



Exergy analysis in the Pulp and Paper Industry

Setúbal Site - The Navigator Company

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Abstract

The Pulp and Paper industry is the highest energy consumer in Portugal. This means that an exergy analysis is extremely relevant in order to better understand the real impacts of this industry and how it can reduce its environmental footprint. The pulp manufacturing process is divided into different stages, with an explanation of what happens in each one. This division has the goal of proposing a standardized way of making this type of analysis to this specific industry, so it becomes easier in future work to compare each stage of the whole process.

An exergy analysis is then performed to a pulp manufacturing process in 2002, specifically to the Kraft process used by The Navigator Company in Setúbal, Portugal. Based on Alexandre Martins' report from 2002, with the aid of an energy audit performed in 2014, it was possible to compute the exergy efficiencies for the digester, washing and black liquor evaporation process, the processing stage, and the recovery boiler and biomass co-generation process which were 41%, 36% and 66%, respectively. The overall efficiency is also calculated, presenting a very low exergy efficiency of 17.5% without taking into consideration the debarking and lime ovens stages, and 7% if all stages are considered.

Keywords

Exergy; Exergy analysis; Exergy efficiency; Pulp and Paper industry;

Resumo

A indústria do Papel é a maior consumidora energética em Portugal. Tal significa que uma análise exérgica é extremamente relevante de modo a compreender os impactos reais desta indústria e como reduzir a sua pegada ecológica. Todo o processo é dividido em diferentes estágios, e mais tarde explicado o que ocorre em cada um deles. Esta divisão tem o objectivo de propor uma forma *standard* de fazer este tipo de análise a esta indústria específica, de modo a facilitar a comparação entre os vários estágios em trabalhos futuros.

Foi feita uma análise exérgica à produção de pasta de papel, mais especificamente ao processo *Kraft* utilizado pela empresa *The Navigator Company* em 2002, em Setúbal, Portugal. Usando os dados de duas fontes distintas, o relatório de Alexandre Martins de 2002 e a auditoria energética efectuada em 2014, foi possível calcular a eficiência exérgica para os processos do digestor, lavagem e evaporação da lúxvia negra, tiragem de pasta e caldeira de recuperação e cogrador de biomassa cujos os valores foram 41%, 36%, 66%, respectivamente. A eficiência total foi também calculada, apresentando valores bastante baixos de 17,5% sem ter em conta os processos de descascamento e caustificação e fornos de cal, e de 7% tendo em conta todos os processos envolvidos.

Palavras Chave

Exergia; Análise exérgica; Eficiência exérgica; Indústria do Papel.

Contents

1.	Introduction.....	1
2.	Bibliographic review.....	4
2.1.	Energy analysis.....	4
2.2.	Exergy analysis.....	5
2.3.	Energy vs Exergy efficiency.....	6
2.4.	Alternative exergy analysis.....	8
2.5.	Legislation context.....	11
2.6.	Paper Industry.....	11
2.6.1.	Exergy analysis in the paper industry.....	14
2.6.2.	Environmental impacts in the paper industry.....	17
2.7.	Pulp and Paper production.....	19
2.7.1.	Setúbal site.....	19
2.7.2.	General process.....	20
2.8.	Setúbal Reports.....	23
2.8.1.	Alexandre Martins' report.....	23
2.8.2.	Energy audit report.....	26
3.	Methodology.....	28
3.1.	Control volumes.....	28
3.2.	Data.....	29
3.2.1.	General equations.....	31
3.2.2.	Efficiencies.....	33
4.	Processes and Results.....	34
4.1.	Pulp Process.....	34
4.1.1.	Digester.....	35
4.1.2.	Washing and Bleaching.....	36
4.1.3.	Processing.....	37
4.1.4.	Recovery Boiler.....	38
4.1.5.	Biomass Co-generation.....	39
4.2.	Exergy flows and efficiencies.....	40
4.2.1.	Digester, Washing and Black liquor evaporation.....	40
4.2.2.	Bleaching.....	43
4.2.3.	Processing.....	45
4.2.4.	Recovery Boiler and Biomass Co-generation.....	46
4.2.5.	Aggregate production process.....	48
5.	Conclusions.....	52
6.	Future work.....	54
	Bibliography.....	55
	Appendix.....	58
	Appendix A – Reports.....	58
	A.1 – Alexandre Martins report's tables and figures.....	58
	A.2 – Energy audit report's tables.....	71
	Appendix B – Other exergy values.....	72

List of Figures

Figure 1 - Energy and exergy flows in a global economic system	5
Figure 2 - Carnot cycle	7
Figure 3 - Example of co-generation process using natural gas.....	8
Figure 4 - Exergy efficiency versus CExC efficiency in the air conditioning of an office building	9
Figure 5 - Extended Exergy Accounting (EEA) method	10
Figure 6 - Top five countries by total final consumption by sector (top) and by sub-sector (bottom) ...	12
Figure 7 - Total world consumption of pulp (top) and paper and board (bottom).....	13
Figure 8 - Number of Confederation of European Paper Industries' mills and total production of pulp (top) and paper and board (bottom)	13
Figure 9 - Energy and exergy efficiencies for each process in a Swedish pulp and paper mill	16
Figure 10 - Woodpulp and woodpulp products worldwide consumption from 2010 to 2060	17
Figure 11 - Evolution of Environmental Impacts of the Confederation of European Paper Industries Pulp and Paper Industry	18
Figure 12 - Carbon emissions from energy combustions (energy consumption) and equivalent biomass energy (raw coal) in CPPI	19
Figure 13 - Kraft Process.....	20
Figure 14 - Pulp and paper production.....	22
Figure 15 - Alexandre Martins' bleaching process	25
Figure 16 - Pulp process	34
Figure 17 - Digester	35
Figure 18 - Washing and Bleaching	36
Figure 19 - Processing	37
Figure 20 - Recovery Boiler.....	38
Figure 21 - Biomass Co-generation	39
Figure 22 – Digester, Washing and Black liquor evaporation	41
Figure 23 – Grassmann's diagram for the Digester, Washing and Black liquor evaporation's main exergy fluxes	42
Figure 24 – Bleaching.....	44
Figure 25 – Recovery boiler and Biomass Co-generation.	46

List of Tables

Table 1 - Exergy factors	6
Table 2 - Efficiencies for sub-sectors of the Dutch Energy Sector.....	9
Table 3 - The conversion of forest products within Swedish forestry and industry based on forests in 1980, measured in PJ (exergy)	14
Table 4 – Specific energy consumption per type of pulp and paper	15
Table 5 - Germany's SEC in the pulp and paper production.....	15
Table 6 - SEC by process using RCF pulping.....	15
Table 7 – SEC comparison between Farla et al. (1997) and Fleiter et al. (2012).....	16
Table 8 – Exergy efficiencies in three different mills	17
Table 9 - Heat exchange in the bleaching process	24
Table 10 - Energy consumption in the digester process in 2014	26
Table 11 - Digester, Washing and Black liquor evaporation's components properties.....	41
Table 12 – Energy balance to Digester, Washing and Black liquor evaporation	41
Table 13 - Exergy values for the digester, washing and black liquor evaporation process	42
Table 14 - Bleaching's components properties	44
Table 15 - Exergy values for the bleaching process	44
Table 16 - Processing's components properties	45
Table 17 - Exergy values for the processing process	45
Table 18 - Recovery boiler and Biomass co-generation's components properties.....	47
Table 19 - Exergy values for the recovery boiler and biomass co-generation process.	47
Table 20 – Component properties of the aggregated process.....	49
Table 21 – Exergy values for the aggregated process stage.....	49
Table 22 – Component properties of the aggregated process with debarking and causticizing and lime ovens stages	49
Table 23 – Exergy values for the aggregated process with debarking and causticizing and lime ovens stages	50
Table 24 – SEC values according to the energy audit of 2014.....	50

Abbreviations

APE	<i>Análise do Ponto de Estragulamento</i>
BFW	Boiler Feeding Water
CEPI	Confederation of European Paper Industries
CExC	Cumulative Exergy Content
COD/AOX	Chemical Oxygen Demand
CPPI	China's Pulp and Paper Industry
CTMP	Chemi-thermomechanical Pulp
DGEG	<i>Direcção Geral de Energia e Geologia</i>
ECF	Elemental Chlorine-Free
EEA	Extended Exergy Analysis
EI	Energy Intensity
ELCA	Exergetic Life Cycle Assessment
HPS	High Pressure Steam
IEA	International Energy Agency
LCA	Life Cycle Assessment
LPS	Low Pressure Steam
MPS	Medium Pressure Steam
NCG	Non-Condensable Gases
OECD	Organization for Economic Cooperation and Development
RB	Recovery Boiler
RCF	Recycled Fibers
SEC	Specific Energy Consumption
TCF	Totally Chlorine-Free
toe	Tonne of Oil Equivalent
UWF	Uncoated Wood Free

1. Introduction

As the world energy demand rises, so does its consumption. The more developed a country is, the more sectors and sub-sectors it has, resulting in higher energy needs. The three main sectors are industry, transportation and households.

Industries are the ones responsible transforming the raw materials into new forms and assembling the final products to be delivered to the consumers whether it be the everyday people or other industries that need those products to produce their own. This sector is also liable for extracting the natural resources that they themselves need to achieve their final product. In Portugal, the biggest energy consumer industry is, by a relatively large margin, the pulp and paper production (DGEG, 2016). This is one of the main reasons why a more in-depth study, such as the one done on this thesis, is vital for the proper development and understanding of new measures and technologies to be implemented. It is also important to note that, in this sector, the main forms of energy are the electricity used to power the mechanical machines and the heat used to either increase or lower the temperatures during manufacturing. The energy production industry provides the energetic necessities of all other industries and sectors across the country. Companies that extract oil, fossil fuels and natural gas as well as coal all fall on this last category. These resources are directed to power plants to produce the necessary energy for the rest of the country. Nowadays, renewable energies are becoming more and more popular and, consequently, starting to substitute some of the previous mentioned industries. The most popular types of alternative energies are solar, wind and hydro, depending on the location and economical availability since putting them together can be quite costly.

Transportation is the sector that allows the allocation of goods and services from one place to another. Whether it is for selling, buying or trading, it is always necessary to have a mean of transport between the provider and the receiver. Cars are the most common type of transportation since they are the most personalized one. They can also carry a small amount of goods relatively safely. Public transports such as buses and subways are almost exclusive for people and they usually cover smaller distances. Trucks serve mainly the purpose of transporting goods. The most versatile modes of transportation are trains and airplanes since they are equally reliable for the transportation of humans as well as other goods. All these vehicles, which are mostly mechanical, use mainly fossil fuels as their source of energy. Imports and exports are one of the pillars of any country's economy, reason why transportation is essential for the proper function of any society. It is also important to note that technological advances especially the ones related to computers have made the need of transporting some goods almost useless, since that product can be readily available without any physical copy. In fact, this can also have a severe impact on other sectors, such as the paper manufacturing one, since there are many situations where there is no need for a physical copy of a document.

The household sector has become more and more relevant notably in the last decades since population has been growing and its quality of life has become an extremely important factor in any developed society. However, the efficiency of the devices being used have not suffered as big improvement as for the other two previously mentioned sectors, although there are some exceptions

such as lighting which has been transitioning from incandescent bulbs to Light Emitting Diodes or LEDs. Electrical appliances, lighting and space heating/cooling are the main consumers of energy in households as electricity represents the main energy carrier followed by heat.

To meet the requirements of the world population some adjustments must be made regarding the usage of devices and processes that need energy to function properly. Efficiency is a good way to measure and improve these equipment or processes to assure that energy sources are not fully depleted before they can be replenished. This is one of the main reasons why calculating efficiency is so important. With society demanding an increase concern for the environment and the reduction of harmful wastes, such as non-condensable gases, CO₂ emissions or alkaline/acidic sewers produced by the paper industry, efficiency analyses at the industry level becomes more and more relevant. It is only through an accurate evaluation of the reality that changes in policies can be more effective. This is not to say that an increase in efficiency leads directly to a decrease in consumption. In fact, there is a phenomena known as the rebound effect that states that as efficiency increases, energy consumption also increases rather than decreasing, since the specific costs of energy diminishes. To decrease primary energy consumption and associated environmental impacts, additional mechanisms are needed.

The most well-known type of efficiency is energy efficiency. It relies purely on the amount of energy being used compared with the one channeled to the desired end-use. Over the past century a new methodology has also been used to estimate efficiency since energy would not suffice when comparing different kinds of processes and equipment. Hence a new concept was developed that combines energy and entropy: exergy. The definition of exergy is the maximum theoretical useful work obtained until a system reaches its thermodynamic equilibrium with the environment. It can also be defined as the minimum theoretical work needed for a system to reach a certain state away from the equilibrium. There are certain characteristics about exergy that should be considered:

- when the environment is specified, a value can be calculated for the system in question, making exergy a property of that system;
- the value of exergy can never be negative since it results from a spontaneous process where the equilibrium can be reached with at least zero work;
- exergy is not conserved but it is destroyed by irreversibilities.

The main objectives of this thesis are to not only present how the pulp manufacturing process occurs in detail, by dividing it in meaningful control volumes, but also do a thorough mass, energy and exergy analysis to the factory in 2002, that is currently owned by The Navigator Company, located in Setúbal, Portugal. This is possible mainly due to data collected from two different reports, one from 2002, written by Alexandre Martins and another from 2014, which is an energy audit performed by Protermia. Finally, since exergy analysis in Portugal is not yet a well-documented approach to the industry sector, specifically when it comes to its largest energy consumer from this sector, the pulp and paper industry, the results displayed here represent one of the first steps made on this regard.

The structure of the thesis is as follows:

- (1) Bibliographic review, where the general concepts are introduced while considering other works made by different authors. In this section, a general description of the factory's main characteristics is provided and previous exergy analysis performed in the pulp and paper industry are explored;
- (2) Methodology, in which the necessary steps to reach the dissertation goals are explained and detailed. Here, the governing equations that are crucial to reach the final results are also presented;
- (3) The results are disclosed as well as discussed, including a comprehensive explanation of the process using the boundaries that were defined for each process and the exergy values for most of the components involved in the manufacturing of pulp;
- (4) Conclusions, where a general assessment of what was discussed and uncovered during the making of this dissertation is made;
- (5) Potential future works are suggested using this document as either inspiration or a source for comparison with other industries.

2. Bibliographic review

2.1. Energy analysis

The first law of thermodynamics states that all energy is conserved, meaning it cannot be lost nor gained, only transformed or, in other words, the total energy of an isolated system remains the same. It is based on this law that energy analyses are made, with the embodied energy of a product being the result of the sum of all the energy required to produce it. Exergy analysis, besides the first law, are also based on the second law of thermodynamics which is related to the entropy of a system and the fact that it cannot decrease if the system is isolated or adiabatic. Due to the dependence on both laws, exergetic analysis are much more useful when comparing different systems.

The energy flow is divided by three main stages: primary, final and useful energy. Primary energy is defined as the natural resource that is extracted from the environment itself. It includes all forms of energy resources that can, in any way, be transformed into any other type of energy, whether it be electrical, heat, chemical or others. These types of energy are considered final energy since they represent the form at which energy is present for commercial use. Usually, final energy is produced in central plants which is then distributed to wherever is needed, although there are many places, especially in the industry sector, that produce their own final energy by using, for example, generators or even, in bigger sites, their own plants. Finally, after acquiring the final form of energy, the equipment that receives it transforms it into useful energy such as heat or mechanical work. This means that useful energy represents the actual form and amount of energy that was used by the end-use devices to produce the desired outcome.

All the previous mentioned stages do not come without losses, which tend to occur between each one. At the primary stage, there might be some losses during the extraction of the resource itself. From primary to final, losses can be accounted for in the extraction, transportation, transformation and distribution. The losses from the final to the useful conversion stages depend on the conversion process and the end-use devices and are related to the energy efficiencies of these devices.

At the primary or final level, in the case of fossil fuels or combustible renewable, energy is the high or low heating content of the fuel or combustible renewable resource. If instead, energy comes from non-combustible renewable sources such as hydro or wind that are directly used to produce electricity, then values depend on the methodology used by the data source. For instance, for the International Energy Agency (IEA) the electricity output is the primary energy because it is first type of energy available in the case of renewable energies (Serrenho, 2013).

2.2. Exergy analysis

Being the most reliable form of asserting the real efficiency of any process, exergy analysis has been developed over the years and, as so, gained importance in the investigation of sustainable alternatives to the current energy situation. Exergy can be divided into three different kinds: mechanical, thermal or chemical. The definitions and differences between each can be found in the literature and other papers such as Ayres (2003), Buhler et al. (2016), or Sciubba and Wall (2007). Mechanical exergy is also known as kinetic or potential energy, whereas thermal exergy is related with heat. Chemical exergy is a little more complex, since it relates to the maximum theoretical work that could be developed in the chemical reaction that combines that substance with reactants present in the environment to produce substances that are in equilibrium with the environment (Ayres, 2003). All these kinds of exergy are measured in relation to a certain state, as the definition of exergy itself states. If an “environmental state” is reached, then there is a mechanical and thermal equilibrium between the environment and the system. Furthermore, if the chemical species are the same, then we also achieve a chemical equilibrium with the environment and the system is in a “dead state” (Rocco et al., 2014; Buhler, 2016).

The stages of exergy flow can be divided in the same way that energy flows are: primary, final and useful exergy (also known as useful work), and are presented in Figure 1.

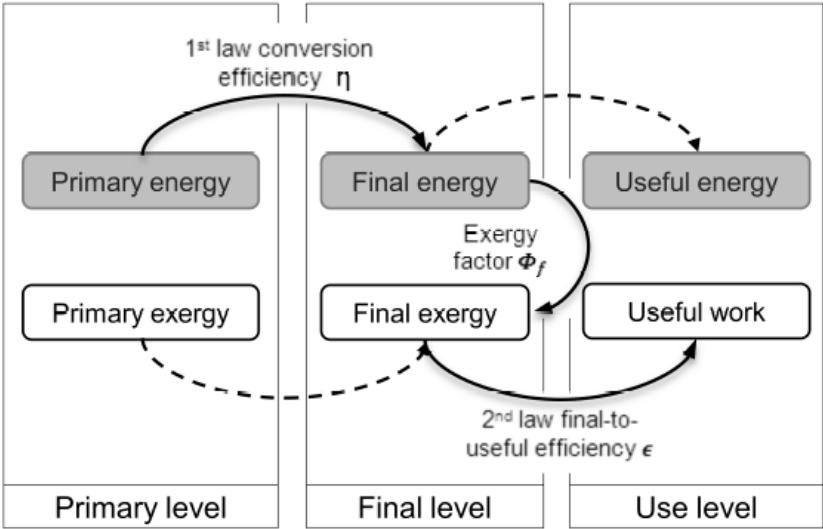


Figure 1 - Energy and exergy flows in a global economic system. Source: Guevara et al. (2014).

Energy can sometimes be converted into exergy by simply applying a conversion factor to it. Table 1 shows these factors for some of the energy carries that can be found in the International Energy Agency (IEA) energy balances. As it can be observed, most combustibles have an exergy factor higher than 1. The reason why this happens is because the chemical exergy of the combustion products are also included in the overall exergy content whilst the IEA only takes the enthalpy of combustion into consideration when calculating the energy balance.

Table 1 - Exergy factors. Source: Serrenho et al. (2014).

Energy Carriers	Exergy Factors
Coal and coal products	1.06
Oil products	1.06
Coke	1.05
Natural gas	1.04
Combustible renewables	1.11
Electricity	1.00
CHP and geothermal heat	0.60

Depending on the initial data, exergy can be directly calculated from the energy given. If this energy is in the form of work (W) then its value is equal to the exergy. If, however, there is heat instead (Q) then it must be multiplied by the Carnot efficiency first, $1 - (T_C/T_H)$, where T_C and T_H are the colder and hotter temperatures in the system, respectively. Finally, if we have a combustible or another energy carrier like the ones presented previously then exergy is equal to energy multiplied by the exergy factor.

When making an exergy analysis, it is also important to distinguish the exergy loss ($\dot{E}x_{loss}$) from the exergy destroyed ($\dot{E}x_{dest}$). $\dot{E}x_{loss}$ is represented by all the non-useful exergy that exits the system, typically by-products of the process that will not be used in any other step. On the other hand, $\dot{E}x_{dest}$ results from the difference between all the exergy entering the system and all the exergy exiting it and is related with the entropy increase in an irreversible process.

2.3. Energy vs Exergy efficiency

Despite being correlated, energy and exergy efficiency, η and ϵ respectively, are different. The energy efficiency of a system provides information about the fraction of energy that is dissipated while the exergy efficiency is also able to express if the process is close to the ideal process since it considers the entropy being created during it.

Reistad (1975) compares these two efficiencies, pointing out the advantages of using each one:

- Energy efficiency is quite accessible and appropriate when the inputs and outputs of the system are the same;
- Exergy efficiency, or effectiveness, “indicates the true thermodynamic performance of the system”. It should be used when comparing the work being achieved by a device with its ideal performance.

Being able to compare any device or energy carrier, regardless of its function or usage, is by far one of the main advantages of exergy analysis. The following examples will show why this is the case as well as demonstrate why an exergy analysis is complementary to an energy one.

Consider a Carnot cycle represent by Figure 2, where our desired output is the work exiting the system.

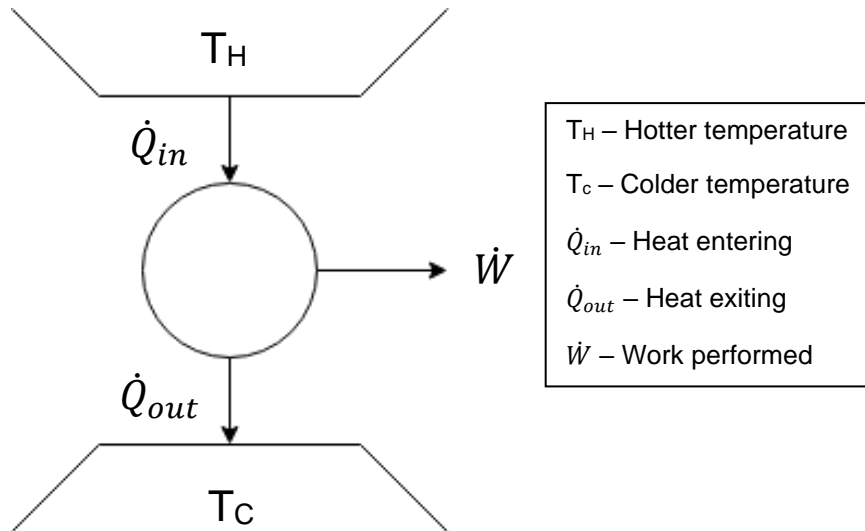


Figure 2 - Carnot cycle.

In this case, the first law (or energy) efficiency involves only \dot{W} and \dot{Q}_{in} (equation 2) where the maximum value is given by:

$$\eta_{max} = 1 - \frac{T_c}{T_H} \quad (1)$$

$$\eta = \frac{\dot{W}}{\dot{Q}_{in}} \quad (2)$$

It will never be possible to achieve an efficiency of 100% or close, since \dot{Q}_{out} cannot be zero. In fact, the maximum efficiency for these cycles is usually about 40%. This can be justified using the second law of thermodynamics: in a steady state cycle, the variation of entropy over time must be zero which means that, since \dot{W} does not contribute to the entropy balance, there must be a \dot{Q}_{out} in order to close the balance. On the other hand, second law efficiency is given by:

$$\varepsilon = \frac{\dot{W}}{\dot{Q}_{in} \left(1 - \frac{T_c}{T_H}\right)} = \frac{\eta}{\eta_{max}} \quad (3)$$

The exergy efficiency provides additional information compared to the energy efficiency because it considers the thermodynamic limits rather than simply what is entering and exiting the system.

Another illustrative example is natural gas being used in a co-generation process. Figure 3 illustrates such transformation with some exemplary energy values for inputs and outputs, where \dot{Q}_{loss} is the energy lost to the environment.

