Life Cycle Assessment of bio-oil produced through lignocellulosic biomass liquefaction

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Abstract

Over the past decade, global concerns about climate change have arisen, prompting countries to transform their economies into drivers of sustainability. Interests in biomass-based goods were renewed, particularly, in the conversion of biomass into fuels. Inserted in this topic, studies have been developed in biofuel produced through lignocellulosic biomass liquefaction. To assess the possible impact of the production of this biofuel on the environment a Life Cycle Assessment (LCA) has been conducted.

Resorting to the support of the *SimaPro* software, the phases of transportation of feedstock, pre-treatment, and manufacturing process under study in each scenario were considered. Additionally, the bio-oil's lower heating value was calculated to know how much quantity of petcoke could be replaced by the liquefied biomass produced and introduced as environmental credits.

A comparative environmental impact evaluation of hexane, heptane, cyclohexanol and user-defined 2-ethyl hexanol as possible solvents used in the production of liquefied biomass, was performed in order to find a possible substitute for 2-ethyl hexanol in *SimaPro* since it is not available in its database. Additionally, tests on biomass sources (Eucalyptus and paper sludges) were made to study the influence of the composition of the biomass in the liquefied biomass. The data on biofuel produced through biomass liquefaction was provided by the company *SECIL*.

The Product Environmental Footprint (PEF) and ReCiPe methodologies were used in calculating the global environmental impact, recommended by the European Commission since the process under study takes place in Portugal.

When comparing both fuels it is shown that it takes almost twice the amount of liquefied biomass to equal the calorific value of petcoke, which is 21.06 Gj/ton when using biomass from Eucalyptus. When using the bio-oil from paper sludges, its LCV is 15.7 Gj/ton.

Through all the analysed scenarios, the best eco-friendly case is the biomass liquefied from Eucalyptus with a mixture of the solvents 2-ethyl hexanol and glycerine from the treatment of waste cooking oil in a proportion of 0.25:0.75, with a single environmental impact score of -1.35 mPt and -1.49 mPt for BATCH and continuous conditions, respectively when PEF was used.

Keywords: Biomass liquefaction, environmental impact, Life Cycle Assessment, *SimaPro*, Product Environmental Footprint, ReCiPe.

Resumo

Nos últimos anos surgiram preocupações globais sobre as alterações climáticas, levando os países a transformar as suas economias em motores de sustentabilidade. Surgiram interesses em bens baseados em biomassa, particularmente, na conversão de biomassa em combustíveis. Inserido neste tópico, têm vindo a desenvolver-se estudos em biocombustíveis produzidos através da liquefação de biomassa lignocelulósica. A fim de avaliar o possível impacto da produção deste combustível no meio ambiente, foi realizada uma Avaliação do Ciclo de Vida (ACV).

Recorrendo ao apoio do software *SimaPro*, foram consideradas as fases de transporte da matéria-prima, pré-tratamento, e processo de fabrico em estudo em cada cenário. Além disso, o valor do poder calorifico inferior do bio-óleo foi calculado de forma a saber que quantidade de petcoque poderia ser substituída pela biomassa liquefeita produzida e introduzida como créditos ambientais.

Foi realizada uma avaliação comparativa do impacto ambiental do hexano, heptano, ciclohexanol e *user defined* 2-etil-hexanol como possíveis solventes usados na produção de biomassa liquefeita, a fim de encontrar um possível substituto para o 2-etil-hexanol no *SimaPro*, uma vez que este não está disponível na sua base de dados. Além disso, foram feitos testes em diferentes fontes de biomassa (Eucalipto e lamas de papel) com o intuito de conhecer a influência da composição da biomassa no liquefeito de biomassa. Os dados sobre os biocombustíveis produzidos foram fornecidos pela empresa *SECIL*.

As metodologias PEF (Product Environmental Footprint) e ReCiPe foram utilizadas no cálculo do impacto ambiental global, recomendado pela Comissão Europeia, já que o processo em estudo tem lugar em Portugal.

