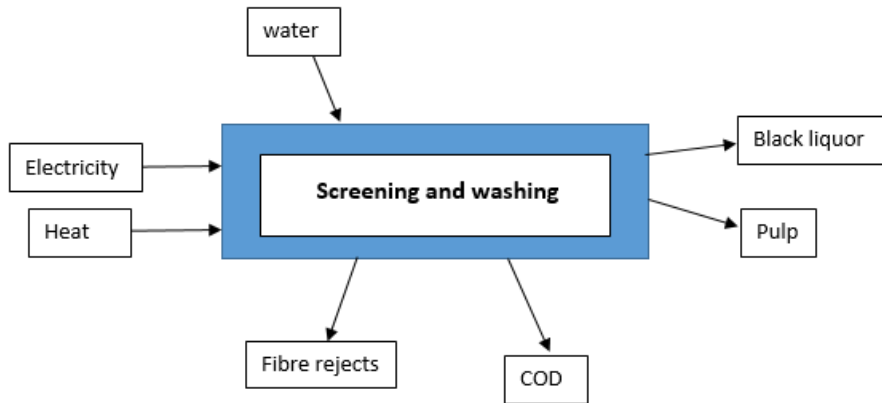
**Steps taken during Calculations and Assumptions made during chemical recovery process inventory compilation.**

The strong Black liquor from the evaporator at 65–80% dry solids content is between 1600 -1900 kg/Adt.

The TRS from the recovery boiler and lime kiln of the chemical recovery process unit was summed up to generate the total TRS emission load in the chemical recovery unit. In addition, the NO<sub>x</sub> and SO<sub>x</sub> form different parts of the chemical recovery unit were also added together to generate the total emission load of the NO<sub>x</sub> and SO<sub>x</sub>.

**5.3.4 Screening and washing processes unit**

In this process unit the brown stock from the digester is washed and screened before it is oxygen delignified. After cooking, the pulp comes out with a spent liquor (black liquor). The black liquor is separated from the pulp by subsequent washing. During the washing, the pulp is separated from the black liquor by treating with washing liquid counter currently. The washing is carried out with a drum washer. After washing, the pulp is screened with pressure screens to remove knots and fibre bundles. In addition, the generated reject is sent back to the digester for re-cooking.



**Figure 5-6:** A flow diagram showing the input and output of the screening and washing process unit.

In table 4.5 the raw input and output data entering and leaving the washing and screening process unit and their units are represented.

**Table 5-4:** Elementary flow of the screening and washing unit (JRC 2000, Bonhivers 2013)

Input & output	Quantity	Range used for the LCA	unit
Pulp	1000±1	1000	Kg/Adt
black liquor	1600-1900	1800	Kg/Adt
Water	2 – 3	2.5	M <sup>3</sup> /Adt

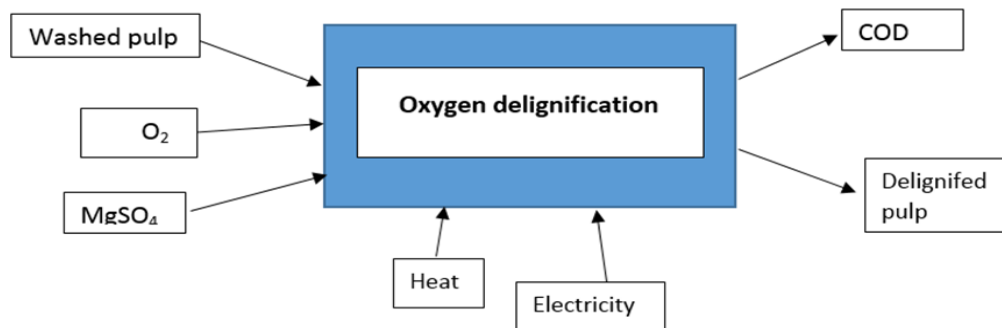
fibre rejects	2 – 20	11	Kg/Adt
COD in a washer	2-4	2	Kg /Adt
Electricity	46±1	46	KWh/Adt
Heat	0	0	MJ/Adt

**Steps taken during Calculations and Assumptions made during washing and screening inventory compilation.**

The total energy use during washing and screening was calculated by summing the heat and electrical energy used during the washing and screening process. This was achieved by converting KWh to MJ by multiplying kWh with 3.6.

**5.3.5 Oxygen delignification**

After washing and screening, the pulp is oxygen delignified depending on the level of pulp brightness require.



**Figure 5-7:** A flow diagram showing the input and output of the oxygen delignification process unit.

Table 4.6 contains raw material input and output, data entering and leaving the Oxygen delignification process unit and their units.

<b>Input &amp; output</b>	<b>Quantity</b>	<b>Range used for the LCA</b>	<b>unit</b>
Washed pulp	1000±1	1000	Kg/Adt



MgSO <sub>4</sub>	0-3	1.5	Kg/Adt
O <sub>2</sub>	5- 25	20	M <sup>3</sup> /Adt
COD	16 – 24	19	Kg/Adt
Delignified pulp	975±1	975	Kg/Adt
Electricity	38±1	38	KWh/Adt
Heat	400±1	400	MJ/Adt

**Table 5-5:** Elementary flow of the oxygen delignification process unit (JRC 2000)

**Steps taken during Calculations and Assumptions made during Oxygen delignification inventory compilation.**

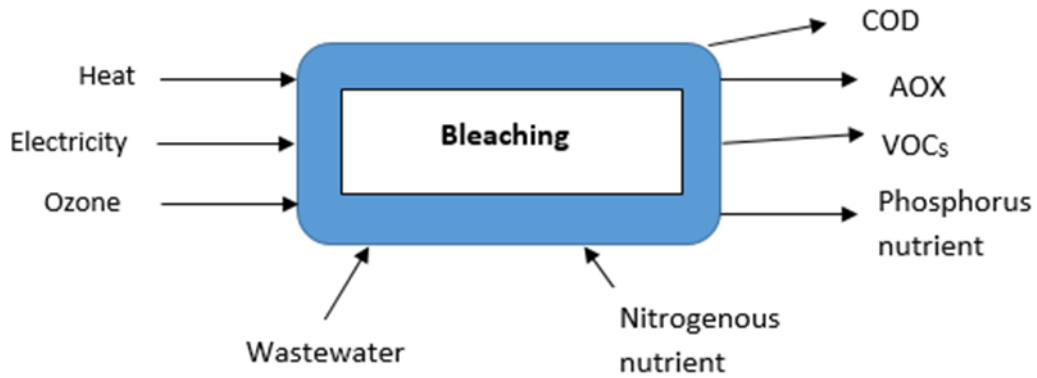
MgSO<sub>4</sub> and O<sub>2</sub> are expressed as 100 % effective chemicals and not as commercial solutions containing various amounts of water.

The overall pulp yield decreases by 1.5 - 2.5%, therefore we multiplied the pulp yield (1000 kg) by 2.5% to get 975 kg (the new quantity of pulp after delignification).

The total energy use during oxygen delignification was calculated by summing the heat and electrical energy used during the wood handling process. This was achieved by converting KWh to MJ by multiplying kWh by 3.6.

### 5.3.6 Bleaching

After oxygen delignification, the pulp is post washed and transferred to the bleaching plant. In the bleaching plant the pulp bleach with respect to the level of brightness needed.



**Figure 5-8:** A flow diagram showing the input and output of the oxygen delignification unit

Table 4.7 represent raw input and output data entering and leaving the Bleaching process unit and their units.

**Table 5-6:** Elementary flow of the bleaching process unit ( Bonhivers 2013, (Suhr et al. 2015))

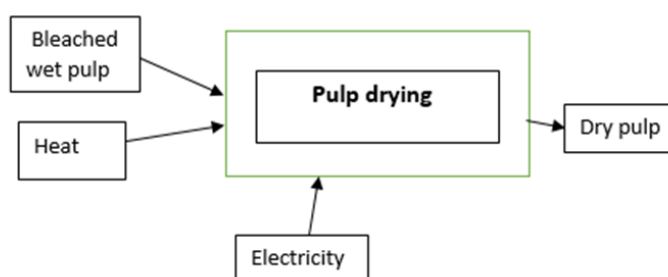
Input & output	Quantity	Range used for the LCA	unit
electricity	70-80	80	KWh/Adt
Heat	500±1	500	MJ/Adt
COD	14-30	17	Kg/Adt
Ozone	0-5	5	Kg/Adt
AOX,	0.1-0.3	0.2	kg/Adt
Chlorine from bleach pulp	0.04-0.4	0.2	Kg /Adt
VOCs	0.1-0.4	0.25	Kg/Adt
Wastewater	20-90	40	M <sup>3</sup> /Adt
Phosphorus nutrient	0,003-0.08	0.06	kg/Adt
Nitrogenous nutrient	0.01-0.4	0.2	kg/Adt
ClO <sub>2</sub>	5±1	5	Kg/Adt
Oxygen delignified pulp	975±1	975	Kg/Adt

**Steps taken during Calculations and Assumptions made during bleaching inventory compilation.**

The calculation and assumption made in table 4.7 is the same with the calculations and assumptions made between table 4.2 to table 4.6.

**5.3.7 Pulp Drying**

In this process the wet pulp produced is dried before transferring them to either the storage unit, paper mill or selling point of the Kraft pulp mill.



*Figure 5-9: a flow diagram showing the input and output of the pulp drying process unit*

Table 4.8 represent raw input and output data entering and leaving the pulp drying process unit and their units.

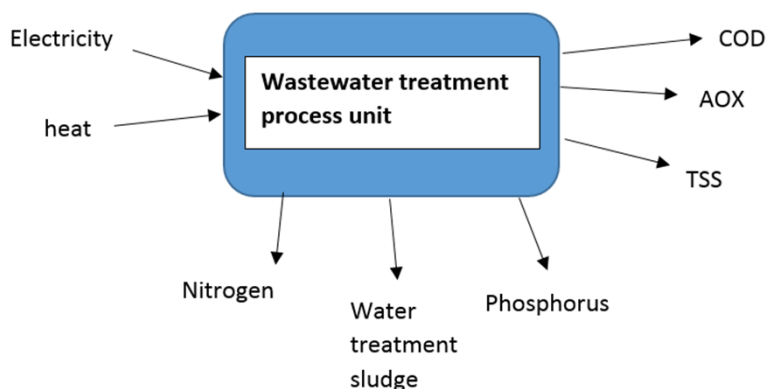
*Table 5-7: Elementary flow of the pulp drying process unit ((Suhr et al. 2015))*

<b>Input &amp; output</b>	<b>Quantity</b>	<b>Value range used</b>	<b>unit</b>
Bleached wet pulp	975±1	975	Kg/Adt
Heat	2850-3580	3280	MJ/Adt
Electricity	105-250	200	KWh/ Adt
Dry pulp	975±1	975	Kg/ Adt

Calculations and Assumptions made during pulp drying inventory compilation is the same with the calculations and assumptions made between table 4.2 to table 4.6.

### 5.3.8 Wastewater treatment

The effluent coming from the Kraft pulp mill are treated before discharging them into the environment.



**Figure 5-10:** A flow diagram showing the input and output of the wastewater treatment process unit

Table 4.9 represent raw input and output data entering and leaving the wastewater treatment process unit.

**Table 5-8:** Elementary flow of the wastewater treatment process unit (Suhr et al. 2015)

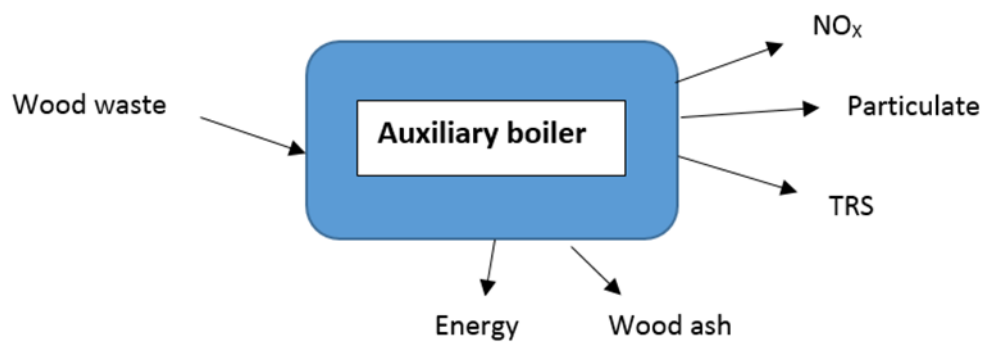
Input & output	Quantity	Range used for the LCA	unit
Water treatment sludge	10±1	10	Kg/Adt
electricity	13±1	13	KWh/Adt
heat	0	0	MJ/Adt
COD	5 – 42	23	Kg /Adt
AOX	0 - 0.3	0.25	Kg/Adt
TSS	0.015 - 7	5	Kg/ Adt
Nitrogen	0.01 - 0.63	0.25	Kg/Adt
phosphorus	0.01 – 110	50	Kg/Adt

Calculations and Assumptions made during pulp drying inventory compilation is the same with the calculations and assumptions made between table 4.2 to table 4.6.

### 5.3.9 Auxiliary boiler

The auxiliary boiler is used for onsite energy production. The vessel produces super-heated steam when the fluid inside the vessel is heated up to the point where it produces

vapours (Rayaprolu 2009).The Heat energy that boil the fluid inside the vessel is produced in the boiler by burning the fuel, which could be either renewable (bark, wood waste and wood reject produced after wood handling process) or non-renewable (coal, natural gas and fossil fuel). The reaction between the three elements (air, fuel, and heat) brings about combustion in the boiler furnace. The combustion generates heat, which boils the fluid (water or any other desired solvent) to produce steam, which is channel to the steam turbine where mechanical energy is converted to electrical energy used in the Kraft pulping mill (Chattopadhyay 2013).



**Figure 5-11:** A flow diagram showing the input and output of the Auxiliary boiler process unit

Table 4.10 represent raw input and output data entering and leaving the auxiliary boiler process unit and their units.

**Table 5-9:** Elementary flow of the Auxiliary boiler process unit (JRC 2000)

Elementary flow	Amount	Range used for the LCA	Unit
Wood ash	9 ± 1	5	Kg/Adt
wood waste	6 ± 2	4	Kg/Adt
energy	108 ± 2	55	MJ/Adt
TRS	0.1 ± 0.2	0.1	Kg/Adt
NOx	0.7 ± 0.1	0.4	Kg/Adt
particulates	1±2	1.5	Kg/Adt

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Calculations and Assumptions made during pulp drying inventory compilation is the same with the calculations and assumptions made between table 4.2 to table 4.6.

While designing the process flowchart, the system boundary is constantly scrutinized according to the cut-off criteria established in this study. Unit process shown not to be significant to the goal and scope of the study were excluded. The total input and output of the selected process unit under the system boundary was recorded between table 4.2-4.10 of the inventory compilation step.

#### ***5.3.10 Determination of Inventory Data relevant to the goal of the study***

The inventory data relevant to the goal of the study was selected based on ranking and prioritization of the elementary flows with respect to their percentage contribution (ISO 14044:2006). To select the relevant inventory for the baseline LCA, we structured and identified the relationship between the elementary flow (inputs and outputs) and the life cycle stages (process units under study). Structuring the life cycle inputs and outputs, helped to prevent double counting because identical elementary flows generated at different units of the life cycle stage were summed-up together. Example NO<sub>x</sub> emission load generated by the evaporator and recovery boiler are treated as one NO<sub>x</sub> emission load by summing-up the NO<sub>x</sub> from the evaporator and NO<sub>x</sub> from the recovery boiler since both processes are part of the chemical recovery process unit. Appendix A represents the identification and structuring stage of the Life Cycle Inventory which is the first step towards determining the key elementary flow of concern. The second step is the contribution analysis. At this point, our focus is to discover the two key elementary flows contributing towards the selected process units within the system boundary. To discover the two key elementary flows, we decided to match each elementary flow with the effected process units. All the elementary flows were arranged on the rows of table 4.11 while the selected process unit in the system boundary were arranged in the column of table 4.11. The interception between each elementary flow and the selected process unit was marked as X. The two elementary flows with the highest number of X were prioritized and ranked as the most impactful elementary flow. The assumption is that elementary flow, which contribute most to the selected process unit, are elementary flow of concern and were prioritized and ranked as the most impactful elementary flows. The table below contains the entire elementary flow entering and leaving the selected process unit. The interception between each elementary flow and the selected process unit is Marked X.

**Table 5-10: The contribution analysis of each elementary flows entering and leaving the selected process units.**

LCI Input /Output	WH	C	CRP	WAS	B	BCP	OD	AB	PD	WWT
Debarked wood (m <sup>3</sup> /Adt)	X	-	-	-	-	-	-	-	-	-
Sawdust (kg/Adt)	X	-	-	-	-	-	-	-	-	-
Bark (kg/Adt)	X	-	-	-	-	-	-	-	-	-
Woodchips (m <sup>3</sup> /Adt)	X	X	-	-	-	-	-	-	-	-
Energy (MJ/Adt)	X	X	X	X	X	X	X	X	X	X
NaOH (kg/Adt)	-	-	-	-	-	-	-	-	-	-
Pulp (Adt)	-	X	-	X	-	-	X	-	X	-
black liquor (kg/Adt)	-	X	X	X	-	-	-	-	-	-
COD (kg/Adt)	-	X	-	X	X	-	X	-	-	X
BOD (kg/Adt)	-	X	-	-	-	-	-	-	-	-
TRS (kg/Adt)	-	X	X	-	-	-	-	X	-	-
Water (kg/Adt)	-	X	X	X	X	X	-	X	-	-
fibre rejects (kg/Adt)	-	-	-	X	-	-	-	-	-	-
MgSO <sub>4</sub> (Kg/Adt)	-	-	-	-	-	-	-	-	-	-
O <sub>2</sub> (kg/Adt)	-	-	-	-	-	-	X	-	-	-
NaClO <sub>2</sub> (Kg/Adt)	-	-	-	-	-	X	-	-	-	-
SO <sub>2</sub> (chemical) Kg/Adt	-	-	-	-	-	X	-	-	-	-
H <sub>2</sub> SO <sub>4</sub> (Kg/Adt)	-	-	-	-	-	X	-	-	-	-
Oxy delignified pulp Kg/Adt	-	-	-	-	X	-	-	-	-	-
Bleaching chemical (ClO <sub>2</sub> ) Kg/Adt	-	-	-	-	-	X	-	-	-	-
Ozone Kg/Adt	-	-	-	-	X	-	-	-	-	-
AOX, Kg/Adt	-	-	-	-	X	-	-	-	-	X
Chlorine from bleach pulp Kg/Adt	-	-	-	-	X	-	-	-	-	-
VOCs Kg/Adt	-	-	-	-	X	-	-	-	-	-
Wastewater Kg/Adt	-	-	-	-	X	-	-	-	-	-
Phosphorus nutrient Kg/Adt	-	-	-	-	X	-	-	-	-	X
Nitrogenous nutrient Kg/Adt	-	-	-	-	X	-	-	-	-	X
Solid waste Kg/Adt	-	-	X	-	-	-	-	-	-	-
Turpentine Kg/Adt	-	-	X	-	-	-	-	-	-	-
Ash Kg/Adt	-	-	X	-	-	-	-	-	-	-
Sludge Kg/Adt	-	-	-	-	-	-	-	-	-	X
Water treatment sludge Kg/Adt	-	-	-	-	-	-	-	-	-	X
TSS /Adt	-	-	-	-	-	-	-	-	-	X
Wood ash Kg/Adt	-	-	-	-	-	-	-	X	-	-
wood waste Kg/Adt	-	-	-	-	-	-	-	X	-	-
particulates Kg/Adt	-	-	X	-	-	-	-	X	-	-
SO <sub>2</sub> (gas) Kg/Adt	-	-	X	-	-	-	-	-	-	-
NO <sub>x</sub> Kg/Adt	-	-	X	-	-	-	-	X	-	-

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After the contribution analysis in Table 4-11, each X was given a numerical equivalent of 10% in order to obtain the percentage contribution of each elementary flow mentioned in table 4.11. The two elementary flows with the highest number of X were ranked and prioritized as the most impactful elementary flow. The two most impactful elementary flows are **Energy** followed by **water**. The relationship between each elementary flow and the process unit was represented as X in table 4.11. Therefore, the percentage contribution of energy is 100% while that of water is 60%. This means that energy affects 10 out of 10 of the selected process units followed by water which affects 6 out of 10 of the selected process units under study. This makes energy and water the two key elementary flows of concern in this LCA study.

The elementary flows listed in table 4.11 were categorized under the following headings mentioned in 4.4.11 as recommended by (ISO 14043, 1997). In subsection 4.4.11 the inventory categories of the Baseline LCA (LCA of the conventional Kraft pulp mill) were discussed.

#### ***5.3.11 Inventory category used for the baseline LCA.***

Seven inventory categories were used in the classification of every elementary flow used in the baseline LCA. The seven inventory categories used are raw material, Energy, Products, By-product, Emissions to the air, Solid waste and Emissions to the water.

**Raw materials:** Feedstock or unprocessed materials used during the production of Kraft pulp. Example wood input, chemical and water.

*Wood:* The two-wood samples used in producing the wood chips used in the production of each conventional Kraft pulp are mentioned as follows, Birch and Pine. The production stage for each of the plants was excluded from the system boundary. At the wood handling process unit, the debarked timber of each wood sample was converted to wood chips ranging between 2-8mm thickness using the sawmill. According to (Suhr et al. 2015) three metric air-dry tonnes of each wood sample will produce 1 Adt of Kraft pulp.

*Water:* Water is another important raw material used in pulp production. Some of the water consumed in the pulp and paper industry is associated with the following process units: cooking, bleaching, chemical recovery unit, washing and screening, auxiliary boiler and oxygen delignification. About 85% of the water consumed in the pulp and paper industry is consumed during Kraft pulp processing stage (JRC 2000). To process a tonne of Kraft



pulp, you will need between 15 to 100 metric tonnes of water (Suhr et al. 2015). Water is used in the conventional Kraft pulp mill in the following ways: as steam during Kraft cooking, for pre-washing of pulp from the digester, for pre-washing of pulp after oxygen delignification and post-washing of the Kraft pulp after bleaching. Finally, water is used as steam in the evaporator of the chemical recovery unit. A telephone survey was used to determine information concerning the amount of water consumed by the selected process units within the system boundary. The table below represents the outcome of the survey. Due to data protection, the names of these companies will not be mentioned here. However, the countries where the Kraft mills are located will be used to identify these pulp mills.

**Table 5-11: The outcome of the survey on water consumption from different country**

<b>Pulp mill Location</b>	Canada	Europe	Ghana	Nigeria	Nigeria	United state
<b>Name of companies</b>	C <sub>1</sub>	E <sub>1</sub>	G <sub>1</sub>	N <sub>1</sub>	N <sub>2</sub>	U <sub>1</sub>
<b>Kraft cooking process.</b>	2m <sup>3</sup>	2m <sup>3</sup>	2m <sup>3</sup>	5m <sup>3</sup>	5m <sup>3</sup>	5m <sup>3</sup>
<b>Pre-washing and screening after oxygen delignification</b>	40m <sup>3</sup>	50m <sup>3</sup>	60m <sup>3</sup>	60m <sup>3</sup>	70m <sup>3</sup>	60m <sup>3</sup>
<b>Chemical recovery unit.</b>	7m <sup>3</sup>	10m <sup>3</sup>	18m <sup>3</sup>	15m <sup>3</sup>	14m <sup>3</sup>	10m <sup>3</sup>
<b>Auxiliary boiler</b>	10 m <sup>3</sup>	10 m <sup>3</sup>	8 m <sup>3</sup>	10 m <sup>3</sup>	10 m <sup>3</sup>	10 m <sup>3</sup>
<b>Post-washing after bleaching process unit</b>	8m <sup>3</sup>	8m <sup>3</sup>	9m <sup>3</sup>	8m <sup>3</sup>	9m <sup>3</sup>	9m <sup>3</sup>
<b>Bleaching chemical preparation</b>	2 m <sup>3</sup>	2 m <sup>3</sup>	3 m <sup>3</sup>	2 m <sup>3</sup>	2 m <sup>3</sup>	1 m <sup>3</sup>
<b>Total water usage in the conventional Kraft pulp mill</b>	67m <sup>3</sup>	82m <sup>3</sup>	100m <sup>3</sup>	100m <sup>3</sup>	100m <sup>3</sup>	85m <sup>3</sup>

From the outcome of the survey, conventional pulp mills operated in developed countries consumed less water than conventional pulp mills operated in developing countries. This is because majority of pulp mill operated in developed countries like Europe, Canada and

United states are equipped with best available techniques and technologies which help in the reduction of water consumed during pulp production.

The values in table 4.13 below were chosen from the range of values provided for each mentioned process unit in table 4.12 during the survey.

**Table 5-12: Estimated amount of water consumed in the conventional Kraft pulp mill**

<b>Process unit (life cycle stages)</b>	<b>Average value of water consumed</b>
Kraft cooking process.	4m <sup>3</sup>
Pre-washing and screening after oxygen delignification.	53.3m <sup>3</sup>
Chemical recovery unit.	15m <sup>3</sup>
Post-washing after bleaching	10m <sup>3</sup>
Bleaching chemical preparation	2m <sup>3</sup>
Auxiliary boiler	9m <sup>3</sup>

From the table mentioned above, the process unit that have the highest impact on water consumption is the **washing and screening process unit** because it consumes an average of 53.3 metric tonnes of water per air dry tonne of pulp during Kraft pulp production.

**Input Chemicals:** These are chemicals required during Kraft pulp production examples are NaOH, O<sub>2</sub>, NaClO<sub>3</sub>, EDTA, H<sub>2</sub>O<sub>2</sub>, O<sub>2</sub>, MgSO<sub>4</sub> and CaO (JRC 2000). NaOH is one of the cooking chemicals used to breakdown the natural binding material holding the components of the wood, MgSO<sub>4</sub> is used to preserve the strength of the pulp during oxygen delignification (Suhr et al. 2015). EDTA acts as chelating agent and it helps in removing metal from hydrogen peroxide bleaching sequence (Pinto et al. 2015).