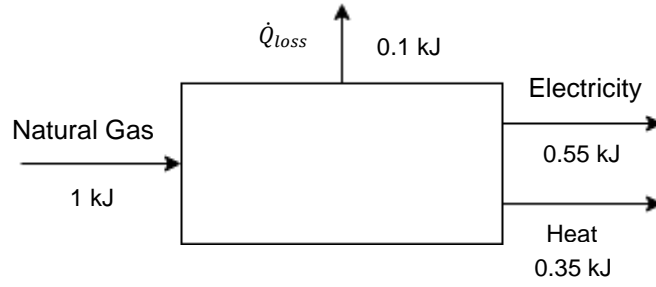


Figure 3 - Example of co-generation process using natural gas.

If the desired output is electricity only and assuming a conversion factor for natural gas of 1.04, then:

$$\eta = \frac{0.55}{1} = 55\% \quad (4)$$

$$\varepsilon = \frac{0.55}{1 * 1.04} = 53\% \quad (5)$$

However, if we have a co-generation process then heat becomes relevant too. Assuming an environmental temperature of 273K and that the temperature of the heat is 773K then efficiencies will change to:

$$\eta = \frac{0.55 + 0.35}{1} = 90\% \quad (6)$$

$$\varepsilon = \frac{0.55 + 0.35 * \left(1 - \frac{273}{773}\right)}{1 * 1.04} = 75\% \quad (7)$$

With this example it is possible to see that not only can there be a considerable discrepancy between the first and second law efficiencies but also that the same process (burning of natural gas, in this case) can yield two very different efficiencies depending on the desired outputs.

2.4. Alternative exergy analysis

Throughout the last decades more complex methods of exergy analysis have been developed to consider different aspects that were felt lacking in previous approaches. Szargut (1978) introduced a new methodology called Cumulative Exergy Content (CExC) where the cumulative exergy consumption of the natural resources along the production line is calculated, resulting in the “resource cost” necessary to create the desired product (Rocco, 2014). This approach differs from a general analysis, since it considers all the natural resources involved in a process, not just in the operation stage. It is also important to note that the units used by CExC are in kJ/unit produced.

Despite being small, there is a difference between energy ($\eta = \eta_{EN}$), exergy ($\varepsilon = \eta_{EX}$) and CExC (η_{CEXC}) efficiencies as it is shown by Table 2 for the different Dutch energy sub-sectors, with the lowest

always being the CExC one. It is important to note here that the exploitation and transformation sub-sectors relate to the transformation of primary energy into secondary energy and the distribution is where secondary energy is transformed into final. Pu et al. (2010) also makes a comparison between exergy and CExC efficiencies but in this case, it refers to three different project proposals on a new air conditioning system in an office building. Figure 4 shows that in this case the difference between the two approaches is much larger than in Ptasinski et al. (2006).

Table 2 - Efficiencies for sub-sectors of the Dutch Energy Sector. Source: Ptasinski et al. (2006).

Sub sector	η_{EN}	η_{EX}	η_{CExC}
Exploitation	0.99	0.99	0.98
Transformation	0.91	0.90	0.87
Distribution	0.99	0.98	0.89
Dutch Energy Sector	0.96	0.96	0.90

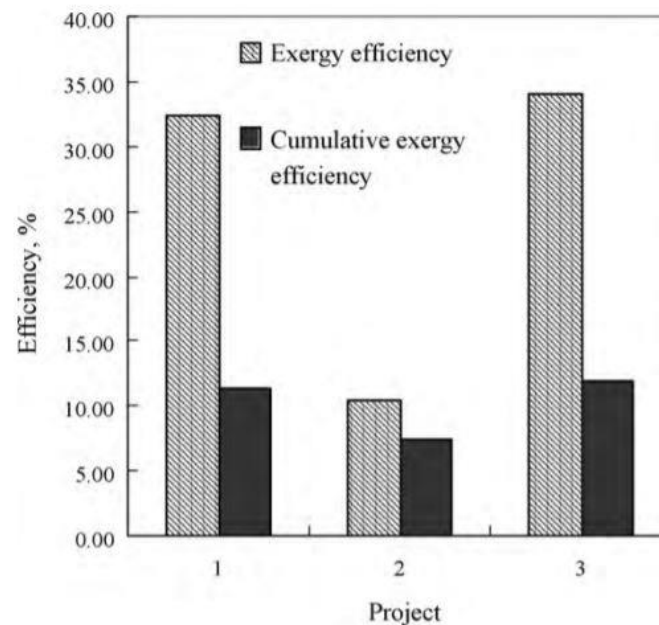


Figure 4 - Exergy efficiency versus CExC efficiency in the air conditioning of an office building. Source: Pu et al. (2010).

Another methodology used is referred to as Exergo-Economics or Thermo-Economics. Here, the general idea is to attribute a price not to the unit of mass but to the specific exergy content of a stream. This methodology can be used for a specific configuration, where the specific cost is obtained in €/J, especially if the same production line has more than one output product. Alternatively, it is also possible to find the “optimal” design point if the configuration can be changed (Sciubba and Wall, 2007). Rocco et al. (2014) describes this method as a monetary costing technique with the purpose of finding

out the minimum economic cost of the final products by determining the best trade-off between efficiency and total system cost. It also points out its major drawbacks:

- heavy dependence of the results on market considerations;
- if the resource is not widely available then this method is difficult to formulate;
- difficulty in properly attributing monetary costs for the environmental remediation activities;
- in more complex production chains, the function that relates the final product cost with the cost of all components is non-linear.

Finally, the most complex exergetic analysis is denominated Extended Exergy Accounting or EEA and it is presented in Figure 5. This approach is a combination of CExC and Thermo-Economics methods with other factors such as labour, capital and environmental costs, this is why it is called “extended” (Seckin et al., 2013). It also includes the Exergetic Life Cycle Assessment (ELCA) which is itself a combination of exergy analysis and Life Cycle Assessment (LCA). The LCA is a procedure that considers every step of a given product, from its extraction to its disposal (including end-use), therefore considering all energy and material flows.

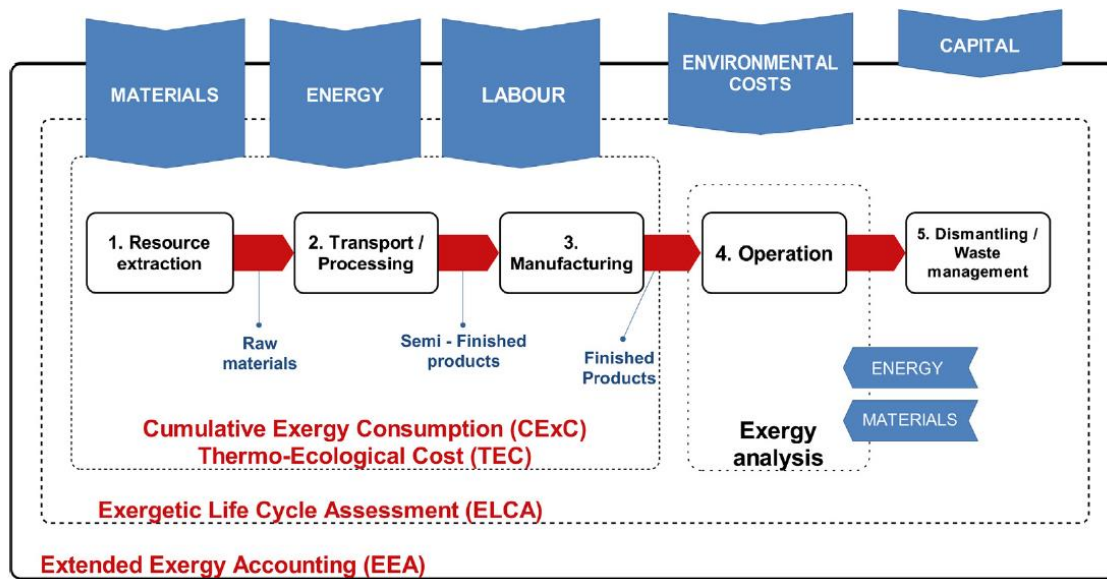


Figure 5 - Extended Exergy Accounting (EEA) method. Source: Rocco et al. (2014).

The way how EEA unifies all these different branches is by converting them all in the same unit: Joule. By doing so, it is now possible to calculate an aggregated efficiency that includes not only processes with intrinsic energy but also economic values that are extremely important in every industry. Since all these factors are considered, EEA efficiencies tend to be much lower than any other efficiency calculated by the other methods. Some applications of this method can be found in Site and Sciubba (2001) for ethanol production or for the Norwegian society by Ertesvåg (2005).

2.5. Legislation context

In Portugal, there is a system responsible for regulating high energy consumption entities known as *Sistema de Gestão dos Consumos Intensivos de Energia* or SGCIE. This legislation concerns companies and facilities that consume or exceed 500 toe/year. SGCIE will, periodically, make an energy audit during which it will evaluate the current situation on site and develop a plan denominated *Planos de Racionalização dos Consumos de Energia*, that will establish minimum efficiency goals and grant benefits to the companies that follow through with it (SGCIE, accessed 22/01/2020). These plans rely on three main indicators:

- Energy Intensity (EI) = Total primary energy consumption [toe] / Gross value added [€];
- Specific energy consumption (SEC) = Total primary energy consumption [toe] / Production volume;
- Carbon Intensity (CI) = Greenhouse gases emissions [kg CO₂] / Total primary energy consumption [toe]

For companies with an energy consumption equal to or above 1000 toe/year it is imposed a 6% improvement on EI and SEC, over a period of 8 years. For the other cases this improvement drops to 4%. For all cases the values of CI cannot increase.

Parallel to this legislation there is the European Union emission trading system (EU ETS). This is the system that the Portuguese Pulp and Paper industry follow. Considered the “cornerstone of the EU's policy to combat climate change and its key tool for reducing greenhouse gas emissions cost-effectively” (European Commission, accessed 03/02/2020), the EU ETS focus is the total CO₂ and other greenhouse gases emissions rather than a specific value like the CI. By using a cap and trade system, the EU ETS establishes a maximum cap of greenhouse gases emissions which will gradually reduce over the years, while also creating allowances that can be traded between companies. By the end of the year companies must have enough allowances to cover their total emissions or be heavily fined for not following these rules. If a company has an excess of allowances, it can save them for future needs or sell them to others that might need them.

2.6. Paper Industry

Ever since the industrial revolution, around 1760, the industry sector has been one of the biggest energy consumers worldwide. As people were substituted by machines, it became more and more clear that the energy necessary to meet the demands was an unavoidable issue. With Figure 6 we can clearly see the main consumers of final energy, which are all from the Organization for Economic Co-operation and Development or OECD. Despite not having the largest percentage, the paper and pulp industry is still considered to be one of the main consumers in these countries, otherwise it would just be included in the “Other” section of the graphic. According to *Direcção Geral de Energia e Geologia* (DGEG, 2016),

the industrial sector is the second largest consumer of the Portuguese total final energy consumption, only surpassed by transportation.

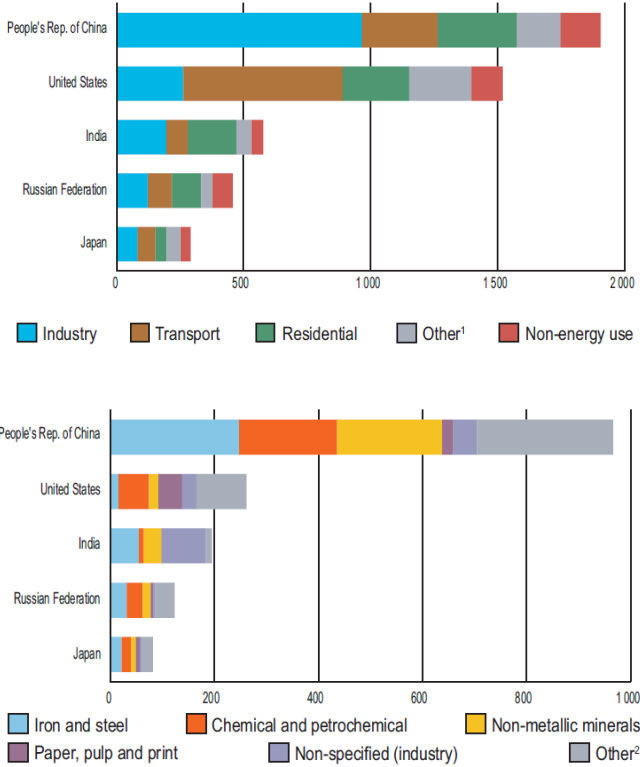


Figure 6 - Top five countries by total final consumption by sector (top) and by sub-sector (bottom). Source: IEA (2017).

According to Ojala et al. (2013) the first countries to industrialize pulp and paper were Great Britain, France and Germany, where production was first mechanized. After that, the main producers were in the northern hemisphere although over the years the dominance was lost to the southern hemisphere. This is explained not only by the natural resources needed but also by the demand, which started to become saturated in some of the northern hemispheric countries. The biggest technological developments that replaced the traditional ways of producing paper occurred in the beginning of the 19th century (Ojala et al., 2013). It was also around this time that cellulose started being produced from the wood fiber and that sulfate and sulfite cellulose technology first appeared. In Portugal, there are records that show that paper was being produced by small mills as far as 1411 but it was only in the 19th century that the production of pulp started (Lopes, 2010).

Even though the pulp and paper industry are not the biggest consumers worldwide, they certainly have a considerable share. About 40% of all industrial wood traded globally is for this industry, as stated by the World Wildlife Fund organization (World Wildlife Fund, accessed 09/07/2018). The Confederation of European Paper Industries or CEPI also publishes several statistics about the consumption and production of pulp and paper worldwide, as seen in Figure 7 and Figure 8. With a consumption of almost 1.4 million tep, the paper and pulp industry is, by far, the biggest industrial consumer of Portugal's final energy. Such relevance comes from the country's history and location, as well as the overall process of which paper is made.

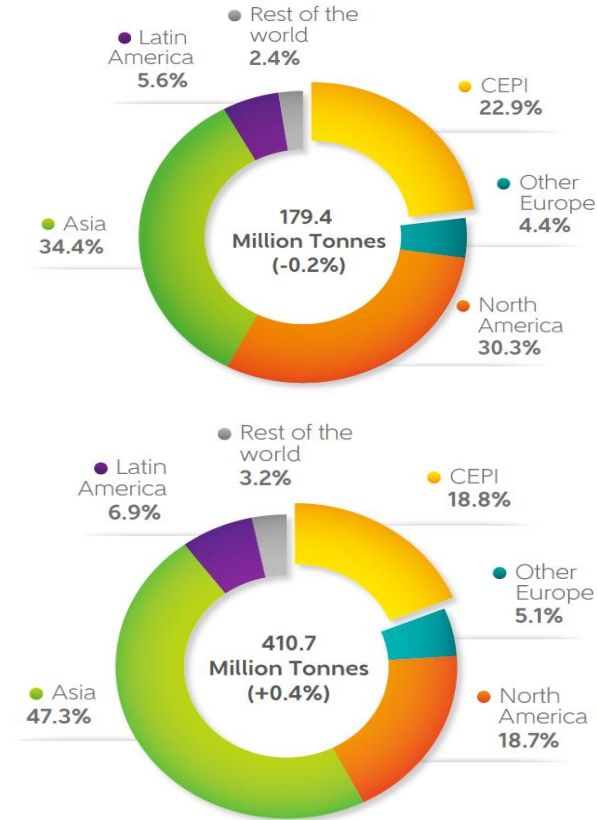


Figure 7 - Total world consumption of pulp (top) and paper and board (bottom). Source: CEPI (2016).

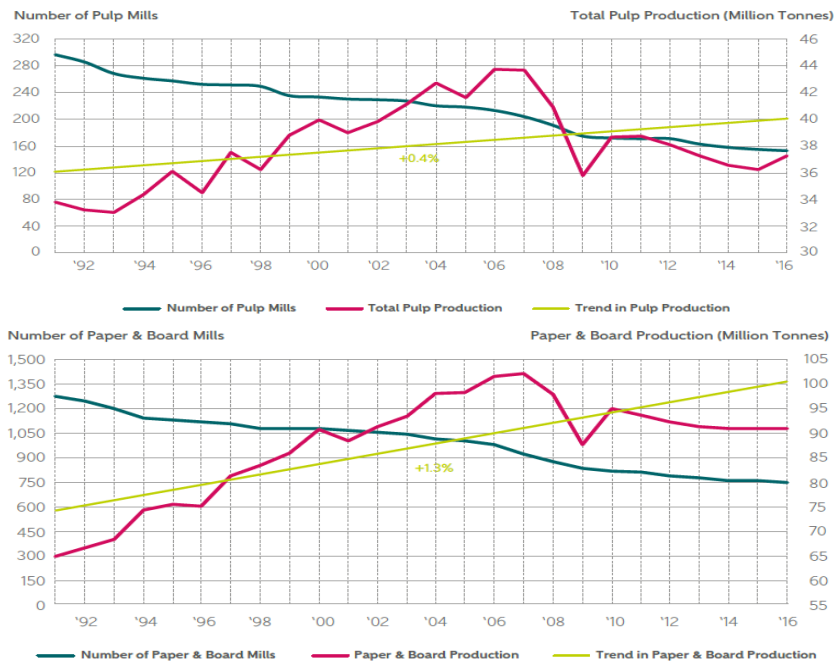


Figure 8 - Number of Confederation of European Paper Industries' mills and total production of pulp (top) and paper and board (bottom). Source: CEPI (2016).

2.6.1. Exergy analysis in the paper industry

There have been several energy and exergy analysis presented in the literature regarding numerous processes and industrial sectors such as Moran (1982) and Szargut et al. (1988). With respect to the pulp and paper business specifically, we can find different approaches such as energy analysis to create the most efficient way of managing the production of electricity and steam in the mill (Sarimveis et al., 2003) or the comparison between an energy and exergy analysis in the sulphide-pulp preparation process located in Turkey (Gemci and Öztürk, 1998). Goran Wall (1987) also did a thorough exergetic review on the different sectors of the Swedish society which included the paper industry. Table 3 shows the results of all forest related products that were presented in that paper.

Table 3 - The conversion of forest products within Swedish forestry and industry based on forests in 1980, measured in PJ (exergy). Source: Wall (1987).

Timber-cutting	394
Timber from stores	23
Waste paper	14
Imports	73
	<hr/>
Total consumption	504
Input to the saw mill industry	178
Input to the pulp and paper industry	266
Use of wood based fuels (lignin)	120
Production of timber ware	133
Production of market pulp	64
Production of paper	114
Firewood	19
	<hr/>
Total production	330

In the production of pulp and paper, the different ways in which the final product can be obtained can be either chemical or mechanical. The main difference between these two is whether the individual fibers are obtained using chemical substances or if the raw material is simply grinded down and mixed with warm water. Both cases are detailed in Harvey (2010). The bleaching process can be described as totally chlorine-free bleaching (TCF) if it only uses H_2O_2 and O_2 or elemental chlorine-free bleaching (ECF) if it also uses ClO_2 . Mechanical pulping has a better source of heat, since the friction in the grinding process of the wood already produces some of the heat necessary to form the pulp, but it also consumes more electricity than chemical pulping. In Harvey (2010), it is also described how the heat loads can affect the general efficiency of the mills. If the nearby district heating has a biomass gasification combined cycle co-generation, then the idea of reducing the factory's heat load should be considered, which will also reduce the electricity generated, and sell the excess biomass to the nearby district heating facility in order to increase the efficiency of electricity generation. The district heating facilities provide the necessary heat for an entire area (district) and their energy usually comes from

natural gas steam boilers (Rosen et al., 2005). These district heating facilities are typically found in colder regions since the heat demand for households is much higher in these countries.

Farla et al. (1997) makes a comprehensive cross-country comparison of eight of the OECD countries on the pulp and paper energy consumptions and efficiencies. Table 4 shows the weighting factors for the specific energy consumption (SEC) on each type of pulp and paper. It is important to note that these values relate to best available techniques used in a specific year, depending on the final product. Fleiter et al. (2012) also calculate these values in Germany, which can be seen in Table 5, along with the SEC results for each process using recycled fibers (RCF) pulping presented in Table 6. The indirect CO₂ emissions refer to the electricity generation (on and offsite) and the direct emissions refer to all fuel combustion processes in the paper mill.

Table 4 – Specific energy consumption per type of pulp and paper. Source: Farla et al. (1997).

	Fuel/heat (GJ/ton)	Electricity (GJ/ton)	Primary (GJ/ton)
Mechanical wood pulp	-2.1	5.3	11.2
Chemical wood pulp	10.0	2.5	16.3
Other wood pulp	-3.0	6.0	12.0
Other fibre pulp	-3.0	6.0	12.0
Recycled fibre input	0.4	1.4	3.9
Newsprint	2.5	1.4	6.0
Printing/writing paper	7.0	2.0	12.0
Sanitary paper	5.0	2.4	11.0
Packaging paper	5.0	1.5	8.8
Other paper	6.0	1.8	10.5

Table 5 - Germany's SEC in the pulp and paper production. Source: Fleiter et al. (2012).

	Energy consumption						CO ₂ emissions ^b		
	SEC electricity [kWh/t]	SEC fuels [GJ/t]	Total electricity [PJ]	Total fuels [PJ]	Total [TJ]	Share [%]	Indirect [Mt CO ₂]	Direct [Mt CO ₂]	Total [Mt CO ₂]
Chem. pulp	639	12.6	3.5	19.5	23.1	10%	0.6	1.0	1.6
Mech. pulp	2200	-2.0 ^a	11.5	-2.9	8.6	4%	2.1	-0.2	1.9
RCF pulp	260	0.5	14.7	8.5	23.2	10%	2.6	0.4	3.1
Paper	530	5.5	44.5	128.2	172.7	76%	8.0	6.6	14.6
Sum			74.3	153.4	227.7	100%	13.3	7.9	21.2

Table 6 - SEC by process using RCF pulping. Source: Fleiter et al. (2012).

Process step	Electricity		Fuels	
	[kWh/t]	[GJ/t]	[kWh/t]	[GJ/t]
Pulping	40	0.14	–	–
Screening	50	0.18	–	–
De-inking (Flotation)	80	0.29	–	–
Concentration and dispersion	40	0.14	150	0.54
Bleaching	30	0.11	–	–
Others	20	0.07	–	–
Sum	260	0.94	150	0.54

Table 7 combines the data from Farla et al. (1997) and Fleiter et al. (2012). It shows that the SECs are very similar between them despite the time and location differences. The most significant differences are the fuel/heat in chemical pulping and the electricity in mechanical pulping. To calculate the values for the paper sector using Table 4, an average between all types of paper was assumed. This was accomplished by simply adding the newsprint, printing/writing, sanitary, packaging and other paper SEC's values for fuel/heat and electricity and convert them into a one single average result.

Table 7 – SEC comparison between Farla et al. (1997) and Fleiter et al. (2012).

Sector	Fuel/Heat from Farla et al. (1997) [GJ/ton]	Fuel/Heat from Fleiter et al. (2012) [GJ/ton]	Electricity from Farla et al. (1997) [GJ/ton]	Electricity from Fleiter et al. (2012) [GJ/ton]
Mechanical Pulping	-2.1	-2	5.299	7.92
Chemical Pulping	10	12.6	2.498	2.300
RCF Pulping	0.4	0.5	1.400	0.369
Paper	5.1	5.5	1.822	1.908

Gong (2005) made an exergy analysis to a pulp and paper mill in Sweden. The results for the energy and exergy efficiencies are displayed in Figure 9. In this specific mill, along with the sulfate pulp mill, there is also a chemi-thermomechanical pulp mill (CTMP) and a paper mill.