Ao comparar ambos os combustíveis demonstra-se que é necessário quase o dobro da quantidade de liquefeito de biomassa para igualar o valor calorífico do coque, que é de 21.06 Gj/ton quando se utiliza biomassa de eucalipto. Ao usar o bio-óleo de lamas de papel, o seu PCI é de 15,7 Gj/ton.

De todos os cenários analisados, o caso mais ecológico corresponde ao biocombustível proveniente de Eucalipto, com uma mistura de solventes 2-etil hexanol e glicerina procedente do tratamento de óleo de cozinha residual, na proporção de 0.25:0.75. apresentando uma pontuação única de impacto ambiental de -1.35 mPt e -1.49 mPt para as condições BATCH e de contínuo, respetivamente quando o método PEF foi aplicado.

Palavras-chave: Liquefação da biomassa, impacto ambiental, Avaliação do Ciclo de Vida (ACV), *SimaPro*, Pegada Ambiental do Produto, ReCiPe.

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List of Abbreviations

CCL - Clean Cement Line Project

R&D – Research and development

PEF - Product Environmental Footprint

LCV - Lower Calorific Value

LCA – Life Cycle Assessment

FAO – Food and Agriculture Organization of the United Nations

HTL – Hydrothermal liquefaction

LCI – Life Cycle Inventory Analysis

LCIA – Life Cycle Impact Assessment

ISO – International Organization for Standardization

FU – Functional Unit

J – joule

kWh – kilowatt-hour

kg – Kilogram

eq. – equivalent

NMVOC – Non-methane volatile organic compounds

PM – Particulate matter

CTUh - Comparative Toxic Unit for humans

DEG/ 2EH – 2-ethyl hexanol

tkm – transportation of 1 tonne over 1 kilometre

RoW – Rest of the World

RER – Europe

Pt – Eco point Indicator

uPt - micropoints

mPt – millipoints

LHV – Lower Heating Value

1 Introduction

This initial chapter starts with a description of the problem followed by the principles and objectives of this work. It also contains the structure of the document. The contextualization of the problem correlates the main challenges related to the energy transition that the world is facing along with the actions that have been taken by Portugal to overcome these problems. Related to this topic, the development of a new biofuel by the company Secil is presented to make its cement production line more environmentally friendly. In the following subchapters, the aim of the work expresses the principal goals in doing this study and how the work is divided.

1.1 Contextualization of the problem

Interests in the progressive replacement of fossil fuels with renewable fuels have been increasing, associated with the need to preserve the environment. With this in mind, a profound reorganization of the value chains of industry, international trade and geopolitics is inevitable.

In the last decade, the energy transition path has been an important topic for both entities and companies, as well as a way of achieving a positive advancement for the economy. However, Portugal remains reliant on imported fossil fuels. As such, Portugal has carried out remarkable progress in developing strategic paths in the renewable energy transition. It includes electricity generation with hydro, wind and solar sources. There are 59 hydroelectric plants and 4 thermoelectric plants that supply energy to the entire country. Wind farms allow the production of electricity for injection into the public distribution grid or, in a decentralized manner, through relatively small turbines, disconnected from the grid. Additionally, future projects comprise the production of green hydrogen, obtained entirely from processes which use energy from renewable sources. One of these plans consists of converting a coal-fired power station in Sines to a hydrogen-driven one. Consequently, green hydrogen can be turned into electricity or synthetic fuels and used for commercial, industrial or mobility purposes.

The Secil group, founded in 1930 in Portugal, is a company based on the production and sale of cement, concrete, aggregates, mortars, and hydraulic lime. It also integrates other companies that operate in complementary areas in the circular economy, in the use of waste as a source of energy and in the production of microalgae. Secil operates in 8 countries with an annual production capacity of 9.75M tonnes.

In these circumstances, the Secil group will implement technological improvements in the cement production plant in Outão, as part of the Clean Cement Line Project (CCL) funded by P2020, Lisbon 2020 and the European Regional Development Fund. This project includes R&D subprojects that aim to eliminate dependence on fossil fuels, increase energy efficiency, own electric energy production, integrate it into the digitalization process and reduce CO_2 emissions.