**Energy:** energy as an important input in the pulp and paper industry (JRC 2000). It affects every part of the Kraft pulping mill. Since we are using gate to gate LCA to look at the pulp production phase of the conventional Kraft pulp mill, it is good to know that the energy used by the discussed Kraft pulp mill is produced onsite from the recovery and Auxiliary boiler. While the energy used for start-up process are non-renewable (Suhr et

al. 2015). Kraft pulp mills might generate below or above the energy required during onsite energy generation. However, the assumption during this study is that the energy consumed plus losses is equal to the energy generated in the Kraft pulp mill under study. The energy consumed in the mill is in form of electrical and heat energy (Environ 2012). The electrical energy used by a Swedish Kraft mill to produce one tonne of pulp is between 600 – 800 kWh while the heat energy used is between 10 – 14 GJ (Suhr et al. 2015). After analysing the percentage of energy consumed by each process unit within the system boundary, we found out that the **chemical recovery process unit** impact extensively on energy because it takes up to 46% of the energy requirement during Kraft pulp production.

*Table 5-13: Tabular representation of each life cycle stage of the non-integrated modified conventional Kraft pulp mill, the pulping production energy and the percentage of the pulping production energy used per life cycle stage (Suhr et al. 2015)*

<b>Process Units of the LCA</b>	<b>conventional Kraft pulping mill (MJ/ton)</b>	<b>Percentage of Pulping production energy consumed</b>
wood handling	438	3%
cooking	2284	16%
Chemical recovery process	6642	46%
Washing and screening	198	1%
Oxygen delignification	562	4%
bleaching	799	6%
Pulp drying	4000	22%
Axillary boiler	108	1%
Bleaching chemical preparation	92	1%
Wastewater treatment	72	0%

**Emissions to the air:** These are pollutant release into the air during the Kraft pulp production. Example of emission to the air are SOX, NOx and TRS (Gavrilescu et al. 2012). These substances have serious impact on the environment and that is why we chose to discuss them. The following emissions originate from the auxiliary boiler and the chemical recovery process unit (JRC 2000). The emission released to the air during energy generation are mentioned in Table 4.15,

**Table 5-14: Emission released to the air during energy generation (JRC,2000)**

<b>Total emission released to the air</b>	<b>Quantity</b>
SOX	0.65 (Kg/Adt)
NOX	2.7 (Kg/Adt)
TRS	0.5 (Kg/Adt)

**Solid waste:** These are fraction of solid waste generated during the production of Kraft pulp. They comprise of inorganic sludge from the chemical recovery process, dreg, green liquor sludge and lime mud (Bajpai 2015). They are also other solid waste generated from other process unit during the pulp production example bark, reject and wood residues from wood handling process unit, sludge from effluent treatment, dust and ash from boilers and furnace (Bajpai 2015).

**Emissions to the water:** These pollutants are release into water bodies from process unit like washing process, screening process, and bleaching etc. Example of main emission to the water are COD, BOD, TSS, and AOX (Lopes et al. 2003). These substances contaminate water source when effluent is discharged carelessly.

**Product:** According to (ISO 14040, 2006) product is defined as any service or goods that can be offered to the market and sold to satisfy consumers need. In the pulp production mill, the main product is the manufactured pulp which is conveyed to the pulp dryer where the pulp is dried before transporting them to either the pulp storage units, paper mill or pulp markets.

**By-product:** These are secondary products generated from the Kraft pulp production process. Example of the by-product generated during Kraft pulp production are Tall-oil, crude sulfate turpentine and extractives.

Furthermore, ranking the life cycle stages based on their contribution towards the most important elementary flow helped to also show the life cycle stage of most importance. The ranking process for the life cycle stages was done by finding process unit which have a significant influence towards energy and water as already demonstrated in table 4.13 and 4.14. Table 4.14 shows that the chemical recovery process is the life cycle stage or process unit with the biggest influence on energy because it consumes 46% of the energy

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required during Kraft pulp production. While the washing and screening process unit in table 4.13 have the biggest influence on the water consumption level.

### **Summary of inventory phase**

A detail description of each unit process in the Kraft pulp mill under study was done in the inventory phase. The source of the data collected, unit conversions and calculations were also explained at the inventory phase of the LCA. During the inventory analysis we discovered energy and water as the two most impactful elementary flows. Energy influence 10 out of 10 of the selected process unit (life cycle stages), making it the top of the chart when discussing elementary flow of concern. According to the inventory, energy is a big issue in the pulp and paper industry. In addition, water influenced 6 out of 10 of the selected process unit, making it the second top of the chart when discussing elementary flow of concern. Furthermore, water footprint in pulp and paper industry is a matter of great concern and need urgent attention. We also discovered that the chemical recovery process unit is the process unit with the highest impact on energy consumption because it consumes up to 46% energy during Kraft pulp production. On the other hand, the washing & screening process unit is the most impactful process unit effecting water consumption because 53.3m<sup>3</sup> of water is consumed by this process unit during Kraft pulp production.

The major elementary flows released during energy generation by the recovery boiler (chemical recovery unit) and bark boiler (auxiliary boiler) are SO<sub>x</sub>, NO<sub>x</sub> and TRS. These elementary flows cause Acidification, Respiratory inorganic, human toxicity, and Climatic change. Therefore, Section 4.5 will analyse the impact of pulp production energy on the environmental impacts (Acidification potential, Respiratory inorganic, Human toxicity, and Climatic change) caused by the release of SO<sub>x</sub>, NO<sub>x</sub> and TRS into the atmosphere using the Environmental impact assessment.

### **5.4 Environmental Impact assessment for pulp production energy and water consumption**

The environmental impact of energy and water use in the conventional Kraft pulp mill was discovered using the mandatory element of the environmental impact assessment phase of the LCA methodology. The first mandatory element used during the environmental impact assessment was the same as those indicated in table 3.1. While the

second mandatory element (classification) and third mandatory element (characterisation) was further used to analyse the environmental impact of energy and water use. See section 4.5.1 to 4.5.4 for details.

#### **5.4.1 Classification (Assigning LCI results to the selected impact categories from Energy as an elementary flow of importance)**

During energy generation in Kraft pulping mill, the recovery boiler as part of the chemical recovery process unit and the bark boiler as part of the axillary boiler, released emissions to the air. The impact of these released emissions is interpreted by matching the released emissions with the environmental problem they create.

**Table 5-15: Elementary flows assigned to the selected impact category (Classification)**

Elementary flow	Impact categories			
	CC	HT	AP	RI
NO <sub>x</sub>	(NO <sub>x</sub> , CC)		(NO <sub>x</sub> , AP)	(NO <sub>x</sub> , RI)
SO <sub>x</sub>		(SO <sub>x</sub> , HT)	(SO <sub>x</sub> , AP)	(SO <sub>x</sub> , RI)
TRS			(TRS, AP)	(TRS, RI)

After the elementary flows were assigned to the selected impact categories, effect of each elementary flow on the selected impact category was quantified by characterisation as discussed in section 4.5.2 and 4.5.3.

#### **5.4.2 Calculation of the category indicator result (characterisation)**

This is the third mandatory element of the environmental impact assessment. At the characterisation stage, each elementary flow is multiple by the characterisation factor to generate an impact score as shown in table 4.17, 4.18 and 4.19. The impact score is a numerical value that indicates the quantity of environmental problem the elementary flow contributes to the environment. The impact score obtained from the characterization is expressed in a unit common to all other elementary flows contributing to that environmental problem. For each elementary flow assigned to an impact category, there is a characterisation factor, which gives a quantitative representation of its importance.

**Table 5-16:** The quantity of each elementary flow and the characterisation factors of each impact categories used for this study

Elementary flows	Quantity of emission (Kg/Adt)	Impact category			
		Climatic Change kg (CO2)	Human Toxicity kg(14DCB)	Respiratory Inorganic kg (PM10)	Acidification kg (SO2)
Emission from both Recovery boiler and Bark Boiler					
SOX	0.65	CF=0	CF=9.60E-02	CF= 0.032	CF=1
NOX	2.7	CF =264	CF=0	CF= 1.50E-04	CF= 0.7
TRS	0.5	CF=0	CF=0	CF= 0.22	CF= 1.88

CF - Represent characterisation factor

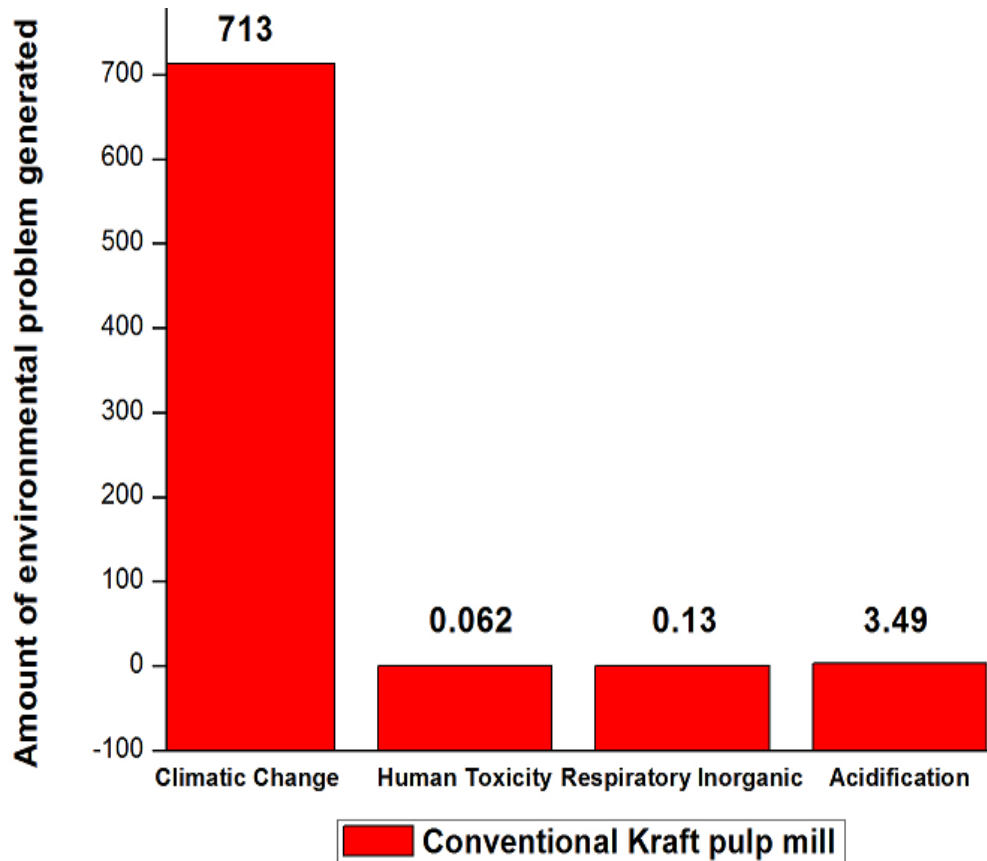
**Table 5-17:** Calculation to achieve the impact score of each impact category

Elementary flow	Impact categories			
	CC	HT	AP	RI
NOx	(2.7* 264)		(2.7* 0.7)	(2.7*1.50E-04)
SOx		(0.65*9.60E-02)	(0.65* 1)	(0.65 *0.032)
TRS			(0.5 1.88)	(0.5*0.22)

**Table 5-18:** Summation of all the impact scores from different impact category to achieve the characterisation of each impact category for the conventional Kraft pulp mill.

Elementary flows	Impact category			
	Climatic Change kg (CO2)	Human Toxicity kg(14DCB)	Respiratory Inorganic kg (PM10)	Acidification kg (SO2)
Emission from Recovery boiler and Bark Boiler				
NOX	713	0.0624	0.0208	0.65
SOX	0	0	0.0004	1.9
TRS	0	0	0.11	0.94
<b>Characterisation</b>	<b>713</b>	<b>0.0624</b>	<b>0.1312</b>	<b>3.49</b>

The outcome of the characterisation was compared and represented in figure 4.12. In figure 4.12, climatic change appears to be the most significant environmental problem.



*Figure 5-12: Environmental problems generated during energy generation in the conventional Kraft pulp mill.*

**5.4.3 Classification (Assigning elementary flow to the selected impact categories from water consumption)**

During Kraft pulp production, 6 out of 10 process units needed water to function effectively, making water the second most important elementary flow in the Kraft pulp production process. In the method of classification discussed in chapter 3, the impact category was assigned to the average water consumed by the selected process unit within the system boundary. The water consumed was matched with the environmental problem created due to water consumption.



**Table 5-19: Elementary flows assigned to the selected impact category (Classification)**

Elementary flow	Impact category
	Fresh water depletion (WD)
Water use during Kraft cooking process (WKC).	(WKC, WD)
Water use during Pre-washing and screening after oxygen delignification (WWS).	(WWS, WD)
Water used in the Chemical recovery unit. (WCRU)	(WCRU, WD)
Post-washing after bleaching (WB)	(WB, WD)
Bleaching chemical preparation (WBCP)	(WBCP, WD)
Auxiliary boiler (WAB)	(WAB, WD)

After the classification, we proceeded with determining the characterisation. But first, we had to find the characterisation factor of the selected impact category (**Fresh water depletion**). The characterisation factor of freshwater depletion is  $1\text{m}^3$  (Brauman et al. 2016).

#### 5.4.4 Characterisation (Calculation of the category indicator result)

As discussed in section 4.5.2, characterisation is the third mandatory element of the environmental impact assessment, achieved by finding the characterisation factor of the impact category as shown in table 4.21. Secondly, matching and calculating the impact score of the selected impact category as shown in table 4.22 and 4.23. Finally, all the impact scores were summed up to achieve the characterisation for freshwater depletion due to water use in the conventional Kraft pulp mill.

**Table 5-20: The characterisation factor of the selected impact category for water use**

Impact category	Abbreviation	Category indicator	Characterisation factor	Characterisation model
Fresh water depletion	WD	Water depletion	$1\text{m}^3/\text{m}^3$	Recipe 2008

**Table 5-21:** The quantity of each elementary flow and the characterisation factors of the selected impact category for water use

Elementary flows	Quantity of water consumed (m <sup>3</sup> /Adt)	Impact category
		Fresh water depletion m <sup>3</sup> /m <sup>3</sup>
Water consumption		
Water use during Kraft cooking process (WKC).	4	CF=1
Water use during Pre-washing and screening after oxygen delignification (WWS).	53.3	CF =1
Water used in the Chemical recovery unit. (WCRU)	15	CF=1
Post-washing after bleaching (WB)	10	CF=1
Bleaching chemical preparation (WBCP)	2	CF=1
Auxiliary boiler (WAB)	9	CF=1

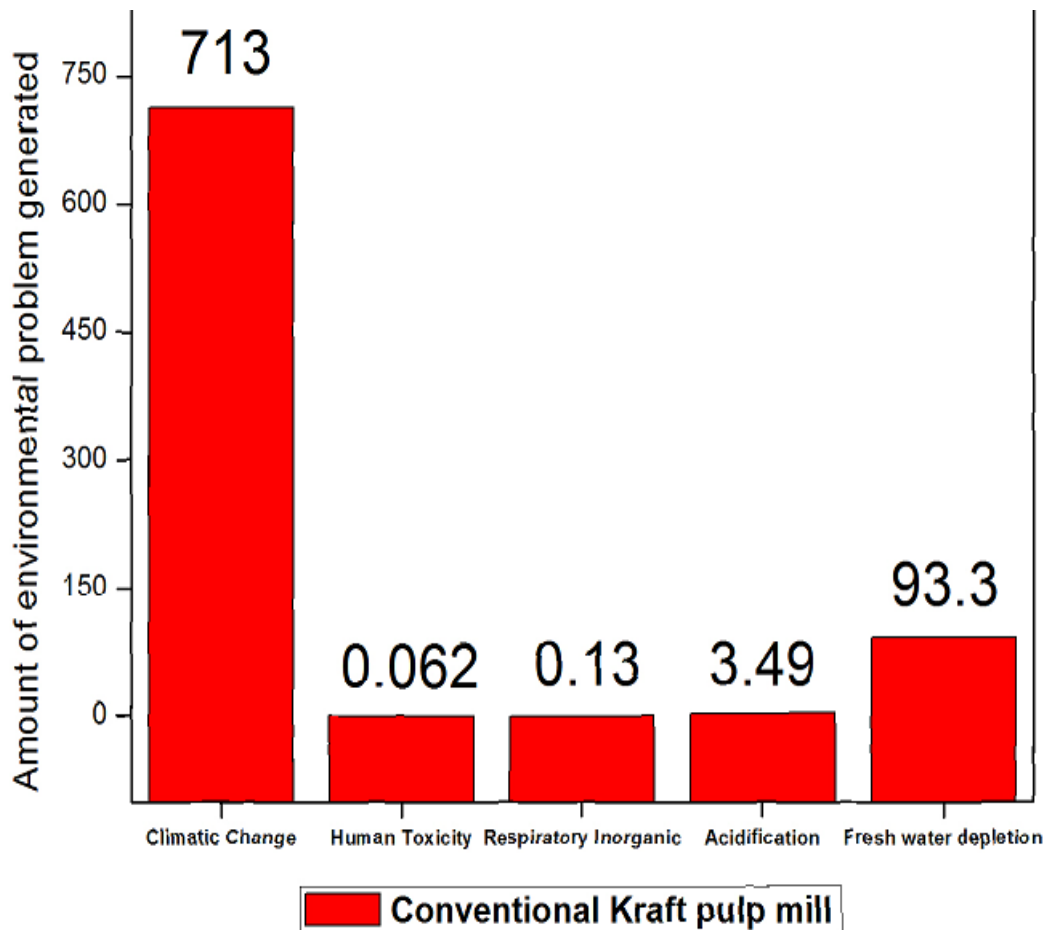
**Table 5-22:** Calculation to achieve the impact score of each impact category

Elementary flow	Impact category
Water use	Water depletion (WD)
Water use during Kraft cooking process (WKC).	$(4 * 1) m^3$
Water use during Pre-washing and screening after oxygen delignification (WWS).	$(53.3 * 1) m^3$
Water used in the Chemical recovery unit. (WCRU)	$(15 * 1) m^3$
Post-washing after bleaching (WB)	$(10 * 1) m^3$
Bleaching chemical preparation (WBCP)	$(2 * 1) m^3$
Auxiliary boiler (WAB)	$(9 * 1) m^3$

**Table 5-23:** Summation of all the impact scores from the impact category to achieve the characterisation of water use in the conventional Kraft pulp mill.

<b>Elementary flow</b>	<b>Impact category</b>
<b>Water use</b>	<b>Water depletion (WD) <math>m^3</math></b>
Water use during Kraft cooking process (WKC).	4
Water use during Pre-washing and screening after oxygen delignification (WWS).	53.3
Water used in the Chemical recovery unit. (WCRU)	15
Post-washing after bleaching (WB)	10
Bleaching chemical preparation (WBCP)	2
Auxiliary boiler (WAB)	9
<b>Characterisation</b>	<b>93.3</b>

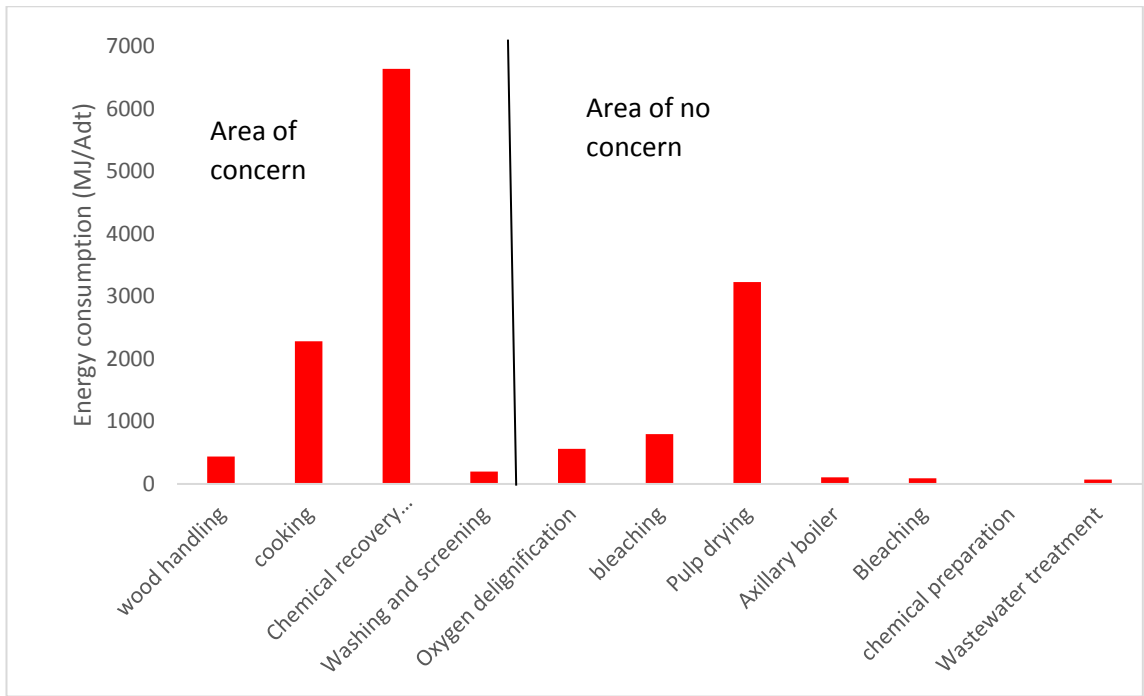
In summary, the entire environmental problem generated because of energy generation and water use in conventional Kraft pulp mill during Kraft pulp production were compared as shown in figure 4.13 and climate change was identified as the most significant environmental problem generated during Kraft pulp production.



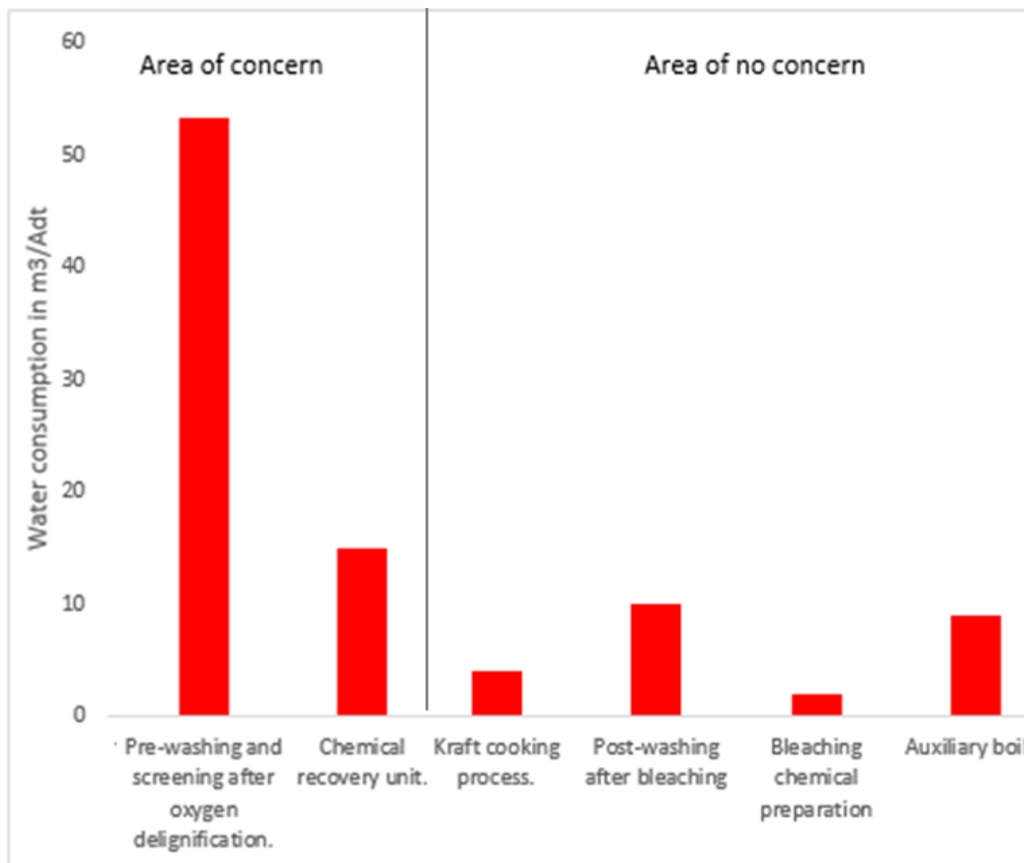
*Figure 5-23: Comparing the environmental problem generated as a result of energy generation and water use in conventional Kraft pulp mill during Kraft pulp production.*

### 5.5 Life cycle interpretation

During the inventory analysis energy and water use were identified as the two key elementary flow of concern. While the chemical recovery unit and the washing and screening process are the two main process units contributing towards the key elementary flows of concern as demonstrated in figure 4.14 and 4.15.



**Figure 5-34:** Energy consumed in a Conventional Kraft Pulp mill



**Figure 5-4:** Average quantity of water consumed in a conventional Kraft pulp mill

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During the environmental impact assessment, climatic change was identified as the most significant environmental problem when compared to respiratory inorganic, acidification potential, human toxicity and freshwater depletion as demonstrated in figure 4.13. After identifying the issues of concern as indicated in the first element of the LCA interpretation phase, I moved to the evaluation stage. Evaluation is the second stage of the LCA interpretation phase. According to (ISO 14044:2006), the purpose of evaluation is to improve confidence and trustworthiness in the LCA result. The result of the LCA was evaluated through consistency check, completeness check and sensitivity check. See sub section 4.6.1, 4.6.2 and 4.6.3 for more details.

### ***5.5.1 Consistency check***

The consistency check finds out whether the assumptions and approaches used to acquire the data used throughout the LCA analysis are consistent. A consistency check was carried out on the ten selected process unit within the system boundary by using the six main characteristics of data acquisition as mentioned in table 4.25. The first characteristic mentioned in the table below is Data source. The main sources of data use for the LCA are from secondary source (S). The rest of the data used were obtained from primary source (P). The second characteristic of data acquisition mentioned in table 4.25 is Data accuracy. The data used for this study was accurate because they were check against different sources. Under data accuracy, the word **Yes** in the table means that the data used in the LCA is accurate regardless of the data age. In addition, the data used in the LCA was data between 1 to 20 years old. Furthermore, the technologies used to either obtain the primary or secondary data used for the LCA were obtained from Best Available Technology (BAT). The time related coverage for data used for this study were from 2000 till date. The geographical coverage of all the data used for this study was collected from Europe, Canada, Nigeria, Ghana or USA as shown in table 4.25. After the consistency check, the outcome was represented in table 4.26.