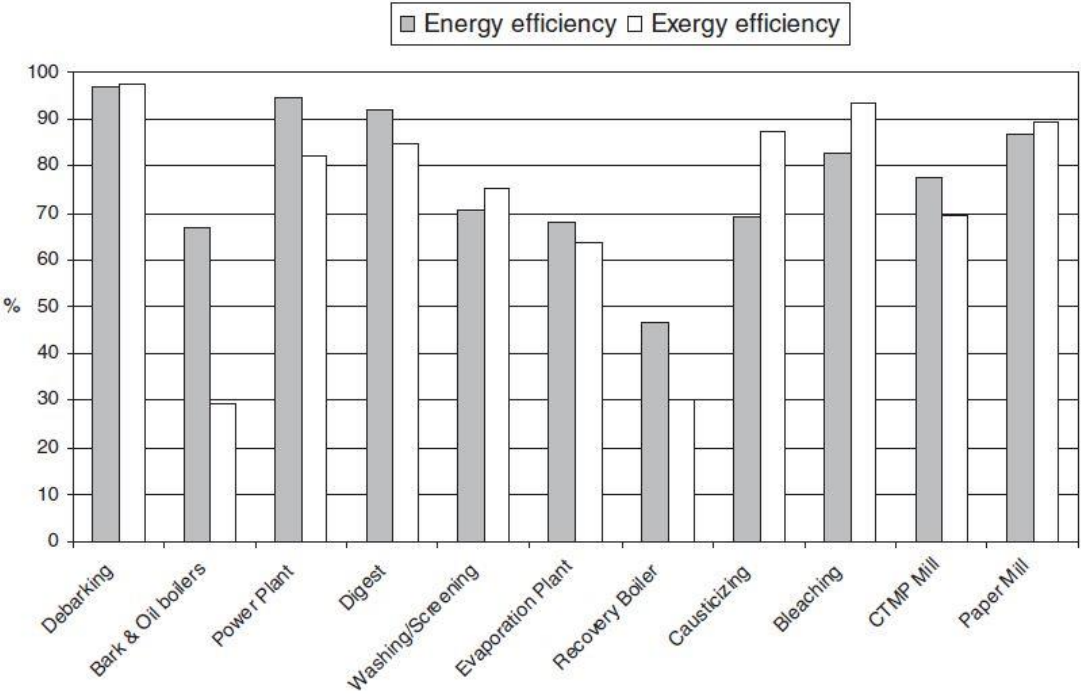


Figure 9 - Energy and exergy efficiencies for each process in a Swedish pulp and paper mill. Source: Gong (2005).

Another example of exergy efficiencies in the pulp and paper industry is presented by Assari et al. (2014) in Table 8, where it presents its own results (PPIG) and compares it to two other papers, Wall (1988) (SCA-Munksund) and the previously mentioned Gong (2005) (Skoghall).

Table 8 – Exergy efficiencies in three different mills. Assari et al. (2014).

Section	PPIG	SCA-Munksund	Skoghall
Depithing	95.59%	99%	97%
Digester	79.47%	99.7%	85%
Washing	93.35	99.1%	79%
Bleaching	82.67%	–	94%
Paper mill	83.5%	86.2%	89%
Steam plant	29.9%	31.3%	29%
Evaporator	69.47	97.1%	97.1%
Soda recovery	28.73%	36.3%	30%
Causticizing	66.4%	87.4%	87%

2.6.2. Environmental impacts in the paper industry

Finally, there is the issue of the environmental impact caused by this industry. The first major one is obviously the amount of natural resources (wood) that are needed. According to a study performed by Carle and Holmgren (2008), plantations covered around 260 million ha worldwide in 2005. The eucalyptus is the most common type of wood used in plantations producing about 33 to 83 m³ per ha per year in Brazil, for instance (Stape et al., 2010). Elias and Boucher (2014) predictions of the worldwide woodpulp consumption, as well as its derived products show an increase (Figure 10) which may lead to the increase of deforestation affecting therefore many different ecosystems. By-products such as waste water (chemical oxygen demand or COD and AOX) and air emissions (CO₂, SO₂ and NOX) are also a source of concern when discussing the paper and pulp industry (Figure 11).

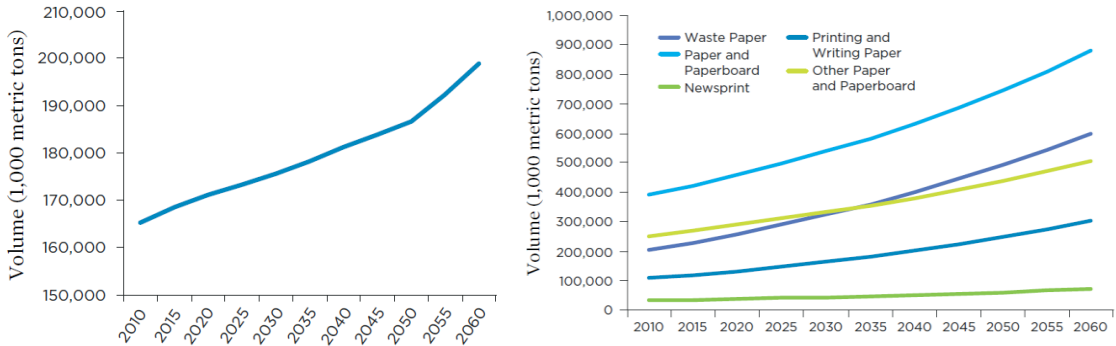


Figure 10 – Expected woodpulp and woodpulp products worldwide consumption from 2010 to 2060. Source: Elias and Boucher (2014).

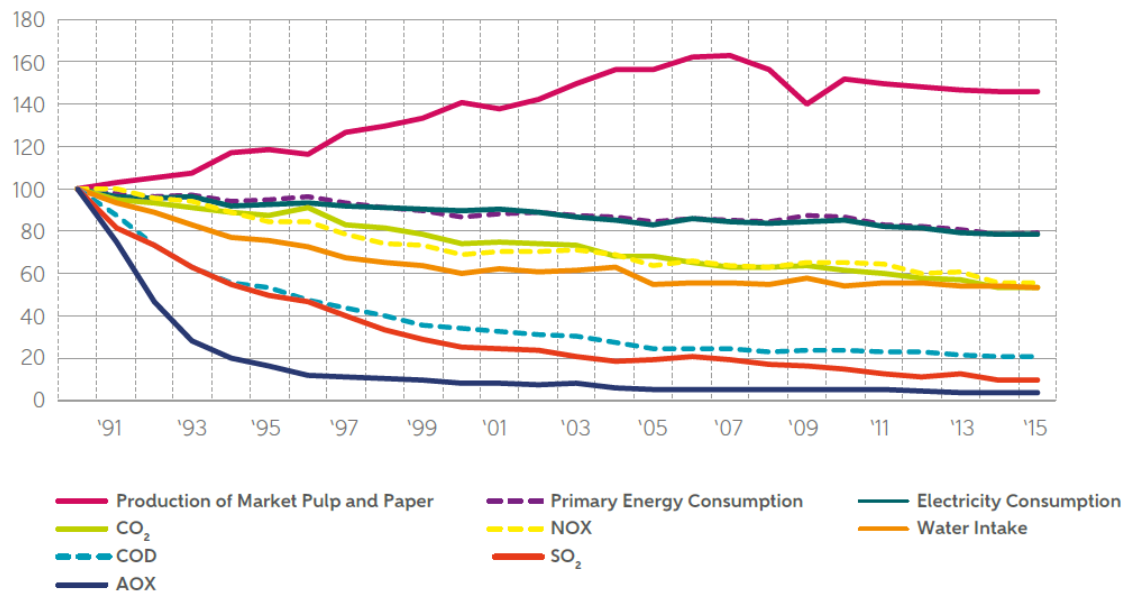


Figure 11 - Evolution of Environmental Impacts of the Confederation of European Paper Industries Pulp and Paper Industry. Source: CEPI (2016).

It should also be mentioned that CO₂ emissions can be greatly reduced if the industry adopts an energy recovery policy using the biomass waste, specifically bark, and if the black liquor is used as an energy source. If this is the case, then both processes can be considered carbon free, if the equivalent of all the biomass used is then replanted. Wang et al. (2016) present the CO₂ emissions that would be produced by China's Pulp and Paper Industry (CPPI) if they were to use raw coal (biomass equivalent) instead of biomass when compared with the emissions they are currently producing (energy consumption). This comparison is showed by Figure 12, where it is clear the impact that this policy would have in the environment.

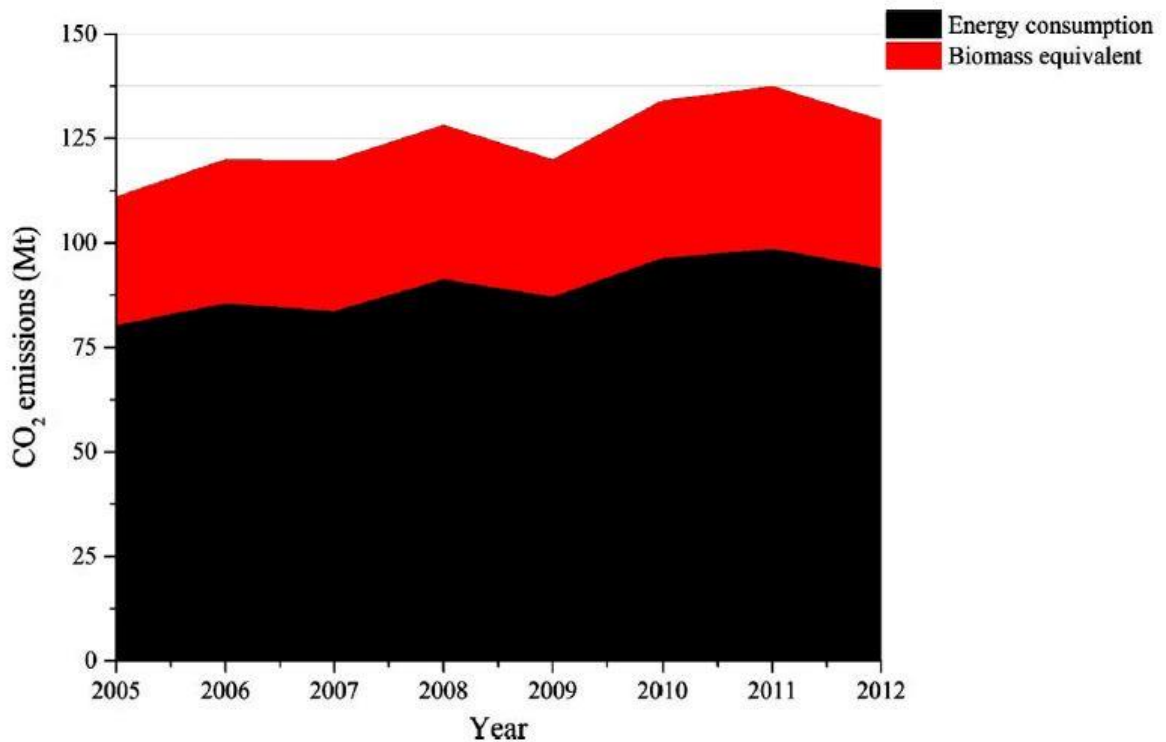


Figure 12 - Carbon emissions from energy combustions (energy consumption) and equivalent biomass energy (raw coal) in CPPI. Source: Wang et al. (2016).

2.7. Pulp and Paper production

2.7.1. Setúbal site

The pulp and paper mill analyzed in this thesis is in the industrial complex of the Miltrena Peninsula, in Setúbal and it is owned by The Navigator Company. More accurately, according to the company (The Navigator Company (1), accessed 28/09/2019), there is precisely one pulp and two paper mills. Nowadays, the site is estimated to produce around 550 thousand tons of bleached eucalyptus kraft pulp per year, using the Kraft Process. The site also includes a natural gas and biomass co-generation plant and a biomass power station. Both paper mills produce Uncoated Wood Free paper (UWF), with the first having two machines producing 275 thousand tons of paper, and the second one (also known as “About the Future”, inaugurated in 2009) producing 500 thousand tons of paper per year, at a rate of 30 meters per second, turning out reels of 10,4 meters wide. This sums up to 775 thousand tons of paper per year only surpassed, in Portugal, by the company’s other site in Figueira da Foz that produces a total of 800 thousand tons of printing and writing paper (The Navigator Company (2), accessed 28/09/2019).

2.7.2. General process

To evaluate the energy efficiencies of this industry, it is necessary to understand how the process works. As to better understand what happens in each stage, the operations can be illustrated by various schematic representations. For instance, Figure 13 is found in Alexandre Martins' (2002) report and gives a detailed idea of how all processes are connected, differentiating the main path of the mass flow from the chemical recovery. Likewise, Figure 14 represents a general description starting with the planting of the tree seeds until the stacks of paper are ready to be distributed to their respective places. It is important to note that although this figure is based on Setúbal's mill, most of these steps are common throughout the whole industry, the difference being, for example, on how the mill obtains its raw material (wood), what type of wood is used or whether it uses recycled paper or not. Some sites only contain either pulp or paper manufacturing, which means that some of the steps presented in the figure simply do not occur at those sites. There are three main parts in the transformation of wood into paper and they are:

- Planting and harvesting the wood;
- Pulp process;
- Paper process

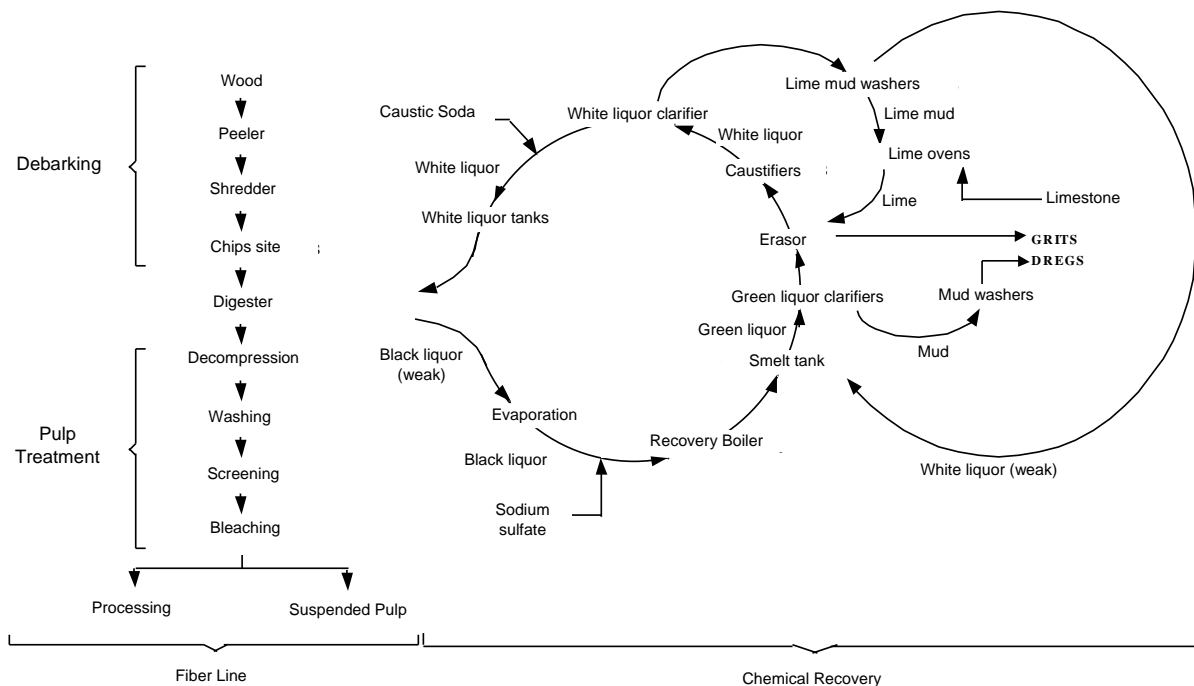


Figure 13 - Kraft Process. Source: Alexandre Martins (2002).

In the first process identified in Figure 14, *eucalyptus globulus* seeds are planted in nurseries, where they grow until they become saplings. At this point, these saplings are transported to the main forest, owned by the company, and taken care of until they mature to fully grown trees. According to the Navigator Company website (The Navigator Company (3), accessed 19/10/2019) the *eucalyptus*

globulus specimen can grow until they reach 40 to 50 meters in height, prefers coastal and low-lying regions (below 700 meters) and temperate damp climates. Furthermore, it produces more paper with the same amount of wood, up to 46% more than many other species. These characteristics make this type of seed the ideal one to be planted in Portugal. However, it is important to assure proper care of these forests, as they represent a serious fire hazard site. In the final stage of this part, the trees are cut down into standard sized logs and transported to the company site where they are stored until needed.

Then, the raw wood is transformed into white pulp. First, the bark, which is the outside part of the wood, is separated from the log itself through a mechanical process, more specifically a peeler. The bark is then directed to the biomass co-generator where it will be used to produce heat and electricity. On the other hand, the logs are chopped into specific sized chips and transported to the digesters where a brownish pulp comes out, as the result of a chemical reaction between the chips and other chemical components. From here, this brown pulp undergoes a washing and bleaching operation to remove any remain components that are not desired in the final pulp composition, giving it a white coloration in the end. Both by-products from washing and bleaching and the digester (mainly lignin for this last one) form what is called the black liquor, which is then directed to the recovery boiler, where a chemical recovery occurs (green liquor) as well as the production of steam, that is redirected to the biomass co-generator. Finally, the white pulp is separated into two different directions, either to be used to produce white pulp sheets, to be sold on the market or be transported to other sites of the company, or to be used to produce paper in the same industrial unit, in which case it is pumped as a slurry to the paper mill, but not before it is refined with specific mineral fillers and other additives in order to strength the bonding between the fibers and improve the optical properties of the paper.

The third and final set of steps performed on this site correspond to the manufacturing of the paper itself. Firstly, the slurry is fed to the headbox at a steady speed, as smooth as possible, onto a continuous fabric loop. Once on the wire, water is drained due to gravity, combined with vacuum and suction procedures, as the paper sheet begins to gain form. Next, the moisture content is further reduced until it reaches about 58 to 60%, as it passes through presses, combined with vacuum, in the operation known as the pre-dryer. From this point on, water can no longer be removed by mechanical means. Before the water in the sheet is evaporated as much as possible in the drying cylinders (using heat) in the post-dryer, there is an intermediate process called the symsizer. Here, a starch solution is applied to improve the interaction between the paper surface and printing inks using rubber-clad rolls. The paper is now wound into jumbo reels (about 60 minutes per jumbo reel which corresponds to 80 tons of paper), which is then processed into smaller reels to sell to clients or sent to a warehouse where robots cut the paper into the different formats. Lastly, the paper is sorted into stacks of 500 sheets called “reams”, wrapped, packed and then palletized to be distributed.

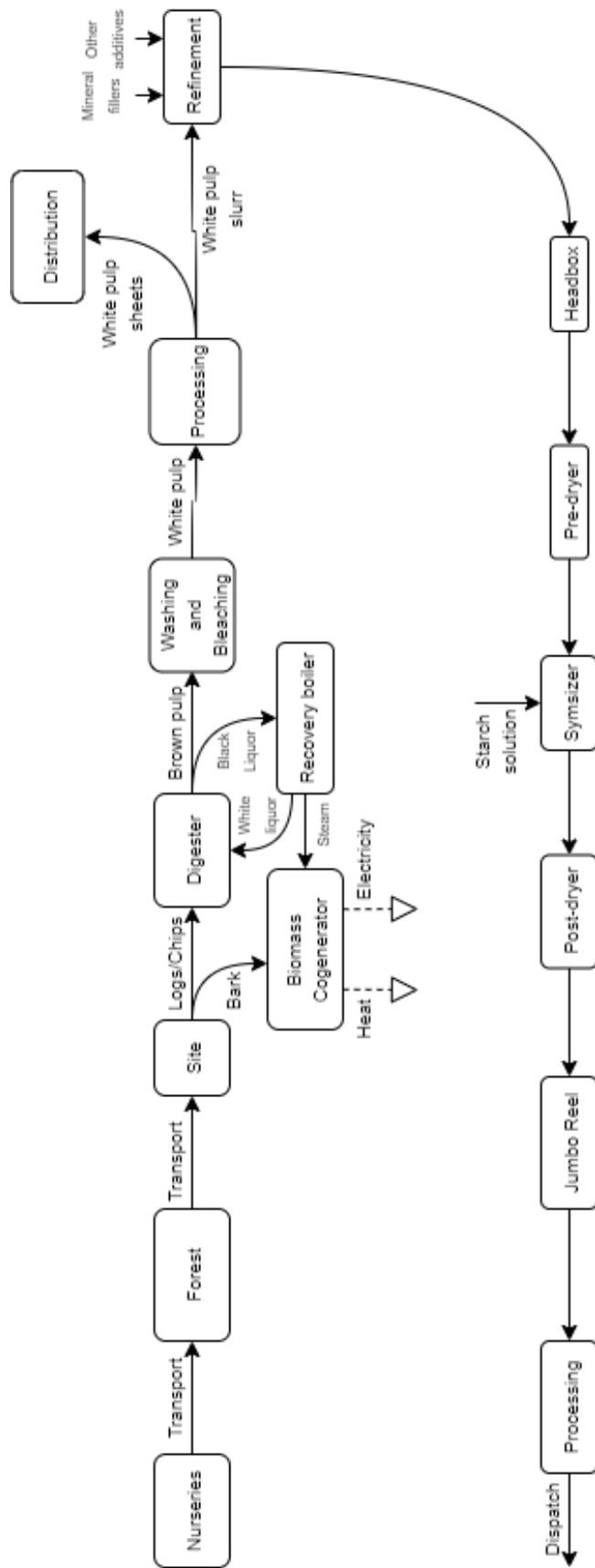


Figure 14 - Pulp and paper production.

2.8. Setúbal Reports

2.8.1. Alexandre Martins' report

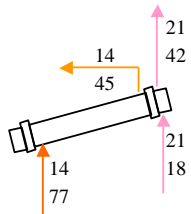
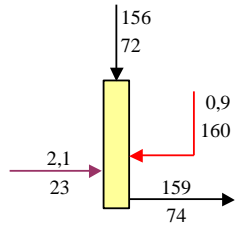
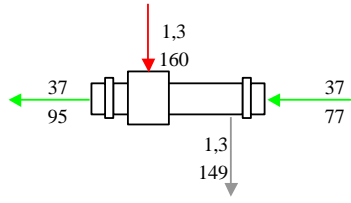
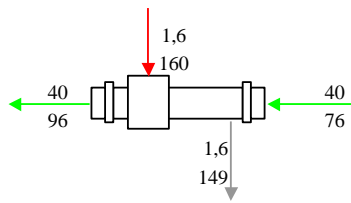
The first part of the report revisits some of the work done before it, regarding other pulp and paper factories, followed by a generic description of the Kraft process and its integration in the factory in order to understand how each part of the process works and the related mass and energy flows. The Kraft process, used to produce the pulp in this factory, is a method that involves mixing wood chips with an alkaline solution of mainly sodium hydroxide and sodium sulfite, also known as white liquor, to create a pulp that is then treated and bleached to achieve the final desired properties. The liquor that results from the first mixture (black liquor) is going to be processed in the recovery boiler and then causticized in order to create the white liquor again.

Then, dividing it into smaller processes, the second part of the report describes in detail what is needed in each stage in terms of actual matter and energy requirements. The focus points are where heat is exchanged since it is possible to evaluate the current situation in the factory from this data. Different figures are also presented for each of the stages, such as Figure 15 as well as the correspondent tables characterizing the heat exchange occurring, to which Table 9 serves as an example. In this part, an analysis known as Pinch Analysis or *Análise do Ponto de Estrangulamento* (APE), in Portuguese, is also presented. This analysis provides crucial insight on the energy balances, optimizing the energy consumption of a given process based on thermodynamic principles. By studying the heat fluxes, it can minimize temperature gradients and therefore the irreversibilities in the system.

The third part of the report is where several options are presented to substitute different parts of the process by alternative ones that would result in a better usage of the energy produced in the factory itself. Most of the alternatives proposed involve either substituting one heat exchanger for two of them or using an alternative component, such as warm water instead of cold water, in the heat exchanger itself. Both solutions have the intention of lowering the temperature differences, therefore increasing the efficiency of the process. It is important to note that this part covers the entirety of the process again and not just one specific section of it.

Final conclusions are presented in the last section of the report, where the author gives his perspective on how his suggestions would be implemented and the conditions that have to be met for that to happen, discussing issues that may occur if in fact they follow through. Lastly, following this are several appendixes with some helpful information collected such as general energy consumption of the factory and more detailed tables of the heat exchanger components of each process.