The Zero Fossil Fuels project is part of the CCL project, in partnership with Instituto Superior Técnico (IST), Center for Nanotechnology and Smart Materials (CENTI) and ThyssenKrupp, with the main objective of completely removing the fossil fuels currently in use. In this project, one strategy comprises the production of biofuel with a calorific value from the liquefaction of lignocellulosic biomass (Energreen) in order to upgrade the fuel mix used today currently. These innovations will promote the development of low-carbon clinker production and consequently the creation of a range of types of cement with a low ecological footprint.

1.2 Aim of work

The main objective of this work is to carry out a study that analyses the environmental impact of bio-oil production through the liquefaction of lignocellulosic biomass using the *SimaPro* software. The impact of the life cycle stages of the bio-oil will be studied and evaluated to define which stages of the process are the main contributors to the environmental impact caused and which impact categories are the most affected.

Two different sources of biomass will be compared, eucalyptus and sludges from the paper industry, at BATCH and continuous conditions. Through a comparative analysis, it will be possible to identify which scenario is the most environmentally friendly, identify which inputs have the largest contribution to the environmental impact and which environmental impacts most influence the environmental load. This environmental punctuation is caused by the impact that is assigned to the different phases of the process. Through this final punctuation, obtained through specific methods, it is possible to compare the different processes and draw conclusions.

The LCIA methods used for this purpose are Product Environmental Footprint (PEF) and ReCiPe, available on *SimaPro* software. These methodologies are the most suitable to use in this study in analysis since their results take into account the European citizens' average impact as reference.

One additional objective of this work is to study the energy efficiency of the biofuel created. To complete this task, a comparison will be made between the lower calorific value (LCV) of fuels.

1.3 Document structure

This document is structured into 6 chapters as follows.

The first and current chapter provides the introduction, context for the work herein developed and the aim of said work. The second chapter (page 3) includes a background of the project developed, approaching subjects such as sustainability, circular bioeconomy, and types of processes to produce energy from biomass. The third chapter presents the applied methodology, explaining the different sub-steps taken to obtain the final results. In Chapter 4, the liquefaction process is described, starting on page 25. Chapter 5 (page 33) includes the results of the LCA of the liquefied biomass, the comparative studies and their results. Finally, in chapter 6, some conclusions and comments are presented on page 59.

2 Literature Review

In this chapter, efforts related to the process of valuing forest residues will be discussed. Taking into account the concept of circular bioeconomy, an attempt was made to relate it to the importance of biomass as a renewable biological resource. Several technologies to produce energy from biomass will be a theme, including the biobased products obtained.