**Table 5-24: Consistency check analysis**

	<b>WH</b>	<b>C</b>	<b>CRP</b>	<b>WAS</b>	<b>B</b>	<b>BCP</b>	<b>OD</b>	<b>AB</b>	<b>PD</b>	<b>WWT</b>
Data source	S	S&P	S&P	S&P	S&P	S&P	S	S&P	S	S
Data accuracy	YES	YES	YES	YES	YES	YES	YES	YES	YES	YES
Data Age	1-20 years	1-20 years	1-20 years	1-20 years	1-20 years	1-20 years	1-20 years	1-20 years	1-20 years	1-20 years
Technology coverage	BAT	BAT	BAT	BAT	BAT	BAT	BAT	BAT	BAT	BAT
Time related coverage	2000-2013	2000-2019	2000-2019	2000-2019	2000-2019	2000-2019	2000-2001	2000-2019	2000-2001	2000-2001
Geographic coverage	Canada Europe Ghana, Nigeria USA	Canada, Europe, Ghana, Nigeria, USA.	Canada, Europe, Ghana, Nigeria, USA.	Canada, Europe, Ghana, Nigeria, USA.	Canada, Europe, Ghana, Nigeria, USA.	Canada, Europe, Ghana, Nigeria, USA.	Canada, Europe, Ghana, Nigeria, USA.	Canada, Europe, Ghana, Nigeria, USA.	Canada, Europe, Ghana, Nigeria, USA.	Canada, Europe, Ghana, Nigeria, USA.

*S- Secondary source, P- Primary source, BAT- Best available technology*

**Table 5-25: Outcome of the consistency check**

Characteristics of data acquisition	Consistency check	Action
<i>Data source</i>	Not consistent	No-action required
<i>Data accuracy</i>	consistent	No-action required
<i>Data Age</i>	Not consistent	No-action required
<i>Technology coverage</i>	consistent	No-action required
<i>Time related coverage</i>	Not consistent	No-action required
<i>Geographic coverage</i>	Not consistent	No-action required

### 5.5.2 Completeness check

The completeness check ensures that the elementary flow going in and out of the selected process units during the inventory analysis are obtainable and complete. The input and output of each process unit in table 4.27 was clearly checked and marked X if obtainable,

followed by a “Yes”. The Yes means that the information obtained for the selected process units are complete and do not need further verification. However, if the response in the box is NO, data is missing from the inventory of the process units. The first action (AR<sub>1</sub>) is to use proxy. Once the missing inventory data is replaced, the next box is completed with a “Yes”. This means that the missing inventory data have been found and a second action is not required. Table 4.27 presents the outcome of the completeness check.

**Table 5-26: A summary of the completeness check**

Process units (Life cycle stage)	Is the inventory data obtainable?	Is the inventory data Complete ?	First action required (AR <sub>1</sub> )	Is the inventory data Complete?	Second action required (AR <sub>2</sub> )
Wood handling	x	Yes	None	Yes	None
Kraft cooking	x	No	Check for proxy	Yes	None
Washing & screening	x	Yes	None	Yes	None
Oxygen delignification	x	No	Check for proxy	Yes	None
Bleaching	x	Yes	None	Yes	None
Bleaching chemical preparation	x	Yes	None	Yes	None
Chemical recovery process	x	Yes	None	Yes	None
Pulp drying	x	Yes	None	Yes	None
Internal waste treatment	x	Yes	None	Yes	None
Axillary boiler	x	Yes	None	Yes	None

X - Entry available



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### **5.5.3 Sensitivity check**

The sensitivity check was used to check the impact of change in assumptions or determine key factors that may have impact on the study outcome (Hauschild et al. 2018). Therefore, the sensitivity check in this study will help evaluate the outcome of using different particle sizes on energy consumption in the conventional Kraft pulp mill. The sensitivity check was carried out in sub section 6.7.1.

## **5.6 Conclusion, limitation, and recommendation**

This is the third element of the LCA interpretation phase. It summarizes what has been discovered in the second and third phase of the LCA with respect to the goal and scope of the study, pointing out the limitations of the study and making recommendations.

### **5.6.1 Conclusion**

The big challenge with the conventional Kraft pulp mill is that it is not environmentally sustainable. This is because it consumes lot of energy and water, which has a lot of impact on the pulp mill environment. Conducting a life cycle assessment on the conventional Kraft pulp mill has provided information to identify areas where the conventional Kraft pulp paper mill can be improved. The result of the inventory analysis and impact assessment has shown the two key elementary flow of concern and the process unit effecting those elementary flows, allowing the industry to improve its environmental performance by changing the way things are done in the Kraft pulp production stage.

### **5.6.2 Limitations**

The data used for the LCA are mostly secondary data. Therefore, could be generated under different conditions (Curran, 2014). The knowledge on how these data were generated is not well known. The locations, age and technologies used to generate this data might vary in different ways reducing the consistency and completeness of the information used for the LCA study.

### **5.6.3 Recommendation**

One of the ways to make the Kraft pulp mill environmentally sustainable is to reduce the impact of energy generation and sustained water pumping on the environment by reducing energy and water consumption. Therefore, reducing the particle size from 8mm currently used in the conventional Kraft process to < 2mm will reduce the total energy

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consumed. According to (Dang and Nguyen 2008) chip thickness is an important dimension that affect the rate at which the cooking liquor penetrate the capillary structure of the woodchips. In fact, when the woodchip thickness is more than 3mm the rate at which the cooking liquor diffuse into the chip is reduced, making the pulp produced non-uniform, with plenty of rejects. In addition, more raw materials like water and chemicals are used.

Secondly, the use of a re-usable liquid (Hexane) as part of the washing process could reduce water consumption. Furthermore, hexane can help absolve the volatile organic compounds released into the air as pollutant after cooking and during the concentration of weak black liquor in the evaporator. The use of hexane as an organic solvent will help in the extraction of value-added compounds from the black liquor as already demonstrated in the outcome of the work done by (Al-Kaabi, Z et al, 2017). Finally, I propose the use of hexane will reduce the amount of water used in the pre-washing and chemical recovery stage of the Kraft pulp, reduce emission release in the air and enable the recovery of value-added chemical. Therefore, the outcome of the experiment in chapter 5 will confirm whether change in woodchip size and the use of hexane as part of the washing liquid will help reduce energy consumption with high emission, water use and generate a value-added compound.

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## Chapter 6- Effect of using different particle size and hexane as part of the Pulp Washing Liquor.

### 6.1 Introduction

In Chapter 4, the inventory phase and the impact assessment phase of the LCA was used to identify energy as the most impactful elementary flow because it affected 100% of the process unit within the system boundary, followed closely by water use, which affected 60% of the selected process unit within the system boundary. Therefore, reducing the particle size from 8mm to < 2mm(0-2mm) and replacing part of the water used during pulp washing with recoverable hexane could help in the reduction of energy consumption, reduction of water consumption and produce value added chemicals. Reducing the energy and water consumption will go a long way towards making the conventional Kraft pulp mill environmentally sustainable and industrially viable. Therefore, in this chapter we will see how reducing the wood particle size from 8mm currently used in the conventional Kraft process to < 2mm (0-2mm) and replacing part of the water during washing with recoverable hexane leads to generation of green crude, reduction of energy and water consumption.

### 6.2 Mass balance of the samples used

Using (Nati et al. 2010) method with modification, the percentage size distribution of the samples used for the experiment was shown in Table 5.1. The size distribution of the samples used was achieved by using a high-performance stainless sieve shaker, ranging from 20  $\mu$ m to 125 mm, Amplitude between 0 - 3 mm with digital setting of 0.1 mm steps in "Closed Loop" amplitude control (Endecott's limited, UK). To separate the woodchips into different particle sizes. The samples retained at different level of the sieve were categorized into 0-2mm for sample retained in the bottom Container of the sieve, 2-4mm for sample retained in the 2mm sieve, 4-8mm for sample retained in the 4mm sieve and > 8mm for particles retained in the 8mm sieve. The percentage mass balance was also recorded respectively in the Table 5.1

**Table 6-1:** Shows the particle size distribution per 10g of the sample used for the experiment

Size of stainless sieve	Particle size retained	Mass balance (%)
8mm sieve	Particles size (>8mm)	0.7
4mm sieve	Particle size (4-8mm)	27.3
2mm sieve	Particle size (2-4mm)	40.5
Container at the bottom of the sieve	Particle size (0- 2mm)	31.7

In summary, the separation of the samples using high performance stainless sieve shakers show that each 10g analysed contains 31.7% of particles size 0-2mm, 40.5% of particle size 2-4mm, 27.3% of particle size 4-8mm and 0.7% of particles above 8mm.

### 6.3 Kraft cooking

In table 5.2 the result obtained from cooking birch sample are shown. The cooking procedure has been discussed in chapter 3. After cooking, the Particle size, cooking time (Mins), Weight of Particle before cooking (g), Weight loss in wood after cooking (g) and Percentage weight loss for Birch and Pine was recorded in Table 5.2 and 5.3.

**Table 6-2:** Outcome of cooking the birch wood samples

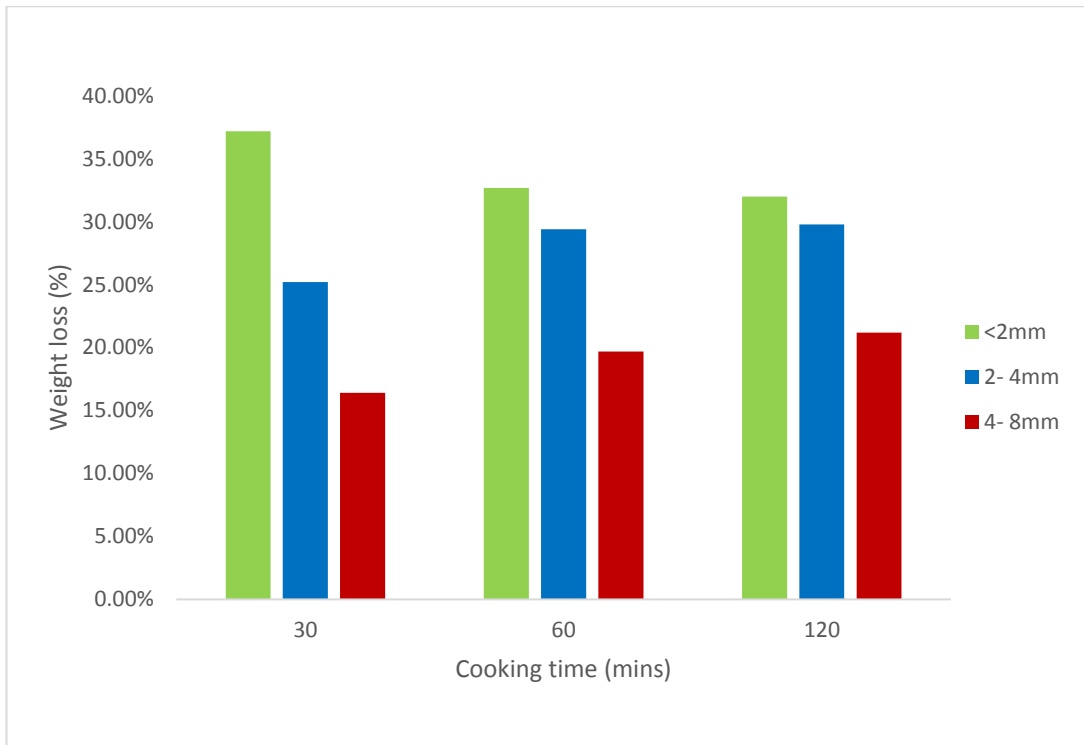
Particle size	Cooking time (Mins)	Weight of Particle before cooking (g)	Weight of Particle after cooking (g)	Weight loss in wood after cooking (g)	Percentage weight loss
2mm	30	10	6.28	3.72	37.2%
2mm	60	10	6.73	3.27	32.7%
2mm	120	10	6.80	3.20	32%
4mm	30	10	7.48	2.52	25.2%
4mm	60	10	7.06	2.94	29.4%
4mm	120	10	7.02	2.98	29.8%
8mm	30	10	8.36	1.64	16.4%
8mm	60	10	8.03	1.97	19.7%
8mm	120	10	7.88	2.12	21.2%

In table 5.3 the result obtained from cooking pine sample are shown. The cooking procedure has been discussed in chapter 3.

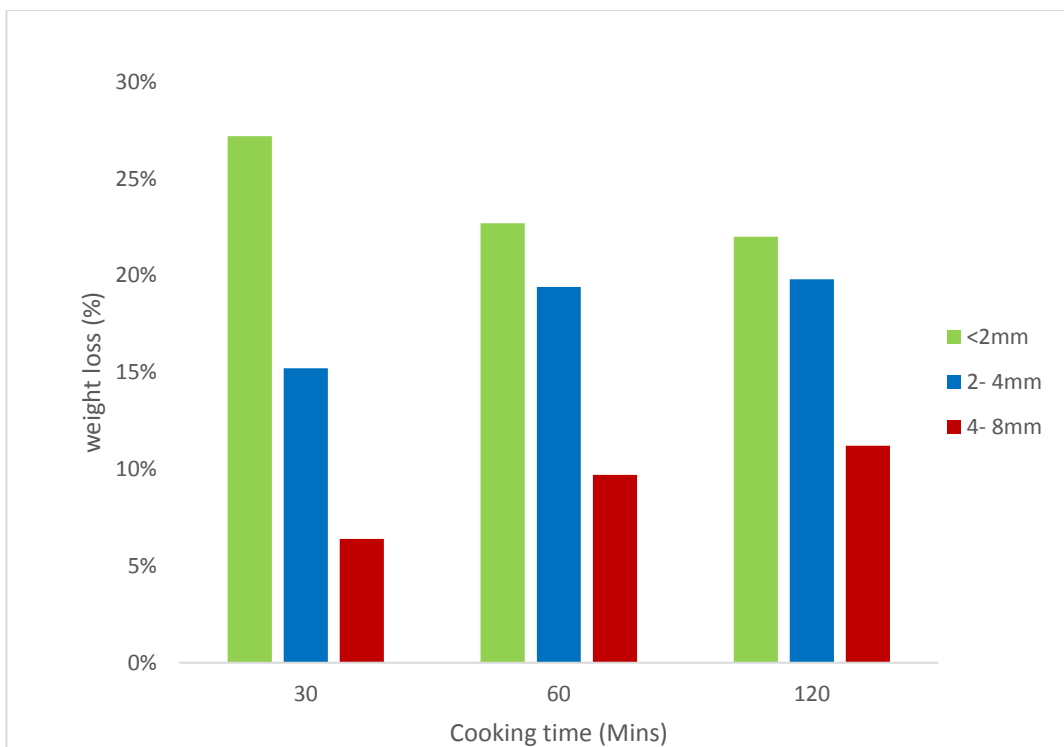
**Table 6-3:** *Outcome of cooking the pine wood samples*

Particle size	Cooking time (Mins)	Weight of Particle before cooking(g)	Weight of Particle after cooking (g)	Weight loss in wood after cooking (g)	Percentage weight loss
2 <sub>30</sub>	30	10	7.28	2.72	27.2%
2 <sub>60</sub>	60	10	7.73	2.27	22.7%
2 <sub>120</sub>	120	10	7.80	2.20	22.0%
4 <sub>30</sub>	30	10	8.48	1.52	15.2%
4 <sub>60</sub>	60	10	8.06	1.94	19.4%
4 <sub>120</sub>	120	10	8.02	1.98	19.8%
8 <sub>30</sub>	30	10	9.36	0.64	6.4%
8 <sub>60</sub>	60	10	9.03	0.97	9.7%
8 <sub>120</sub>	120	10	8.88	1.12	11.2%

In Figure 5.1 and 5.2, the relationship between particle size, cooking time and the rate of delignification under Kraft cooking condition is shown. The Y axis of the bar chart in Figure 5.1 and 5.2 represents the weight loss in percent of the wood samples while the X axis represents the cooking time, which is 30mins, 60mins and 120mins. The cooking time is the time it takes the lignin material binding the cellulose and hemicellulose together in the wood to disintegrate. In Figure 5.1 and 5.2, the green legend represents particle size 0-2mm; the blue legend represents particle size 2-4mm and the red legend represents particle size 4-8mm.



**Figure 6-1:** The relationship between size (thickness) of woodchips, cooking time and the rate of delignification for birch sample.



**Figure 6-2:** The relationship between size (thickness) of woodchips, cooking time and the rate of delignification for pine sample.

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Figure 5.1 and 5.2 depicts that smaller woodchip require less cooking time and less energy consumption because the cooking time is directly proportional to the amount of heat energy consumed when cooking the wood sample. In addition, the Kraft cooking experiment helped us to also understand that smaller particle size experience faster rate of delignification due to increase in the chips surface area (Drzymala 1993). While big particle sizes require longer cooking time and larger heat energy, increasing the total pulp production energy consumed. Furthermore, the larger particle size experience slower rate of delignification, meaning that the wood sample must cook for a longer time to encourage proper diffusivity of the cooking liquor and the effective cooking of the woodchips. After independently cooking the woodchips for 30min using the batch cooking process, particle size 0-2mm experienced a weight loss of 37.2% for birch and 27.2% for pine, particle size 2-4mm experienced a weight loss of 25.20% for birch and 15.20% for pine, while particle size 4-8mm experience a weight loss of only 16.40% for birch and 6.40% for pine, when the weight of the woodchips after cooking was subtracted from the original weight of the woodchips before cooking. However, fresh particle sizes 0-2mm was cooked under the same cooking conditions with a different cooking time (60mins). After cooking at 60mins, particle size 0-2 mm experienced a weight loss of 32.70% for birch and 22.70% for pine, particle size 2-4mm experienced a weight loss of 29.40% for birch and 19.40% for pine and particle size 4-8mm experience a weight loss of 19.70% for birch and 9.70% for pine, when the weight of each woodchip after cooking was subtracted from the original weight of the woodchips before cooking. The last batch of woodchips was cooked with the same cooking condition at a different cooking time. After cooking for 120min, particle size 0-2mm experienced a weight loss of 32% for birch and 22.00% for pine, particle size 2-4mm experience a weight of 29.80% for birch and 19.80% for pine. Particle size 4-8mm experienced a weight loss of 21.20% for birch and 11.20% for pine. Figure 5.1 and 5.2 was used to demonstrate the relationship between cooking time, particle size and the rate delignification.

Finally, Figure 5,1 and 5.2 shows that smaller particle size (<2mm cooked in 30min) experienced fast delignification rate due to larger surface area. Particle size 0-2mm cooked in 30mins was identified as the ideal particle size for Kraft biorefinery because it took a shorter time to disintegrate the lignin material binding the cellulose and hemicellulose of the wood sample together. This implies that energy is conserved, and less emission released when particle size 0-2mm is used. During Kraft cooking, the

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cooking time is directly proportional to the energy consumed. Therefore, the longer the cooking time the larger the energy consumed. However, the shorter the cooking time the smaller the energy consumed. In other words, chip thickness is directly proportional to the rate of delignification. The difference in the percentage weight loss between birch and pine indicates the difference in the two-wood sample. Birch as a hardwood cook faster with lower Kappa number while pine as a softwood cook slower with higher Kappa number indicating the rate of delignification is faster in birch as compared to pine.

#### 6.4 Outcome of the liquid-to-liquid extraction



*Figure 6-3: Liquid to liquid extraction of the black liquor from the birch wood sample.*

Figure 5.3 shows the picture of the hexane mixed with black liquor sample from birch wood during the liquid–liquid extraction experiments. Figure 5.3 is significant because it shows there was a separation between the organic phase and the aqueous phase with extraction taking place after agitating the black liquor from birch wood sample with hexane. To obtain the amount of organic compound extracted from the black liquor after the Liquid - Liquid extraction, the weight of the black liquor after 90 mins of extraction was subtracted from the weight of the black liquor before extraction.

Table 5.4 and 5.5 s representation of all the parameters measured and calculated before and after the Liquid – Liquid Extraction of the nine samples obtained from cooking each particle size (PS). Each of the PS was cooked at three different cooking time ( $C_{T \text{ mins}}$ ) to obtain the strong Kraft Spent Liquor (SKSL). The table also contain recorded weight of empty vial + weight of black liquor before extraction (WEV + BLBE) and weight of black



liquor at 90 mins after extraction (WEV+ BLAE). Further explanation of the abbreviations in the tables 5.4 and 5.5 can be found in section 3.6.5.

**Table 6-4:** *The results obtained before and after the liquid–liquid extraction Experiment of birch sample*

Particle sizes	Cooking time (mins)	WEV + BLBE (g)	WEV+ BLAE (g) @90mins
2mm	30	11.89	10.03
2mm	60	11.80	10.20
2mm	120	11.89	10.23
4mm	30	11.77	11.09
4mm	60	12.64	11.29
4mm	120	11.95	10.55
8mm	30	11.93	11.69
8mm	60	11.92	11.49
8mm	120	12.81	12.28

**Table 6-5:** *The results obtained before and after the liquid–liquid extraction experiments of pine sample.*

Particle sizes	Cooking time	WEV + BLBE (g)	WEV+ BLAE @90mins
2mm	30	11.89	10.53
2mm	60	11.80	10.69
2mm	120	11.89	10.81
4mm	30	11.77	11.36
4mm	60	12.64	10.75
4mm	120	11.95	11.02
8mm	30	11.93	11.83
8mm	60	11.92	11.70
8mm	120	12.81	11.53

#### **6.4.1 Effect of using hexane as part of the washing liquid**

Using hexane as 50% of the washing liquid reduced the volume of water consumed in the washing and screening process unit from 53.3 m<sup>3</sup> to 26.7m<sup>3</sup> and the amount of water

consumed in the chemical recovery process unit from 15 m<sup>3</sup> to 7.5m<sup>3</sup> during Kraft pulp production. For details on how the volume of water consumed was obtain, see chapter 4. Also visit chapter 6 to see how the environmental impact assessment was used to examine the influence of water consumption on Kraft pulp mills. In addition, hexane was used to extract organic compounds (green crude) which add value to the Kraft pulp mill. In table 5.6 and 5.7, the amount of extractable organic compound extracted with Hexane from the black liquor is shown.

**Table 6-6:** *Percentage of Green crude present in birch wood.*

Particle size (mm)	Cooking time	(W <sub>EV+L</sub> + BL <sub>BE</sub> )	(W <sub>EV+L</sub> + BL <sub>AE</sub> ) @ 90mins	Amount of extractable organic compounds extracted by hexane (g)
<2mm	30	11.89	10.03	1.86
<2mm	60	11.80	10.20	1.60
<2mm	120	11.89	10.23	1.57
4mm	30	11.77	11.09	0.68
4mm	60	12.64	11.29	1.35
4mm	120	11.95	10.55	1.40
8mm	30	11.93	11.69	0.24
8mm	60	11.92	11.49	0.45
8mm	120	12.81	12.28	0.53

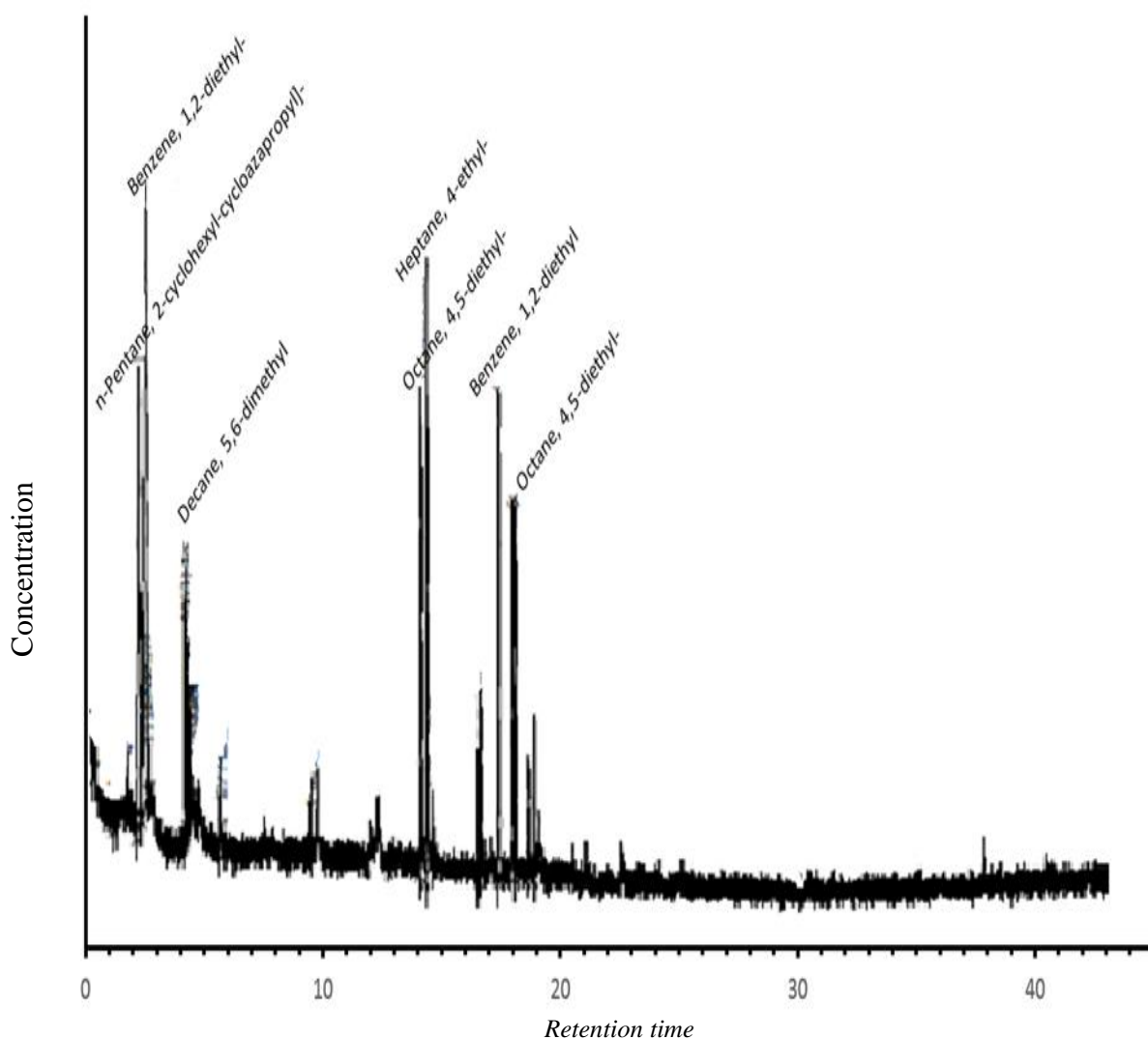
**Table 6-7:** Percentage of Green crude present in pine wood.