Table 9 - Heat exchange in the bleaching process. Source: Martins (2002). → mass flow (kg/s)
temperature (°C)

Equipment	Description	ΔH (kW)
Chlorine dioxide heating heat exchanger		1925
D0 stage stand-pipe		2143
Tower D1.1 filtrate heat exchanger		2816
Tower D1.2 filtrate heat exchanger		3361

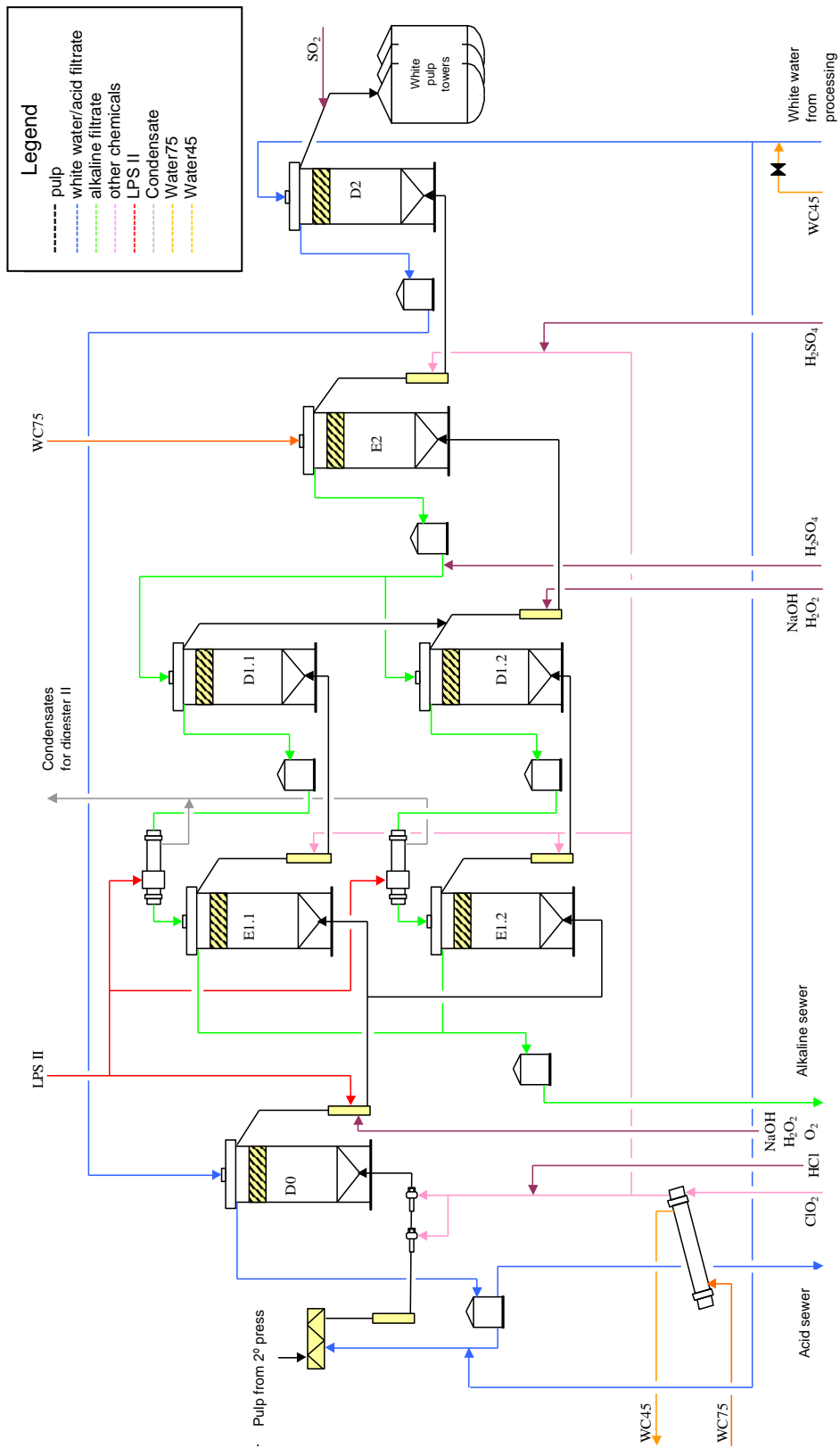


Figure 15 - Alexandre Martins' bleaching process. Source: Martins (2002).

2.8.2. Energy audit report

This document (Bento et al., 2016) follows a standard approach to this type of examinations, presenting tables, graphs and figures as well as moderately in-depth explanation of the entire pulp manufacturing process.

The report starts by giving a description of the site history and how it operates nowadays, followed by a general characterization of the entire pulp process. The subsequent sections go into a comprehensive analysis of the energy consumption in each main part of the factory, finishing with the factory total consumption. In all these sub-sections we can find the same information: every step involved in this specific process, a table, exemplified by Table 10, with its energy consumptions, such as electricity or steam, among others, where it can be improved and the energy counters. There is also a chapter about general services (electrical, compressed air and illumination) that account for all other aspects not mentioned previously. Finally, the authors leave some commentaries regarding energy saving options and opportunities that might help improve the facility consumption. One of the main suggestions made in this section is the installment of electricity meters throughout the facility in order to have a better understanding of the machines and other equipment consumption during the year. Another suggestion is the substitution of conventional motors for high efficiency ones when the former needs to be repaired or replaced and it is economically viable.

Table 10 - Energy consumption in the digester process in 2014. Source: Bento et al. (2016).

Factory's Total	Jan -14	Feb -14	Mar -14	Apr -14	May -14	Jun -14	Jul -14	Aug -14	Sep -14	Oct -14	Nov -14	Dec -14	TOTAL
Functioning hours	h												
Pulp production	tAD												
PULP BLEACHING													
Functioning hours													
Bleaching	h												
Chemicals preparation	h												
Bleached pulp production													
Bleached Pulp	tAD _{brans}												
Energy Input													
Electricity	MWh												
3,6 GJ/MWh	GJ												
Medium pressure steam	t												
2,844 GJ/t	GJ												
Low pressure steam	t												
2,77 GJ/t	GJ												
Total energy inputs	GJ												
Energy outputs													
Condensates	t												
0,419 GJ/t	GJ												
Total energy consumption	GJ												
Specific energy consumption – referring to bleached pulp													
Electrical	GJ/tAD _{bransq&elt}												
Heat	GJ/tAD _{bransq&term}												
Global	GJ/tAD _{bransq}												
Specific energy consumption – referring to total pulp													
Electrical	GJ/tAD _{elt}												
Heat	GJ/tAD _{term}												
Global	GJ/tAD												

When discussing the energy aspects, the report points out the main consumer for each section as well as the main electrical consumer. For instance, in the digester operation, the main consumer is thermal energy in the form of low and medium pressure steam in the digesters and the low pressure steam in the black liquor evaporators. As for electrical expenses, the most relevant are the sieves medium tension motors and pulp and liquor pumps. Also, there are no energy counters in any section of the factory which means that the electrical consumption was estimated through historical registries.

There are numerous differences between the data provided by Alexandre Martins' report and this one. The main difference is that the first one focusses on the heat exchange happening while the second merely points out the energy consumption for every segment. This means that there are practically no mass flows provided in the audit since they are not necessary for any of the calculations done in these reports. The second major difference is how the data is presented. While Alexandre Martins disregards the energy with the enthalpy involved (in kW), the audit displays a table with the energy consumption in GJ, allowing an easy month by month analysis. Lastly, because of this clearer way to present the data, it is possible to include in the final results other parts of the manufacturing process, such as the wood reception and preparation, the caustification and lime ovens and what it is denominated as the renewable co-generation station, which is set by the recovery boiler, the biomass boiler and the steam turbines.

3. Methodology

First, it is crucial to notice that this thesis only considers the making of pulp, disregarding the production of paper itself. This is because the data available from both the Alexandre Martins' report (2002) and the factory energy audit (2016) only regards the pulp production process. Furthermore, neither of these reports contain all the information necessary to make a thorough exergy analysis, reason why some of the data had to be estimated or inferred based on other similar reports.

Finally, it is important to keep in mind that there is no standardized way to present the results for an exergy analysis of a pulp factory. Since that is the case and taken into consideration that one of the objectives of this paper is to present a way of doing so, the results were presented in two different ways. The first gives an explanation of the whole process separating each one by objective. The second presents the results of the exergy efficiencies for each process as well as for the whole operation.

3.1. Control volumes

Given the complexity of the pulp manufacturing process, it was necessary to divide it into several different control volumes. Setting the boundaries of each process is fundamental not only to understand what is happening at each stage, but also to evaluate any results that are calculated afterwards. As such, the entire process is divided into:

- Digester;
- Washing and Bleaching;
- Processing;
- Recovery Boiler;
- Biomass Co-generation.

The main reason why the information is presented in this way is because each process has a defined purpose. The digester is where the raw material (wood/chips) is transformed into a pulp (brown in this case), with the black liquor produced as a by-product. This liquor will be very important later to produce high pressure steam, which will then be used to produce energy and other types of steam. From here, the pulp enters the washing and bleaching segment where the pulp will acquire the properties necessary to create high quality paper. Any nodes or not fully cooked segments of pulp will be returned to the digester, ensuring the best possible pulp characteristics while also wasting the least possible amount of wood. The processing is where all the pulp that was not sent to the paper mill will be dried, cut into sheets and stored. Parallel to all of this, we have the recovery boiler where the black liquor is concentrated and transformed into the green liquor while also producing high pressure steam. Finally, there is the biomass co-generation process where the high pressure steam is used to produce electricity and medium and low pressure steam.

Not all parts of the factory were described, namely the preparation of wood and the causticizing and lime ovens. The first one simply debarks the eucalyptus and turns it into small chips, while the second one is where the green liquor is transformed into white liquor which will be used in the digester. The reason why the debarking of wood is not considered in this thesis is because there is no data regarding the main flows thus making an exergy analysis impossible to accomplish. It can be assumed, however, that, since only electricity is used, and there are not many reasons why temperatures would vary much from ambient other than the friction in the debarking machines, the energy and exergy efficiencies might be similar as seen in Gong (2005). The causticizing and lime ovens are much more complex processes with various flows, mainly chemical, most of which are not presented in either of the reports or even the literature. This means that it would be nearly impossible to make any exergy analysis for this stage of the manufacturing.

3.2. Data

To obtain the most accurate results possible, the exergy was calculated using the data from both reports and other bibliographic materials. Martins (2002) divided the entire manufacturing into each specific process whereas the energy audit had a different method. It is in this last one, however, that the electricity for each stage and some of the missing mass flows are given. Since the audit has the most compact approach of all, the boundaries defined by it are as follows:

- Digester, Washing and Black liquor evaporation;
- Bleaching;
- Processing;
- Recovery Boiler and Biomass Co-generation.

By using this approach, it was feasible to estimate many of the values such as liquors, condensates, electricity and even biomass. Equations 8, 9 and 10 represent the ratio used to calculate the black and green liquor and the biomass in 2002, respectively, using the data from 2014. The black liquor and the condensates leaving the digester, washing and evaporation system were calculated simply by assuming that the proportionality between the brown pulp and black liquor was the same in 2002 and 2014, whereas for the green liquor, the concentrated black liquor and the weak white liquor had to take in consideration. The biomass mass flow rate takes the medium and low pressure steams it can produce into account. Equation 11 was used to calculate the air ratio using the data from Assari (2014). Also, regarding the mass flows, some were determined to close the mass balance of the process, namely the white liquor, the processing water and the combustion products. Closing the mass balance means that the mass flow of one the components is estimated in such a way that the total mass flow entering the system is equal to the total mass flow that is exiting it. When it comes to the electricity, both reports give the electricity's specific energy consumption for the entire factory, with the energy audit also providing it for each process. That being the case, it is possible to find how much electricity was consumed in 2002 for each process, by diving both values and obtaining the increase/decrease of

electricity consumption, assuming all machinery and electrical appliances had this same increase/decrease in their efficiencies.

$$\text{Black liquor ratio} = \frac{\text{Brown pulp production}_{2014}}{\text{Black liquor}_{2014}} \quad (8)$$

$$\text{Green liquor ratio} = \frac{\text{Green liquor}_{2014}}{\text{Black liquor (strong)}_{2014} + \text{White liquor (weak)}_{2014}} \quad (9)$$

$$\text{Biomass ratio} = \frac{\text{Biomass}_{2014}}{\text{MPS}_{2014} + \text{LPS}_{2014}} \quad (10)$$

$$\text{Air ratio} = \frac{\text{Air}_{\text{Assari (2014)}}}{\text{Black liquor (strong)}_{\text{Assari (2014)}}} \quad (11)$$

One of the main components of the entire process is steam. It is used to heat up other elements at every single stage, whether it be by direct injection or in heat exchangers. In order to obtain reasonable results, it was necessary to assume that the transportation of this steam was adiabatic, meaning there is no heat loss and, since pressure remains constant along the pipes that carry this steam, temperature remained constant. This condition does not apply to every single flow, only to those with unknown temperatures. Another important aspect about steam flows is that the same process might, at different times, use different flows with different temperatures. As such, to compact the information as much as possible, the mass flows were compared and, in the case of being similar, a single flow with a weighted average mass flow and temperature was considered. Otherwise, if one of the mass flows was significantly higher than the others, the mass flow rate and temperature of that flow was considered.

Exergy was divided into physical, chemical and total. Physical exergy is the sum of mechanical and thermal exergy and depends on the mass flows, temperatures, pressures and specific calorific values whereas chemical exergy depends on the composition of each component. Most of this information is presented in Martins (2002) except for the white liquor and condensates mass flow rates mentioned before as well as their temperatures. For those, the same temperature as the one given by Assari et al. (2014) was presented. It is also from this paper that most of the chemical exergy values were calculated. To do so, the physical exergy for each component was determined and then subtracted from the total exergy. This methodology was applied to all liquors (black, white, green and weak white), pulps (unbleached, bleached and white sheet) and chips. Regarding steam and condensates/water, the chemical exergy values were taken from Szargut (2007) and applied to these specific flows whereas the chemical exergy of biomass was taken from Ptasinski et al. (2007).

3.2.1. General equations

Energy and exergy efficiencies of each process depend directly on their inputs and outputs. Therefore, it is crucial to calculate these values as accurate as possible. The expression for the mass balance for a steady-state open system, where subscripts “in” and “out” represent what is entering and exiting the system, respectively, can be written as:

$$\sum \dot{m}_{in} = \sum \dot{m}_{out} \quad (12)$$

In a similar way, the energy balance for a steady-state open system can be expressed as:

$$\sum \dot{E}_{in} = \sum \dot{E}_{out} \quad (13)$$

Considering a stationary state, negligible kinetic and potential energies, that heat (\dot{Q}) is positive if it is entering the system and work (\dot{W}) is positive if it is exiting the system, then the energy equation can also be written as:

$$\frac{dE}{dt} = \dot{Q} - \dot{W} + \sum \dot{m}_{in} \bar{h}_{in} - \sum \dot{m}_{out} \bar{h}_{out} = 0 \quad (14)$$

$$\dot{Q} - \dot{W} = \sum \dot{m}_{out} \bar{h}_{out} - \sum \dot{m}_{in} \bar{h}_{in} \quad (15)$$

$$\dot{Q} - \dot{W} = \sum \dot{m}_{out} (\bar{h}_{f,out}^0 + \Delta \bar{h}_{out}) - \sum \dot{m}_{in} (\bar{h}_{f,in}^0 + \Delta \bar{h}_{in}) \quad (16)$$

$$\dot{Q} - \dot{W} = \sum \dot{m}_{out} \bar{h}_{f,out}^0 - \sum \dot{m}_{in} \bar{h}_{f,in}^0 + \sum \dot{m}_{out} \Delta \bar{h}_{out} - \sum \dot{m}_{in} \Delta \bar{h}_{in} \quad (17)$$

In equations 16 and 17, \bar{h}_f^0 and $\Delta \bar{h}$ represent the enthalpy of formation and enthalpy variation (in regard to a reference temperature T_0), respectively, which are the variables involved in the calculation of the total enthalpy, \bar{h} . The heat that has to be provided (positive) or released (negative) for a reaction to occur, when the reactants and products are in the reference conditions, is denominated heat of reaction, $\dot{Q}_{reaction}$, and it is given by:

$$\dot{Q}_{reaction} = \sum \dot{m}_{out} \bar{h}_{f,out}^0 - \sum \dot{m}_{in} \bar{h}_{f,in}^0 \quad (18)$$

Thus, the energy balance can be rewritten as:

$$\dot{Q} - \dot{W} = \dot{Q}_{reaction} + \sum \dot{m}_{out} \Delta \bar{h}_{out} - \sum \dot{m} \Delta \bar{h}_{in} \quad (19)$$

The general exergy balance for steady-state can be given by:

$$\dot{E}x_Q - \dot{E}x_W + \sum \dot{E}x_{in} - \sum \dot{E}x_{out} - \sum \dot{E}x_{dest} = 0 \quad (20)$$

Where:

$$\dot{E}x_Q = \dot{Q} \left(1 - \frac{T_C}{T_H} \right) \quad (21)$$

$$\dot{E}x_W = \dot{W} \quad (22)$$

$\dot{E}x_Q$ and $\dot{E}x_W$ represent the exergy exchange in the boundaries of the system in the form of heat and work, respectively. The exergy associated with the mass flows entering and exiting the system are given by $\dot{E}x_{in}$ and $\dot{E}x_{out}$, respectively. $\dot{E}x_{dest}$ is exergy that is destroyed during the process and cannot be avoided. T_C and T_H simply refer to the colder and hotter temperatures of the system. Utlu and Kincay (2013) and Moran et al. (2010) are two examples of the various places where these equations (or equivalents) can be found.

Regarding exergy itself, the physical component can be calculated through the enthalpies, entropies and kinetic and potential energies, like it is showed in equation 23, based on an equivalent expression from Moran et al. (2010). The difference between the enthalpies and entropies at the state considered and the reference one can be easily obtained through the specific heat c_p , the state and reference temperatures, T_1 and T_0 respectively, perfect gases constant, R , and state and reference pressures, p_1 and p_0 respectively. These expressions are presented in equation 24 and equation 25 and are derived from Atmaca and Yumrutas (2014).

$$\dot{E}x_{ph} = \dot{m} \left(\Delta h - T_0 \Delta s + \frac{v^2}{2} + gz \right) \quad (23)$$

$$\Delta h = h_1 - h_0 = c_p (T_1 - T_0) \quad (24)$$

$$\Delta s = s_1 - s_0 = c_p \ln \frac{T_1}{T_0} - R \ln \frac{p_1}{p_0} \quad (25)$$

Equation 24 can be used if the pressure is approximately constant and equation 25 is valid only for perfect gases. In many cases the substance is not in this form but rather a liquid. Therefore, the equation no longer needs to take pressure into consideration, and it can be written as:

$$\Delta s = c_p \ln \frac{T_1}{T_0} \quad (26)$$

The total exergy of the system can be described as the sum of both the physical and chemical exergy, as expressed in equation 27.

$$\dot{E}x_t = \dot{E}x_{ph} + \dot{E}x_{ch} \quad (27)$$

3.2.2. Efficiencies

Moran et al. (2010) describes energy efficiency as:

$$\eta = \frac{\text{energy output (desired)}}{\text{energy input}} \quad (28)$$

Identically, exergy efficiency is defined as:

$$\varepsilon = \frac{\text{exergy output (desired)}}{\text{exergy input}} \quad (29)$$

Since exergy is directly related with the amount of work performed in a system, the second law efficiency might be better suited to take this information into consideration. Equation 30, found in Cullen and Allwood (2010b), is an example of the previous statement.

$$\varepsilon = \frac{\text{work output}}{\text{maximum possible work output}} \quad (30)$$

Which is the same as:

$$\varepsilon = \frac{W_{max,output}}{W_{max,input}} \quad (31)$$

4. Processes and Results

This chapter presents the main results of this thesis. The tables and graphics presented are the result of applying the theoretical analysis followed by the methodology previously mentioned. The different sub-chapters will include the results using Alexandre Martins' and the energy audit reports for each separate process. The first part of this chapter presents the results of dividing each process by its objective as explained in the chapter 3, since in all previous exergy studies performed to other pulp industries, do not present any standardized way of dividing each process. The second part of this chapter is dedicated to results of the exergy analysis performed to the Setúbal mill.

4.1. Pulp Process

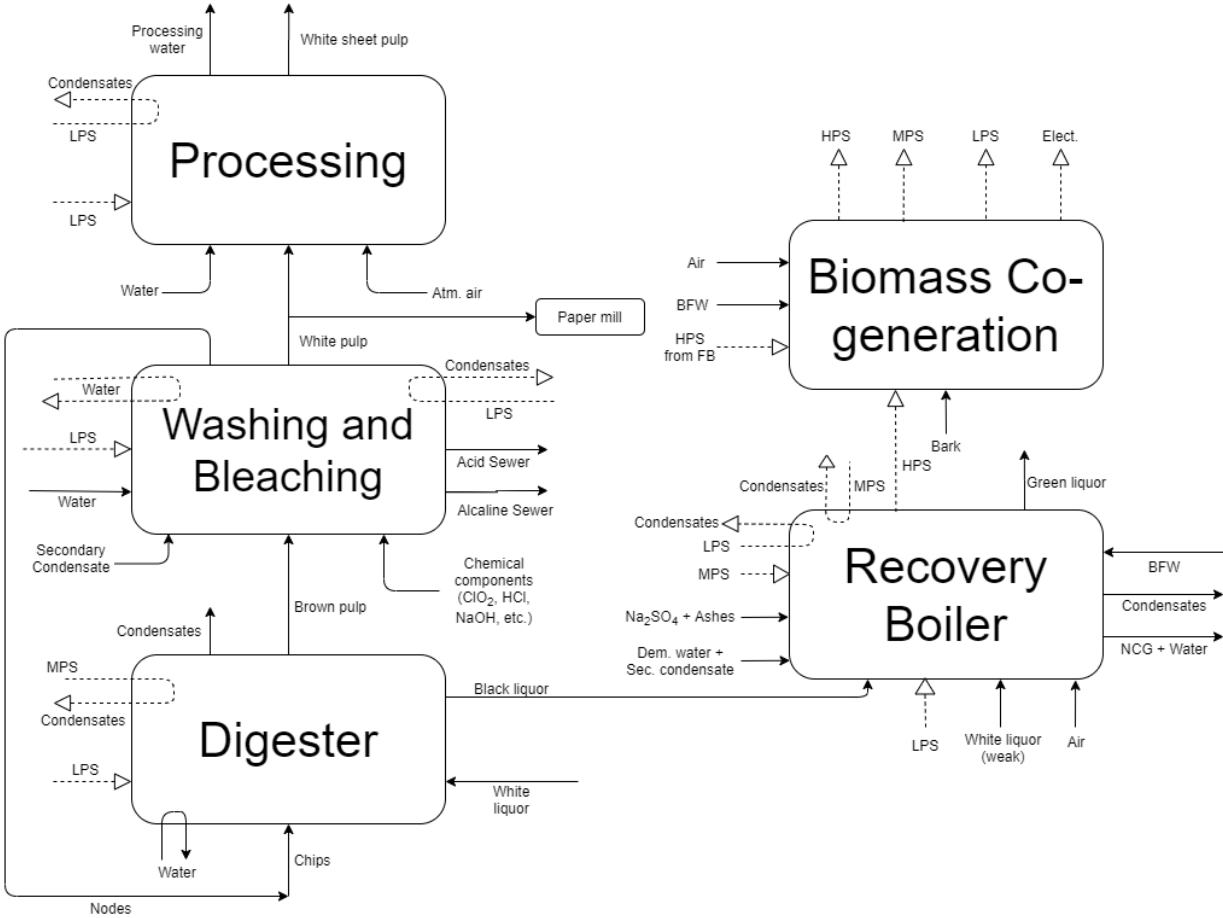


Figure 16 - Pulp process.

Pulp production is divided into a series of separate but interconnected stages, as it is shown by Figure 16. Despite the general description given before, it is necessary to understand each part of the process, since it is what both reports present in their analysis and where the results presented in the next sub-chapter are obtained from. As such, the following parts will go into detail of what happens in each of the different stages. Notice that, even though electricity is only represented as an output of the biomass co-generation process, every single process consumes it to power the necessary machines.