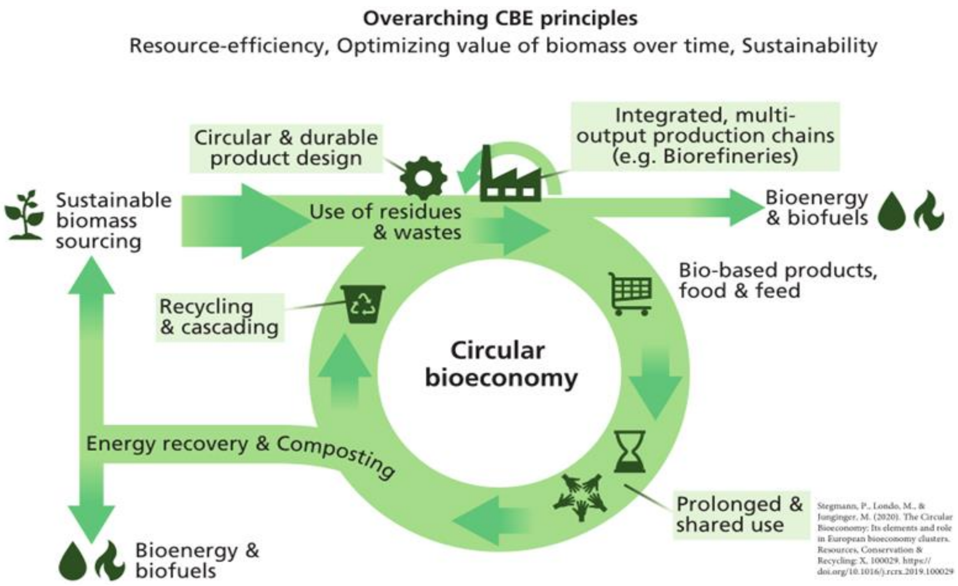
2.1 Circular Bioeconomy

The drive towards a more environmentally friendly economy is necessary in a world threatened by climate change. The Sustainable Development Goals (SDGs) and the Paris Climate Agreement gave global, overarching societal objectives for future decades. Its 17 goals address the challenges that the world face, including poverty, inequality, health, climate change, environmental degradation, irresponsible consumption and production and justice and peace. The Paris Climate Agreement limit global warming to 1.5 Celsius degrees, which can be reached by reducing greenhouse gas emissions. To achieve such sustainable development, bioeconomy becomes a crucial subject in this process.

According to the Food and Agriculture Organization (FAO) of the United Nations, bioeconomy is defined as “knowledge-based production of goods and services and the use of biological resources, processes and methods to provide goods and services in a sustainable manner in all economic sectors”. It also covers the services related to biobased products, such as intellectual property rights, consulting, R&D, marketing, sales, servicing of machinery, administration, etc. Bioeconomy aims to drive circularity by applying the principles of the circular economy - reuse, repair and recycle.

Bioeconomy and circular economy are complementary concepts. The circular economy is a model of production and consumption, which involves sharing, reusing, repairing, and recycling existing materials and products in order to extend the life cycle of the products. Consequently, this approach implies the reduction of waste to a minimum and reuse which could save companies money while reducing total annual greenhouse gas emissions. [1], [2]

Figure 1 represents the circular bioeconomy strategy as a framework to reduce the dependence on natural resources; transform manufacturing; promote sustainable production of renewable resources; and finally, promote their conversion into several biobased products and bioenergy while creating new jobs and industries. [2]



Stegmann, P., Londo, M., & Junginger, M. (2020). The Circular Bioeconomy: Its elements and role in European bioeconomy clusters. Resources, Conservation & Recycling: X, 100029. https://doi.org/10.1016/j.rcrx.2019.100029

Figure 1 The European Commission's circular bioeconomy and its elements (adapted from [2])

Limitations associated with the circular bioeconomy are related to the risk of leading to the use of forests at a large scale and consequently, the production of bioenergy may lead to increased CO_2 emissions in the short term. This corresponds to a risk of depletion of biomass carbon stocks, increased atmospheric CO_2 concentrations and contribution to climate change. [2]

Another concern with the circular economy is that efficiency gains often lead to rebound effects in terms of increased production and consumption, thereby not meeting perceived environmental objectives. For example, the fuel efficiency gain for vehicles may lead to more driving, resulting in more greenhouse gas emissions. As a result, these possible environmental improvements cannot necessarily be achieved only by substituting products based on fossil resources with bio-based ones. Since circular economy and bioeconomy focus on resources (renewable materials, material recycling), they fail to address synergies between wider ecological processes and ecosystem services. For example, besides the competition for fresh water and food production, intensifying biomass production may conflict with other social, economic, and environmental functions of forests. [2]–[4]

Even though, biobased products seem to be the best option in the mitigation of climate change and expanding resource security compared to fossil-based solutions, it might imply a rise in the price of these goods due to an increase in the demand for these products. [2], [5] Additionally, the industrial cultivation of favoured species could threaten biodiversity.

By applying different bioeconomy policies, the European Union and some of its Member States like Germany developed and follow their bioeconomy strategies. These measures proposed by the European Parliament attempt to adopt a circular economy action plan, calling for additional measures to achieve a carbon-neutral, environmentally sustainable, toxic-free and fully circular economy by 2050, including stricter recycling rules and binding targets for use and consumption of materials by

2030. Recently, it released measures to speed up the transition towards a circular economy, as part of the circular economy action plan. The proposals include boosting sustainable products, empowering consumers for the green transition, reviewing construction product regulations, and creating a strategy for sustainable textiles. [1][6] All of these countries present their definition of bioeconomy but have in mind the principal goal of the need to replace fossil resources in industrial and energy production with renewable biomass.