Particle sizes	Cooking time	$W_{EV} + L + BL_{BE}$	$W_{EV} + L + BL_{AE}$ @90mins	Amount of Green crude extracted (g)
<2mm	30	11.89	10.53	1.36
<2mm	60	11.80	10.69	1.11
<2mm	120	11.89	10.81	1.08
4mm	30	11.77	11.36	0.41
4mm	60	11.64	10.75	0.89
4mm	120	11.95	11.02	0.93
8mm	30	11.93	11.83	0.10
8mm	60	11.92	11.70	0.22
8mm	120	11.81	11.53	0.28

Therefore, the extract from the birch wood sample was subjected to a qualitative analysis using GC/MS because the birch wood sample generated more quantity of extractable organic compound than the pine wood sample as shown in table 5.6 and 5.7. In addition, the GC/MS results obtained from the birch wood samples are explained in section 5.5.

### 6.5 The GC/MS experiment

Figure 5.4 is a chromatogram with different patterns representing the constituent of the extract obtained after washing the pulp of particle size 2mm cooked in 30 min with washing liquid containing 50% hexane. During the Kraft cooking and liquid to liquid extraction, particle size 2mm cooked in 30mins showed more prospect than any other particle size based on the result of the Kraft cooking and liquid to liquid extraction as represented in Figure 5.1, 5.2 and Table 5.4, 5.5. The method used to achieve the result of the GC/MS has been already described in section 3.6.6 of chapter 3. The X-axis of the chromatogram represents the retention time. It is the time it took the analytes to pass through the GC Column and reach the mass spectrometer detector (Chauhan et al. 2014). While the peaks on the Y-axis reflect the concentration of the specific analytes present in the extract. Figure 5.4 shows that the organic compounds present in the extract contain a higher concentration of the following aromatic hydrocarbon represented at the peaks of the chromatogram below.



**Figure 6-4:** Chromatogram of hexane black liquor extract for particle size 0-2mm cooked for 30min, identified peaks and names of compounds showing those peaks.

### 6.5.1 Analysis of the GC/MS result

Table 5.8 represent few of the highest peaks from the GC/MS results obtained from particle size 2mm cooked in 30mins. The result obtained after analysing the extract from liquid-liquid extraction were sorted and represented according to their Area, retention time, category and compound name. The lignin in the black liquor depolymerised during Kraft cooking and the product generated comprise of aromatic compound, naphthenic compound and paraffinic compound as shown in table 5.8. During the gas chromatograph, majority of the aromatic and naphthene had weaker interaction with the stationary phase of the GC column (Chauhan et al. 2014). As a result, the aromatic and naphthene had shorter retention time compared to the paraffins.

**Table 6-8:** GC/MS result obtained from analysing black liquor of particle size 2mm cooked in 30mins

Retention time (R) mins	Area of the chromatograph (%)	Aromatic (A), paraffin (P) and Naphthene (N)	Name of compound
18.9	6.74	A	Benzene, 1,2-diethyl-
8.8	6.66	P	Heptane, 4-ethyl-
9.1	6.13	N	n-Pentane,2-cyclohexyl-5-[1-cycloazapropyl]-
18.7	4.92	A	Benzene, 1,2-diethyl
21.4	4.48	P	Octane, 4,5-diethyl-
21.4	3.84	P	Octane, 4,5-diethyl-
9.1	3.56	N	n-Pentane,2-cyclohexyl-5-[1-cycloazapropyl]-
21.9	3.26	P	Decane, 5,6-dimethyl-
22.0	3.17	P	Decane, 5,6-dimethyl-
10.5	3.05	P	n-Butyl ether
44.2	2.18	A	1-Naphthalenepropanol, alpha. - ethenyldecahy
77.3	1.58	P	Octane, 4,5-diethyl-
20.8	1.33	P	Decane, 5,6-dimethyl-
20.8	1.16	P	Undecane, 5-methyl
22.7	0.88	P	Dodecane, 2-methyl-6-propyl-
22.5	0.67	P	Heptane, 3,4,5-trimethyl-
77.6	0.67	P	Methyl3-(1-pyrrolo) thiophene-2-carboxylate
77.8	0.62	P	Octane, 4-ethyl-
78.6	0.43	P	1-((1-Butoxypropan-2-yl) oxy) propan-2-yl 2,3,4,5,6
81.3	0.43	P	Acetic acid, hydrazino-, ethyl ester
15.1	0.4	P	Hexa(methoxymethyl)melamine
77.1	0.39	P	Heptane, 4-propyl
77.3	0.37	A	3-Indolethanamine, 6-fluoro-5-methoxy
80.1	0.33	P	Urea, 2-propenyl
77.1	0.32	P	Methane, tert-butoxymethoxy-

Tall Oil

Therefore, more than 50% of the GC/MS results obtained from the nine samples were analysed and categorised into aromatics (A), naphthene (N) and paraffin (P) as represented in the table below.

In Table 5.9 the number of Aromatics, naphthene and paraffin in more than 50% of each GC/MS analysed sample starting from particle size 2<sub>30</sub> – 8<sub>120</sub> (meaning particle size 2mm cooked in 30mins to particle size 8mm cooked in 120mins) are shown. When

depolymerised organic compounds are not immediately extracted, the broken carbon to carbon bonds undergo condensation to form paraffinic long chains (Xu et al. 2014). Therefore, the quantity of paraffins in the Strong Kraft spent Liquor samples represented in table 5.9 increased with a decrease in Aromatics and Naphthene with an increase in the cooking time. Despite the condensation reaction, particle size 2mm cooked in 30mins still stood out as the best particle size because it contains the highest aromatic composition by percentage. The reduction of naphthene cooking time from 60 mins to 120 mins was clear evidence of the condensation reaction. If we watch the aromatic side of the table, we can see that the aromatic composition is constantly reducing from particle size 2mm to 8mm because the depolymerised organic compounds were undergoing condensation reaction to form long chains while the extractable monomers are decreasing.

**Table 6-9:** Number of Aromatics, naphthene and paraffin obtained from analysing above 50% of the GC/MS result from nine SKSL samples

Particle size (mm)	Total analysed area in without Colum Bleed	A (%)	N (%)	P (%)
2,30	57.57	20.00	9.69	27.88
2,60	72.74	18.59	2.20	51.95
2,120	51.26	12.44	0.00	38.82
4,30	56.94	13.10	1.89	33.95
4,60	50.72	12.71	0.00	37.97
4,120	52.88	11.68	0.00	41.2
8,30	61.64	14.08	0.00	47.56
8,60	50.48	12.43	0.92	37.13
8,120	50.80	8.44	0.41	41.95

The discovered aromatic, Naphthenic and paraffinic compounds obtained from the birch black liquor sample were normalized and represented on a ternary diagram in section 7.4 of chapter 7. The method used to normalize the values of the aromatic; naphthene and paraffin are shown in section 3.6.6 of chapter 3.

**Table 6-10:** The normalized GC/MS results from nine SKSL sample from birch wood

Particle size (mm)	Total analysed area for each sample	Normalized A (%)	Normalized N (%)	Normalized P (%)
2,30	57.57	34.7	16.9	48.4
2,60	72.74	25.6	3.0	71.4
2,120	51.26	24.3	0.0	75.7
4,30	50.94	26.8	3.8	69.4
4,60	50.72	25.1	0.0	74.9
4,120	52.88	22.1	0.0	77.9
8,30	61.64	22.8	0.0	77.2
8,60	50.48	24.6	1.8	74.0
8,120	50.80	16.6	0.8	82.6

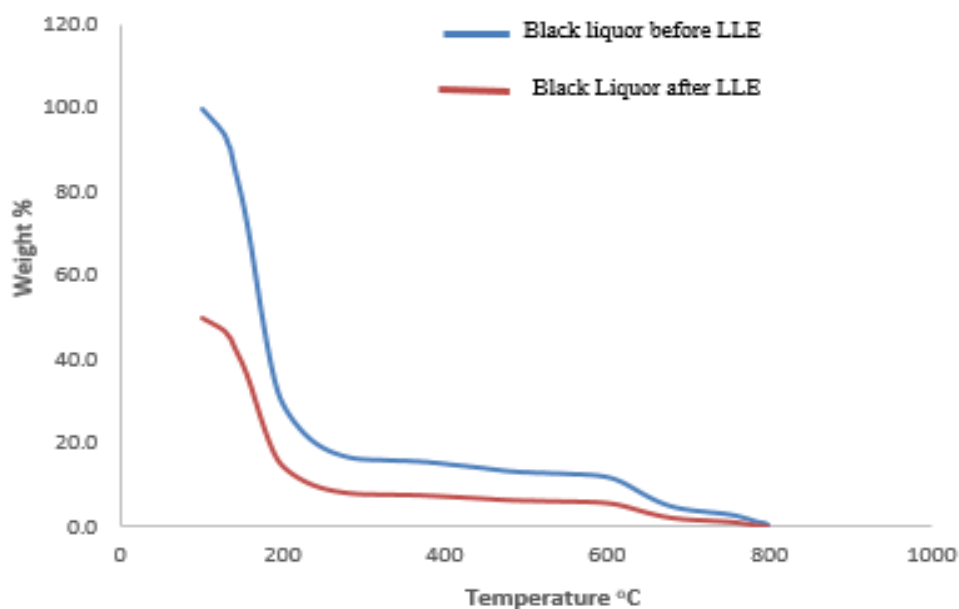
The GC/MS have shown that the hexane extract contains extractable organic compounds. The aromatics compound in the GC/MS sample shows the presence of lignin which can be converted to valuable monomers. Nevertheless, it would have been better if they were more aromatics in the analysed sample because lignin has more aromatics than paraffin's. On the contrary the results of the GC/MS in Table 5.9 have shown more paraffin than aromatics. This is because the monomers in the SKSL experienced self-condensation (Salvapati et al. 1989) during the formation of radicals like tall oil and turpentine due to internal factors like change in temperature, nature of reactant, concentration of reactant etc. Finally, particle size 2mm cooked in 30mins remains the preferred choice of particle size because short cooking time increase extractable chemicals as shown in table 5.4 and 5.5. However, the raffinate from the nine samples underwent a quantitative analysis in order to determine the amount of extractable in the SKSLs. The quantitative Analysis was carryout using a Thermo Gravimetric Analysis (TGA).

### **6.5.2 The TGA outcome**

The purpose of the TGA was to find the amount of low molecular weight compounds the hexane has extracted from the strong Kraft spent liquor (SKSL) after liquid-liquid extraction. The result was plotted on an excel sheet as shown In Figure 5.5, 5.6 and 5.7. Figure 5.5 shows 50% weight difference between the amount of organic compounds present in the SKSL before and after liquid-liquid extraction for particle size 0-2mm

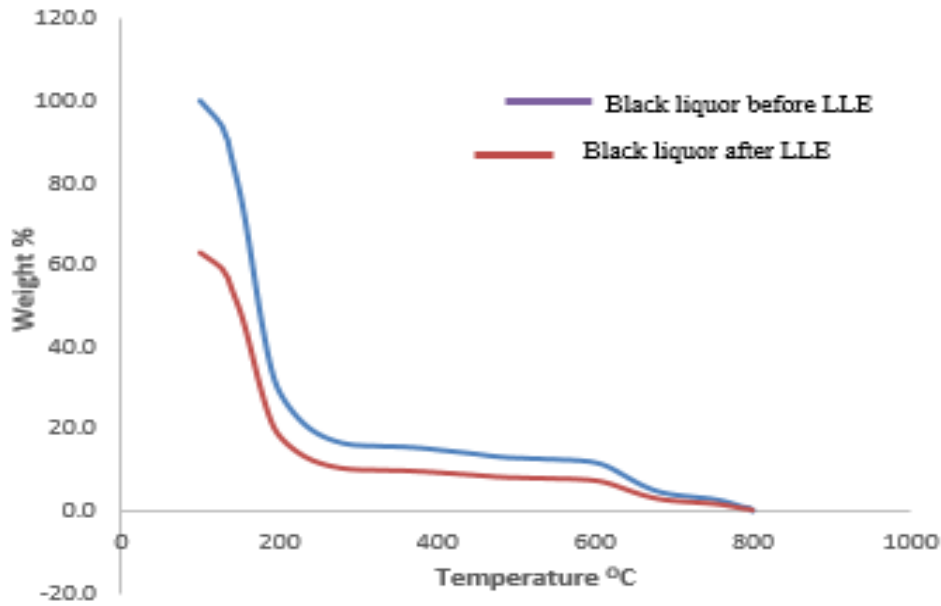
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cooked in 30min. Therefore, 50% of the low molecular weight compounds were extracted from the SKSL. Figure 5.6 shows 27% weight difference between the amount of organic compounds present in the SKSL before and after liquid-liquid extraction for particle size 2-4mm cooked in 30min. Therefore, 27% of the low molecular weight compounds were extracted from the SKSL. Figure 5.7 shows 15% weight difference between the amount of organic compounds present in the SKSL before and after liquid-liquid extraction for particle size 4-8mm cooked in 30min. Therefore, 15% of the low molecular weight compounds were extracted from the SKSL.

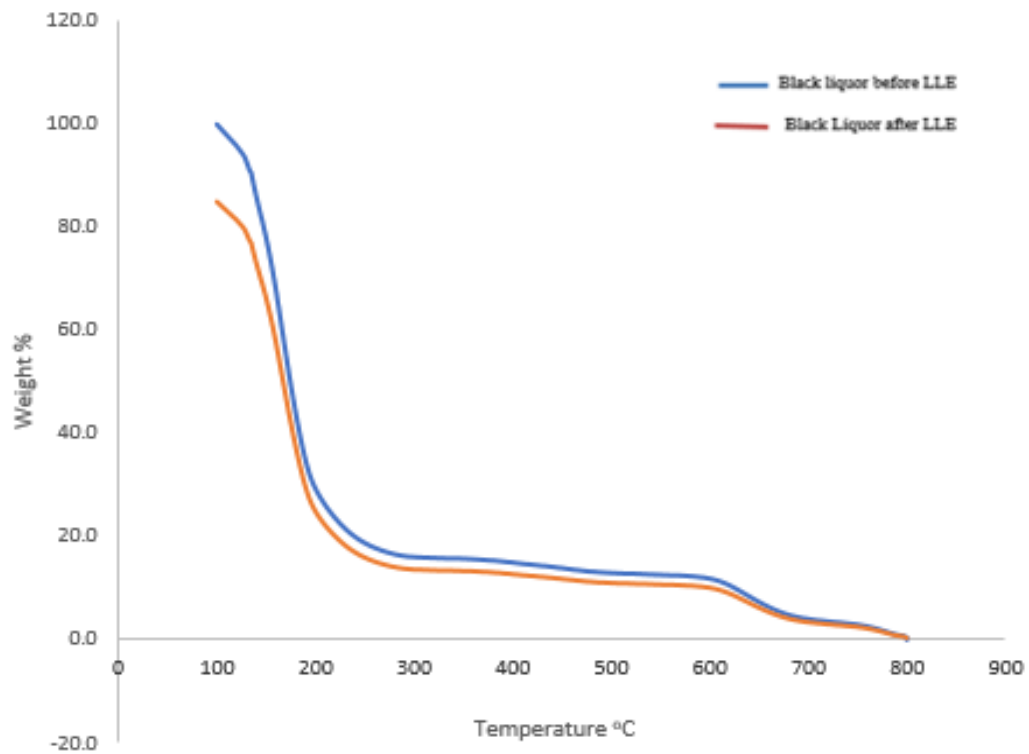


**Figure 6-5:** Shows the amounts of organic compounds extracted from the SKSL of particle size 0-2mm cooked in 30mins after liquid-liquid extraction.





**Figure 6-6:** Shows the amounts of organic compounds extracted from the SKSL of particle size 2-4mm cooked in 30mins after liquid-liquid extraction



**Figure 6-7:** Shows the amounts of organic compounds extracted from the SKSL of particle size 4-8mm cooked in 30mins after liquid-liquid extraction

Table 5.11 shows the particle size and the percentage of organic compound present in the black liquor after extraction. However, to calculate the percentage amount of organic

compound extracted by hexane, the percentage amount of organic compound left in the black liquor after liquid-liquid extraction was subtracted from 100. This procedure was adopted for all nine samples.

**Table 6-11:** *The percentage of organic compound present in the black liquor and hexane after liquid-liquid extraction of the birch wood sample*

Particle size	Cooking time	Percentage amount of organic compound in the black liquor after cooking	Percentage amount of organic compound left in the black liquor after liquid-liquid extraction	Percentage amount of organic compound present in hexane after Liquid-liquid extraction
0-2mm	30mins	100%	50%	50%
0-2mm	60mins	100%	51%	49%
0-2mm	120mins	100%	51%	49%
2-4mm	30mins	100%	63%	27%
2-4mm	60mins	100%	54%	46%
2-4mm	120mins	100%	43%	47%
4-8mm	30mins	100%	85%	15%
4-8mm	60mins	100%	67%	23%
4-8mm	120mins	100%	75%	25%

Table 5.12 shows the percentage amount of extractable organic compound based on initial dry wood mass for the nine samples as discussed in the experimental methodology in chapter 3. The percentage amount of extractable organic compound based on initial dry wood mass for the nine samples was calculated by dividing the amount of extractable organic compound in 10g of birch wood by weight of dry wood sample before cooking. This is equivalent to  $WBL_{BE} - WBL_{AE} / WDW_s$ .

**Table 6-12:** Percentage amount of green crude based on initial dry wood mass for the nine samples

Particle size	Cooking time	Amount of extractable organic compound in 10g of birch wood.	weight of dry wood sample before cooking	percentage amount of organic compound based on initial dry wood mass for the nine samples
<2mm	30mins	1.86g	10g	18.6%
<2mm	60mins	1.60g	10g	16.0%
<2mm	120mins	1.57g	10g	15.7%
4mm	30mins	0.68g	10g	6.8%
4mm	60mins	1.35g	10g	13.5%
4mm	120mins	1.40g	10g	14.0%
8mm	30mins	0.24g	10g	2.4%
8mm	60mins	0.45g	10g	4.5%
8mm	120mins	0.53g	10g	5.3%

## 6.6 Conclusion

The experimental outcome of the Kraft cooking using different particle size, solvent extraction, GC/MS analysis and TGA analysis have shown that particle size 2mm cooked in 30mins contains the highest extractable organic compound in percentage (%) than other particle sizes because short cooking time increase extractable chemicals as shown in table 5.8. In addition, the total energy used during cooking is directly proportional to the time of cooking. Therefore, particle size cooked in 60mins will consume twice the energy required for particle size cooked in 30mins. So, using particle size 0-2mm in Kraft pulping mill is more sustainable, than 2-4mm and 4-8mm. Also, extract from black liquor with small particle size can shift the financial outcome and increase profit made from the pulp and paper industry. The economic relevance of choosing particle size <2mm is further explained in section 7.2.3.

Therefore, the experimental outcome in this chapter confirms that a change in woodchip sizes used in the Kraft pulping mills while extracting value-added compounds from black liquor using hexane will:

- a) Reduce pulping production energy as explained in section 5.3.
- b) Reduce excess water consumption as explain in section 5.4.1.

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c) Reduce environmental problems generated during pulp production in the conventional Kraft pulping mill.

d) Generate value added chemical as shown in section 5.4.

Finally, it is evident that particle size <2mm (0-2mm) cooked in 30mins and hexane as 50% of the washing liquid has proved to be more sustainable because it consumed less energy, less water and generate approximately 19% of extractable value-added organic compounds (Green crude) based on initial dry wood than other particle sizes.

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## Chapter 7 Life Cycle Assessment of a Kraft biorefinery

### 7.1 Introduction

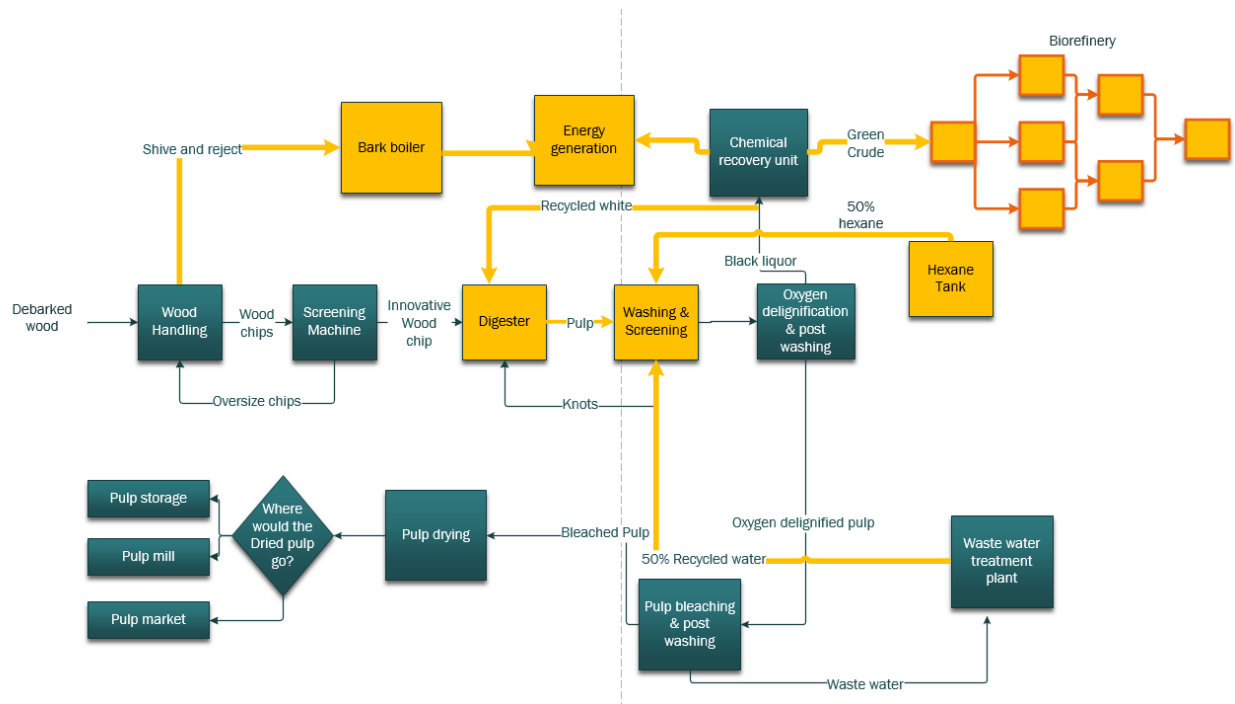
In chapter 5 we discovered that the Particle size  $< 2\text{mm}$  cooked in 30mins and incorporating hexane as 50% of the pulp washing liquid made the Kraft pulp mill more sustainable because less energy and water is consumed reducing the amount of environmental problem generated and value-added organic compounds (green crude) produced. The output of the empirical methodology is applied to the new conventional Kraft pulp mill called Kraft biorefinery. The outcome is measured using the LCA methodology.

The first phase of the LCA methodology started with the goal of the study, followed by the scope of the study, which includes the product system boundary, functional unit, impact categories, quality of data required and the cut-off criteria. In the second phase of the LCA, the relevant materials, energy and emissions entering and leaving the system was discussed. The third phase of the LCA methodology is the environmental impact assessment. This phase of the LCA involves assigning inventory data to impact categories and modelling the inventory data to fit in with the impact category in a way that goes in line with the goals and scope of the study. In the interpretation phase of the LCA methodology, the different outcome of the second and third phase is used to identify significant issues, evaluate the outcome of the inventory analysis and environmental impact assessment through sensitivity, completeness, and consistency check. Lastly, the LCA methodology was used to carry out a comparative study between the conventional Kraft pulp mill and Kraft biorefinery to decide the more environmentally sustainable and industrially viable mill between the two with any limitations and recommendations.

### 7.2 The goal of the study

The goal of this study is to use the four phases of the life cycle assessment to determine the impact of using particle size  $< 2\text{mm}$  cooked for 30mins and hexane as 50% of the pulp washing liquid on pulp production energy with high emissions and water consumption while extracting value-added chemicals from the black liquor. The targeted audience are the pulp and paper production industries globally and research institutions interested in the environmental sustainability and industrial viability of Kraft pulping mill.