4.1.1. Digester

Before reaching the digester itself, the chips are pre-heated with flash steam in the silo and both flash and low-pressure steam (LPS) in the steam impregnator. The flash steam comes from cyclones used during the process while the LPS comes from the co-generation. Entering from the top, the chips are mixed with the white liquor right from the start, where a chemical reaction occurs between the two. Most of the lignin is separated from the wood fibers that are going to exit at the bottom of the digester as a brownish pulp. Along the digester, black liquor is extracted, reheated and mixed again with white liquor to maintain a constant temperature at certain levels of the digester itself. In this case, the heat used to raise the temperature of the black liquor is medium pressure steam (MPS). It is also important noting that the flash vapor mentioned before comes from flash chambers that use black liquor as well. Warm water is used to cool down the black liquor that exists the digester and is to be transported to the recovery boiler. Finally, all the condensates, which include those exiting the flash chambers and the ones formed by the MPS, are sent to a central collector. Figure 17 represents this entire operation, with the main flows of mass and heat clearly shown.

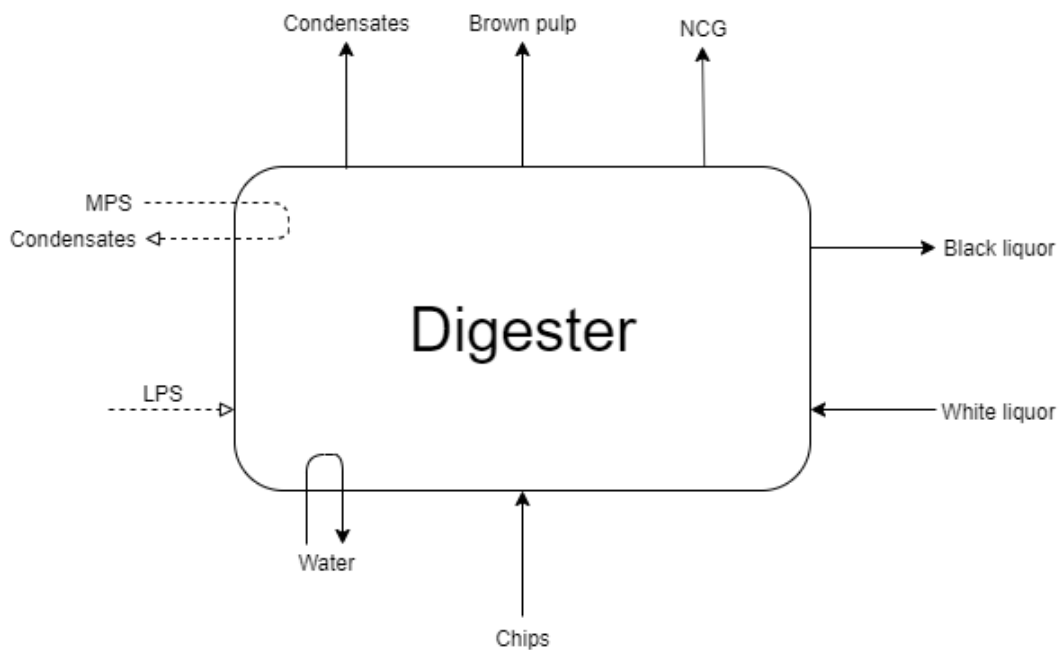


Figure 17 – Digester.

4.1.2. Washing and Bleaching

The brownish pulp now needs to be washed and bleached so any lignin or other undesired materials that remained in the brown pulp can be separated from it. This washing process occurs in counter flow, meaning that as the brown pulp is being transported in one direction, the water is running in the opposite direction, towards the bottom of the digester. At this point, some nodes are extracted from the pulp and mixed with the chips that are going to be processed in the digester. There are condensates known as secondary condensates that also help the washing process and produce filtrate. Immediately after being washed, chemical components such as chlorine dioxide (ClO_2), sodium hydroxide (NaOH), hydrogen peroxide (H_2O_2), sulfur dioxide (SO_2) and even sulfuric acid (H_2SO_4), as well as oxygen (O_2) are added, giving the pulp its final white coloration. To help the chemical reactions taking place, hot water is used to pre-heat the chlorine dioxide and wash the pulp at a later stage while low pressure steam is directly injected to pre-heat the pulp. LPS is also used to heat alkaline filtrates in-between different stages of this process, which is created during the process and exits it as alkaline sewer. Finally, the condensates formed by the steam are directed to the central collector. All these features can be put together and resumed as it is showed by Figure 18. The excess components and chemical products that result from this reaction are drained, creating both an acid and an alkaline sewer and the bleached pulp is stored in silos, ready to be used.

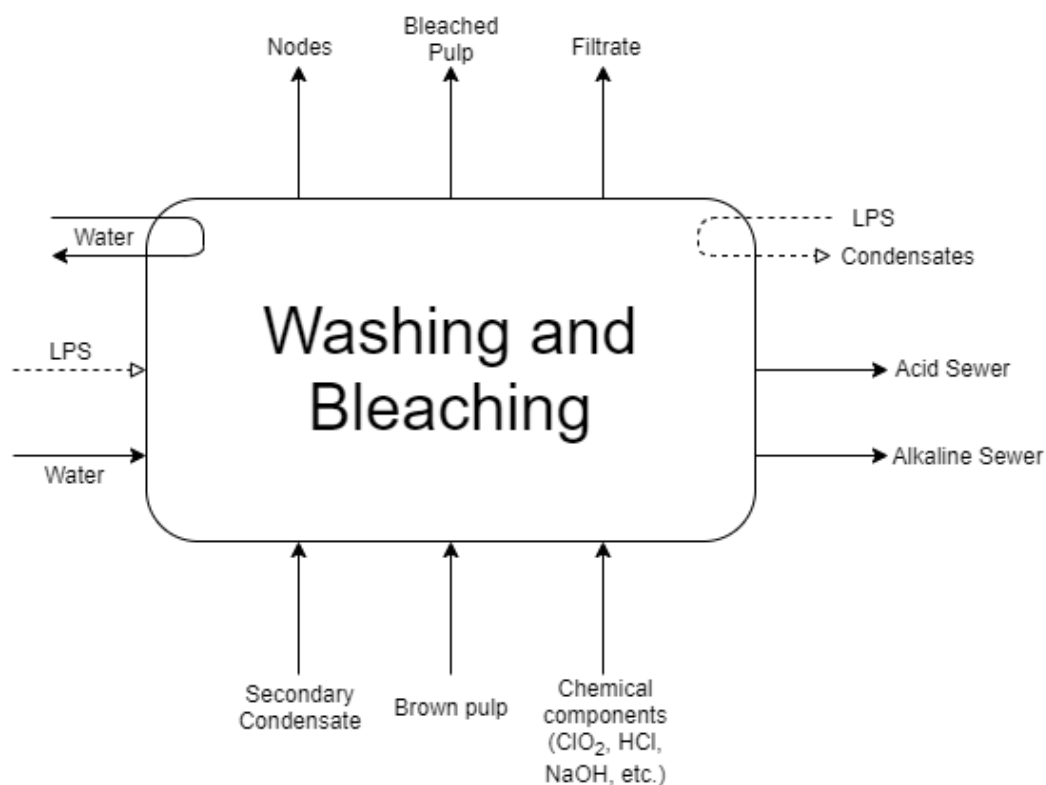


Figure 18 - Washing and Bleaching.

4.1.3. Processing

After being bleached, about 1/3 of the white pulp is sent directly to the paper mill, whereas the remaining 2/3 are going to be cut in order to be transported or sold to other mills. The main elements in this section are the warm and cold water used to dilute the pulp to an acceptable level of consistency and the atmospheric air necessary for the dryer to remove the excess water, as it is shown by Figure 19. Two different low pressure steams, along with flash steam, are also used to further aid this procedure. This flash steam is obtained using some of the condensates that are formed from one of the LPS. Processing water and condensates, due to the condensation of both LPS, are also formed during this process. At the end of the line mechanical presses and rolls help form the final shape of the pulp, with the final step being the cutting of it into the desired sizes.

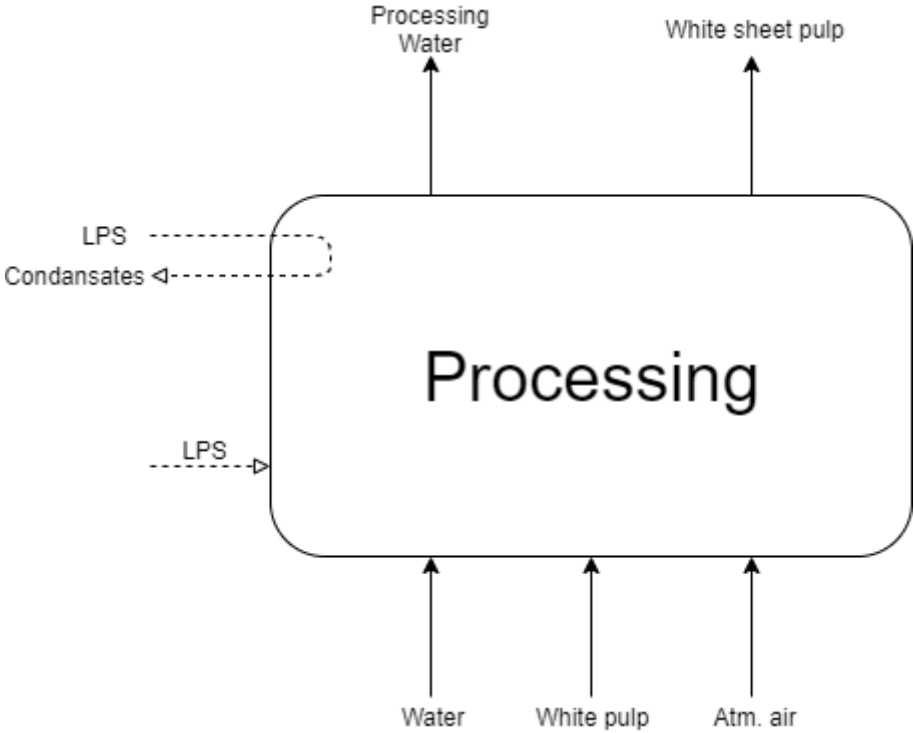


Figure 19 - Processing.

4.1.4. Recovery Boiler

One of the main components of the entire mill is the recovery boiler. Figure 20 represents the main mass flows. The purpose of this device is to reclaim some of the chemical components expended in the digester, while producing high pressure steam (HPS) at the same time. To do so, the black liquor coming from the digester process needs to be concentrated first before it enters the recovery boiler itself, which can be accomplished by two evaporation stages. In the first one, the weak solution of black liquor goes through a series of ascended film tubular evaporators that transform it into an intermediate solution. Then, to create a stronger, more concentrated substance, it undergoes another evaporation step, using weak and intermediate solutions. Both phases use low pressure and flash steam (using the LPS condensates) and create some by-products such as condensates (from the flash chambers), non-condensable gases (NCG) and another three different kinds of condensate: secondary and dirty, which are both directed to their own collectors and contaminated which will go to the causticizing. As a side operation, these dirty condensates that result from the evaporation are cleansed in the procedure known as stripping, using the flash steam produced in the second evaporation stage. Water is used in both stages to cool the dirty condensates and the NCG. Before reaching the chamber, the black liquor is pre-heated with MPS. Now, using pre-heated atmospheric air, sodium sulfate (Na_2SO_4) and ashes that came from electrofilters, and low and medium pressure steam, the combustion occurs inside a chamber where the ashes are melted to form what is called smelt and the high pressure steam is directed to both the biomass co-generator and a HPS collector. This steam is produced due to the evaporation of the boiler feeding water (BFW) that comes from a tank. The smelt is used to produce green liquor after being mixed with weak white liquor. Additionally, the condensate from the LPS and MPS used to pre-heat the air is delivered to a flash tank where, with the addition of demineralized water, it produces boiler feeding water to be supplied to the biomass co-generator, fuel-oil generator and the combustion chamber itself.

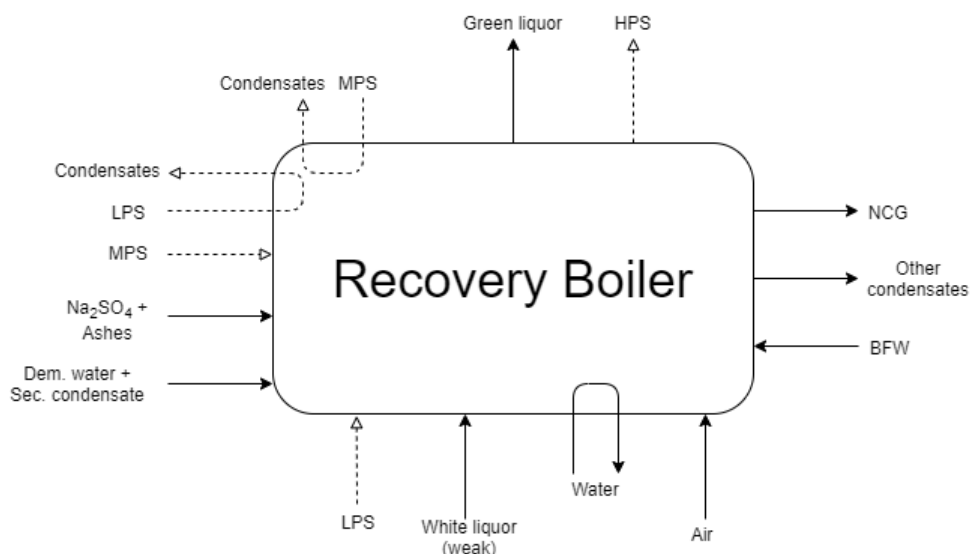


Figure 20 - Recovery Boiler.

4.1.5. Biomass Co-generation

The main energy carriers used in the factory are steam and electricity, which are mostly produced in the biomass co-generator. Air is pre-heated in heat exchangers using high pressure steam before it enters the combustion chamber and mixes with the bark. The HPS produced by the reaction goes directly to the HPS collector. The HPS that enters the turbine comes from this collector combined with a fraction that came directly from the recovery boiler. Here is where the different types of steam (MPS and LPS) and electricity are produced. There are two distinct LPS: one for the processing area and the other for the rest of the pulp and paper mill. Furthermore, for maximum possible extraction of electricity, there is a second turbine. This electricity is distributed throughout the whole factory, including all mechanical devices. In fact, the electricity production goes beyond the mills' needs, with the excess being fed to the national grid. Another important aspect is the fact that sometimes, especially at the beginning of the day, there is not enough high pressure steam to sustain the demand of the entire site. At this point, there is a fuel-oil boiler responsible for helping the co-generator reach its requirements to function properly. Figure 21 represents the stream of masses exchange during this operation.

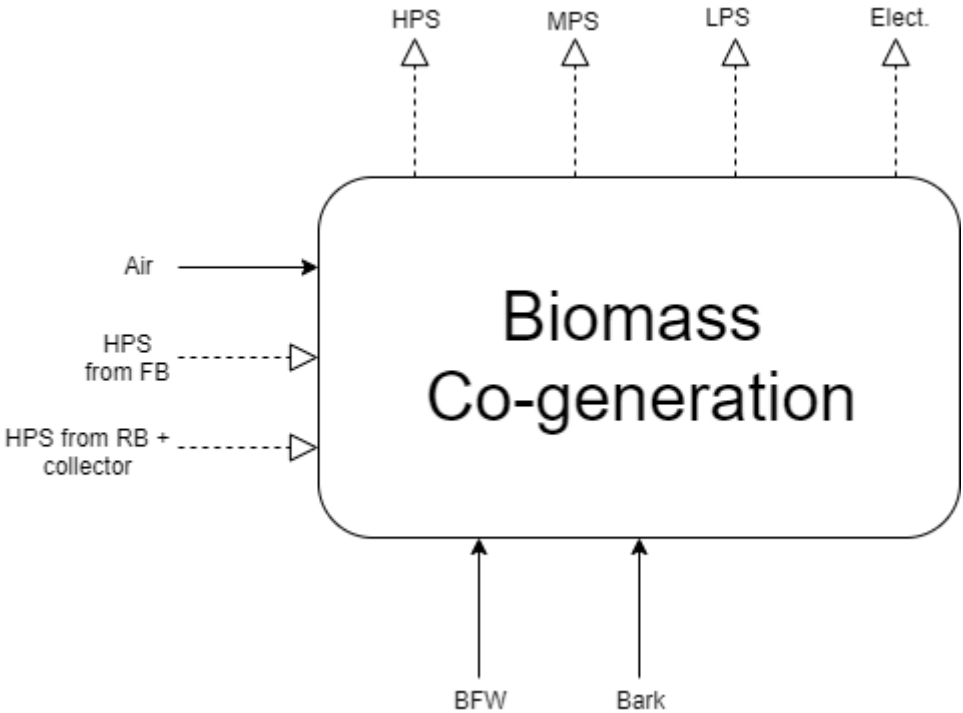


Figure 21 - Biomass Co-generation.

4.2. Exergy flows and efficiencies

The first step when calculating the exergy values of any system is to define the conditions at which each component is entering or exiting it. The main variables that come into play are mass flows (\dot{m}), temperature (T), specific heat (c_p) and, in the case of gases, pressure (p). All these values can be found in the tables presented in the following sections, along with the enthalpy and entropy variation, Δh and Δs , respectively. After defining all properties, exergy values can finally be presented for each process. This includes physical exergy (Ex_{ph}), chemical exergy (Ex_{ch}) and total exergy (Ex_t). There is a distinction between three main types of water depending on the average temperature at which they are: plain water usually has a temperature of 25°C, warm water is around 45°C (Water45) and hot water is around 75°C (Water75).

In 2002, the specific consumption of electricity was 1.951 GJ/ton whereas in 2014 this value was 1.335 GJ/ton, meaning there was a decrease in the specific energy consumption of around 46%. Taking this value into consideration and knowing the specific consumption of electricity for each process in 2014, the electricity consumed in 2002 for each process can be estimated. Also regarding electricity, it is not represented in the figures of any process, as entering the system, but it is always considered in the exergy balance.

4.2.1. Digester, Washing and Black liquor evaporation

In 2002, the production of brown pulp was about 1392 tons/day, whereas in 2014 this value was 1594 tons/day. This means there was, approximately, an 14.5% increase in brown pulp production between 2002 and 2014. This percentage was used to obtain both the black liquor leaving the evaporation process and the one entering the recovery boiler. This is possible since the 2014 black liquor's mass flow is known, which can then be used to calculate the value in 2002. Also, in this case, the white liquor is closing the mass balance, since it was the only unknown variable. The temperature of the MPS entering this stage is the average result of all the flows involved in it. All non-condensable gases (NCG) along with the water used in the evaporators as well as the three types of condensates leaving them (dirty, contaminated and secondary) were assumed to be irrelevant and therefore are not considered in all balances. For the energy balance, presented in Table 12, the heat of reaction was taken from Courchene et al. (2005), where it was presented in $kcal/kg_{chips}$ and converted to kJ/s using the known mass flow rate of the chips. Figure 22 represents this process, Figure 23 is the Grassmann diagram for the main flows and Table 11 and Table 13 are the exergy results involved in this stage.

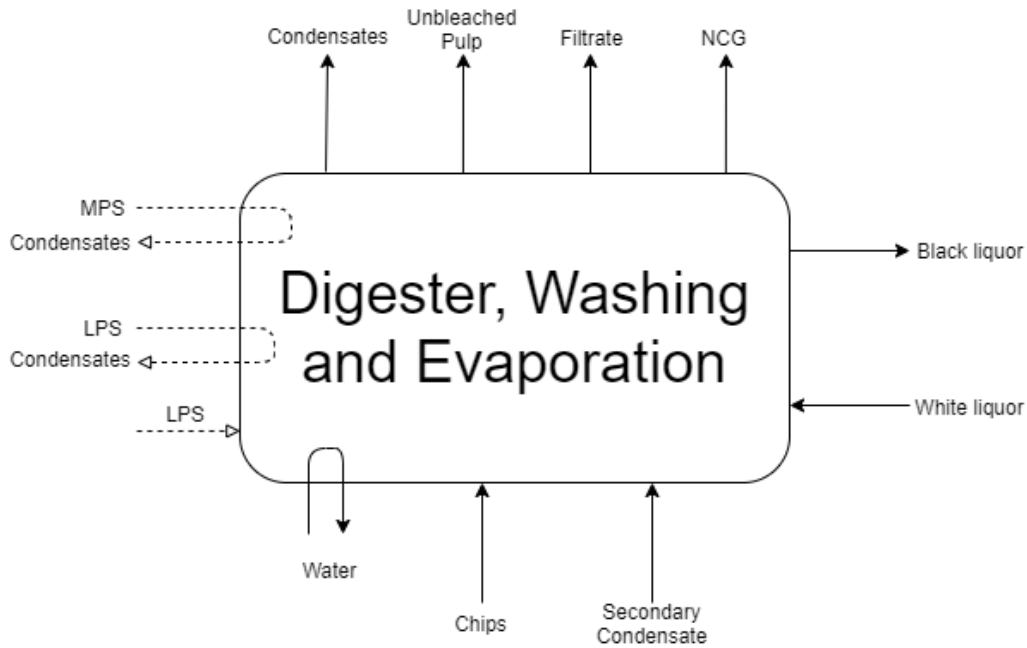


Figure 22 – Digester, Washing and Black liquor evaporation.

Table 11 - Digester, Washing and Black liquor evaporation's components properties. ⁽¹⁾ – closes the mass balance; ⁽²⁾ – calculated from energy audit; ⁽³⁾ – from Assari et al. (2014).

Component	$\dot{m}[\text{kg/s}]$	$T[^\circ\text{C}]$	$p[\text{kPa}]$	$c_p[\text{kJ/kgK}]$	$\Delta h[\text{kJ/kg}]$	$\Delta s[\text{kJ/kgK}]$
Chips	55	25	-	2.52	0	0
White liquor	86.88 ⁽¹⁾	90 ⁽³⁾	-	4.22	274.04	0.83
LPS	23.50	160	460	-	2770	6.92
MPS	11	255.50	1150	-	2950.50	6.88
Water	341	25	-	4.18	0	0
Water45	137	44	-	4.18	79.42	0.26
Sec. Condensate	106	75	-	4.15	207.50	0.64
Water75	153	84	-	4.18	246.62	0.75
Water45	317	56	-	4.18	129.58	0.41
Black liquor	20.08 ⁽²⁾	87	-	3.70	229.40	0.70
Condensates	28.90	100 ⁽³⁾	-	4.21	315.83	0.94
Filtrate	178	77	-	4.08	212.16	0.66
Unbleached pulp	63	76	-	3.47	176.97	0.55

Table 12 – Energy balance to Digester, Washing and Black liquor evaporation. ⁽¹⁾ – from Courchene et al. (2005).

$\dot{m}\Delta h_{in}[\text{MJ/s}]$	$\dot{m}\Delta h_{out}[\text{MJ/s}]$	$\dot{W}[\text{MJ/s}]$	$\dot{Q}_{react}[\text{MJ/s}]$
154.2	141.5	-9.3	18.4 ⁽¹⁾

Table 13 - Exergy values for the digester, washing and black liquor evaporation process.