2.2 Biomass

Biomass energy or Bioenergy corresponds to the energy produced by recently living organisms. The known forms of bioenergy available are heat, fuels and electrical power.

Biomass matter is derived from organic materials, including plants, animals, and microorganisms or from a biochemical perspective, cellulose, lignin, sugars, fats and proteins. It can absorb atmospheric carbon while it grows and returns it into the atmosphere when consumed, all in a relatively short amount of time. Because of this, biomass use creates a closed-loop carbon cycle.

Through the process of photosynthesis, plants capture the sun's energy by converting carbon dioxide (CO_2) from the air and water into carbohydrates, i.e., compounds composed of carbon, hydrogen, and oxygen. When they are burned, they turn back into carbon dioxide and water and release the sun's energy they contain. In this way, biomass functions as a sort of natural battery for storing solar energy. [7], [8]

2.2.1 Types of biomasses

Biomass can be used as a viable, sustainable source of renewable energy. Nowadays, wood and agricultural products, landfill gas and biogas, solid waste, and alcohol fuels like ethanol and biodiesel are the main types of sources of biomass, supported by Figure 2.

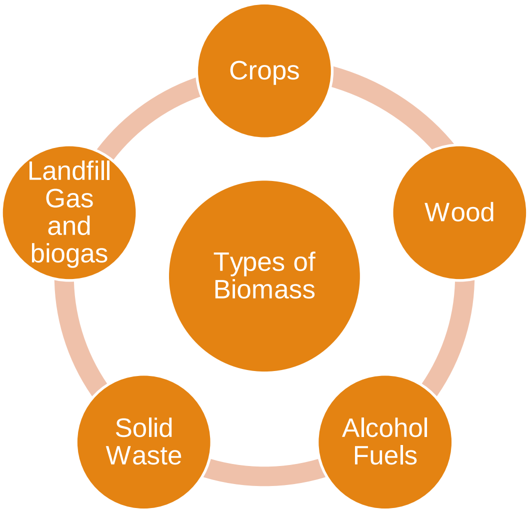


Figure 2 Types of biomasses.

Agricultural biomass is a relatively broad category of biomass that includes: the food-based portion of crops (corn, sugarcane, soybeans), the non-food-based portion of crops (corn stover [leaves, stalks, and cobs]), rice husks and animal waste. For large-scale power generation, wood is often used as a biomass. It includes logs, chips, bark, and sawdust and is of importance as a source of wood for timber and pulp, ecosystem structure and carbon stocks. As highlighted previously, plants remove carbon dioxide, a greenhouse gas, from the atmosphere when they grow. Burning biomass releases CO_2 but growing plants for use as biomass fuels may also help keep carbon dioxide levels balanced. [9]

Another type of biomass is the category of alcohol fuels, which include ethanol or biodiesel. Ethanol is an alcohol fuel (ethyl alcohol) obtained from fermenting the sugars and starches found in plants and then distilling them. Any organic material containing cellulose, starch, or sugar can be made into ethanol. Biodiesel is a liquid fuel produced from a chemical reaction with alcohol and new and used vegetable oils and animal fats. [10]

Solid waste, which results from various human activities, without utility or economic value for those who discard it, turns waste into a usable form of energy. One ton of garbage contains about as much heat energy as 0.25 tons of coal. Burning solid waste decreases the amount of garbage dumped in landfills by 60 to 90%, which in turn reduces the cost of landfill disposal. Moreover, it is more advantageous to make use of energy in the garbage than to bury it, where is not used.[11]

Biogases (methane gases) are produced by the anaerobic decomposition or thermochemical conversion of biomass. During the anaerobic decomposition of biomass, anaerobic bacteria consume and break down biomass and produce biogas without oxygen. Anaerobic bacteria live naturally in soils, in water bodies such as swamps and lakes, in the digestive tracts of humans and animals like in municipal solid waste landfills. The gas collected in municipal solid waste landfills is called landfill gas. This gas can be used to produce electricity, or for cooking and lighting. [9], [12]

Knowing the different source types of biomasses, parameters like availability, cost, distance to the processing facility, end-product or other factors will determine the viability of using any particular type of biomass.