### 7.2.1 Product System description for the proposed Kraft biorefinery under study



**Figure 7-1:** Schematic drawing of a Kraft biorefinery

With respect to this study, Kraft biorefinery is defined as a Kraft pulp mill integrated with biorefinery techniques to produce pulp, energy, and value-added organic compounds. The proposed Kraft biorefinery begins with introducing logs of wood into the milling machine where it is crushed and screened using a sieve with mesh size 2mm to achieve the targeted particle size. The oversize chips were conveyed back to the sawmill where they were re-chipped to the required chip size bringing about an increase in energy consumption during the wood handling. The innovative particle (< 2mm) was transferred to the digester where they were cooked in 30mins at a temperature of 175°C. During the cooking, the energy required is four times less than the energy required to cook the conventional particle size (2-8mm). After cooking, the pulp was discharged into a blow tank from the bottom of the digester using a blow unit through the blow valve. From the blow tank, the pulp was unloaded into a pulp washer where the washing liquid contains 50%: 50% volume ratio of hexane and water in a solid to liquid ratio of 1:10 L/W (Liquid to water ratio). After washing, the pulp was filtered and transferred to the oxygen delignification unit. After the pulp was oxygen delignified, the pulp was pre-washed, bleached, post washed, and sent to the pulp dryer. The dry pulp is transferred to either a paper mill for making papers, cardboard or used as specialty cellulose. The spent liquor from the pulp washing unit and oxygen delignification unit is transferred to the spent liquor collection unit where the

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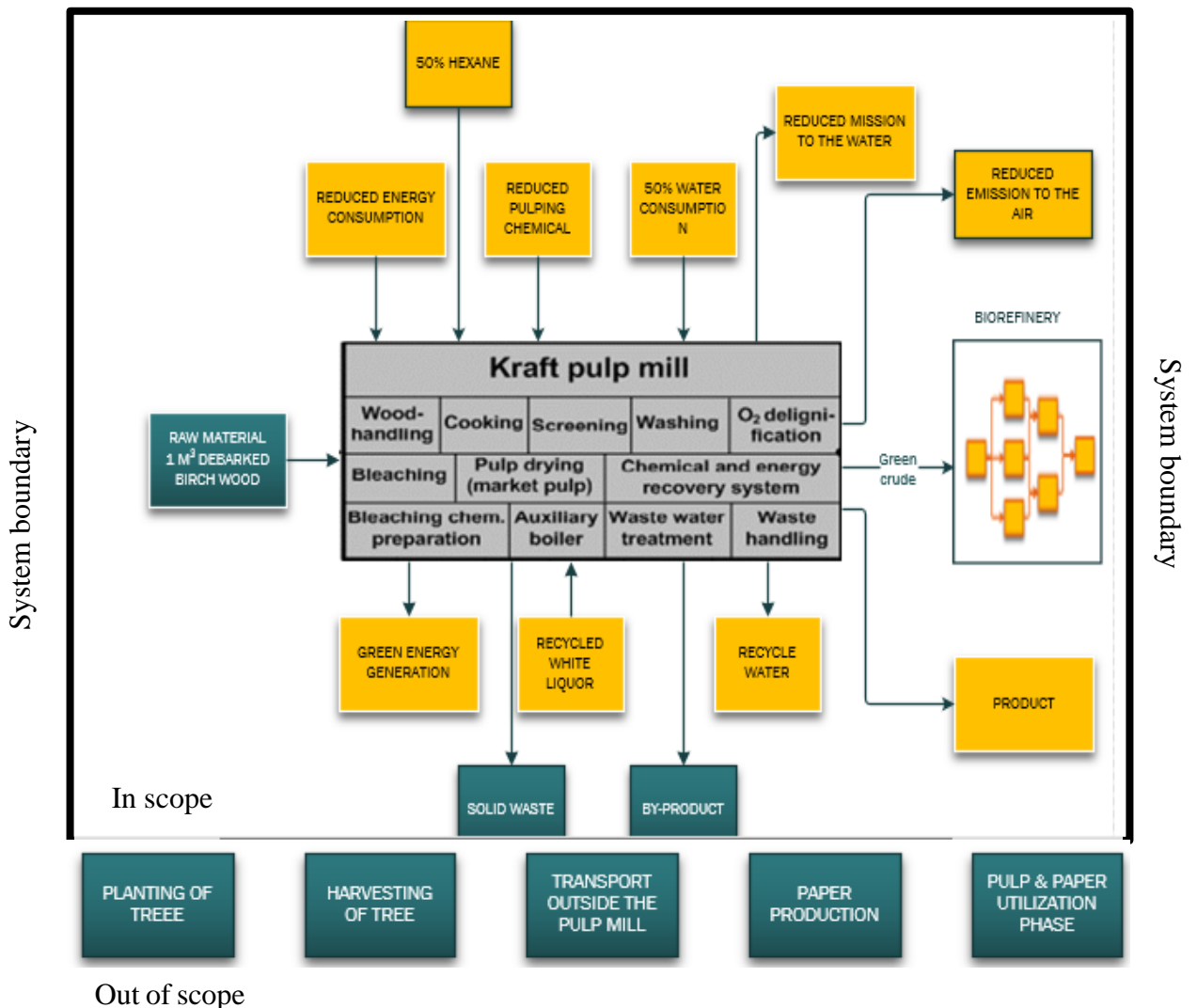
spent liquor pass through a separation technique called liquid to liquid extraction. After the extraction, the extract containing hexane and extractable organic compound are transferred into a collection tank while the raffinate containing water, few soluble organic and inorganic compound was transferred to the multiple evaporators. However, the high-pressure extract containing hexane and extractable organic compound was transferred from the collection tank to the flash tank where the pressure and temperature of the extract is regulated to enhance hexane recovery (de Yuso et al. 2013). The vaporized hexane is condensed at a low temperature and a pressure of 2 bar to regenerate liquid hexane, which is pumped back into the washing unit while water and fresh hexane is added to replace losses. The extractable organic compound is pumped into a storage tank from where it is transferred to a biorefinery or used as a drop-in fuel (Kumar et al. 2020). In the multiple evaporators, the raffinate (weak black liquor) is concentrated. The concentrated black liquor is transferred into the recovery boiler where it undergoes combustion to generate molten smelt and steam for energy production (JRC 2000). The white liquor is reproduced from the smelt (green liquor) through a recausticizing process (Suhr et al. 2015). Finally, the lime used in the recausticizing process is recovered through the calcining process (JRC 2000). The Product System boundary of a proposed Kraft biorefinery represent the major unit processes in the proposed Kraft biorefinery. The conditions used in establishing the system boundary was chosen based on the goal of the study. According to ISO 2007, systems cannot be compared unless they share the same boundary. The system boundary used in this chapter 6 is the same as the system boundary chosen in chapter 4 because we intend to compare the conventional Kraft pulp mill with the proposed Kraft biorefinery. Energy was identified as the most impactful elementary flow in chapter 4 because each life cycle stage selected for this Life Cycle Assessment was affected by energy. The output of the experiments in chapter 5 confirmed that using particle < 2mm cooked in 30mins and hexane as 50% washing liquid could cut down the consumption of energy, reduce water consumption and generate value added product. If the energy is cut down by using particle size < 2mm and hexane as 50% of the washing liquid, the amount of environmental problem generated by energy consumption is also reduce. Note, the process in green are modifications due to integration of biorefinery and the use of best available techniques and technology. While the process in red are the AS-IS process of the conventional Kraft pulp mill without modification.

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### 7.2.2 *System boundary for the proposed biorefinery*

The system boundary used for performing the LCA study in this chapter is the same as the system boundary mentioned in chapter 4 of this thesis. The system boundary comprises of all the Input, output, and process units within the proposed Kraft biorefinery. Within the scope of the system boundary, we have the following elementary flow including the energy generated, energy consumed, material input and output, emission release to the air, emissions released to the land, emission release to the water, by-product, solid waste, green crude, and pulp flowing in and out of the selected process units. Outside the scope of the system boundary, we have a list of activities excluded from the system under study because they are outside the goal and scope of the study. These activities include planting of trees, harvesting of trees, Transportation outside the pulp mill, paper production and utilization phase. The system boundary of the proposed Kraft biorefinery is further categorised into two levels: areas of concern and area of no concern. The areas of concern are process unit within the system boundary which experienced the direct impact of using particle size < 2mm cooked for 30mins and hexane as 50% of the pulp washing liquid. Example, the wood handling process unit had to change from 2-8mm to < 2mm resulting in an increase in energy consumption from 90MJ/ton to 468MJ/ton. Secondly, the energy consumption and cooking time of the Kraft cooking process unit changed from 120mins to 30mins resulting in a decrease in energy consumption from 2254MJ/ton to 571MJ/ton. Thirdly, there was a change in the number of multiple evaporators used in the chemical recovery unit, an addition unit called the extraction unit and a change in the amount of energy consumed from 6642 MJ/ton to 4786MJ/ton. Finally, the total water consumed in the washing and screening process unit was reduced from 93.3m<sup>3</sup> to 59.15m<sup>3</sup>. Therefore, the four mentioned process unit are called the area of concern. While areas of no concerns are process units within the system boundary, which do not experience the direct impact of using particle size < 2mm cooked for 30mins and hexane as 50% of the pulp washing liquid. All the other process units mentioned in the system boundary belongs to this category. In summary, the proposed Kraft biorefinery consumes less energy, less water, release less emission and generate an additional product known as green crude.





**Figure 6.2** Overview of the system boundary for the Proposed Kraft pulp mill under study

### 7.2.3 The functional unit

The functional unit is 1 air dry tonne of pulp. Therefore, the outcome of using innovative particle size < 2mm cooked for 30min and hexane as 50% of the pulp washing liquid in the proposed Kraft Biorefinery would be measure per function unit. The same Cut-off criteria used in chapter 4 was also used in chapter 6.

### 7.2.4 Quality of data used in the inventory.

The data used in chapter 6 met the requirements mentioned in chapter 4. For more detail see page 4.3.5. Some of the data used in designing the proposed Kraft biorefinery were calculated. However, it is also difficult to assess precision as discussed in chapter 4,

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because many conversions were done in other to unify the unit of all the elementary flow used in the inventory analysis.

### ***7.2.5 Conclusion of the goal and scope phase***

This study was conducted to identify the impact of using particle size <2mm cooked in 30mins and hexane as 50% of the pulp washing liquid on energy use, water consumption and the amount of environmental problem generated while extracting value chemicals from the black liquor. The functional unit of the LCA study is 1 air dry tonne of pulp from the proposed Kraft biorefinery. The selected system boundary was the same with the conventional Kraft pulp paper mill excluding the Areas of concern and Areas of no concerns. The system boundary was selected based on the goals of the study and cut-off criteria. Finally, all the data selected for the LCA study was based on data quality requirements.

## **7.3 Inventory compilation / analysis**

The inventory phase of chapter 6 will focus on the area of concern. We are going to discuss only the area of concern because these are the process units that experienced direct impact of using particle size < 2mm cooked for 30mins and hexane as 50% of the pulp washing liquid. During the inventory analysis, we defined each process unit, and explained the calculations and assumption used to determine the new value of the elementary flows. Example of processes discussed are wood handling process unit, Kraft cooking process unit, chemical recovery process unit, washing and screening process unit.

### ***7.3.1 Wood handling***

The wood handling process unit of the Kraft biorefinery is still the same as that of a conventional Kraft pulp mill except that the energy consumption is different due to the production of particle size < 2mm(0-2mm).

#### **Calculations and Assumptions made during the wood handling inventory compilation.**

The total energy used during the wood handling was calculated by summing the heat and electrical energy used during the wood handling process. The total energy calculated was all in MJ.

All the assumptions, calculations and conversion made in the wood handling section of chapter 4 is the same for the wood handling phase of the Kraft biorefinery except for the

energy used. According to particle size 1.6 mm (in the range of 0-2mm) consumed 468 MJ, Particle size 3.2mm (in the range of 2-4mm) consumed 180 MJ and particle size 6.35mm (in the range of 4-8mm) consumed 90 MJ. Therefore, Table 6.1 below presents the energy consumed during wood handling process unit.

**Table 7-1: Energy consumed during wood handling**

<b>Particle size</b>	<b>Energy (MJ)</b>
<2mm	468
2-4mm	180
4-8mm	90

In summary, the average energy used during the wood handling process unit of a conventional Kraft pulp mill and the proposed Kraft biorefinery is represented in table 6.2.

**Table 7-2: The amount of energy used during wood handling process for a Conventional Kraft pulp mill and a Kraft biorefinery.**

<b>Process unit</b>	<b>Conventional Kraft pulp mill Input &amp; output</b>	<b>Quantity</b>	<b>Kraft biorefineries Input &amp; output</b>	<b>Quantity</b>	<b>unit</b>
<b>Wood handling process unit</b>	Energy	90	Energy	468	MJ/Adt
	Particle size	2-8	Particle size	<2 (0-2mm)	mm

Therefore, using particle <2mm instead of 2-8mm lead to an increase in the amount of energy consumed during wood handling.

### **7.3.2 Kraft cooking process unit**

The Kraft cooking process unit of the proposed Kraft biorefinery is the same as that of a conventional Kraft pulp mill except that the energy consumption varies due to the use of particle size <2mm instead of 2-8mm.

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### **Calculations and Assumptions made during the Kraft cooking inventory compilation.**

The total energy used during the Kraft cooking was calculated by adding the heat and electrical energy used during the Kraft cooking process. The total energy consumed in the cooking process unit was measured in MJ.

All the assumptions, calculations and conversion made in the Kraft cooking section of chapter 4 is the same for the Kraft cooking phase of the Kraft biorefinery except for the energy used. The result of the Kraft cooking experiment in chapter 5 depicts that particle size <2mm cook faster than particle size 2-4mm and 4-8mm due to large surface area which increase the rate at which the cooking chemical diffuse into the woodchip sample. So, smaller particle size cooks faster. Secondly, the cooking time is directly proportional to the rate of delignification and the quantity of energy consumed as demonstrated in chapter 5. In this study, we assumed that the energy required to cook particle size 4-8mm is equivalent to the energy required to cook particle size 2-8mm. According to (JRC 2000), the total energy required by Kraft cooking process unit to cook particle size 2-8mm in 120 mins is equivalent to 2284MJ/ton. The table below contains the energy consumed at each cooking time.

*Table 7-3: The relationship between cooking time and the energy consumption*

<b>Particle size</b>	<b>Cooking time</b>	<b>To energy required during cooking.</b>
2-8mm	2 hours	2284MJ/ton
2-4mm	1 hour	1.142MJ/ton
0-2mm	0.5 hour	571MJ/ton

Therefore, using particle 0-2mm instead of 2-8mm lead to a reduction in energy consumed during Kraft cooking.

#### **7.3.3 Washing and Screening process unit**

In this process the brown stock from the digester is washed and screened before it is oxygen delignified. After cooking, the pulp comes out with a spent liquor (black liquor). The black liquor is separated from the pulp by subsequent washing. During the washing,

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the pulp is separated from the black liquor by treating with washing liquid counter currently. During the washing process, hexane was used as 50% of the washing liquid resulting in a reduction of the total amount of water consumed in the washing and screening process unit from 93.3m<sup>3</sup> in a modified conventional Kraft pulp mill to 59.15m<sup>3</sup> in a Kraft biorefinery.

#### **7.3.4 Chemical recovery unit**

The chemical recovery process unit of a Kraft biorefinery is the same as that of a conventional Kraft pulp mill except that an additional unit called extraction unit is added to the chemical recovery process of the proposed Kraft biorefinery. Also, the amount of energy consumed in the chemical recovery unit is reduced. The extraction unit was used to extract value-added chemical from the proposed Kraft biorefinery.

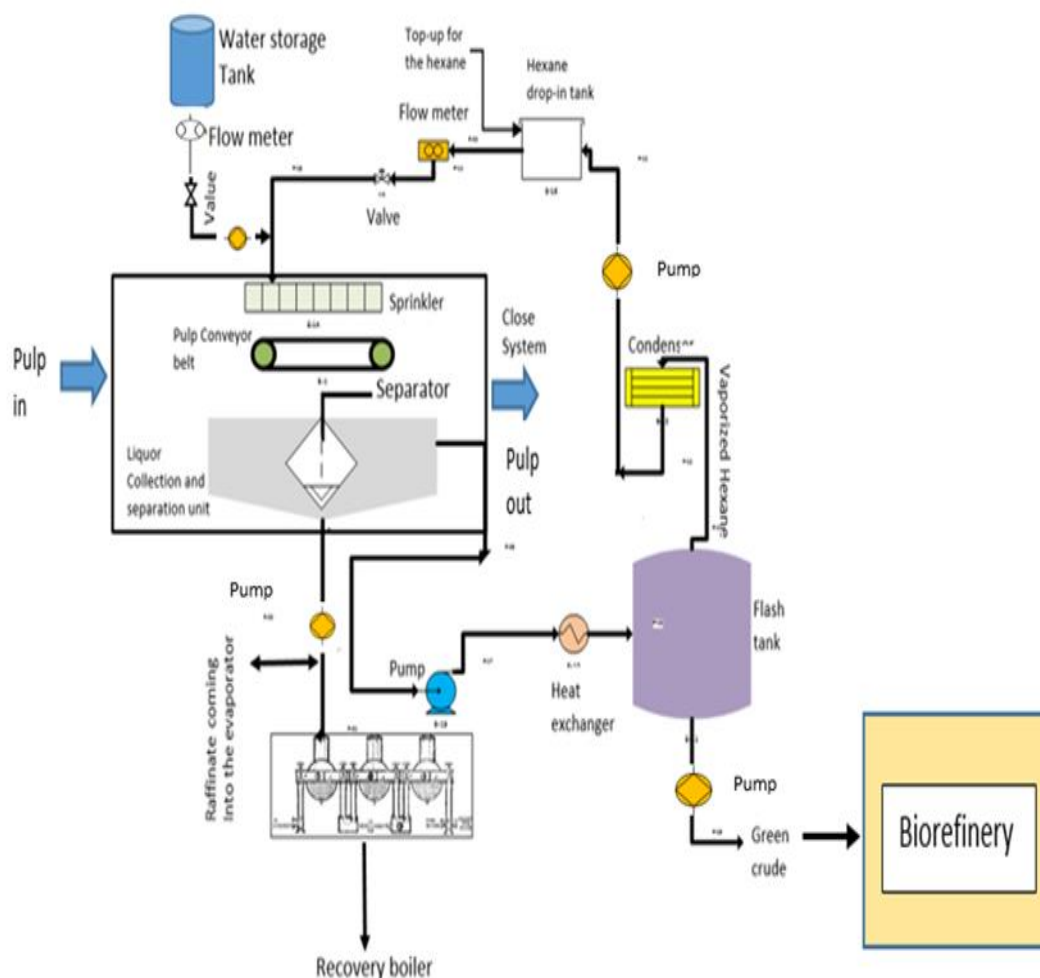
##### **The extraction unit**

The extraction unit is a part of the chemical recovery process unit of the proposed Kraft biorefinery. This additional unit is one of the key features that makes the proposed Kraft biorefinery different from the conventional Kraft pulp mill. In the proposed Kraft biorefinery, the extraction process started from the washing and screening process unit until the point where the hexane is recycled back to the hexane storage tank. The hexane extract is transferred to the extraction storage unit, where it can be used as a drop-in fuel for refineries (Mante et al. 2016) or transferred to the biorefinery where it is further process into other products. Finally, the raffinate containing the rest of the organic and inorganic compound are transferred to the evaporator where the white liquor is recycled back to the digester and the rest of the black liquor is utilized for the generation of steam used for energy production (Vakkilainen 2000). The Schematic diagram of the extraction process unit is shown below.

The total electricity consumed by the extraction process unit = electricity consumed by the pumps pumping the hexane extract + the amount of electricity consumed, by the pump transferring the extract into the flash tank (with pressure decrease to 1 bar) + the amount of electricity consumed by the pump transporting the condensed hexane to the hexane drop-in-tank (with pressure increase of 2 bars) with a loss of 0.1%.

The total electricity consumed by the extraction process unit = electricity consumed by the pumps pumping the hexane extract + the amount of electricity consumed, by the pump transferring the extract into the flash tank (with pressure decrease to 1 bar) + the amount

of electricity consumed by the pump transporting the condensed hexane to the hexane drop-in-tank (with pressure increase of 2 bars) with a loss of 0.1%.



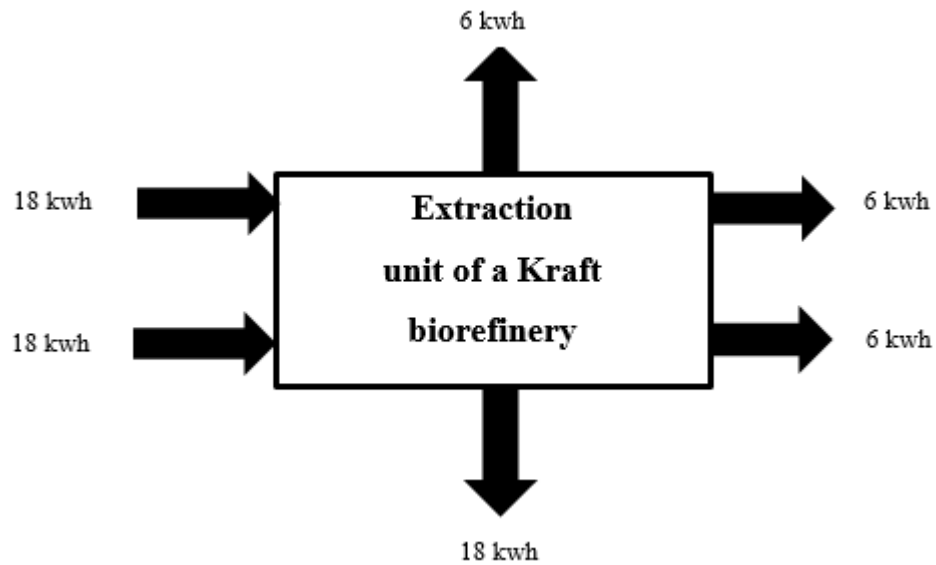
**Figure 7-2:** The extraction process unit designed using Aspen Plus software

The flow meter attached to the water tank measures the volume of water leaving the water tank through the valve. The same applies to the flow meter attached to the hexane collection tank. The immiscible liquids were combined in the ratio of 1:1 to form the washing liquid. The washing liquid is pumped to the sprinkler, which discharge the washing liquor on the pulp conveyed by the conveyor belt. The washing liquid helps to wash off both organic and inorganic compound from the pulp. After washed, the organic and inorganic substance from the pulp goes into the liquid collection and separation unit. In this unit, the separator splits the hexane extract and the raffinate. The hexane extract is pumped into the Flash tank where the hexane vaporizes under a pressure of 153mmHg and temperature of 25<sup>0</sup>C leaving the organic compounds, which are transferred to the biorefinery or used directly as a drop-in fuel. The vaporized hexane is condensed and

pumped back into the hexane drop-in tank. Also, the raffinate is pumped into the evaporator where the water content of the raffinate is reduced. From the evaporator, the strong black liquor is transferred to the recovery boiler where it is burnt to produce steam used for energy generation. The green liquor produced in the recovery boiler is recycled to produce white liquor that is transferred back to the digester.

**The energy consumption of the extraction unit**

The total energy consumed by the extraction process unit is equivalent to electricity consumed by the pumps pumping hexane extract into the flash tank at a pressure of 1 bar, plus the pumps pumping raffinate into the evaporator, plus the pump pumping the extracted organic compound from the flash tank to the biorefinery, plus electricity consumed by the pumps pumping the hexane and water into the sprinkler, plus electricity consumed by the pumps pumping the evaporated hexane at a pressure of 153mmHg at 25°C to the hexane storage tank with a loss of 0.1%. The total energy consumed in the extraction process unit is equivalent to 72Kwh.



*Figure 7-3: Energy balance in the extraction unit*

Therefore, using hexane as 50% of the washing liquid leads to energy savings in the chemical recovery unit. The details are shown in table 6.4.

**Table 7-4:** Compares the energy consumption between the chemical recovery process of a conventional Kraft pulp mill and a Kraft biorefinery for a non- integrated bleached Kraft pulp.

<b>Process unit</b>	<b>Conventional Kraft (MJ/ADt)</b>	<b>Proposed Kraft biorefinery (MJ/ADt)</b>
extraction	0	259.2
evaporator	4208	2104
Recovery boiler	826	826
causticizing	72	72
Lime kiln	1536	1536
<b>Total Different</b>	<b>6642</b>	<b>4786</b>

The wood handling process unit, Kraft cooking process unit, washing & Screening process unit. and the chemical recovery process unit are the process unit within the system boundary which experienced the direct impact of using particle size < 2mm cooked for 30mins and hexane as 50% of the pulp washing liquid. However, input and output entering and leaving this area of concern were categories under the following headings described in 6.4.4.

### **7.3.5 The major inventory areas addressed by the proposed Kraft biorefinery**

**Raw material:** These are feedstock or unprocessed materials used during the production of Kraft pulp. Example: wood, chemicals used during Kraft pulp production and water.

**Wood:** The size of woodchips used for the proposed Kraft biorefinery is called innovative woodchip. It is innovative because particle size < 2mm has been experimentally tested and proven more sustainable than the conventional particle sizes (4-8mm). Particle thickness < 2 mm cooked for 30mins contains high value extractable chemicals when compared with other particle sizes. In addition, the innovative particle sizes help in energy and water savings when compared with other particle sizes. The experimental result in chapter 5 reveals that particle size < 2mm cooked in 30mins are better than using particle size 2-4mm and 4-8mm cooked in 30mins. However, the innovative particle size (Particle size < 2mm cooked in 30mins) is produced during wood handling by re-chipping and screening the oversize conventional particle through a screen aperture between 0-2mm in size.

**Water:** water is an important resource in the proposed Kraft biorefinery and the second elementary flow of concern as discussed in chapter 4. Water effects 60% of the life cycle



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stages selected in the system boundary of the LCA. The water consumption of the proposed Kraft biorefinery per tonne of pulp is reduced to 50% by adding hexane in the washing and screening process unit. Also, water in form of steam used in the evaporator of the chemical recovery unit was reduced from 100% to 50% due to the use of hexane as 50% washing liquid. Furthermore, using hexane as 50% of the pulp washing liquid in the proposed Kraft biorefinery helps to reduce the number of evaporators required and reduce the energy consumption and the level of emission released in the air from the chemical recovery unit. The used hexane is recovered under reduced pressure at room temperature while 50% of the water in the raffinate is transferred to the evaporator where the solid content of the black liquor is increased from 15% to 85% before burning in the recovery boiler to generate steam for energy generation. The extractable organic compound generated is recycled and re-used. The average amount of water consumed in both conventional Kraft pulp mill and Kraft biorefinery are shown in table 4.11.