Component	$\dot{E}x_{ph}[kJ/s]$	$\dot{E}x_{ch}[kJ/s]$	$\dot{E}x[kJ/s]$
Chips	0	566500	566500
White liquor	2271	124514	126785
LPS	16639	12403	29041
MPS	9890	5806	15696
Water	0	17050	17050
Water45	333	6850	7183
Sec. Condensate	1661	5300	6961
Electricity	-	-	9348
Water75	3304	7650	10954
Water45	1998	15850	17848
Black liquor	421	109814	110235
Condensates	986	1445	2431
Filtrate	2954	8900	11854
Unbleached pulp	857	194946	195803

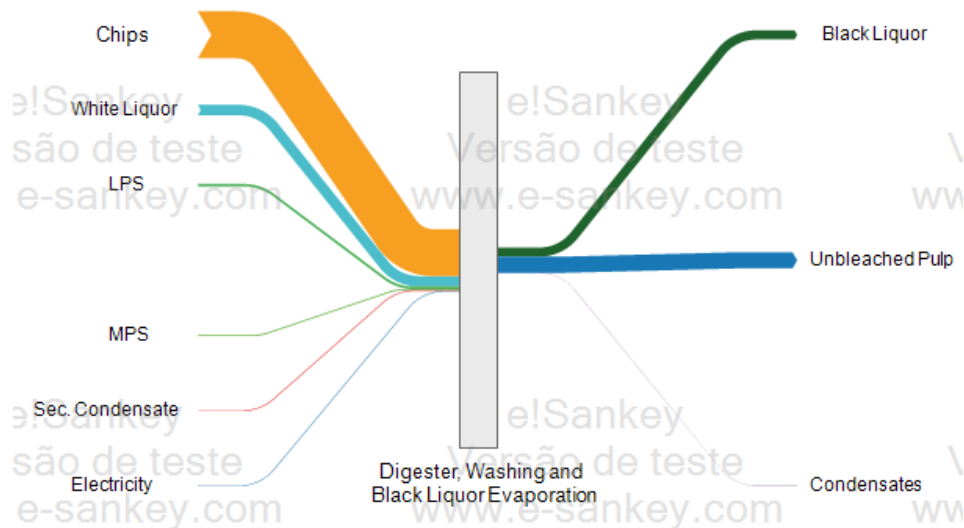


Figure 23 – Grassmann's diagram for the Digester, Washing and Black liquor evaporation's main exergy fluxes.

Using equation 19, we can see that the energy balance for the digester, washing and black liquor evaporation process is not closed. However, the gap represents approximately only 2.5% of $\dot{m}\Delta h_{in}$, which is a very small part of the overall energy involved during this process. This difference can be easily explained by the fact that not all the components are being taken into consideration, as explained earlier in this section.

Another important aspect for this analysis is the difference between the exergy loss ($\dot{E}x_{loss}$) and the exergy destroyed ($\dot{E}x_{dest}$). In this case, the exergy loss is represented mainly by the filtrate and the condensates which amount to 14.3 MJ. On the other hand, the exergy destroyed during this process is about 429.4 MJ, which is clearly much larger than the exergy loss. Therefore, any solutions to increase efficiency of this process should first look at ways to decrease the exergy destroyed during it.

Regarding the exergy efficiency, some considerations must be made. The most important one is that the heat that is being used to pre-heat the chips, pulp and liquors is inside the boundary considered. Consequently, in order to take this heat into account, the condensates are subtracted to the total exergy entering the process resulting in an exergy efficiency represented by:

$$\varepsilon = \frac{\dot{E}x_{unb. pulp} + \dot{E}x_{black liquor}}{\dot{E}x_{chips} + \dot{E}x_{elect.} + \dot{E}x_{white liquor} + \dot{E}x_{sec. cond.} + \dot{E}x_{LPS} + \dot{E}x_{MPS} - \dot{E}x_{condensates}} = 41\% \quad (32)$$

When compared with Gong (2005) and Assari et al. (2014) this efficiency is much smaller than the average for this process presented in these papers. This is to be expected since typically the average efficiency between two or more processes is higher than the real one of all of them combined. Aside from that, there are other explanations of why the efficiency value presented is low. First, any of the assumptions made, whether it is the calculation of the black liquor, the electricity or the chemical exergy, might be, either collectively or individually, creating an underestimated result. The value that deviates the most from all others comes from the chips and, since for this case there is only chemical exergy involved, it is possible that the specific chemical exergy used for this component is overestimated. Another possible scenario is that, in 2002, this process had in fact this low efficiency. Although it is unlikely, the fact is that there is a large amount of heat associated to the digester, washing and evaporation process and this energy carrier is the least efficient of all.

4.2.2. Bleaching

The bleaching process is the only one that is not complete since neither reports give any data regarding the mass flows of most of the main chemical components (NaOH, H₂O₂, SO₂, H₂SO₄ and O₂). This means that it is impossible to calculate the exergy efficiency for this process. Table 14 presents only five of the main mass flows instead of all of them, with Table 15 representing its exergy values. Furthermore, the values of Δh and Δs from the ClO₂ are negative because this component enters the system at a lower temperature than the considered reference temperature of T₀ = 25°C. The value for the ClO₂ chemical exergy was not found. This process can be seen in Figure 24.

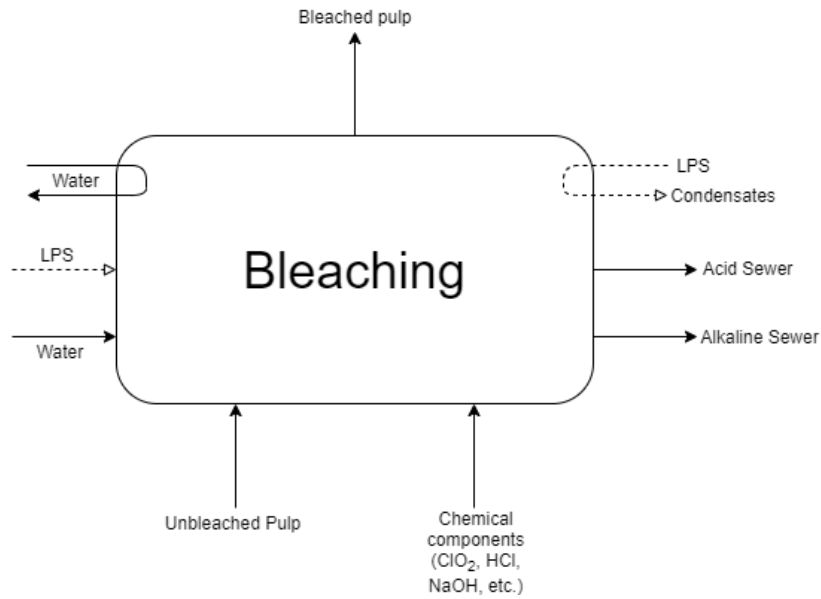


Figure 24 – Bleaching.

Table 14 - Bleaching's components properties.

Component	$\dot{m}[\text{kg/s}]$	$T[^\circ\text{C}]$	$p[\text{kPa}]$	$c_p[\text{kJ/kgK}]$	$\Delta h[\text{kJ/kg}]$	$\Delta s[\text{kJ/kgK}]$
Unbleached pulp	63	76	-	3.47	176.97	0.55
ClO ₂	21	18	-	3.83	-26.81	-0.09
LPS	0,90	160	460	-	2770	6.92
Condensate	2.80	149	-	4.18	518.32	1.45
Bleached pulp	15.32	60	-	3.89	136.15	0.43

Table 15 - Exergy values for the bleaching process.

Component	$\dot{E}x_{ph}[\text{kJ/s}]$	$\dot{E}x_{ch}[\text{kJ/s}]$	$\dot{E}x_t[\text{kJ/s}]$
Unbleached pulp	857	19609	20466
ClO ₂	6.71	-	-
LPS	637	475	1112
Electricity	-	-	8365
Condensate	237	140	378
Bleached pulp	113	47501	47614

4.2.3. Processing

Processing is the only stage that uses two different types of low pressure steams, LPS and LPS_p. As showed, LPS_p has a considerable higher pressure than LPS, which will obviously affect Δh and Δs . It is important to state again that not all the bleached pulp leaving the previous process is consumed, with approximately 2/3 used for processing whilst the rest is used in the paper factory. In this case, the processing water is closing the mass balance. Table 16 and Table 17 show the properties of the processing's components and their exergy values, respectively.

Table 16 - Processing's components properties. ⁽¹⁾ – Closes the mass balance

Component	$\dot{m}[\text{kg/s}]$	$T[^\circ\text{C}]$	$p[\text{kPa}]$	$c_p[\text{kJ/kgK}]$	$\Delta h[\text{kJ/kg}]$	$\Delta s[\text{kJ/kgK}]$
Bleached pulp	10.59	45	-	3.47	69.4	0.23
Atm. Air	54	25	-	1.01	0	0
LPS _p	14	170	630	-	2780.35	6.80
LPS	1.8	160	460	-	2770	6.92
Water45	29	40	-	4.18	62.70	0.21
Water	200	25	-	4.18	0	0
Condensates	14	138	-	4.18	472.34	1.34
Processing water	230.39 ⁽¹⁾	68	-	4.18	179.74	0.56
White sheet pulp	11	96	-	1.67	118.57	0.36

Table 17 - Exergy values for the processing process.

Component	$\dot{E}x_{ph}[\text{kJ/s}]$	$\dot{E}x_{ch}[\text{kJ/s}]$	$\dot{E}x_t[\text{kJ/s}]$
Bleached pulp	24	32827	32851
Atm. Air	0	0	0
LPS _p	10551	7389	17940
LPS	1274	950	2224
Water45	44	1450	1494
Water	0	10000	10000
Electricity	-	-	371
Condensates	1006	6900	7906
Processing water	2727	11520	14246
White sheet pulp	134	16075	16210

The exergy loss during this process is about 22.2 MJ, represented by the processing water and condensates, and the exergy destroyed is equal to 26.5 MJ. Similarly to the digester stage, in the processing stage, the destruction of exergy is higher than the loss. However, the difference between these two results is much smaller than in the digester, washing and evaporation process, meaning in this case, reducing either of these will yield positive results in the overall efficiency of process in question.

The exergy efficiency for this part of the process is given by:

$$\varepsilon = \frac{\dot{E}x_{white\ sheet\ pulp}}{\dot{E}x_{bleached\ pulp} + \dot{E}x_{LPS_p} + \dot{E}x_{LPS} + \dot{E}x_{elect.} - \dot{E}x_{condensates}} = 36\% \quad (33)$$

This stage of the manufacturing process is not very efficient since it uses a considerably large portion of hot water to dilute the pulp. Furthermore, despite being an efficient way to pre-heat the air and dry the pulp, low pressure steam still represents heat, the least efficient form of energy. It is not possible to compare this value with others in the literature, since all the bleached pulp exiting the bleaching process goes directly to the paper manufacturing.

4.2.4. Recovery Boiler and Biomass Co-generation

Figure 25 represents this stage of the pulp process. Na₂SO₄ plus the ashes and the non-condensable gases plus water were not presented in any reports. The bark entering the biomass chamber has a composition that can be found in Klock (accessed 20/08/2019). Table 18 and Table 19 present the component properties and exergy values for this part of the process, respectively, with the combustion products closing the mass balance. From equations 9 and 10, the value of the proportion between the bark and the steam was about 12% and between the green liquor and the weak white liquor plus the strong black liquor was around 83%. To calculate the air entering the recovery boiler, the amount of air is about 5.44 times more than the amount of strong black liquor. The temperature of the MPS exiting the system is calculated assuming adiabatic flow and therefore is the highest temperature found during the entire pulp manufacturing process.

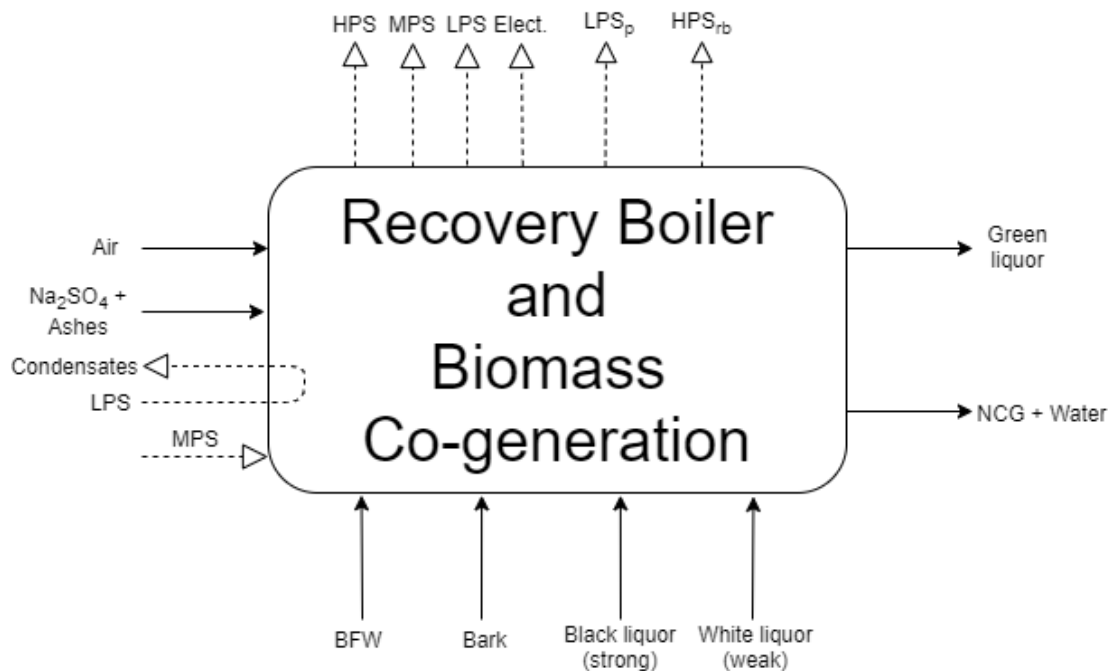


Figure 25 – Recovery boiler and Biomass Co-generation.

Table 18 - Recovery boiler and Biomass co-generation's components properties. ⁽¹⁾ – closes the mass balance.

Component	$\dot{m}[\text{kg/s}]$	$T[^\circ\text{C}]$	$p[\text{kPa}]$	$c_p[\text{kJ/kgK}]$	$\Delta h[\text{kJ/kg}]$	$\Delta s[\text{kJ/kgK}]$
Bark	9.71	25	-	2.52	0	0
Air	209.82	25	-	1.01	0	0
White liquor (weak)	66	46	-	4	84	0.27
MPS	3.30	216	1150	-	2856.77	6.70
LPS	0.8	160	460	-	2770	6.92
Water	803.60	25	-	4.18	0	0
Black liquor (strong)	34	110	-	2.96	251.60	0.74
BFW	99	120	193	4.18	397.10	1.16
HPS	37	424	6200	-	3233.83	6.61
Comb. Products	248.37 ⁽¹⁾	-	-	-	-	-
Water 45	803.60	33.67	-	4.18	36.23	0.12
MPS	18	273	1150	-	2987.80	6.95
LPS	32	160	460	-	2770	6.92
LPS _p	11	170	630	-	2780.75	6.80
HPS _{rb}	48	424	6200	-	3233.83	6.61
Condensates	22.30	100	-	4.21	315.83	0.94
Green liquor	83.77	90	-	3.60	234	0.71

Table 19 - Exergy values for the recovery boiler and biomass co-generation process. ⁽¹⁾ – consumed electricity; ⁽²⁾ – produced electricity.

Component	$\dot{E}x_{ph}[\text{kJ/s}]$	$\dot{E}x_{ch}[\text{kJ/s}]$	$\dot{E}x_t[\text{kJ/s}]$
Bark	0	161588	161588
Air	0	-	0
White liquor (weak)	187	10863	11049
MPS	2835	1742	4577
LPS	566	422	989
Water	0	40180	40180
Black liquor (strong)	1028	185982	187010
BFW	5187	4950	10137
HPS	46729	19528	66257
Electricity ⁽¹⁾	-	-	116
Water 45	415	40	455
MPS	15263	9500	24763
LPS	22657	16889	39546
LPS _p	8295	5806	14100
HPS _{rb}	60621	25333	85954
Condensates	761	1115	1876
Green liquor	1869	87067	88937
Electricity _p ⁽²⁾	-	-	37272

The recovery boiler produces high pressure steam which will later be used in the co-generation process. However, not all HPS goes directly from the recovery boiler to the turbine producing electricity and the other steams. As mentioned previously, there is a high pressure steam collector that will store most of HPS produced. Therefore, one of the components entering the system is the HPS coming from this collector and the other one corresponds to the one exiting the recovery boiler, namely HPS_{rb} . It is also important to note that the bark, air and water entering the system are at the reference temperature which means they do not contribute to the physical exergy of the system.

The exergy loss during the recovery boiler and biomass co-generation process is minimal since, in this case, it is only represented by the condensates that amount to 1.9 MJ. On the other hand, the exergy destroyed is about 187.8 MJ, a much larger sum than the previous mention exergy loss. Therefore, any measures to increase efficiency for this process should start by reducing the exergy destroyed during it.

Regarding the exergy efficiency of this process, it is given by:

$$\varepsilon = \frac{\dot{E}x_{MPS} + \dot{E}x_{LPS} + \dot{E}x_{LPS_p} + \dot{E}x_{HPS_{rb}} + \dot{E}x_{green\ liquor} + \dot{E}x_{electricity_p}}{\dot{E}x_{bark} + \dot{E}x_{white\ liquor\ (weak)} + \dot{E}x_{MPS} + \dot{E}x_{LPS} + \dot{E}x_{black\ liquor\ (strong)} + \dot{E}x_{BFW} + \dot{E}x_{HPS} + \dot{E}x_{electricity} - \dot{E}x_{condensates}} = 66\% \quad (34)$$

In Gong (2005) the average exergy efficiency value for this process is about 47%, which means that this facility has a better performance when it comes to its energy production. It is, however, impossible to identify which stage deviates the most from the values given by Gong (2005) since they are divided differently.

To obtain this efficiency, many conjectures had to be made. Despite all these assumptions, the mass flowrate difference between the fuels (bark and strong black liquor) plus the air and the combustion products is small (about 11 kg/s) which can be easily justified by the smelt produced in the recovery boiler itself. This means that the assumptions made should be close to their real value if they were to be measured at the site.

4.2.5. Aggregate production process

The pulp manufacturing involves all the previous mention processes with the addition of the debarking and causticizing and lime ovens stages. Table 20 and Table 21 refer to the properties and exergy of the entire process analyzed in this thesis, while Table 22 and Table 23 also include debarking and causticizing. It is also important to note that these efficiencies do not include the chemical components used in the bleaching process, meaning that the exergy efficiencies here presented are overestimated in relation to the real ones.

Table 20 – Component properties of the aggregated process.

Component	$\dot{m}[\text{kg/s}]$	$T[^\circ\text{C}]$	$p[\text{kPa}]$	$c_p[\text{kJ/kgK}]$	$\Delta h[\text{kJ/kg}]$	$\Delta s[\text{kJ/kgK}]$
Chips	55	25	-	2.52	0	0
White liquor	86.88	90	-	4.22	274.30	0.83
White liquor (weak)	66	46	-	4	84	0.27
Bark	13.51	25	-	2.52	0	0
Bleached pulp	4.73	60	-	3.89	136.15	0.43
White sheet pulp	11	96	-	1.67	118.57	0.36
Green liquor	83.77	90	-	3.60	234	0.71
HPS	7.20	424	6200	-	3233.83	6.61

Table 21 – Exergy values for the aggregated process stage. ⁽¹⁾ – produced electricity.

Component	$\dot{E}x_{ph}[\text{kJ/s}]$	$\dot{E}x_{ch}[\text{kJ/s}]$	$\dot{E}x_t[\text{kJ/s}]$
Chips	0	566500	566500
White liquor	2273	124514	126787
White liquor (weak)	187	10863	11049
Bark	0	161588	161588
Bleached pulp	35	14662	14697
White sheet pulp	134	16075	16210
Green liquor	1869	87067	88937
HPS	9093	3800	12893
Electricity _p ⁽¹⁾	-	-	19072

The exergy efficiency for the pulp manufacturing (without debarking and causticizing and lime ovens stages) is given by:

$$\varepsilon = \frac{\dot{E}x_{white\ sheet\ pulp} + \dot{E}x_{green\ liquor} + \dot{E}x_{HPS} + \dot{E}x_{electricity_p}}{\dot{E}x_{chips} + \dot{E}x_{white\ liquor} + \dot{E}x_{white\ liquor\ (weak)} + \dot{E}x_{bark} + \dot{E}x_{electricity}} = 17.5\% \quad (35)$$

Table 22 – Component properties of the aggregated process with debarking and causticizing and lime ovens stages.

Component	$\dot{m}[\text{kg/s}]$	$T[^\circ\text{C}]$	$p[\text{kPa}]$	$c_p[\text{kJ/kgK}]$	$\Delta h[\text{kJ/kg}]$	$\Delta s[\text{kJ/kgK}]$
Chips	55	25	-	2.52	0	0
Bark	13.51	25	-	2.52	0	0
Bleached pulp	4.73	60	-	3.89	136.15	0.43
White sheet pulp	11	96	-	1.67	118.57	0.36
HPS	7.20	424	6200	-	3233.83	6.61

Table 23 – Exergy values for the aggregated process with debarking and causticizing and lime ovens stages. ⁽¹⁾ – produced electricity.

Component	$\dot{E}x_{ph}[kJ/s]$	$\dot{E}x_{ch}[kJ/s]$	$\dot{E}x_t[kJ/s]$
Chips	0	566500	566500
Bark	0	161587	161588
Bleached pulp	35	14661	14697
White sheet pulp	134	16075	16210
HPS	9093	3800	12893
Electricity _p ⁽¹⁾	-	-	6336

The final exergy efficiency for this whole process is given by:

$$\varepsilon = \frac{\dot{E}x_{white\ sheet\ pulp} + \dot{E}x_{HPS} + \dot{E}x_{electricity_p}}{\dot{E}x_{chips} + \dot{E}x_{bark}} = 7\% \quad (36)$$

Both these efficiencies are extremely low for such a high energy consuming process. As previously showed, the efficiency in each stage is considerably low, in particular the processing, which can justify why the overall efficiencies are so low. Another reason is the fact that in all the processes, there is a large amount of exergy that is being destroyed, particularly during the digester, washing and black liquor evaporation process.

Unfortunately, it is not possible to compare neither of these efficiencies with the values presented in the literature since in those cases, the case study always includes the paper manufacturing and, consequently, does not include the processing stage. Since this is the least efficient process, it would not be reasonable to compare the overall efficiencies with other case studies where the processing is not part of the pulp manufacturing process.

Another important value in this analysis is the specific energy consumption (SEC). Since this value is given for the main processes, as well as the total one in the 2014 audit, showed by Table 24^(*), it can be compared with Table 7 previously presented.

Table 24 – SEC values according to the energy audit of 2014.

	Electricity [GJ/ton]	Fuels/Heat [GJ/ton]
<i>Debarking</i>		
<i>Digester, Washing and Black Liquor Evaporation</i>		
<i>Bleaching</i>		
<i>Processing</i>		
<i>Causticizing and Lime Ovens</i>		
<i>Recovery Boiler and Biomass Co-generation</i>		
<i>Total</i>		

^(*) Due to confidentiality issues this data is not displayed. If you need the data please contact the author António Felizardo (antonio.pfelizardo@gmail.com)

By comparing both previously mentioned tables, we can observe that although the SEC value for the electricity is approximately 53% and 58% lower in the Setúbal site than it was in Farla et al. (1997) and Fleiter et al. (2012) for chemical pulping, respectively, that is not the case for the SEC values of the fuels/heat. In this case, the SEC is about 41% higher than in Farla et al. (1997) and 25% higher than in Fleiter et al. (2012), which, even though most of the analysis here presented is for the factory in 2002, could further explain why exergy efficiencies are so low, since heat is the least efficient form of energy.

5. Conclusions

To make an energy or exergy analysis it is important to first master its basic concepts. That is why their meaning as well as their differences are pointed out along this thesis. By having a better understanding of why exergy analysis is superior to an energy one, it becomes obvious why transitioning from one to the other is necessary. Enabling an accurate comparison between different machines, processes or even entire compounds is crucial when the primary objective is to point out where the main consumptions are while assessing areas suitable for improvement. This is only possible with an extensive exergy analysis, reason why it should be implemented to every economical sector.

Pulp manufacturing is a specific, highly complex process with many different mass flows and operating temperatures that need to be taken into consideration. Understanding the distinction from what enters the main flow and what is used just to help it reach its necessary temperatures as well as the desired outputs from the by-products will produce more significant results. Separating the stages into objective focused processes, where the boundaries are well defined, is a good way of achieving a better comprehension of the entire process while simplifying its multiple steps. This should always be the first step when making an exergy analysis regardless of the industry that is being studied. Ultimately there would be a standardized way of dividing each industry so that it was possible to compare each step properly. The solution proposed here is the one that makes the most sense when discussing chemical pulping for paper production.