2.2.2 Biomass energy pros and cons

The use of biomass presents several advantages:

- Biomass fuel is carbon neutral. Since it has already been through a photosynthesis process, the absorption of carbon dioxide has already happened.
- It has a high-profit margin for biomass producers. It is cheaper to make and made of residues, when the source is waste.
- It is a renewable resource;
- The use of waste materials reduces landfill disposals;

- It is cheaper than fossil fuels. Fossil fuel production requires a heavy outlay of capital.

Biomass also has its shortcomings.

- The energy obtained from biomass is not efficient as that from fossil fuels;
- It may lead to deforestation. Taking into account several biomass sources, wood is the main source of bioenergy, so great quantities of wood and waste product need to be used to produce the desired amount of power;
- Biomass energy plants require space, limiting the areas where is possible to place a plant.

2.3 Biomass conversion pathways

There are several methods to extract biomass energy, as illustrated in Figure 3. These routes include mechanical extraction and thermochemical and biological conversion, sectioned into several processes.

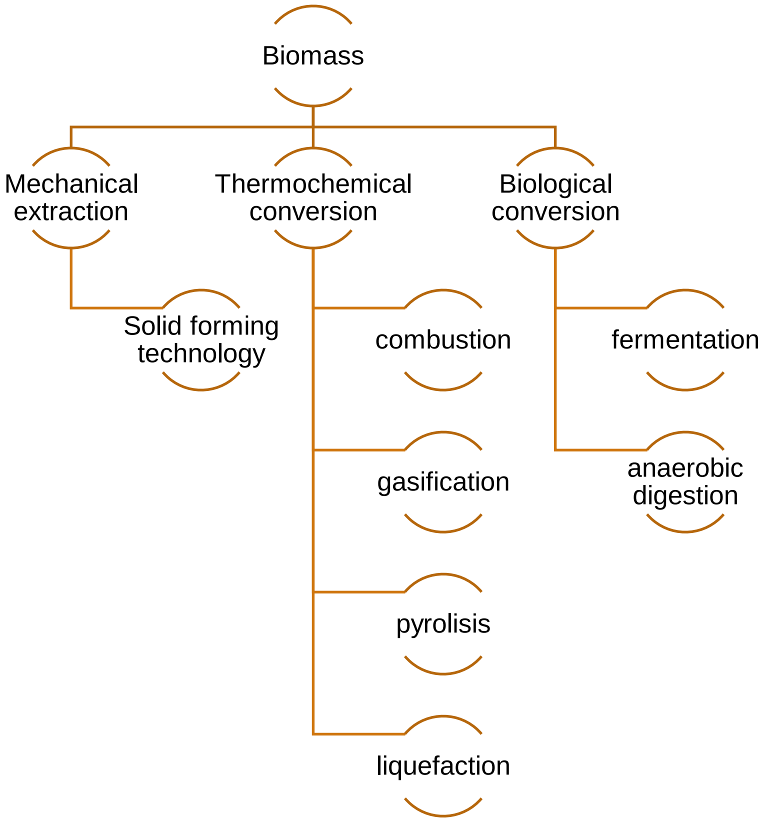


Figure 3 Methods to extract biomass energy.

Mechanical conversion of biomass includes crushing biomass, densification, chipping and grinding and drying.

In biological conversion, the main extraction routes are fermentation and anaerobic digestion. Fermentation is a process which contributes to the production of about 80% of the world's ethanol.

Anaerobic digestion involves using anaerobic microorganisms to convert biomass into biogas (methane and carbon dioxide as the main gaseous products) through decomposition. [13]

Finally, thermochemical conversion techniques like combustion, gasification, pyrolysis and liquefaction include the release of chemical energy stored during photosynthesis. This occurs because the chemical bonds between adjacent carbon, hydrogen and oxygen molecules are broken.

2.3.1 Biomass thermochemical conversion pathways

A significant part of the research into renewable energy has been devoted to the production of biofuels from biomass, with a variety of several thermochemical conversion processes having been explored.