***Input chemical:*** Many chemicals are used in pulp production. Some of the chemicals are for cooking, pulp strength preservation, delignification, bleaching etc. an additional chemical used in proposed Kraft biorefinery that is not used in the conventional Kraft pulp mill is Hexane. Hexane is used for two purposes: washing the pulp yield after cooking in the digester and extraction of organic compound in the chemical recovery stage. Also, the changes caused in input parameter like the use of particle size < 2mm helped in the reduction of bleaching chemical, reducing the amount of pollution released during the pulp production because the pulp is almost bleached depending on the amount of brightness required after cooking and oxygen delignification.

***Emission to air:*** There are emissions released into the atmosphere from the recovery boiler and auxiliary boiler during their operation. Since energy is the elementary flow of most concern as indicated in chapter 4. The amounts of emission released depend on the amount of energy generated by the recovery and bark boiler or the amount of energy consumed by the entire process unit. When the generation level is high, the emission level is also high and when the generation or consumption level is low, the emission level is low. Example of major elementary flows released during energy generation by the recovery boiler (chemical recovery unit) and bark boiler (auxiliary boiler) are SO<sub>x</sub>, NO<sub>x</sub> and TRS.

**Energy:** Energy is an important input in proposed Kraft biorefinery just as it is in conventional Kraft pulp mill. During the wood handling, the proposed Kraft biorefinery use more energy than the conventional Kraft to crush the woodchip particle into smaller sizes. While in cooking and chemical recovery unit, the proposed Kraft biorefinery consumes less energy than the conventional Kraft pulp mill. We assumed that the energy used in both the conventional Kraft pulp mill and the proposed Kraft biorefinery are renewable and are generated by the recovery boiler (chemical recovery unit) and bark boiler (Auxiliary boiler). For every Mega joule of energy generated, there is an equivalent amount of emission release into the environment. Table 4.11 shows, that energy affect 100% of the selected process unit within the system boundary. Energy reduction is one of the major goals of the proposed Kraft biorefinery. Due to a change in the input parameter (woodchip thickness) and the used of hexane for black liquor extraction, the energy consumed in the proposed Kraft biorefinery was reduced from approximately 15000MJ to 12000MJ with 20% energy savings.

**Table 7-5:** *The different in energy consumed in the conventional Kraft pulp mill and Kraft biorefinery.*

<b>Process Units of the LCA</b>	<b>Conventional Kraft pulping mill (MJ/ton)</b>	<b>Kraft biorefinery (MJ/ton)</b>
wood handling	468	90
cooking	2284	571
Chemical recovery process	6642	4786
Washing and screening	198	198
Oxygen delignification	562	562
bleaching	799	799
Pulp drying	4000	4000
Axillary boiler	108	108
Bleaching chemical preparation	92	92
Wastewater treatment	72	72
Approximated Total energy	15000	12000

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During the life cycle inventory phase of the LCA, we summarized the major inventory areas addressed by the proposed Kraft biorefinery. The total energy used in the proposed Kraft biorefinery is less than energy used in the conventional Kraft pulp mills. Since energy and water are the most impactful elementary flows contributing towards the selected process units of the conventional Kraft pulp mill under study as shown in table 4.11, the energy and water consumed in a Kraft biorefinery was examined from an environmental perspective at the life cycle impact assessment stage as shown in section 6.5.

#### **7.4 Environmental impact assessment**

According to ISO 14040, the Environmental impact assessment stage is the third stage of the LCA. In this LCA, Pulp production energy generated from biomass and the amount of water consumed during pulp production was examined from an environmental perspective using the environmental impact assessment. The major elementary flows released during energy generation by the recovery boiler (chemical recovery unit) and bark boiler (auxiliary boiler) are SO<sub>x</sub>, NO<sub>x</sub> and TRS. These elementary flows affect Acidification potential, Disability Adjusted Life Years (DALY), Human toxicity potential (HTP) and Global warming. Therefore, Section 6.5.1 will discuss the impact of pulp production energy on the selected environmental impacts (acidification, respiratory inorganic, human toxicity, and climatic change) caused by the release of SO<sub>x</sub>, NO<sub>x</sub> and TRS using the Environmental impact assessment.

##### ***7.4.1 The impact of the total pulp production energy on acidification potential, respiratory inorganic, human toxicity, and climatic change using Environmental impact assessment***

The third phase of the LCA was used to study the impact of energy consumed during Kraft pulp production on Acidification potential, Respiratory inorganic, Human toxicity, and Climatic change. Every energy generated from biomass in the Kraft pulp mill produce an amount of emission (Suhr et al. 2015). Therefore, a reduction in the amount of energy consumed per tonne of pulp will reduce the amount of energy generated and emission released during the generation. Table 6.6 present the sources of energy used during pulp production, the amount of energy consumed, and the levels of emission released from both the conventional Kraft pulp mill and the proposed Kraft biorefinery.

**Table 7-6: Energy consumed, and emission released by the conventional Kraft pulp mill and the proposed Kraft biorefinery**

Elementary flow	Conventional Kraft pulp mill (Suhr et al. 2015)	The proposed Kraft biorefinery (calculated value)
<b>Energy source</b>	15000 MJ/Adt	12000 MJ/Adt
The recovery and bark boiler		
<b>Emission release to air</b>		
SOX	0.65 (Kg/Adt)	0.52 (Kg/Adt)
NOX	2.7 (Kg/Adt)	2.16 (Kg/Adt)
TRS	0.5 (Kg/Adt)	0.4 (Kg/Adt)

To determine the impact of the pulp production energy on acidification potential, respiratory inorganic, human toxicity and Climatic change, the three-mandatory element of the environmental impact assessment was used to study the emission release into the air during pulp production. The environmental impact assessment phase started with the first mandatory element which involves the selection of category indicators and characterisation models used to study the impact of the pulp production energy on acidification potential, respiratory inorganic, Human toxicity, and Climatic change. Table 6.7 shows the selected category indicators and characterisation models used to study the impact category listed in table 6.7.

**Table 7-7: Impact category, Category indicators and characterisation.**

<b>Impact category</b>	<b>Abbreviation</b>	<b>Category indicator</b>	<b>Characterisation model</b>
<b>Acidification</b>	AP	Acidification potential	Recipe 2008
<b>respiratory inorganic</b>	RI	Disability Adjusted Life Years (DALY).	Eco-indicator 99
<b>Human toxicity</b>	HT	Human toxicity potential (HTP).	USES-LCA model
<b>Climatic change</b>	CC	Global-warming potential	Recipe 2008

In the second mandatory element of the environmental impact assessment phase, the emission released during energy generation as shown in table 6.6 were assigning to the selected impact categories. This is known as classification. Table 6.8 shows the classification of emissions released to the air from the pulp mills and the selected impact categories.

**Table 7-8 :** Classification of emissions released to the air from the pulp mills and the selected impact categories.

Elementary flows	Quantity of emission (Kg/ADt)	Impact category			
		Climatic Change kg (CO2)	Human Toxicity kg(14DCB)	Respiratory Inorganic kg (PM10)	Acidification kg (SO2)
Emission from the Recovery boiler and Bark Boiler					
SOX	0.52	CF=0	CF= 9.60E-02	CF= 0.032	CF=1
NOX	2.16	CF =264	CF=0	CF= 1.50E-04	CF= 0.7
TRS	0.4	CF=0	CF=0	CF= 0.22	CF= 1.88

CF - Represent characterisation factor.

In the third mandatory element of the environmental impact assessment phase, the effect each elementary flow has on the selected impact category was quantified by characterisation. Table 6.9 shows the characterisation of acidification potential, respiratory inorganic, Human toxicity, and Climatic change.

**Table 7-9:** The characterisation of acidification potential, respiratory inorganic, Human toxicity, and Climatic change

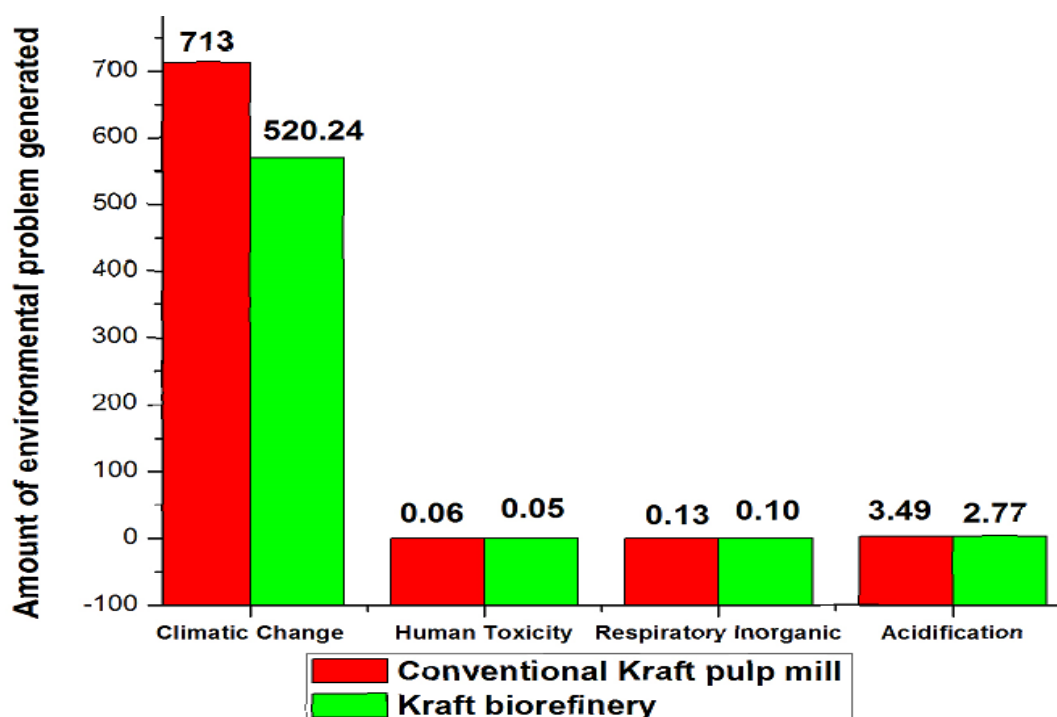
Elementary flows	Impact category			
	Climatic Change kg (CO2)	Human Toxicity kg (14DCB)	Respiratory Inorganic kg (PM10)	Acidification kg (SO2)
Emission from Recovery boiler and Bark Boiler				
SOX	0	0.04992	0.0166	0.52
NOX	570.24	0	0.0003	1.5
TRS	0	0	0.088	0.752

Table 6.10 shows a comparison between the environmental problem generated from the Conventional Kraft pulp mill and the Kraft biorefinery.

**Table 7-10:** The difference between the environmental problems caused by the conventional Kraft pulp mill and the proposed Kraft biorefinery

Impact categories	Conventional Kraft pulp mill	Kraft biorefinery
Climatic Change	713	570.24
Human Toxicity	0.0624	0.04992
Respiratory Inorganic	0.1312	0.1049
Acidification	3.49	2.772

After the third stage of the life cycle impact assessment, climatic change appeared to be the most significant environmental problem in both the conventional Kraft pulping mill and the proposed Kraft biorefinery as represented in figure. 6.4.



**Figure 7-4:** Different between the level of environmental problem generated for both conventional Kraft mill and Kraft biorefinery.

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Therefore, looking at pulp production energy from an environmental perspective using environmental impact assessment, we can conclude that the proposed Kraft biorefinery is more environmentally friendly because it contributes less towards climatic change when compared to the conventional Kraft pulp mill.

### **7.5 Studying the influence of increasing water consumption during pulp production on freshwater depletion using environmental impact assessment stage**

The third phase of the LCA was used to study the influence of increasing water consumption during pulp production in both conventional Kraft pulp mill and the proposed Kraft biorefinery. According to literature, we already know that the amount of water consumed during pulp production is between 15 - 100 metric tonnes of water per air dry tonne of pulp (JRC 2000). Using hexane as 50% of the washing liquid has help to reduce the average water consumption during prewashing and screening from 53.3m<sup>3</sup> (conventional Kraft pulp mill) to 26.7m<sup>3</sup> (proposed Kraft biorefinery). Also using hexane as the washing liquid reduced the amount water in form of steam consumed in the evaporators of the chemical recovery unit from 15m<sup>3</sup> to 7.5m<sup>3</sup>. The process water reductions achieved in the proposed Kraft biorefinery due to using hexane as part of the pulp washing liquid is equivalent to 37% of the total water consumed during Kraft pulp production. Table 6.11 shows the average amount of water consumed by the conventional Kraft pulp mill and the proposed Kraft biorefinery.

**Table 7-11: Average amount of water consumed in the conventional Kraft pulp mill and proposed Kraft biorefinery**

<b>Process unit (life cycle stages)</b>	<b>Average volume of water consumed in the conventional Kraft pulp mill.</b>	<b>Average volume of water consumed in the Kraft biorefinery.</b>
Kraft cooking process.	4m <sup>3</sup>	4m <sup>3</sup>
Pre-washing and screening after oxygen delignification.	53.3m <sup>3</sup>	26.65m <sup>3</sup>
Chemical recovery unit.	15m <sup>3</sup>	7.5m <sup>3</sup>
Post-washing after bleaching	10m <sup>3</sup>	10m <sup>3</sup>
Bleaching chemical preparation	2m <sup>3</sup>	2m <sup>3</sup>
Auxiliary boiler	9m <sup>3</sup>	9m <sup>3</sup>

To determine the impact of water consumption on freshwater depletion, the three-mandatory element of the environment impact assessment was used to study how increase or decrease in water consumption contributes towards freshwater depletion. The environmental impact assessment phase started with the first mandatory element which involves the selection of category indicators and characterisation models used to study the impact of water consumption on freshwater depletion. Table 6.12 shows the selected category indicators and characterisation models used to study the impact category listed in table 6.12.

**Table 7-12: Impact category, Category indicators and characterisation model**

<b>Impact category</b>	<b>Abbreviation</b>	<b>Category indicator</b>	<b>Characterisation model</b>
<b>Freshwater depletion</b>	WD	Fresh water depletion potential	Recipe 2008

In the second mandatory element of the environmental impact assessment phase, the average water consumption during pulp production as shown in table 6.11 were assigning



to the selected impact categories. This is known as classification. Table 6.13 shows the classification of water consumed by process units of the pulp mill and the selected impact category.

**Table 7-13:** Water consumption in the proposed Kraft biorefinery assigned to the impact categories.

Elementary flows	Quantity of water consumed (m <sup>3</sup> /Adt)	Impact category
		Fresh water depletion m <sup>3</sup> /m <sup>3</sup>
Water consumption		
Kraft cooking process.	4	CF=1
Pre-washing and screening after oxygen delignification.	26.65	CF =1
Chemical recovery unit.	7.5	CF=1
Post-washing after bleaching	10	CF=1
Bleaching chemical preparation	2m <sup>3</sup>	CF=1
Auxiliary boiler	9m <sup>3</sup>	CF=1

CF - Represent characterisation factor.

In the third mandatory element of the environmental impact assessment phase, the effect water consumption has on freshwater depletion was quantified by characterisation. Table 6.14 shows the characterisation of freshwater depletion.

**Table 7-14: The characterisation of freshwater depletion**

Elementary flows	Quantity of water consumed (m <sup>3</sup> /Adt)	Impact category
		Fresh water depletion m <sup>3</sup> /m <sup>3</sup>
<b>Water consumption</b>		
Kraft cooking process.	4	4
Pre-washing and screening after oxygen delignification.	26.65	26,65
Chemical recovery unit.	7.5	7.5
Post-washing after bleaching	10	10
Bleaching chemical preparation	2	2
Auxiliary boiler	9	9

Table 6.10 shows comparison between the environmental problem generated due the amount of water consumed in the conventional Kraft pulp mill and the Kraft biorefinery.

**Table 7-13: The difference in the level of freshwater depletion for a conventional Kraft pulp mill and the proposed Kraft biorefinery during Kraft pulp production**

Impact categories	Conventional Kraft pulp mill	Kraft biorefinery
Fresh water depletion	93.3	59.15

Finally, freshwater depletion was very significant in the conventional Kraft pulping mill than the proposed Kraft biorefinery because the amount of fresh water consumed in the former is more than the amount of fresh water consumed in the later.

In summary, we can see that energy have the most significant effect on Climatic change when compared to acidification potential, respiratory inorganic and Human toxicity. The level of climate change caused due to the amount of energy consumed in the conventional Kraft pulp mill increased by 20% as compared to the amount of climate change caused

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by the energy consumed in the Kraft biorefinery. Secondly, we can conclude that the use of hexane as 50% of pulp washing liquid in the Kraft biorefinery reduced the amount of water consumed during pulp production by 37%. This implies that the proposed Kraft biorefinery will reduce Freshwater depletion unlike the conventional Kraft pulp mill.

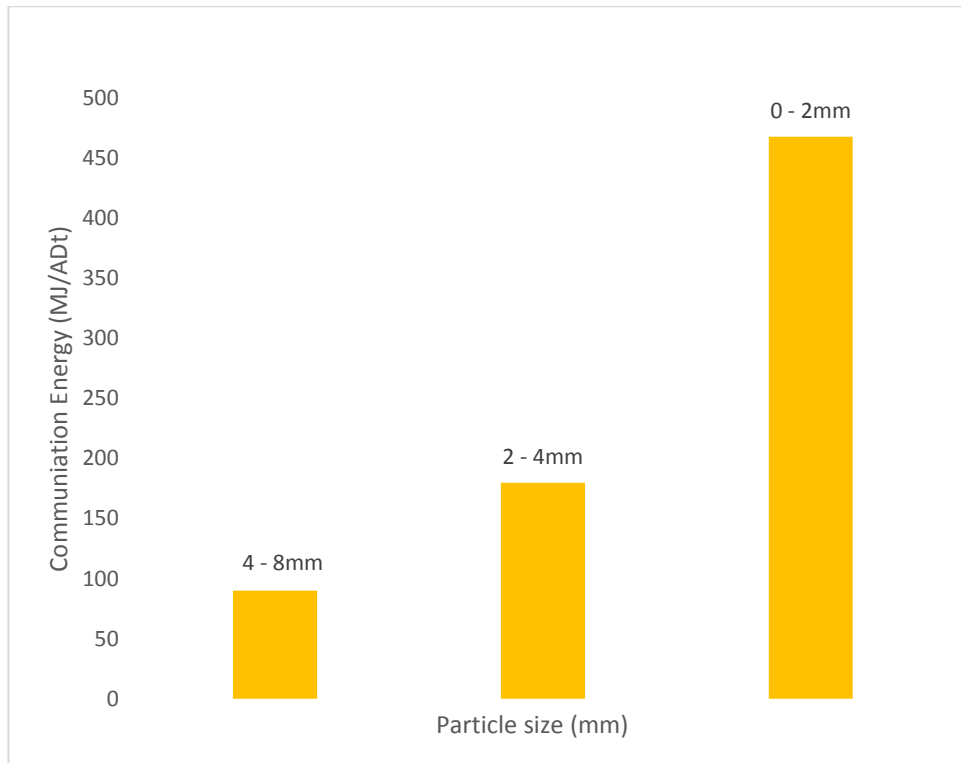
## **7.6 Life cycle interpretation**

The first element of the interpretation phase is to identify significant issues in the LCA study. The significant issue is that Conventional Kraft pulp mill consumes more energy, lots of water and create more environmental problems. But the use of particle size < 2mm cooked in 30mins and hexane as 50% of the washing liquid in Kraft biorefinery has help reduced energy consumption by 20%, fresh water consumed by 37% and reduced the level of environmental problem created by the two key elementary flows.

The second element of the interpretation phase is evaluation. According to ISO 2006, the purpose of evaluation is to improve confidence and trustworthiness in the LCA outcome /outcomes. The evaluation will be carried out through sensitivity check, completeness check, and consistency check. The completeness and consistency check have already been discussed in chapter 4. Therefore, the sensitivity check will be discussed in section 6.7.1.

### **7.6.1 Sensitivity check**

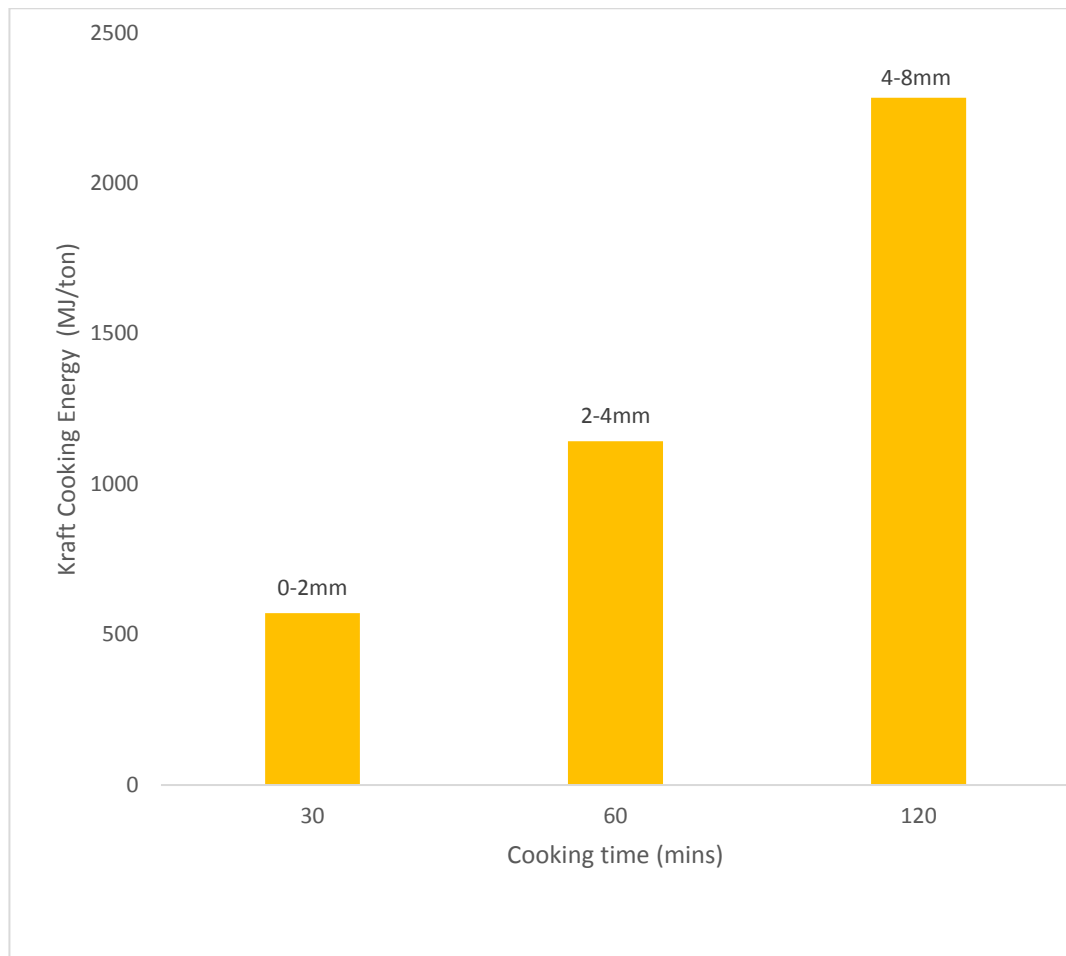
This sensitivity check was used to show that particle size < 2mm (0-2mm) cooked in 30mins is the best particle size and cooking time to achieve a reduction in energy consumption. Since energy consumption is a major issue of concern during Kraft pulp production, we decided to carry out a sensitivity check on wood handling process unit and Kraft cooking process unit to know the direct impact of different particle size on the energy consumption of these areas of concerns. In other words, the first sensitivity checks as demonstrated in figure 6.5 below was on wood handling process unit.



**Figure 7-5:** *The difference in the comminution energy during the wood handling process*

Figure 6.5 was used to show the effects of using Particle sizes (4-8mm, 2-4mm and 0-2mm) cooked in 30, 60 and 120mins on energy consumption. Figure 6.5 clearly shows that different particle size requires different comminution energy. The bigger the particle size the less the comminution energy required and vice versa. Therefore, during the wood handling process, particle size 4-8mm consumed the least energy while particle size 0-2mm consumed the highest energy.

The second sensitivity check as demonstrated in figure 6.6 was on Kraft cooking process unit. This was to show the effect of cooking time on the level of energy consumption in a Kraft pulp mill during pulp production.