Regarding the Setúbal factory, the main conclusion that is drawn in this work is that the processing stage is the least efficient process studied, contrary to what is presented by Assari et al. (2014) and Gong (2005) in which both conclude that this occurs in the recovery boiler process. It is important to note here that for this thesis the recovery boiler and biomass co-generation are not presented separately as in the two previously mentioned case studies. This means that it is possible that the exergy efficiency of the recovery boiler process in Setúbal's mill is low but, since it is presented along with the biomass co-generation process, that efficiency is not the lowest. For this case study, the possibility of eliminating the processing stage and send all the bleached pulp directly to the paper factory should be considered. Furthermore, there are many opportunities to improve in every step. All the processes have a very significant amount of exergy destruction, which always surmount the exergy loss. This means that, to improve the efficiency of the processes, solutions should look into prolonging the time that each step takes, thus decreasing irreversibilities and, consequently, decreasing the exergy destruction. This could be achieved by, for example, increasing the number of stages that it takes to increase the temperature of one component, thus lowering the temperature difference in each stage. The exergy loss might be more difficult to decrease since most stages involve chemical reactions that produce by-products that cannot be avoided as they are part of the reaction itself.

Finally, energy audits should consider extending their data collection to include mass flows and temperatures of all the components involved in the process. This would obviously require either more manpower or more time to complete it as well as a better understanding of the entire process. It may not be called an "energy audit" anymore but it would provide the necessary data to create other analysis,

namely the exergy one. In addition, the legislation should consider adding exergy consumptions to its reports and policies should change accordingly so that countries and businesses can make their decisions based on a more accurate read of their current circumstances.

6. Future work

Despite the results presented, there are several ways to not only improve the work that has been made but also build upon it.

Firstly, going directly to the site and collect the necessary data, like mass flows, temperatures, and other forms of energy consumption would yield the best results when calculating energy and exergy, especially the latter one. Furthermore, by travelling to the factory it would also be possible to have a better understanding of how the different processes occur nowadays and what exactly the interactions between each components are, such as what enters the main stream, what is used to assist it (for instance, reaching the final temperatures) or what is released as waste.

Another suggestion is to implement the methodology in other factories, industries or even other economic sectors. Currently, there are a huge amount of studies about energy and energy efficiencies throughout the whole specter of these sectors. However, despite been growing in popularity, exergy is still an alien term for most people, including those in the scientific community. This is most notable in Portugal, where there are very few studies published regarding this topic, especially when it comes to specific industries. It would be extremely interesting to compare the exergy results from the Setúbal site with other ones or the pulp and paper industry in general with the cement one, since these are the two largest consumers in the industry sector in Portugal. The outcome of this kind of study would be a much more accurate assessment of the current energy crisis and possibly alert and prevent new ones.

Finally, with the increasing understanding of the exergy theory, new methodologies might arise. As mention before, there are other types of exergy analysis such as CExC, Thermo-Economics or EEA. Applying these approaches to this case study would yield more precise results as well as other output values, relevant and more significant to other professional advisors. For instance, applying the Thermo-Economics procedure would help the financial managers have a better understanding of where exactly the factory is spending more money and perhaps find ways to work around it.

All of these suggestions intent to reach the ultimate stage where the owners of such product manufacturing factories or service providers would have the best information and data not only to increase their profits but also to help people with higher responsibilities, such as politicians, improve the current measurements being implemented to increase economic growth and decrease the environmental footprint.

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Appendix

Appendix A – Reports

A.1 – Alexandre Martins report's tables and figures

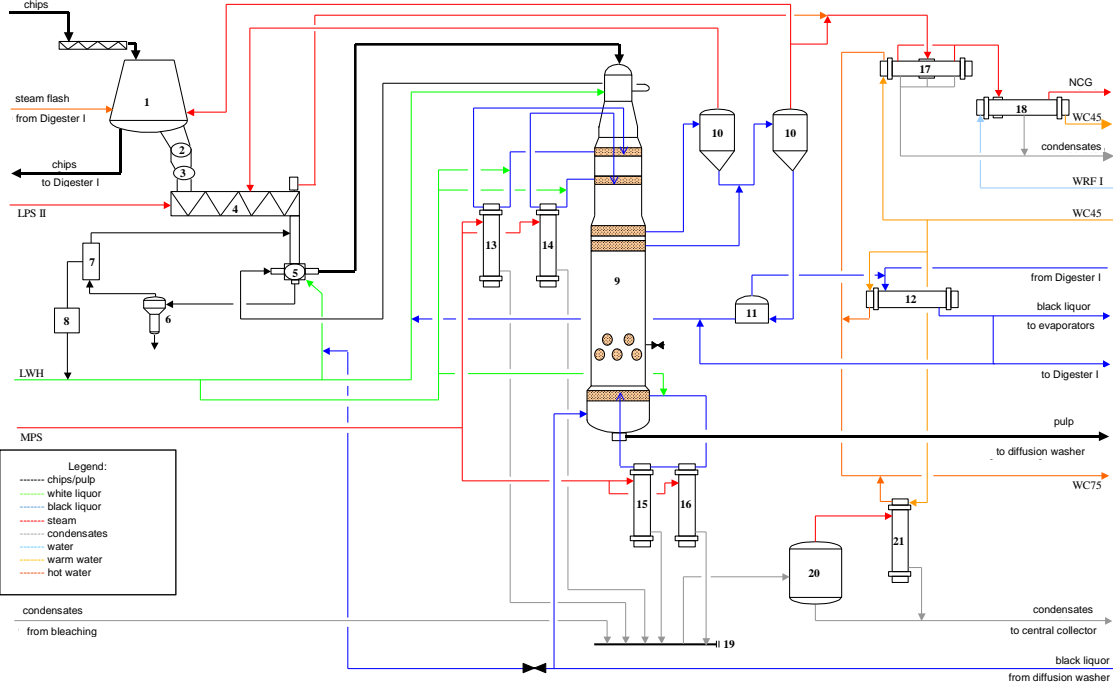


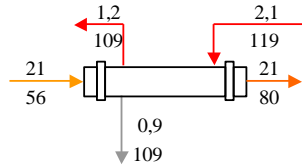
Figure A.1.1 - Digester's mass flows. Source: Martins (2002).

Table A.1. 1 - Heat exchange in the digester. Source: Martins (2002).

mass flow (kg/s) →
temperature (°C)

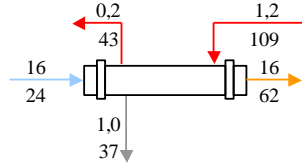
Component	Description	ΔH (kW)
Chip silo		10704
Steam impregnator (DC I)		1783
Upper circulation C5 heat exchanger (DC I)		6141
Lower circulation C6 heat exchanger (DC I)		3979
Washing circulation C8 heat exchanger (DC I)		762

Condenser
(DC I)



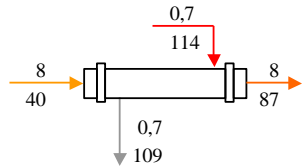
2122

Post-
condenser
(DC I)



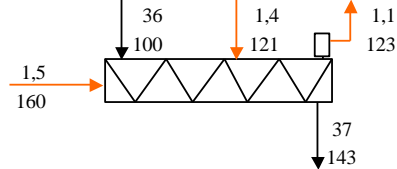
2478

Flash
condenser
(DC I)



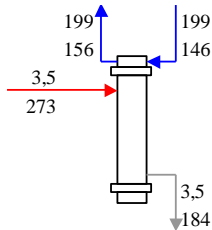
1478

Vapor
impregnator
(DC II)



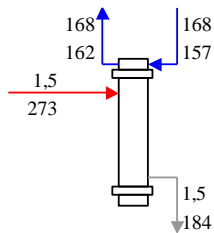
4073

Upper
circulation C5
heat
exchanger
(DC II)



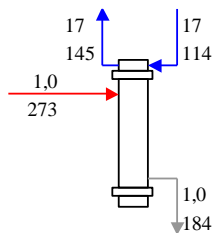
7737

Lower
circulation C6
heat
exchanger
(DC II)



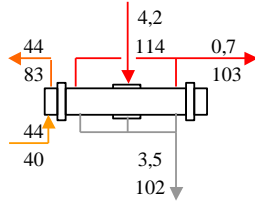
3423

Washing
circulation C8
heat
exchanger
(DC II)



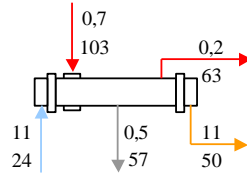
2159

Condenser
(DC II)



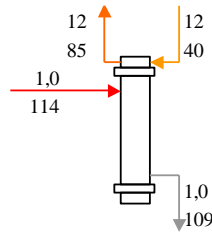
7966

Post-
condenser
(DC II)



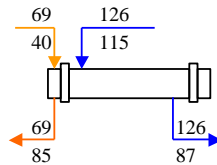
1157

Flash
condenser
(DC II)



2200

Black liquor
cooler



12994

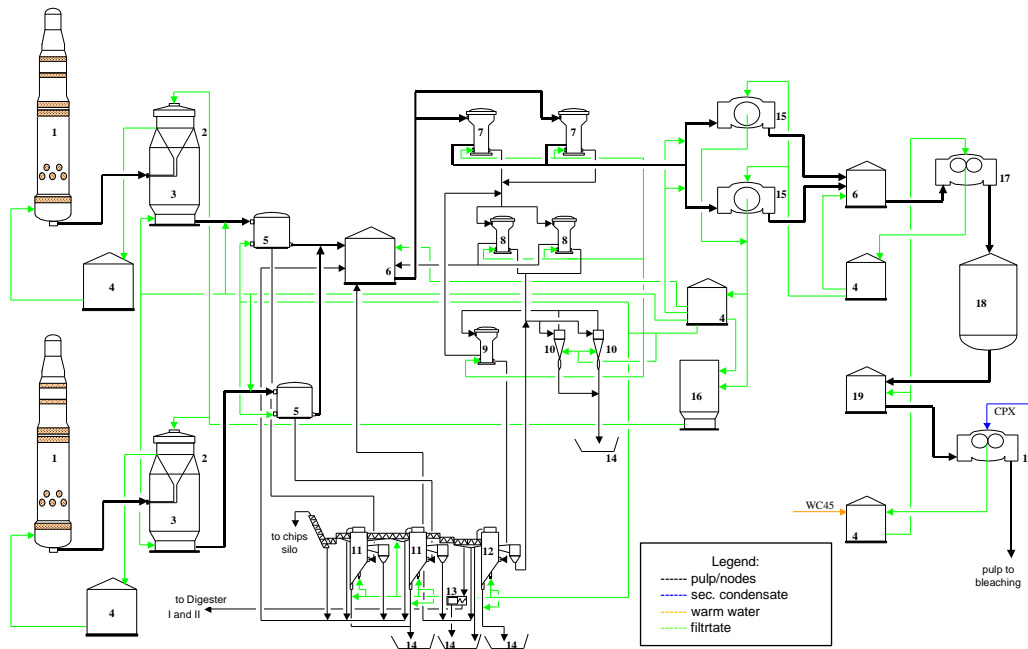


Figure A.1.2 - Washing's mass flows. Source: Martins (2002).

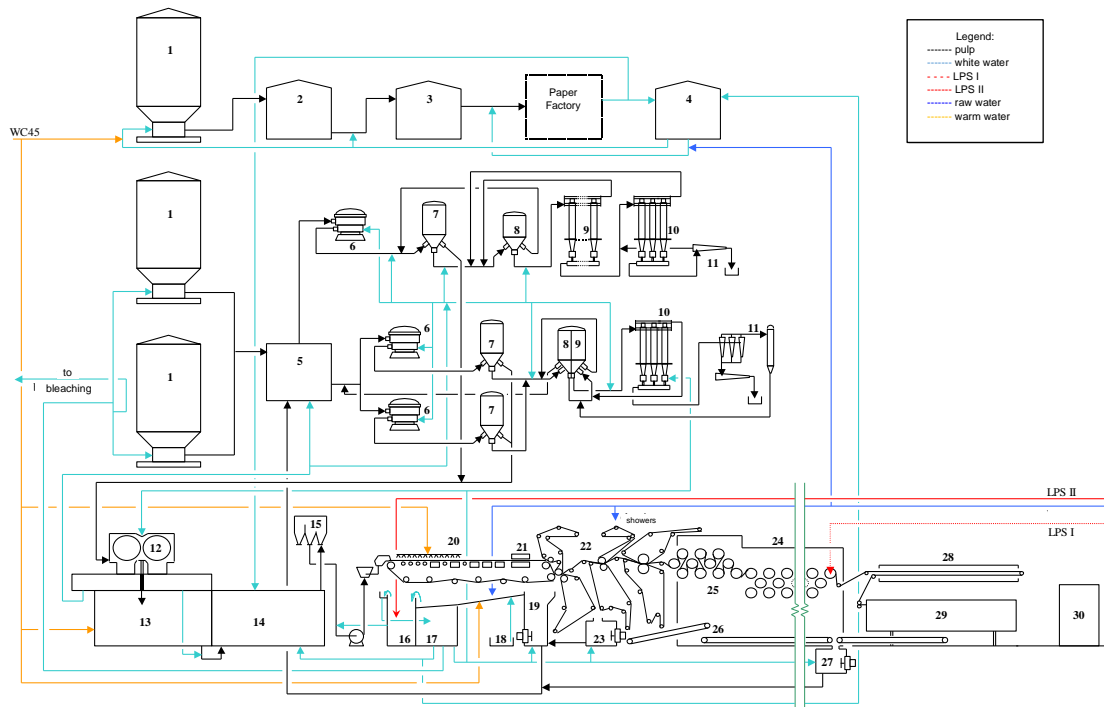


Figure A.1.4 - Processing's mass flows. Source: Martins (2002).

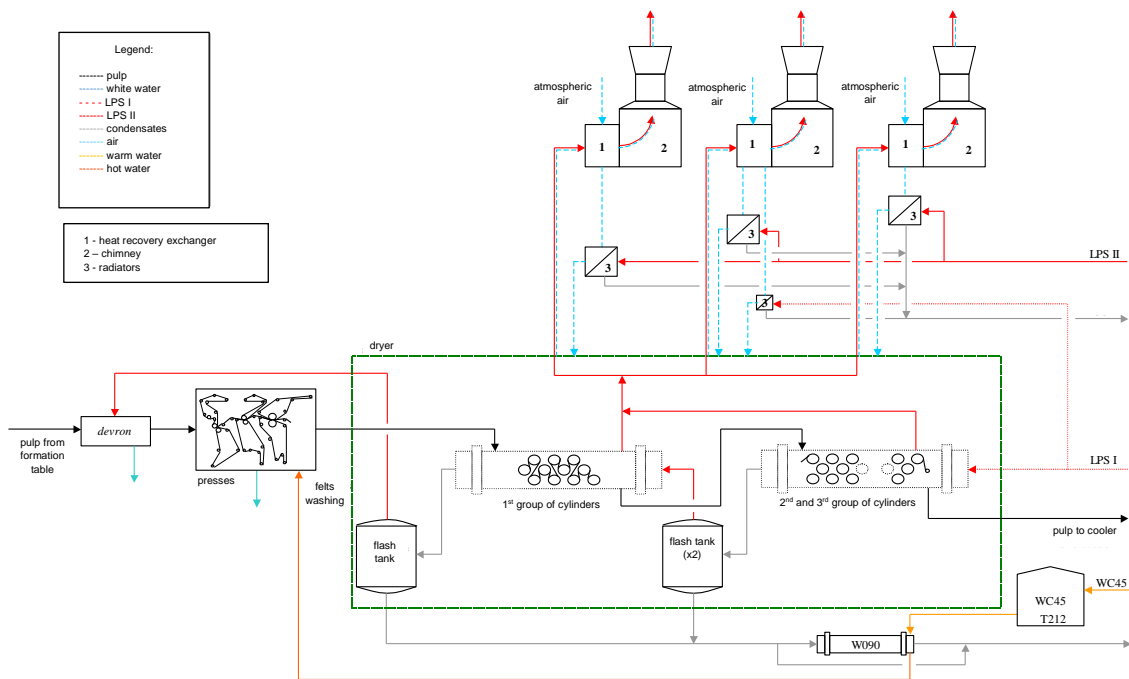
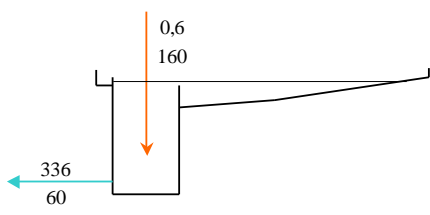
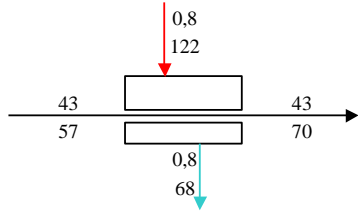
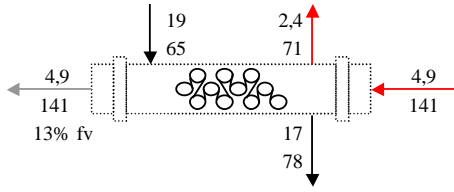
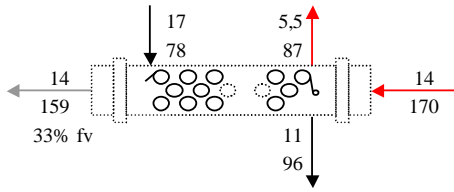
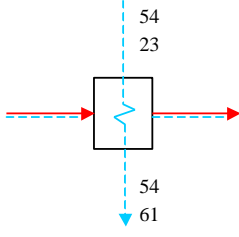
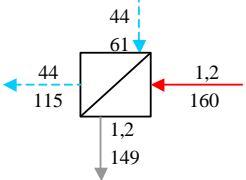


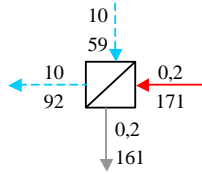
Figure A.1.5 - Air supply and drying vapor in the processing. Source: Martins (2002).

Table A.1. 2 - Heat exchange in the processing. Source: Martins (2002).

mass flow (kg/s) →
temperature (°C)

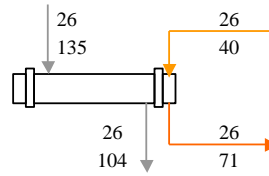
Component	Description	ΔH (kW)
Water box of the machine		1405
<i>devron</i>		1955
1 st group of cylinders		6148
2 nd and 3 rd group of cylinders		13202
Heat recovery exchangers		3167
Air radiators for the dryer		2575

Air radiator
for the
pockets



374

Water
exchanger for
washing felts
(W090)



3310

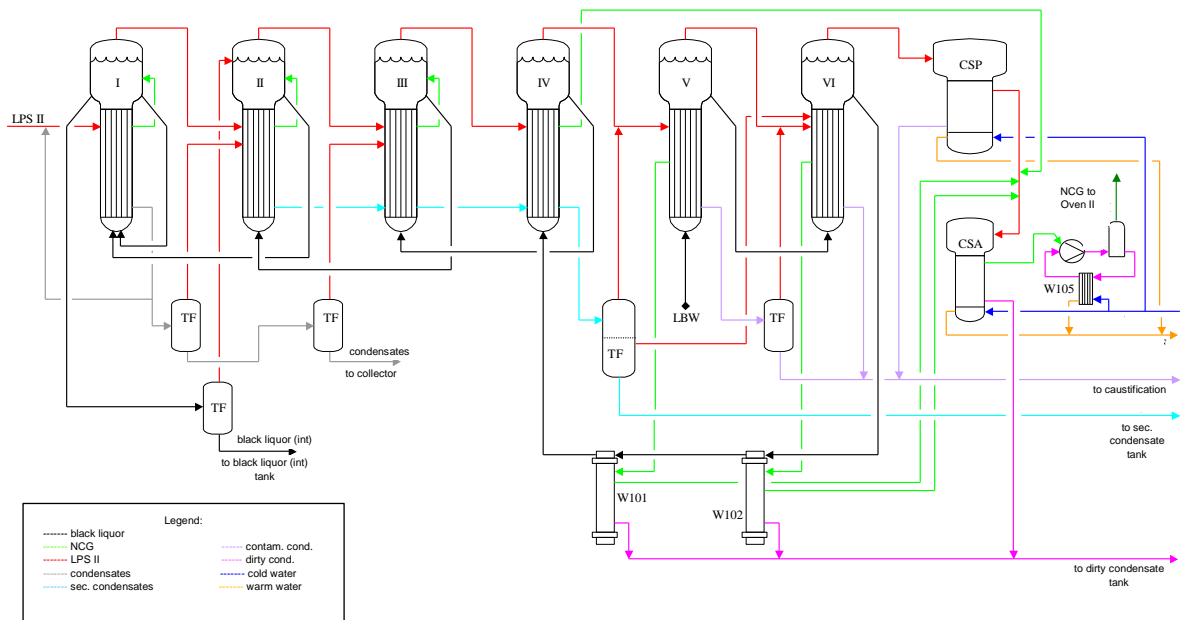
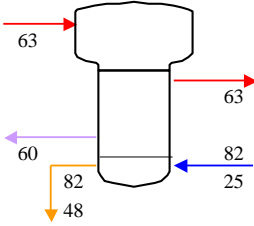
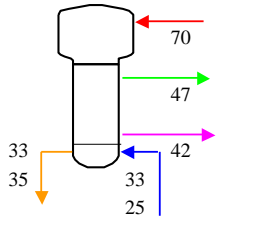


Figure A.1.6 - First evaporation stage's mass flows. Source: Martins (2002).

Table A.1. 3 - Heat exchange in the first evaporation stage. Source: Martins (2002).

Component	Description	ΔH (kW)
Main surface condenser		7682
Auxiliary surface condenser		1311

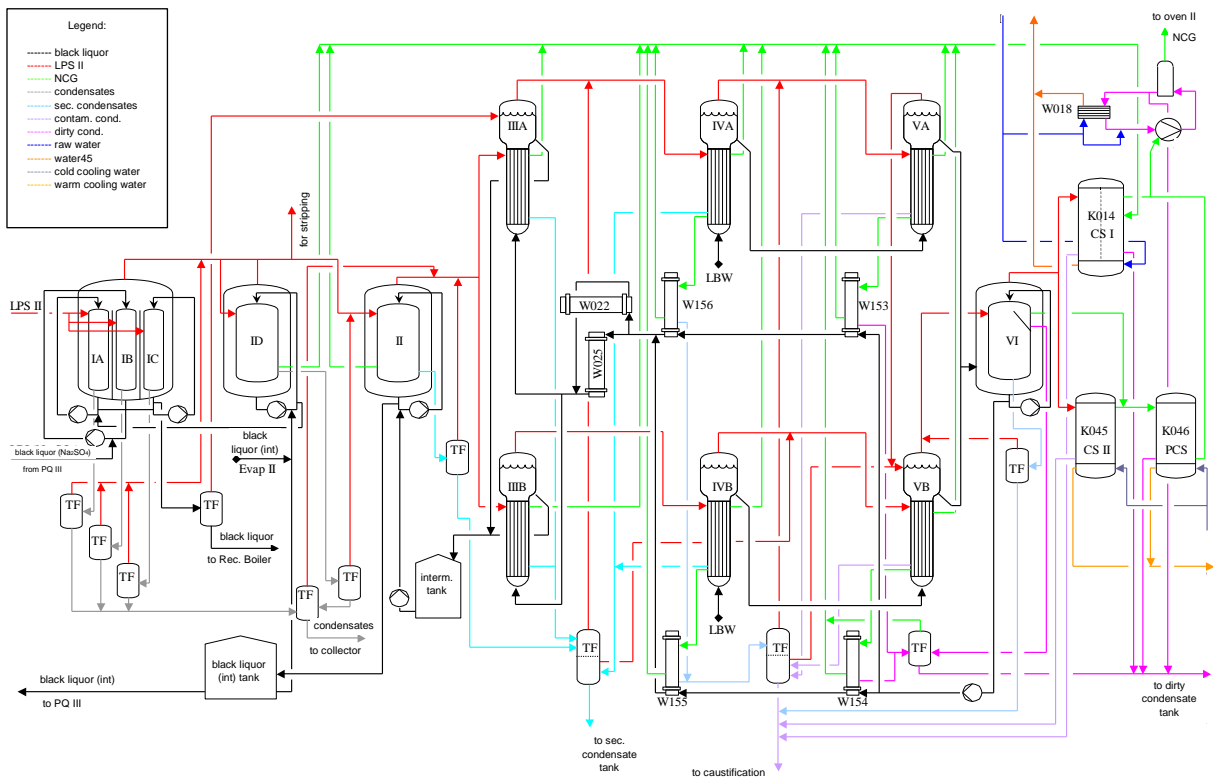


Figure A.1.7 - Second evaporation stage's mass flows. Source: Martins (2002).