The three main components of biomass are cellulose, hemicellulose, and lignin. Depending on the type of biomass, the concentrations of each component may vary, which will significantly affect the quality of biomass feedstock. Contents of cellulose, hemicellulose, and lignin can reach 40–60%, 15–30%, and 10–25%, respectively.

Reinforcing the idea of restricting the use of fossil resources, interest in forest-based goods was renewed since they are biodegradable and reusable products with a smaller ecological footprint. Thus, lignocellulosic biomass presents itself as a reliable candidate for fulfilling future energy demands.

Biomass is the only resource that can be directly converted into valuable forms of energy (bioenergy and biofuels) in any form (liquid, solid or gas) through thermochemical conversion pathways like combustion, gasification, pyrolysis, and liquefaction. [14]

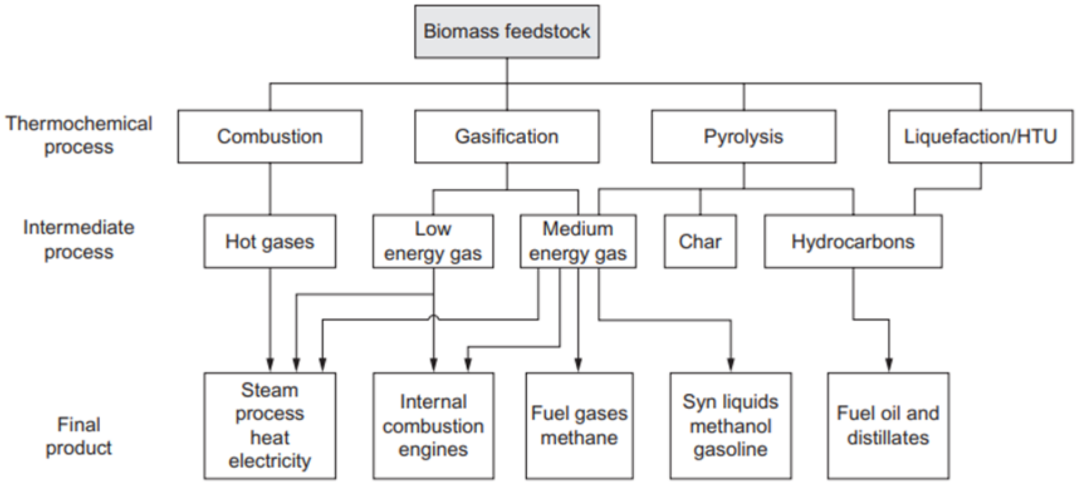


Figure 4 Thermochemical conversion routes for biomass to biofuels. (adapted from [15]**)**

As the flow chart depicts (Figure 4), biomass can be converted into fuels, chemicals or electric power.

2.3.2 Combustion

Biomass combustion is a simple thermo-chemical conversion process that occurs in the presence of air. It has replaced coal as a renewable source of energy in many power plants, and heat and power are the main products of the direct combustion of biomass. Combustion can be split into four stages: drying, pyrolysis, volatile combustion and char combustion.

The efficiency of the biomass combustion reaction has a significant dependency on the particle size and properties of feedstock, the temperature of the reaction, and the combustion atmosphere.[16] Economically, despite being a relatively simple process, it is not the best strategy to utilise biomass since combustion releases polluting contaminants like CO_2, SO_2, NO_X and solid waste in the end products.[17]

2.3.3 Gasification

The gasification process thermo-chemically converts an organic feedstock (liquid or solid fuel) into its gaseous components, which depend on the gasification temperature.

Synthesis gas or syngas is composed of H_2 and CO, which are primarily formed above 1200 °C. At lower gasification temperatures, the product gas is formed containing CO, H_2, CH_4, and CO_2 and, possibly, tar compounds, which may adversely affect gasification performance and downstream end-uses. Tar and ash are produced as by-products which may add value and provide different accounting routes for GHG emissions during gasification.