**Figure 7-6:** Demonstrates the relationship between cooking time, particle size and energy consumed

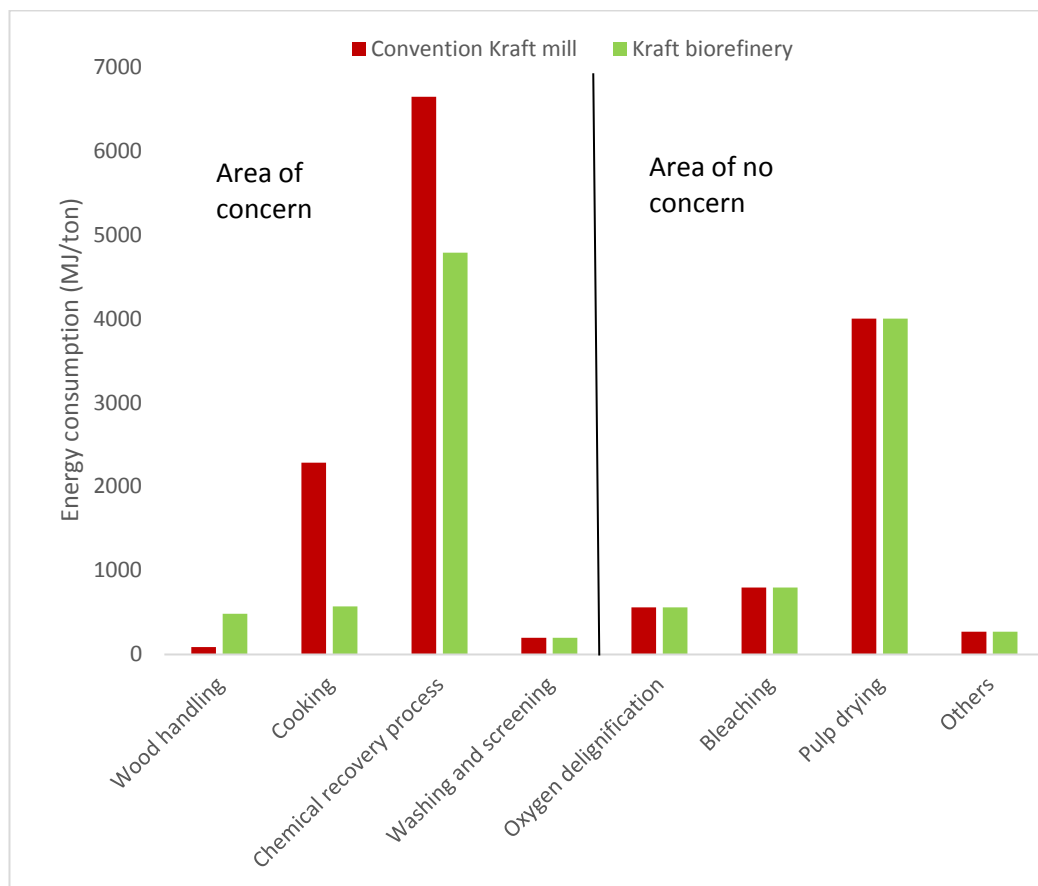
Particle size < 2mm cooked for 30 mins achieve a higher level of delignification at a lower energy consumption than particle size 4-8mm cooked for 120 mins. However, figure 6.6 shows that particle size < 2mm (particle size with the highest rate of delignification) consumed 571 MJ/Adt while particle size 4-8mm (particle size with a lower rate of delignification) consumed 2284 MJ/Adt. This confirms that smaller particle size cooked at a shorter cooking time enhance the extraction of lignin more than large particle size cooked at a longer cooking time. Finally, figure 6.6 above shows the effect of different particle sizes on energy use at different cooking time during Kraft cooking. In conclusion, the sensitivity check shows that there was a change in energy consumed during wood handling and Kraft cooking due to change in particle size and cooking time. Completeness and consistency check are part of the interpretation phase which has not been discussed in this chapter. The Completeness check ensures that the full-required information and data from all phases have been used and available for interpretation while

consistency check determines whether the assumptions, methods and data used are consistent between the life cycle stages. These stages of the interpretation phase were already analysed and explained in chapter 4.

The third element of the interpretation phase is to discuss the conclusion and make recommendation.

### 7.6.2 Conclusion

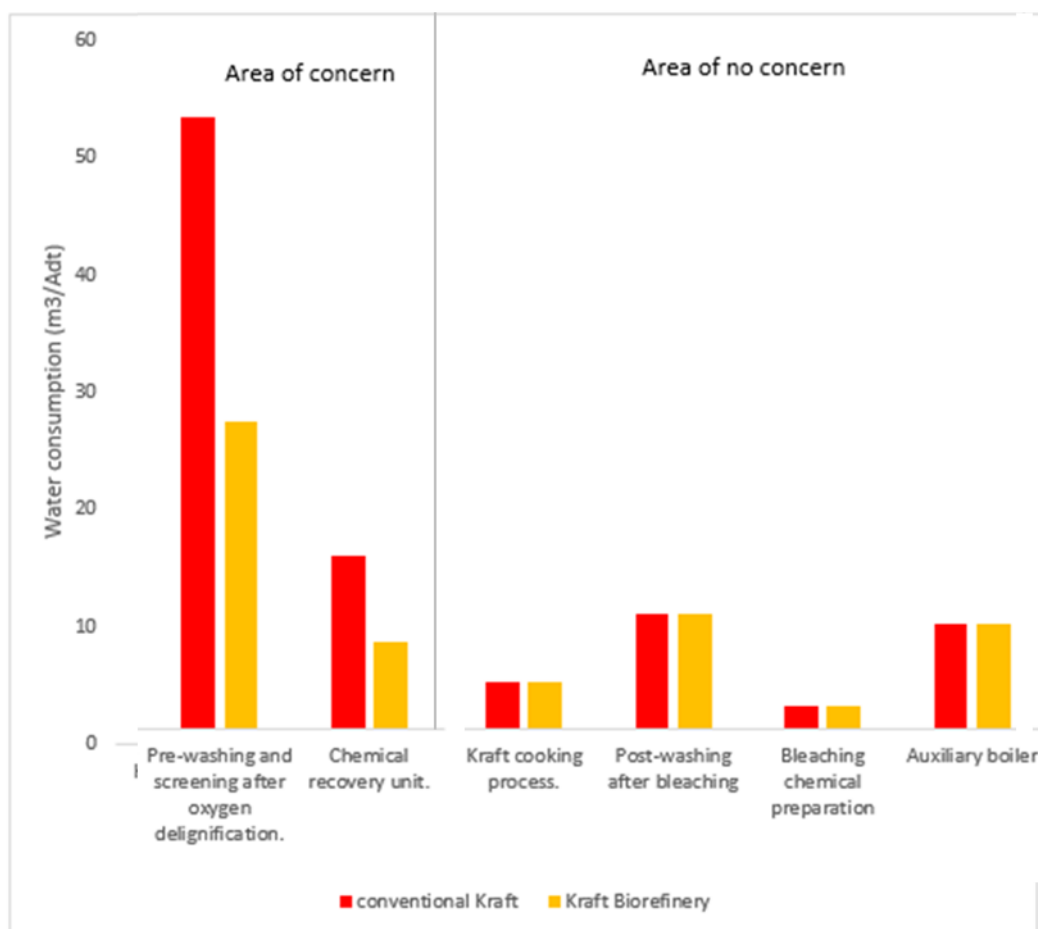
Figure 6.7 demonstrates the difference in the energy consumed in the Kraft pulp mill under study during pulp production using particle size 0-2mm and 50% hexane as part of the pulp washing liquid in the Kraft biorefinery instead of particle size 4-8mm and 100% water as the pulp washing liquid in the conventional Kraft pulp mill.



**Figure 7-7:** Difference in energy consumed in a Kraft biorefinery and a conventional Kraft pulp mill.

The decision to use particle size <2mm instead of 4-8mm and 50% hexane as part of pulp washing liquid instead of 100% water, increased the energy consumption during wood handling and decrease the energy consumption during Kraft cooking and chemical recovery process unit, in general the total energy consumed in the Kraft pulp mill was reduced by 20%.

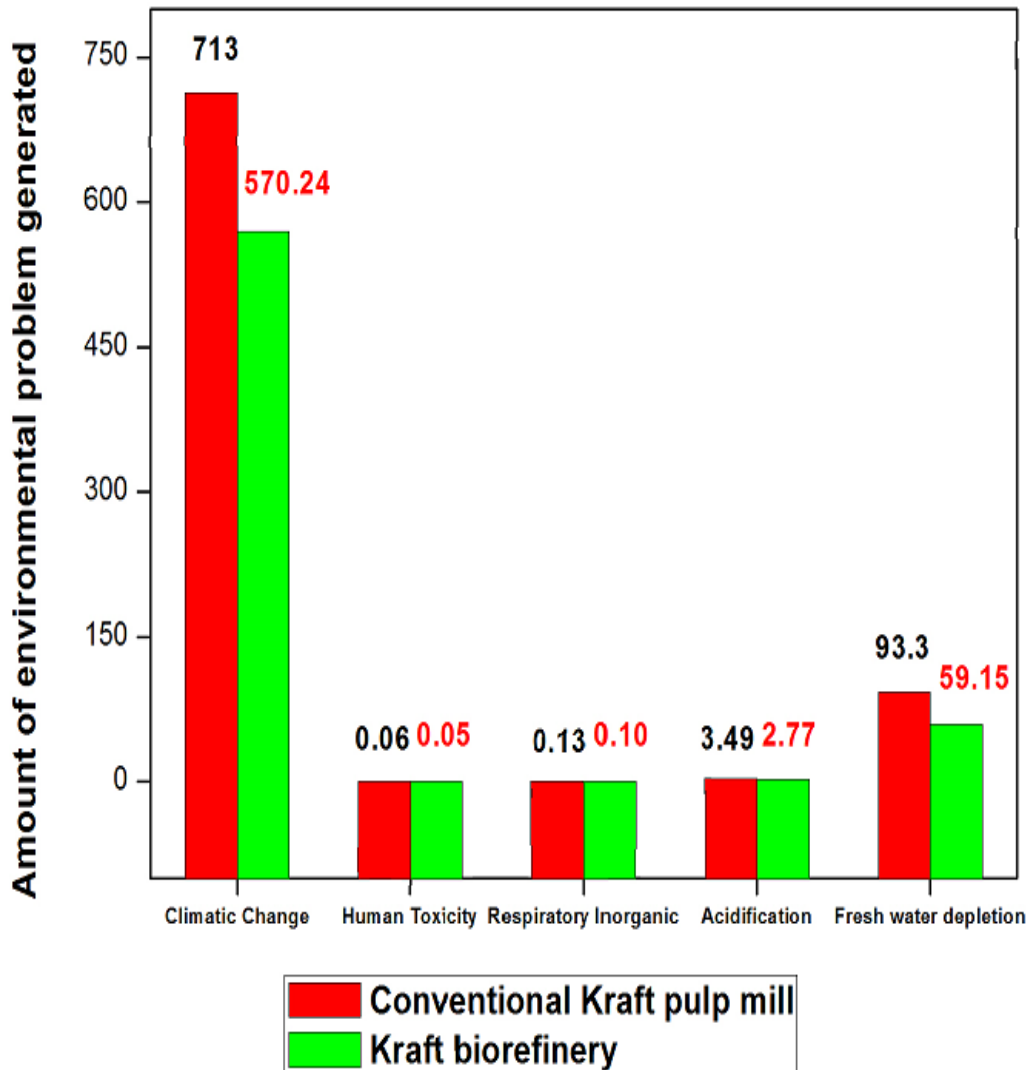
In addition, 50% hexane combined with 50% water was used as part of the washing liquid in the Kraft biorefinery while 100% water was used in the conventional Kraft pulp mill. Figure 6.8 represent the amount of water consumed in the area of concern and the area of no concern of the conventional Kraft pulp mill and Kraft biorefinery.



**Figure 7-8:** The difference between water consumed in conventional Kraft pulp mill and Kraft biorefinery.

Using 50% hexane combined with 50% water in the Kraft biorefinery instead of 100% water in the conventional Kraft pulp mill during the Kraft pulp production have reduced the amount of water consumed by 37%. The chemical recovery unit, the washing and screening process units of the conventional Kraft pulp mill and Kraft biorefinery are where the significant changes in water consumption took effect.

Figure 6.9 shows the following environmental problems (Acidification potential, climatic change, respiratory inorganic, freshwater depletion, and human toxicity) created during energy generation and freshwater consumption in the Kraft pulp mills under study.



**Figure 7-9:** Comparing the entire environmental problem generated as a result of energy generation and Freshwater use in conventional Kraft pulp mill and Kraft biorefinery during Kraft pulp production

The use of particle size < 2mm cooked in 30mins and hexane as 50% of the washing liquid also effected the significant environmental problem discussed in this study. From the figure 6.9, the Kraft biorefinery appears to be more environmentally sustainable when compared to the conventional Kraft pulp mill. Finally, we can see from figure 6.9 that climatic change is the most significant environmental problem among the five environmental problems discussed in this study.



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### **7.6.3 Limitations**

Majority of the data use for the LCA are from the literature, therefore we are not certain about the conditions the data was generated. This is a big challenge because the correctness of the data used in the LCA determines how accurate the outcome of the LCA will be. In addition, we observe they were some gaps and inconsistency because the secondary data used were from diverse source, with different data age and geographical coverage. Also, scarcity of impact data and models to carry out life cycle impact assessment is another limitation experienced during the LCA study.

### **7.6.4 Recommendation**

Hexane was the only immiscible liquid used during the liquid-to-liquid extraction. It will be an amazing idea to use different extraction liquids for the extraction of the green crude and run a sensitivity check to compare the impact of change in extraction liquid on the amount of green crude extracted from the black liquor. Finally, the outcome of the comparative study in chapter 6 suggests that using particle < 2mm cooked in 30mins and 50% hexane as the washing liquid in Kraft pulp mill makes the mill environmentally sustainable and industrially viable.

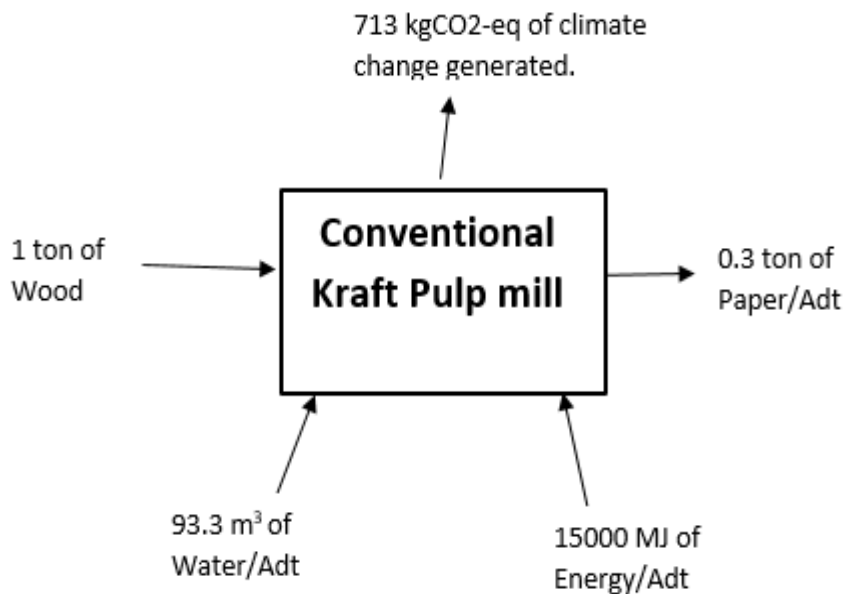
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## Chapter 8- Why Kraft biorefinery should replace conventional Kraft pulping mill

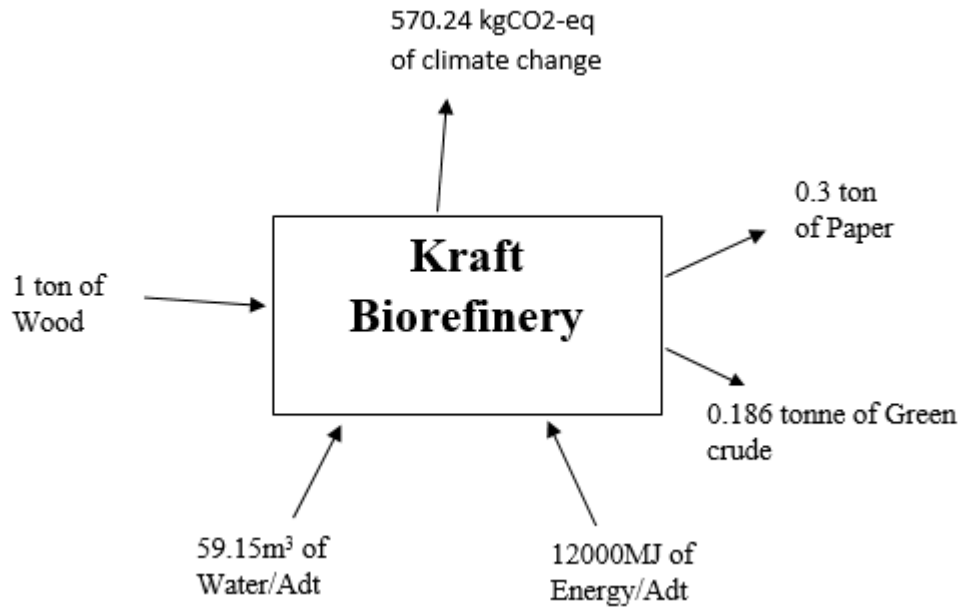
### 8.1 Introduction

In chapter 7 selected inputs and outputs from Kraft biorefinery and the conventional Kraft pulp mill were compared to determine which mills is more environmentally sustainable and industrially viable.

The schematics diagram in figure 7.1 and 7.2 shows the difference between the conventional Kraft pulp mill and Kraft biorefinery. This chapter is dedicated towards proving why Kraft biorefinery should replace conventional Kraft pulping mill. The focus is on energy, water, additional products generated in the Kraft pulp mill and impact of climate change on the environment and human health. So, we would commence by shading light on the focus of the chapter starting from energy.



**Figure 8-1:** Schematic diagram of a conventional Kraft pulp mill using particle size 4-8mm from birch wood cooked in 2 hours and 100% water as the washing liquid ( please correct)



**Figure 8-2:** Schematic diagram of a Kraft biorefinery using particle size <2mm(0-2mm) from birch cooked in 30mins and hexane as 50% of the washing liquid.

## 8.2 Energy

Energy as a very important resource is utilized in the pulp and paper industry in the form of heat and electricity. Pulp and paper industry is seen as a main user of not only energy but consumes in abundant natural resources like wood, water and so on (Suhr et al. 2015). As discussed in chapter 4, energy is identified as the elementary flow of most concern because it effects 100% of the entire process unit under the system boundary. Since 1980, modern technology, unceasing enhancement of the techniques used in the pulp and paper manufacturing, increase in recycling and improved management system have assisted in the systematic reduction of environmental footprints (Rondinelli and Vastag 2000). About 80 - 90% of emissions generated per tonne of pulp produced were reduced due to the introduction of BAT's (JRC 2000). Pulp and paper industries are the highest consumer and generator of renewable energy (Suhr et al. 2015). In fact, more than half of energy consumed in the pulp and paper mill under study is renewable. Increase in energy efficiency and decrease in the amount of fossil fuel consumption is a significant problem for the pulp and paper sector and has both economic and environmental effects (Szabó et al. 2009). Irrespective of the effort made to reduce the energy consumption the total energy demand of the process is still intense (Thollander and Ottosson 2008). The Pulp and Paper industry are in the list of the industries with the potential risk of carbon leakage (Reinaud 2008). Carbon footprint is another huge challenge encountered by the industry

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because of energy production and utilization (Zhao et al. 2019). Therefore, the use of particle size 0-2mm cooked for 30mins and hexane as 50% of the washing liquid in the washing and screening process unit as demonstrated in chapter 5 and analysed using the LCA in chapter 6 has shown that Kraft biorefinery is more environmentally sustainable than the conventional Kraft pulp mill in terms of energy use and emission release to the air.

The amount of energy consumed by the pulp industry is compared with energy consumed by energy intensive industries like steel and aluminium industries (Reddy and Ray 2011). In 2015, the amount of energy consumption per tonne of pulp in a Swedish conventional Kraft pulp mill was equivalent to 2.24 barrels of oil equivalent. However, the energy was reduced to 1.99 barrels of oil equivalent by converting the conventional Kraft pulp mill to Kraft biorefinery. This is to say that the idea of a Kraft biorefinery will help save a huge amount of energy, which will on the other hand save cost for investors because energy can take a reasonable amount of the operational cost and as well reduce a significant amount carbon footprint. Industrial process like pulp and paper manufacturing, ramp up energy use because it takes approximately between 12GJ – 17GJ to produce a tonne of pulp from a conventional Kraft pulp mill (Suhr et al. 2015). Therefore, introducing Kraft biorefinery will not only help improve the energy efficiency but also reduce the cost of production. The idea of a Kraft biorefinery will help address the amount of energy use in pulp production. The Kraft Biorefinery could achieve this goal by using woodchip thickness < 2mm instead of 4-8mm as already demonstrated in chapter 6. Particle size < 2mm have shown to be more sustainable because it consumed less total pulp production energy than other particle sizes. According to EDF energy 2018, the cost of electricity per kWh from 18th September on a standard tariff was equivalent to 18.14p. Table 7.1 shows the implication of using different particle size on the cost of energy consumed in both conventional Kraft pulp mill and Kraft biorefinery.

**Table 8-1: Different particle size and effect on production energy**

<b>System Under study</b>	<b>Total energy consumed (MJ/Adt)</b>	<b>The equivalent of the total energy consumed in Kwh = (0.28*MJ/Adt)</b>	<b>Cost of energy per Kwh</b>	<b>Cost of energy Use per tonne of pulp</b>
Conventional kraft pulp mill	15000	4200	18.14pence	£761.88
Kraft Biorefinery	12000	3360	18.14pence	£ 609.50

Table 7.1 clearly shows that the cost of purchasing the total energy used in the conventional Kraft pulp mill and the Kraft biorefinery are different. Therefore, the cost implication of using particle size < 2mm in the Kraft biorefinery is far less than the cost of using particle size 4-8mm in the conventional Kraft pulp mill. In summary, the outcome of Table 7.1 is one of the reasons that Kraft biorefinery should replace a conventional Kraft pulp mill. Kraft biorefinery consume less energy and acquire less energy cost than the conventional Kraft pulp mill. Table 7.2 clearly demonstrates the energy savings achieved by choosing particle size < 2mm instead of particle size 4-8mm and the use of hexane mixed with water in the pulp washing & screening process unit.

**8.2.1 Energy savings for using particle size <2mm cooked in 30 mins and hexane as 50% washing liquid.**

The energy savings for using particle size < 2mm cooked in 30 mins and hexane as 50% washing liquid was calculated by finding the difference between the total energy consumed in a conventional Kraft pulp mill and Kraft biorefinery. Table 7.2 shows the quantity of energy saved by replacing a conventional kraft pulp mill with a Kraft biorefinery.

**Table 8-2: Energy savings**

Energy saving (MJ/Adt)	The energy equivalent in KWh/t (0.28*MJ/Adtt)	Energy Cost saved per tonne of pulp
3000	840	£ 152.38

In other words, a non-integrated pulp Swedish mill producing 250,000 Adt of a bleached Kraft pulp per annum with particle size < 2mm cooked in 30 mins and hexane as 50% washing liquid would save approximately £38,000,000 per annum on energy cost.

### **8.3 Water**

Another resource that is of great important in the pulp and paper industry is water. As shown in chapter 4, it affects 60% of the process unit within the system boundary. In United States up to 17000 gallons of water are used per ton of pulp, suggesting the industry to be the largest user of water (Bajpai 2018). In addition, the industry is the second biggest water footprint in Europe. However, many actions have been taken to reduce both freshwater use and wastewater production in the pulp and paper industry due to raising issue of water scarcity. In addition, different government regulation has made the issue of water use in the pulp and paper industry a very crucial topic of discussion (Tewari et al. 2009).

#### **8.3.1 The impact of hexane as part of the washing liquid on the level of water consumed in a Conventional Kraft pulp and a Kraft biorefinery**

Introduction of hexane as part of the washing liquid become a huge impact in the Kraft pulping industry. According to (Andersson,2015) the evaporator is one of the most energy intense equipment in a Kraft pulp mill. After washing and screening, all the weak black liquor is transported to the evaporator. The evaporator begins to concentrate the weak black liquor containing 15% solid to strong black liquor containing 75% to 85% solid. Therefore, huge amount of energy is required to convert the weak black liquor to strong black liquor. The proposed concept will help to reduce the amount of water use in pulp production. This concept will decrease the energy required to convert the weak black liquor to strong black liquor, since the number of evaporators use in the chemical recovery unit will reduce. Also, the quantity of water used in the washing and screening process

unit of the Kraft biorefinery has halved as shown in Table 7.4 due to the use of hexane as 50% of the washing liquid. Bear in mind that the cost enquired to purchase the hexane used in the prewashing stage of the conventional Kraft pulping mill is not in any way close to what is required to purchase the evaporators plus the evaporators operating and maintenance cost. Therefore, using hexane as a washing liquid do not only save energy, but it also reduces water consumption.

**Table 8-3:** *Difference in water consumption and effects on the cost of operation for a conventional Kraft pulp mill and Kraft biorefinery due to use of hexane*

	Conventional Kraft pulp	Kraft biorefinery
<b>Percentage of water used in the washing and screening unit</b>	100%	50%
<b>Total quantity of water used</b>	93.3m <sup>3</sup>	59.15m <sup>3</sup>
<b>Cost of water consumed</b>	177.3 pounds	112.4 pounds

We should also remember that using hexane in Kraft pulp mill has economic implications.

### **8.3.2 Water and energy saving due to the use of Hexane**

Assuming the average quantity of water required by the washing unit of a conventional Kraft pulp mill is 93.3m<sup>3</sup> (100%) per ton of pulp. Using only 50% instead of 100% water in pulp production will reduce the amount of water to 59.15m<sup>3</sup> per ton of pulp with water savings of 34.15m<sup>3</sup>. The use of hexane in Kraft biorefinery is one of the easy ways to control and reduce the amount of water used in the Kraft pulp mill because this also reduce the volume of wastewater generated in the Kraft pulp mill. According to Mogden formula, the higher the water consumed in the Kraft pulp mill, the higher the effluence produce and the trade effluence charge per cubic metre (Walker 2000). However, the lower the water consumed in the Kraft mill, the lower effluence and water charge imposed on the Kraft pulp mill. According to southwest water, 1m<sup>3</sup> of water cost £1.9. Therefore, the cost of 34.15m<sup>3</sup> of water saved per ton of pulp is equivalent to 64.9 pounds. If 64.6 pound is saved per ton of pulp by reducing the water consumed, producing 250,000 tons of pulp

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will save £16,225,000 per annum. In summary, Kraft biorefinery should replace conventional Kraft pulp mill because Kraft biorefinery consumes less water in the washing and screening process unit reducing the water footprint of the industry.

### 8.3.3 *Green crude analysis*

The hexane extract (green crude) is nothing until a value is put on it. The value of the green crude will depend on the composition. Therefore, GC/MS analysis of the hexane extract obtained from the Liquid-to-liquid extraction experiment on the nine samples of the strong black liquor acquire from particle size <2mm, 2-4mm and 4-8mm cooked for 30, 60 and 120 mins shows the present of very important compounds which can be extracted and used for different purpose. The GC/MS Library for particle size <2mm cooked in 30mins shows that the extract from particle size <2mm cooked for 30mins contains 34.7% Aromatic, 16.8% Naphthene, 48.5% Paraffin. Just like fossil crude oil, green crude cannot be completely separated into its individual components, although the percentage of the components listed above can be identified. The details of the percentage values of the extractable organic compound were obtained and discussed in chapter 3 and 5. In summary, the green crude obtained from the back liquor of particle size <2mm cooked for 30 mins during hexane extraction shows better potential to be converted to value-added product because it contains the highest percentage of extractable Aromatics. Therefore, the green crude's major compositions were plot on a crude oil ternary diagram to determine the green crude equivalent of crude oil. Since particle size <2mm cooked for 30mins is the preferred choice of particle size, the Aromatic, Naphthene and Paraffin from the particle was plot on a crude oil ternary diagram as shown in figure 7.4. The respective apex of the triangle in figure 7.3 signifies 100% of the compound on the Apex. and 0% of the other compounds on each sides of the triangle diagonal from the apex. For example, Aromatic hydrocarbon is 100 % at A but 0% at B & C likewise paraffin's and naphthene's.