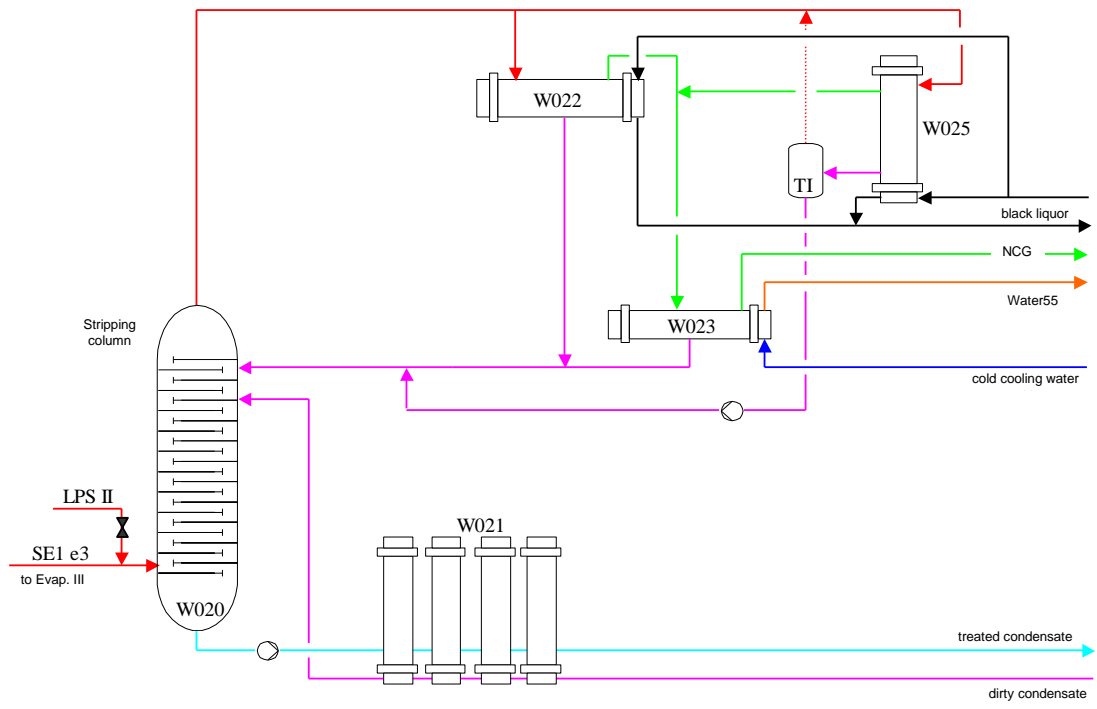
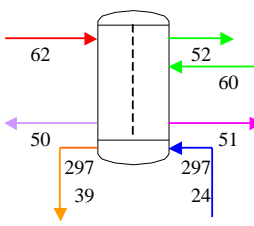
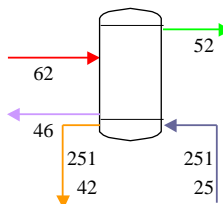
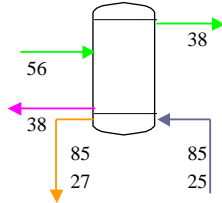
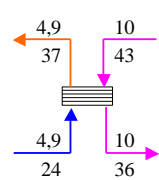
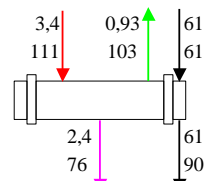
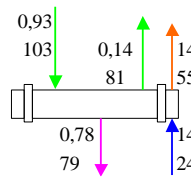
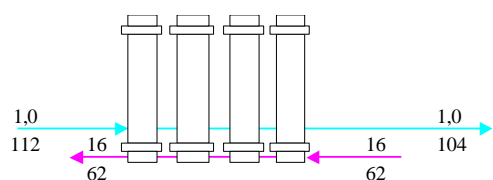


Figure A.1.8 - Stripping's mass flows. Source: Martins (2002).

Table A.1. 4 - Heat exchange in the second evaporation stage and stripping. Source: Martins (2002).

Component	Description	ΔH (kW)
Surface condenser I		18580
Surface condenser II		17679
Surface post-condenser		706
Vacuum pump dirty condensate cooling heat exchanger		271
Reflux condenser stripping column		5774
Tuning condenser		1836
Dirty condensate pre-heater		642

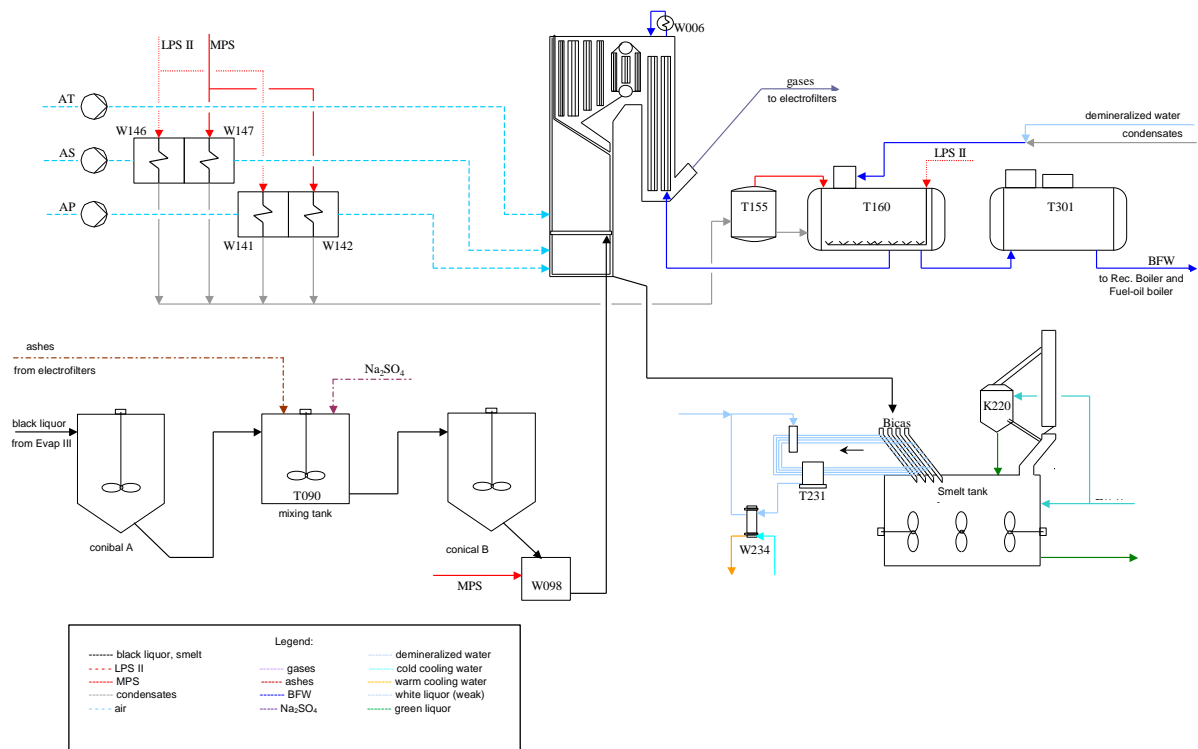


Figure A.1.9 - Recovery boiler's mass flows. Source: Martins (2002).

Table A.1. 5 - Heat exchange in the biomass boiler. Source: Martins (2002).

Component	Description	ΔH (kW)
Combustion air pre-heating heat exchangers		3480

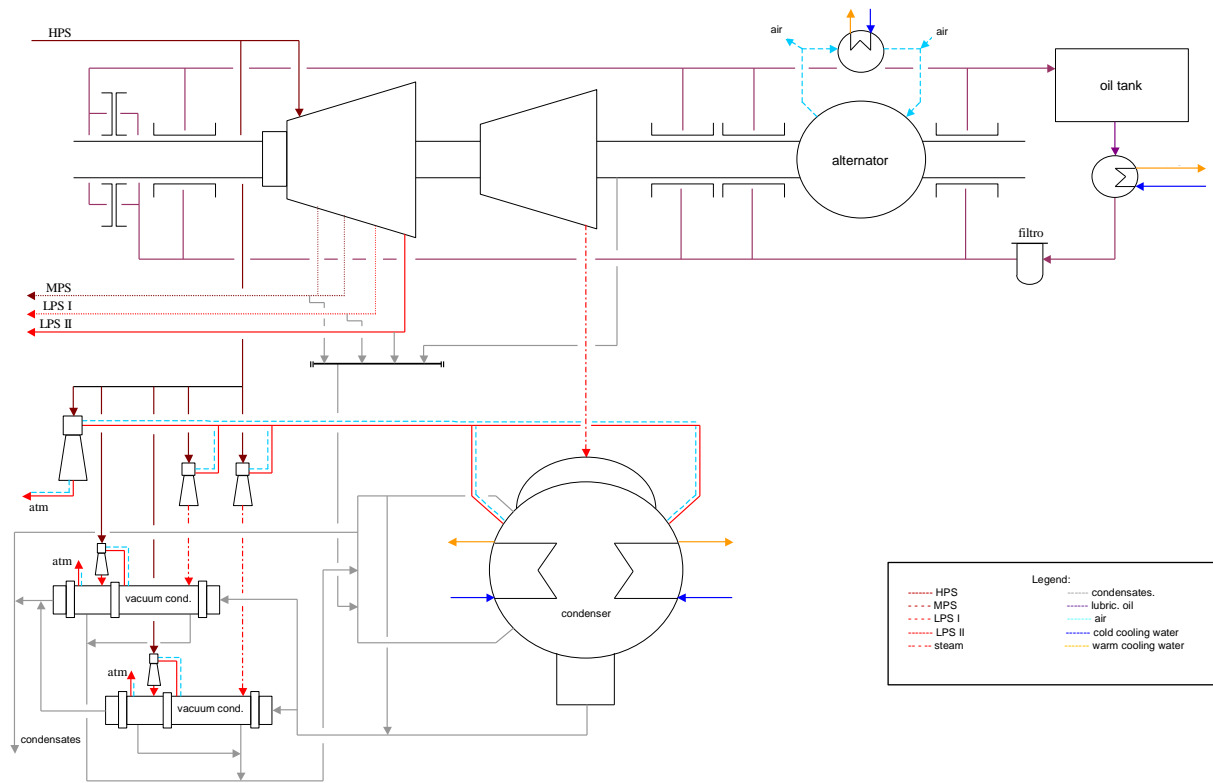


Figure A.1.10 - Biomass co-generation turbine's mass flows. Source: Martins (2002).

Table A.1. 6 - Heat exchange in the biomass co-generation turbine. Source: Martins (2002).

Component	Description	ΔH (kW)
Lubricant oil cooling heat exchanger		73
Alternator cooling air cooling heat exchanger		1916
Turbine condenser		41386
Vacuum condensers		640

Table A.1. 7 - Average raw pulp production. Source: Martins (2002).

Raw pulp	tAD/day
Digester I	553
Digester II	839
Total	1392

Table A.1. 8 - Average white pulp production. Source: Martins (2002).

White pulp	tAD/day
Market	915
Suspended	409
Total	1324

A.2 – Energy audit report's tables

Due to confidentiality issues this data is not displayed. If you need the data please contact the author António Felizardo (antonio.pfelizardo@gmail.com)

Appendix B – Other exergy values

Table B. 1 - Lower heating value and chemical exergy of fuels. Source: Ptasiński et al. (2007).

Fuel	LHV _{org} (kJ/kg organic)	LHV _{org} (kJ/kg biomass)	β (-)	e_{ch} (kJ/kg biomass)
Coal	31047	24839	1.067	26638
Vegetable oils	37558	37558	1.074	40338
Straw	18064	14619	1.128	16506
Treated wood	18886	15290	1.119	17129
Untreated wood	18904	14812	1.122	16634
Grass/plants	18624	13101	1.125	14760
Sludge	19617	8197	1.118	9249
Manure	19148	7506	1.116	8427

Table B. 2 - Chemical exergy of water and other elements. Source: Szargut (2007).

<i>Substance</i>	<i>State</i>	<i>Molecular mass</i>	<i>Enthalpy of devaluation</i>	<i>Standard chemical exergy</i>
		M, kg/kmol	D° , kJ/mol	$e^{\circ}_{x,ch}$, kJ/mol
H ₂ O	g	18.01534	0	9.5
H ₂ O	l	18.01534	-44.012	0.9
H ₃ PO ₄	s	98.0013	-76.26	89.6
H ₂ S	g	34.080	946.61	812.0
H ₂ SO ₄	l	98.077	153.25	163.4

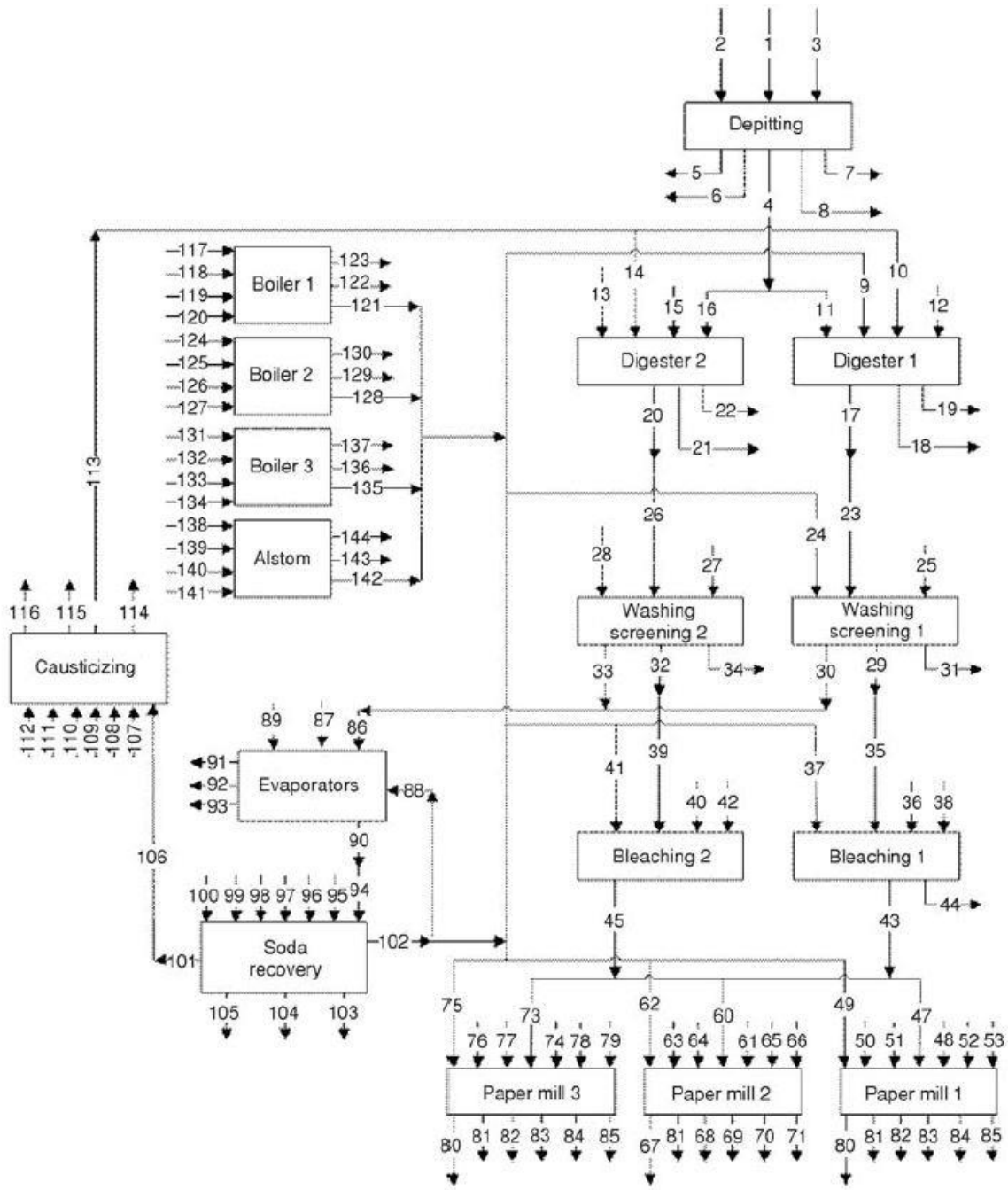


Figure B.1 - Bagasse chemical pulping. Source: Assari et al. (2014).

Table B. 3 - Exergy balance in the bagasse chemical pulping process. Source: Assari et al. (2014).

State no. in fig. 1	Fluid	Mass flow rate [ton/tp]	Temperature [°C]	Pressure [kPa]	Exergy flow [MJ/tp]
1	Raw bagasse	2.69	25		26605.89
2	Water	23.52	35		34.34
3	Electricity	–	–		753.3
4	Depitted bagasse	2.33	25		23999
5	Pit	0.23	25		2185
6	Water	9.09	30		1.54
7	Waste water	14.51	30		2.32
8	Waste bagasse	0.13	25		1186.88
9	Steam	0.78	170	785	630.41
10	Caustic	0.97	25		1415.61
11	Bagasse	0.8	25		8240
12	Electricity	–	–		162.57
13	Steam	1.6	170	785	1309.72
14	Caustic	1.85	25		2699.87
15	Bagasse	1.53	25		15759
16	Electricity				169.31
17	Pulp and liquor	2.4	100		10200
18	Steam	0.1	150	100	49.02
19	Waste	0.05	100		24.51
20	Pulp and liquor	4.28	100		18190
21	Steam	0.6	150	100 kPa	294.15
22	Waste	0.1	150		49.02
23	Pulp and liquor	2.4	70		10200
24	Water	3.6	75		51.66
25	Electricity	–	–		325.15
26	Pulp and liquor	4.28	70		18190
27	Water	5.5	75		93.78
28	Electricity	–	–		470.18
29	Pulp	2	60		6202
30	Black liquor	3.7	60		4297.58
31	Waste	0.3	60		58.69
32	Pulp	3.75	60		11628.75
33	Black liquor	4.51	60		5238.41
34	Waste	1.52	60		147.95

Table B.3 (cont.) - Exergy balance in the bagasse chemical pulping process. Source: Assari et al. (2014).

State no. in fig. 1	Fluid	Mass flow rate [ton/tp]	Temperature [°C]	Pressure [kPa]	Exergy flow [MJ/tp]
35	Brown pulp		50		
36	Hypo		75		
37	Saturated steam	0.24	130	270.1	151.21
38	Electricity	–	–		140.63
39	Brown pulp	3.67	50		11380.67
40	hypo	0.72	75		9.1
41	Saturated steam	0.48	130	270.1	280.93
42	Electricity	–	–		198.22
43	White liquor	1.42	40		4403.42
44	Waste materials	0.94	75		82.41
45	White liquor	3.27	40		10140.27
46	Waste materials	1.6	75		748.88
47	Pulp	1.83	35		2674.83
48	Waste paper	0.04	45		597.4
49	Steam	2.26	140	360	1521.4
50	Water	8.73	35		9.25
51	Water	0.9	55		5.34
52	Brought pulp	0.05	35		1108.85
53	Electricity	–	–		640.69
54	Paper	0.36	45		7983.72
55	Condensate	1	100		34.36
56	Water	4.05	35		2.83
57	Waste water	6.24	25		0
58	Water	0.9	45		2.41
59	Waste condensate	1.26	100		43.29
60	Pulp	1.51	35		4682.51
61	Waste paper	0.05	45		724.25
62	Steam	1.76	140	360	1185.06
63	Water	7.11	35		7.91
64	Water	0.8	55		4.74
65	Brought pulp	0.04	35		887.08
66	Electricity	–	–		714.42
67	Paper	0.29	45		6431.33
68	Condensate	1	100	100	34.36
69	Water	3.25	35		2.27
70	Waste water	5.17	25		0

Table B.3 (cont.) - Exergy balance in the bagasse chemical pulping process. Source: Assari et al. (2014).

State no. in fig. 1	Fluid	Mass flow rate [ton/tp]	Temperature [°C]	Pressure [kPa]	Exergy flow [MJ/tp]
71	Water	0.8	45		2.14
72	Waste condensate	0.76	100	100	26.11
73	Pulp	1.68	35		5209.68
74	Waste paper	0.02	45		289.7
75	Steam	2.39	140	360	1609.26
76	Water	8.4	35		7.16
77	Water	0.4	55		2.37
78	Brought pulp	0.04	35		887.08
79	Electricity	–	–		975.65
80	Paper	0.35	45		7761.95
81	Condensate	1.8	100	100	61.85
82	Water	3.53	35		2.47
83	Waste water	6.66	25		0
84	Water	0.4	45		1.07
85	Waste condensate	0.19	100	100	6.52
86	Stripping liquor	8.2	60		9536
87	Water	1.99	30		40.59
88	Steam	2.62	141	375	1770.07
89	Electricity	–	–		89.77
90	Strong black liquor	1.56	102		8582.4
91	Water	1.99	50		10.65
92	Waste condensate	7.19	60	20	58.89
93	Condensate	2.08	90	70 kPa	55.83
94	Strong black liquor	1.56	95		8584.2
95	Water	6.83	120		354.66
96	Steam	1.2	207		1075.44
97	Fuel oil	0.36	65		1473.8
98	Air	8.48	25		0
99	Weak wash liquor	2.21	55		376.25
100	Electricity	–	–		601.95
101	Green liquor	1.7	95		1810.53
102	Steam	5.67	345	2945	6153.76
103	Exhaust gas	10.4	119		479.06
104	Water	0.7	210		635.74
105	Waste	2.17	274		594.58
106	Green liquor	1.7	90		1810.53
107	Water	1.24	50		5.11

Table B.3 (cont.) - Exergy balance in the bagasse chemical pulping process. Source: Assari et al. (2014).

State no. in fig. 1	Fluid	Mass flow rate [ton/tp]	Temperature [°C]	Pressure [kPa]	Exergy flow [MJ/tp]
108	Natural gas	0.05	20		193.83
109	Sodium carbonate	0.13	65		1.23
110	Air	1.16	25		0
111	Water	0.19	25		0
112	Electricity	–	–		193.8
113	White liquor	0.8	90		1167.51
114	Weak wash liquor	1.72	55		296.23
115	Exhaust gas	1.53	536		451.61
116	Waste material	0.42	65		68.53
117	Water	0.86	108		33.15
118	Fuel oil	0.08	60		3274.72
119	Air	5.62	25		0
120	Electricity	–	–		71.8
121	Steam	0.69	280	785	621.71
122	Exhaust gas	5.7	188		669.81
123	Waste water	0.17	160		17.97
124	Water	1.11	108		43.29
125	Natural gas	0.07	20		3184.87
126	Air	2.1	25		0
127	Electricity	–	–		92.43
128	Steam	0.95	220	785	840.75
129	Exhaust gas	2.17	115		201.42
130	Waste water	0.16	164		46.45
131	Water	0.81	108		31.59
132	Natural gas	0.06	20		2725.75
133	Air	1.89	25		0
134	Electricity	–	–		131.7
135	Steam	0.71	220	785	628.3
136	Exhaust gas	1.95	126		147.65
137	Waste water	0.1	95		11.99
138	Water	9.98	120		570.72
139	Natural gas	0.55	20		25019.12
140	Air	9.49	25		0
141	Electricity	–	–		312.98
142	Steam	8.91	250	785	8524.28
143	Exhaust gas	10.04	224		1402.79
144	Waste water	1.07	95		137.08