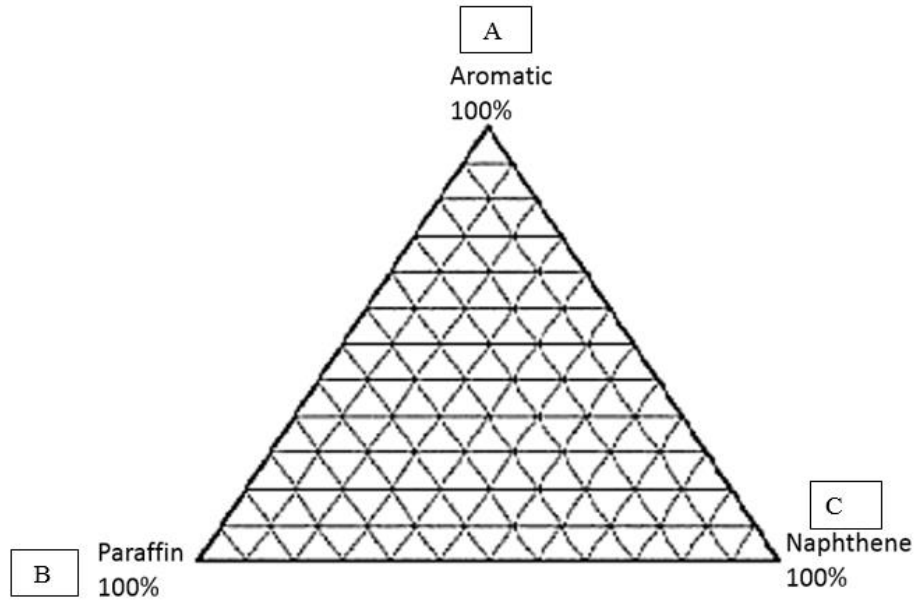


Figure 7-3: A Temporary Diagram

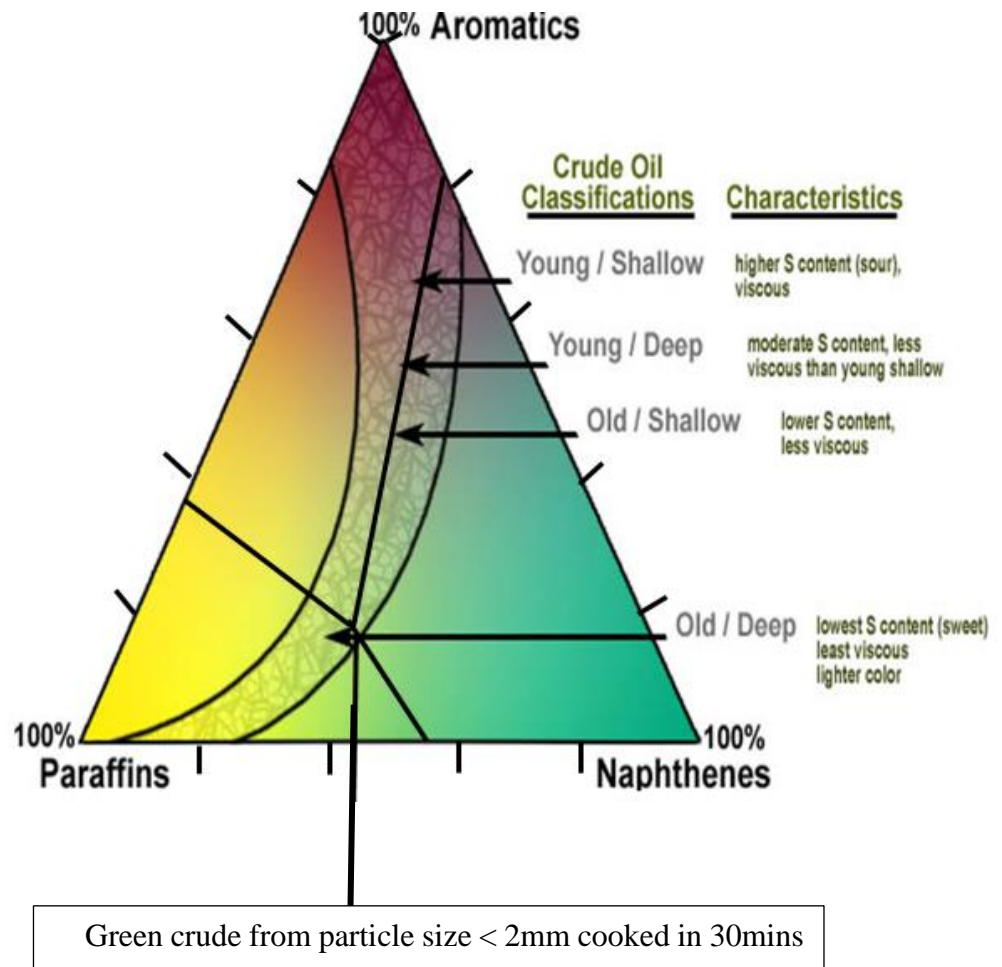


Figure 8-4: The Green crude from birch particle size < 2mm cooked in 30mins plotted on a Crude oil Ternary diagram(Terry 2001)

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The three designated boundaries plotted on the Ternary diagram in Figure 7.4 shows that the discovered green crude is in the same category as the Old/Deep crude oil. The old/deep crude oil is the type of crude buried deeply for a long time. The Old/deep crude oil has low viscosity, low density and very low sulphur content (Simanzhenkov and Idem 2003). The mentioned qualities make Old-deep crude the most favourite type of crude. Unfortunately, only 5% of the world's crude oil reserves are of this quality (Carter and Flaherty 2017). The crude with this type of quality is found primarily in the Appalachian basin in the Marcellus Formation in the state of New York, Pennsylvania, and Ohio (Burruss and Ryder 2014). This type of sweet crude oil is referred to as Pennsylvania grade crude. According to figure 7.4 the discovered green crude falls in the same category as the Pennsylvania crude. The ARG group pricing categories on the 4th of May 2019 show that the price of Pennsylvania crude is \$62.08. One Barrel/0.12 tonne of Pennsylvania crude cost \$62.08 (One barrel = 0.12 tonne). In the extraction unit of the Kraft biorefinery, particle size <2mm cooked for 30mins generated 0.186 tonne of green crude per air dry tonne of pulp after the hexane is recycled back to the hexane tank under a vapour pressure of 153mmHg at 25°C. If 0.12 tonne of Pennsylvania crude = \$62.08, 0.186 tonnes of green crude = \$99.22. Therefore 1 tonne of birch wood produced 0.186 tonne of green crude = \$99.22. Apart from the fact that the green crude has similar features as Pennsylvania crude, green crude can be another opportunity of generating green hydrocarbons. The formation of fossil crude takes 175-200 million years to form fossil hydrocarbon (Wong et al. 2015), in addition, the investment cost is very high, and finally the entire process is not environmentally friendly (Hao and Van Brown 2019). Therefore, green hydrocarbon (green crude) could be best alternative towards producing a sustainable and environmentally friendly hydrocarbon. The products from a conventional Kraft pulp mill and Kraft biorefinery were compared and it was found that both are almost the same except for the product called green crude produced by the biorefinery. Green crude/ green hydrocarbon is the only product that is not produced in the conventional Kraft pulp mill. Earlier in this chapter we defined green crude, its formation, characterisation and compared it with fossil crude to enable us to put a value on it. According to figure 7.4, green crude is equivalent to the Pennsylvania grade crude. If 0.186 tonne of green crude from 1 Adt of pulp generate \$99.22 for the Kraft pulp mill, 250000 Adt of Kraft pulp per annum will yield 46,500 tonnes of green crude. And this quantity of green crude will generate \$4,613,730 for the Kraft pulp mill. This additional product from the Kraft biorefinery shows a better prospect and makes the kraft mill

economically viable. Finally, the green crude is one of the reasons the conventional Kraft pulp mill should be replaced with Kraft biorefinery.

### 8.3.4 *Impact of climatic change on human health and the environment*

The table below clearly shows the difference in the environmental problem (climatic change) caused by the two systems under study.

**Table 8-4:** *The difference in the amount of climatic change caused by a conventional kraft pulp mill and Kraft biorefinery*

<b>Emission released and environmental problem caused</b>	<b>Conventional Kraft pulp mill</b>	<b>Kraft biorefinery</b>
Climatic Change	713 kgCO <sub>2</sub> -eq	570.24 kgCO <sub>2</sub> -eq

#### **Impact of climatic change on human health and environment:**

Climatic change has direct and indirect effect on human health. Examples of direct effect are heat waves, air pollution and aero – allergens while indirect effect are water borne diseases, Malnutrition, social and economic disruption (Beniston 2002). According to (recipe 2008) the impact of climatic change depends on the region of the globe effected because the way regions are protected by nature or social economic factors differ. Secondly, the impact of climate change also depends on how long humans are exposed (Hauschild and Huijbregts 2015). When humans are exposed for a large time scale, the human system begins to adapt, making the damage done less. However, when humans are exposed within a short time scale, they damage done by climatic change on human health is more due to the inability of the body to adjust to a change in the environment in a short time (Hauschild and Huijbregts 2015). Furthermore emission of greenhouse gases encourage the increase in radiative forces which increase the temperature of the atmosphere and oceans resulting in sea rise leading to flooding and accidental death, perturbation in rainfall and warmer oceans which may have important effect on crop yield, water availability and marine production (Pedrono et al. 2016). Warmer climate will have a serious impact on all living species, leading to displacement or extinctions (Pauls et al. 2013). Therefore, the introduction of Kraft biorefinery will reduce the impact of climatic change on human health and environment within the Kraft pulp mill since Kraft biorefinery use less energy, which generates less of those emissions that cause

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global warming leading to climatic change. Therefore, the conventional Kraft mill should be replaced by a Kraft biorefinery.

#### **8.4 Conclusion**

In summary the proposed Kraft biorefinery should replace the conventional Kraft pulping mill because the proposed Kraft biorefinery consumes approximately 12000MJ/Adt while the conventional Kraft pulp mill consumes approximately 15000MJ/Adt saving the mill 3000MJ/Adt which is equivalent to 840 KWh. However, 840 KWh is equal to £152.38 at 18.14 pence per KWh (EDF Energy 2018). For a Kraft pulp mill that produce 250,000 tonnes of pulp per annum, adopting the proposed Kraft biorefinery will save the Kraft pulp mill approximately £38,000,000 per annum. Secondly, the conventional Kraft pulp mill consumes 93.3m<sup>3</sup> per ton of pulp while the proposed Kraft biorefinery consumes 59.15m<sup>3</sup> of water per ton of pulp saving the Kraft pulp mill huge trade effluence charge. During operation, the Kraft pulp mill release emissions like SO<sub>x</sub>, NO<sub>x</sub> and TRS. These emissions generate environmental problems like Climatic Change, Respiratory Inorganic and Acidification. The LCA identified climate change as the most significant environmental problem generated during Kraft pulp production. The amount of climatic change generated by the conventional Kraft mill is equivalent to 713 kgCO<sub>2</sub>eq and this was reduced by 20% to approximately 570.24 kgCO<sub>2</sub>eq by the proposed Kraft biorefinery. Finally, the proposed Kraft biorefinery has shown to be more environmentally sustainable and industrially viable because the Kraft biorefinery consume less energy, less water, cause less climate change and generate green crude which can be used as drop-in fuel. On the other hand, green crude can be refined to produce important bio-chemicals which can be an additional source of revenue for the Kraft pulp mill.

The Kraft biorefinery and the conventional Kraft pulp mill were compared to determine which among them is more environmentally sustainable and economically viable. The outcome explains why Kraft biorefinery should replace conventional Kraft pulp mill.

Table 7-7 is a summary of the energy consumption during Kraft pulp production in a conventional Kraft pulp mill and a Kraft biorefinery.

**Table 7-7: Energy consumption during Kraft pulp production**

<b>Product system under study</b>	<b>Total energy consumed /Adt of pulp</b>	<b>Cost of energy consumed /Adt of pulp</b>	<b>Cost of total energy consumed in producing 250,000 Adt of pulp per annum</b>
Conventional Kraft pulp mill	15000	£761.88	£ 190,470,000
Kraft biorefinery	12000	£ 609.50	£ 152,375,000

Kraft biorefinery should replace the conventional Kraft pulp mill because Kraft biorefinery consumes less energy resulting in less environmental harm. Therefore, Kraft biorefinery is more environmentally sustainable and industrially viable.

Table 7-8 is a summary of water consumed during the Kraft pulp production in a conventional Kraft pulp mill and a Kraft biorefinery.

**Table 7-8: Water consumed during Kraft pulp production.**

<b>Product System under study</b>	<b>Total water consumed /Adt of pulp</b>	<b>Cost of total water consumed /Adt of pulp</b>	<b>Total cost water consumed in producing 250,000 Adt of pulp per annum</b>
Conventional Kraft pulp mill	93.3m <sup>3</sup>	£ 177.3	£ 44,325,000
Kraft biorefinery	59.15m <sup>3</sup>	£ 112.4	£ 28,100,000

Kraft biorefinery should replace the conventional Kraft pulp mill because Kraft biorefinery would cause less freshwater depletion due to less water consumption therefore

Kraft biorefinery is more environmentally sustainable. Table 7-9 is a summary of the environmental problem generated during Kraft pulp production in the conventional kraft pulp paper mill and Kraft biorefinery. The following assumptions were used. Emissions between 0.0001-5.000 is categorised as **significant**. Between 50 - 150 is categorised as **more significant** while 400-800 is categorised as **most significant**. Therefore Table 7-9 also demonstrate that Kraft biorefinery is more environmentally sustainable than conventional Kraft pulp mill.

**Table 7-9: Environmental problem generated**

<b>Product System under study</b>	<b>Environmental problem generated</b>	<b>Quantity generated per Adt of pulp</b>	<b>Level of significance</b>
Conventional Kraft pulp mill	Climatic Change	713	Most significant
	Human Toxicity	0.0624	significant
	Respiratory Inorganic	0.1312	significant
	Acidification	3.49	significant
	Fresh water depletion	93.3	More significant
Kraft biorefinery	Climatic Change	570.24	Most significant
	Human Toxicity	0.04992	significant
	Respiratory Inorganic	0.1049	significant
	Acidification	2.772	significant
	Fresh water depletion	59.15	More significant

Kraft biorefinery should replace the conventional Kraft pulp mill due to the level of environmental problem generated during pulp production. Climate change is the most significant environmental problem as indicated in table 7-9 and the level of climate change cause by the conventional Kraft pulp mill is more when compared with the level of climate change caused by the Kraft biorefinery.

Finally, Kraft biorefinery generate an additional product called green crude during pulp production. This product makes the Kraft biorefinery both economically and industrially viable than the conventional Kraft biorefinery. 186kg of green crude is produced per ton of pulp. 186kg of green crude cost £73.4 therefore the total revenue generated @ 250,000 Adt per annum is equivalent to £18,575,000.

In summary table 7.10 show that Kraft biorefinery is more economically viable than the conventional Kraft pulp mill.

**Table 7.10:** Cost and revenue of Energy, Water and Green crude generated during the Kraft pulp production.

	<b>Conventional Kraft pulp mill</b>	<b>Kraft biorefinery</b>
Total cost of water consumed in producing 250,000 Adt of pulp per annum.	£ 190,470,000	£ 152,375,000
Cost of total energy consumed in producing 250,000 Adt of pulp per annum.	£ 44,325,000	£ 28,100,000
Total revenue generated from green crude @ 250,000 Adt per annum.	£ 0	£ 18,575,000.

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the use of the multi-disciplinary approach involving LCA, and empirical methodology have help discover that the use of particle size <2mm cooked in 30mins and recoverable hexane during pulp washing reduce energy consumption and water consumption resulting in lower environmental impact and green chemicals produced from wood.



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## Chapter 9 - Summary of the conclusions and recommendations for future works.

### 9.1 Summary of conclusion

In this research a multi-disciplinary approach involving life cycle assessment (LCA) and empirical methodology was used to improve the environmental sustainability and industrial viability of the conventional Kraft pulp mill. Firstly, the LCA as the main methodology was used to provide background information needed to identify areas where the conventional Kraft pulp paper mill can be improved while the empirical methodology was used to demonstrate how the change in input parameters like wood particle thickness and the use of a re-usable liquid as part of the washing liquid reduced water consumption, energy use, level of climate change and enable the recovery of extractable chemicals in the form of green Crude.

#### 9.1.1 Summary of the experimental methodology

The experimental methodology was used to show that change in wood particle thickness and the use of a re-usable liquid as part of the washing liquid could reduce water consumption, energy use, and level of climate change and enable the recovery of extractable chemicals in the form of a green crude. Five main experimental steps were taken to achieve this purpose. First, the reduced wood samples were separated into different Particle sizes using sieves of different aperture. The separated particles were cooked using Kraft cooking technique. After cooking, the Kraft pulp was washed using water and hexane. Green crude was extracted from the black liquor using Liquid – Liquid extraction (LLE) technique. The extract from the Liquid – Liquid extraction (LLE) was analysed using a gas chromatography / mass spectroscopy (GC/MS) while the black liquor before and after LLE extraction was analysed with a TGA (Thermogravimetric analysis). The experimental outcome represented in chapter 5, depicts that reducing the particle size from 8mm currently used in the conventional Kraft process to < 2mm and replacing half of the water used during washing with recoverable hexane, reduce energy consumption, reduce water consumption, reduced the level of climate change, and generates an extractable chemical called the green crude.

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### ***9.1.2 Summary of the LCA Methodology***

The four phases of the LCA methodology were used to provide background information needed to identify areas where the conventional Kraft pulp paper mill can be improved. In Chapter 4, LCA methodology was used to identify the two key elementary flow of concern to the selected process units under the system boundary and the process units affected most by the mentioned elementary flows. Also, identify the most significant environmental problem generated during Kraft pulp production. Each phase of the LCA and their outcomes demonstrated how the LCA methodology helped to achieve the study objective. The goal and scope phase of the LCA described the product system studied, functional unit, system boundaries, quality of data required, the LCA limitations and the cut-off criteria. The outcome of the goal and scope phase confirmed that 10 process unit was selected for the LCA study. The inventory phase of the LCA study showcased the flowchart of each process unit, energy input, material input, material output, environmental emissions and waste associated with the conventional Kraft pulp paper mill. During the inventory analysis, a detail description of each process unit mentioned in the system boundary of the conventional Kraft pulp paper mill under study, the source of data use for the study, methods of calculation and specific units used was explained. The percentage contribution of each elementary flow was also discussed in the inventory phase. The selected elementary flow during the inventory analysis were compiled under the following headings: energy input, raw material inputs, solid waste, release to air, water and soil. The outcome of the inventory phase discovered energy and water as the two key elementary flow of concern to the selected process units under the system boundary while the chemical recovery process unit and the washing & screening process unit are the process units affected most by the mentioned elementary flows. The environmental impact assessment phase of the LCA was used to identify the most significant environmental problem generated during Kraft pulp production. During the environmental impact assessment, the mandatory elements were used to study the different environmental problems generated during energy consumption and water consumption in the conventional Kraft pulp mill. The outcome of the environmental impact assessment as demonstrated in Figure 4.13 shows that climatic change is the most significant environmental problem generated during Kraft pulp production. In the interpretation phase of the LCA, important concerns based on the outcome of the inventory analysis and environmental impact assessment were evaluated to improve confidence and trustworthiness in the LCA result. The conclusion based on the outcome

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of the second and third phase of the LCA indicated that the conventional Kraft pulp mill is environmentally unsustainable because of the amount of energy consumed, amount of water consumed, and the level of climate change generated during Kraft pulp production. Recommendation on possible ways to resolve the important concerns were explained with limitation. The use of particle size  $< 2\text{mm}$  and a re-usable organic compound as part of a washing liquid as recommended in chapter 4 was applied to the new conventional Kraft pulp mill called Kraft biorefinery. A comparative study between the conventional Kraft pulp paper mill and the Kraft biorefinery using the LCA methodology as demonstrated in chapter 6 was used to measure the difference in energy consumption, water consumption and the environmental problems generated during Kraft pulp production. During the study, the goal and scope phase defined the objective of the study which is to identify the impact of using particle size  $< 2\text{mm}$  cooked in 30mins and hexane as 50% of the pulp washing liquid on energy consumption, water consumption and the environmental problems generated during Kraft pulp production. The goal and scope phase of the LCA also described the product system studied, functional unit, system boundaries and quality of data used for the inventory. The inventory phase of chapter 6 focused on how the key elementary flows of concern identified in chapter 4 effect the process units in the system boundary called the areas of concern. After the inventory analysis, the pulp production energy and water consumption were examined from an environmental perspective using the third phase of the LCA (environmental impact assessment). Finally, the outcome of the comparative study in chapter 6 suggests that using particle  $< 2\text{mm}$  cooked in 30mins and 50% hexane as the washing liquid in the conventional Kraft pulp mill reduced 20 % of the energy consumed, 37% of fresh water consumed and 20% of the most significant environmental problem generated during Kraft pulp production.

### ***9.1.3 Future works***

- It will be good to use the same empirical methodology to determine the green crude content of other soft and hard woods apart from birch and pine.
- For more reliable and better outcome, inventory used for the LCA should be mostly from primary source with the same representativeness, technology, time and geographical coverage.
- When carrying out the environmental impact assessment, it will be good to include the optional steps which include normalisation and weighting.

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- Scarcity of impact data and models to carry out life cycle impact assessment affect the outcome of LCA. Additional information to support the relationship between important inventory results and the environment are missing therefore some of the important inventories listed in the life cycle inventory phase of the LCA are ignored. Embarking on research that will help in the development of easy impact pathway for impact categories and characterisation model connecting elementary flows from inventory to area of protection will help reduce uncertainty and improve the reliability of LCA results.
  - It will be good if different organic compounds are used for the Liquid-to-liquid extraction process. In the end sensitivity analysis should be carried out to check the reliability of the results and the sustainability of the extraction solvents.

## APPENDICES A

*Structuring the elementary flows entering and leaving the selected process unit within the system*

LCI Input/output	Wood Handling	Cooking	Chemical Recovery Process	Washing And Screening	Bleaching	Oxygen Delignification	Axillary boiler	Pulp Dryer	Waste Water Treatment	Total
Debarked wood (m <sup>3</sup> /ton)	6	-	-	-	-	-	-	-	-	6
Sawdust (kg/ton)	9	-	-	-	-	-	-	-	-	9
Bark (kg/ton)	6	-	-	-	-	-	-	-	-	6
Woodchips (m <sup>3</sup> /ton)	15*	15*	-	-	-	-	-	-	-	30
Energy (MJ/ton)	438*	2284*	6642*	198*	799*	562*	108*	3228*	72*	14.423
NaOH (kg/ton)	-	-	-	-	-	-	-	-	-	50
Pulp (ton)	-	1000*	-	1000*	-	1000*	-	975	-	3975
black liquor (kg/ton)	-	1800*	1800*	1800*	-	-	-	-	-	5400
COD (kg/ton)	-	20	-	4	14	10	-	-	42	90
BOD (kg/ton)	-	10	-	-	-	-	-	-	-	10
TRS (kg/ton)	-	2	0.07	-	-	-	0.1	-	-	2.17
Water (kg/ton)	-	-	-	3	-	-	-	-	-	3

fibre rejects (kg/ton)	-	-	-	20	-	-	-	-	-	20
MgSO <sub>4</sub> (Kg/ton)	-	-	-	-	-	3	-	-	-	3
O <sub>2</sub> (kg/ton)	-	-	-	-	-	25	-	-	-	25
Oxygen delignified pulp Kg/ton	-	-	-	-	975	-	-	-	-	975
Ozone Kg/ton	-	-	-	-	5	-	-	-	-	5
AOX, Kg/ton	-	-	-	-	0.1	-	-	-	0.3	0.4
Chlorine from bleach pulp Kg/ton	-	-	-	-	0.04	-	-	-	-	0.04
VOCs Kg/ton	-	-	-	-	0.1	-	-	-	-	0.1
Waste water Kg/ton	-	-	-	-	40	-	-	-	-	40
Phosphorus nutrient Kg/ton	-	-	-	-	0.06	-	-	-	110	110.06
Nitrogenous nutrient Kg/ton	-	-	-	-	0.09	-	-	-	0.63	0.72
green liquor, lime mud, dredge Kg/ton	-	-	60	-	-	-	-	-	-	60
Turpentine Kg/ton	-	-	2	-	-	-	-	-	-	2
Ash Kg/ton	-	-	0.5	-	-	-	-	-	-	0.5
Sludge Kg/ton	-	-	-	-	-	-	-	-	0.9	0.9

Ash Kg/ton	-	-	0.5	-	-	-	-	-	-	0.5
Sludge Kg/ton	-	-	-	-	-	-	-	-	0.9	0.9
Water treatment sludge Kg/ton	-	-	-	-	-	-	-	-	10	10
TSS Kg/ton	-	-	-	-	-	-	-	-	7	7
Wood ash Kg/ton	-	-	-	-	-	-	9	-	-	9
wood waste Kg/ton	-	-	-	-	-	-	6	-	-	6
particulates Kg/ton	-	-	1.9*	-	-	-	1	-	-	2.9
SO <sub>2</sub> (gas) Kg/ton	-	-	0.402*	-	-	-	-	-	-	0.402
NO <sub>x</sub> Kg/ton	-	-	3.83*	-	-	-	0.7	-	-	4.53

(\*) represent every output or input that has been calculated.

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