Despite the potential of syngas to produce heat, power, and chemical products, it is not commercially sustained due to low-cost fossil oil and natural gas availability. Nonetheless, it can be used in combustion in a boiler to produce heat and electricity via combustion in reciprocating engines and gas turbines or converted to a liquid bio-fuel or substitute natural gas (SNG) for injection into gas grids. [16]

2.3.4 Pyrolysis

In a pyrolysis reaction, the organic matter is decomposed into liquid (usually called bio-oil), solid, and gaseous products in an environment devoid of oxygen.

Depending on the heating rates and/ or the residence time of the pyrolysis vapour in the reactor, pyrolysis can be broadly classified into slow and fast pyrolysis. When the process occurs under low-temperature conditions and longer hot vapour residence times, the production of charcoal is favoured (slow pyrolysis). At higher temperatures and longer residence times, the gas from biomass is preferred, and moderate temperatures and short hot vapour residence times are ideal for forming liquids (fast pyrolysis).

Attending the conditions of the reaction, typically occurs between 300 and 800 °C, where the pyrolysis can convert biomass directly into solid (biochar), liquid (bio-oil), and gaseous products (bio-gas), each of which will have their commercial value.

Pyrolysis provides a less process-intensive and lower-cost pathway to biomass-derived fuels and chemicals than traditional thermochemical strategies, which involve sequential gasification (generally affording syngas, a mixture of primarily carbon monoxide and hydrogen) and subsequent catalytic upgrading. [16], [18]

2.3.5 Liquefaction

Hydrothermal liquefaction (HTL) is defined as a thermochemical pathway at which the lignocellulosic feedstock, wet or dry, is effectively decomposed into renewable liquid fuel, i.e., it involves heating aqueous slurries of biomass or organic wastes at elevated pressures to produce an energy carrier with increased energy density, a liquid bio-crude. Occurs at temperatures between 250 °C and 375 °C and at pressures up to 180 bar.

Furthermore, hydrothermal liquefaction presents a higher efficiency strategy and has less consumption of energy when compared to pyrolysis because of the better physicochemical properties. The bio-crude obtained from hydrothermal liquefaction has an oxygen content of 10–20 wt.%, with a heating value typically higher than those obtained from the conventional pyrolysis process. [16], [17]

In acid liquefaction, biomass decomposition generates small, unstable and reactive fragments that can repolymerize into different compounds. It takes place at low temperatures (150-420ºC) and in a variable pressure range between 1 and 240 bar. [19]

2.4 Biorefinery

The biorefinery concept has been developed for manufacturing biofuels, organic chemicals, polymers, and other products from biomass. It is analogous to petroleum refineries or petrochemical industries and uses biomass as feedstock instead of non-renewable sources. The biorefinery integrates biomass conversion processes and equipment to produce a vast range of transport biofuels, energy and chemicals.

Therefore, from the conversion of biomass monomers (lignin, cellulose and hemicellulose), it is possible to obtain commercially useful products, such as cleaning products, detergents, dyes, hydraulic fluids, inks, lubricants, packaging materials, inks and coatings, paper, plastic fillers, polymers and solvents. [20], [21]

2.4.1 Added-value products

As highlighted earlier, bioenergy production and several other valuable products of our daily life deriving from biomass have received significant attention in the last few years. Various thermochemical and biochemical pathways are used to successfully application of lignocellulosic biomass.

The catalytic conversion of renewable biomass to green and platform chemicals has also been extensively investigated. A platform chemical corresponds to a chemical that can serve as a substrate for the production of various other higher value-added products. Hemicellulose (one of the major components of biomass) for example, can depolymerize into simpler sugars such as glucose, arabinose and xylose; cellulose degrades into its monomer, glucose, which later decomposes into different compounds. As a result, numerous organic acids such as succinic, formic, citric, levulinic, and carboxylic acids have also been obtained as added-value products from biomass. [22], [23]

The major component of lignocellulosic biomass is cellulose, as it is possible to get numerous compounds. Through route A, in Figure 5, occurs a catalytic conversion of cellulose into several fuels and chemicals through glucose. By route B, it is possible the conversion of cellulose into various chemicals and fuels by a one-pass catalytic process in the presence of a multifunctional catalyst.

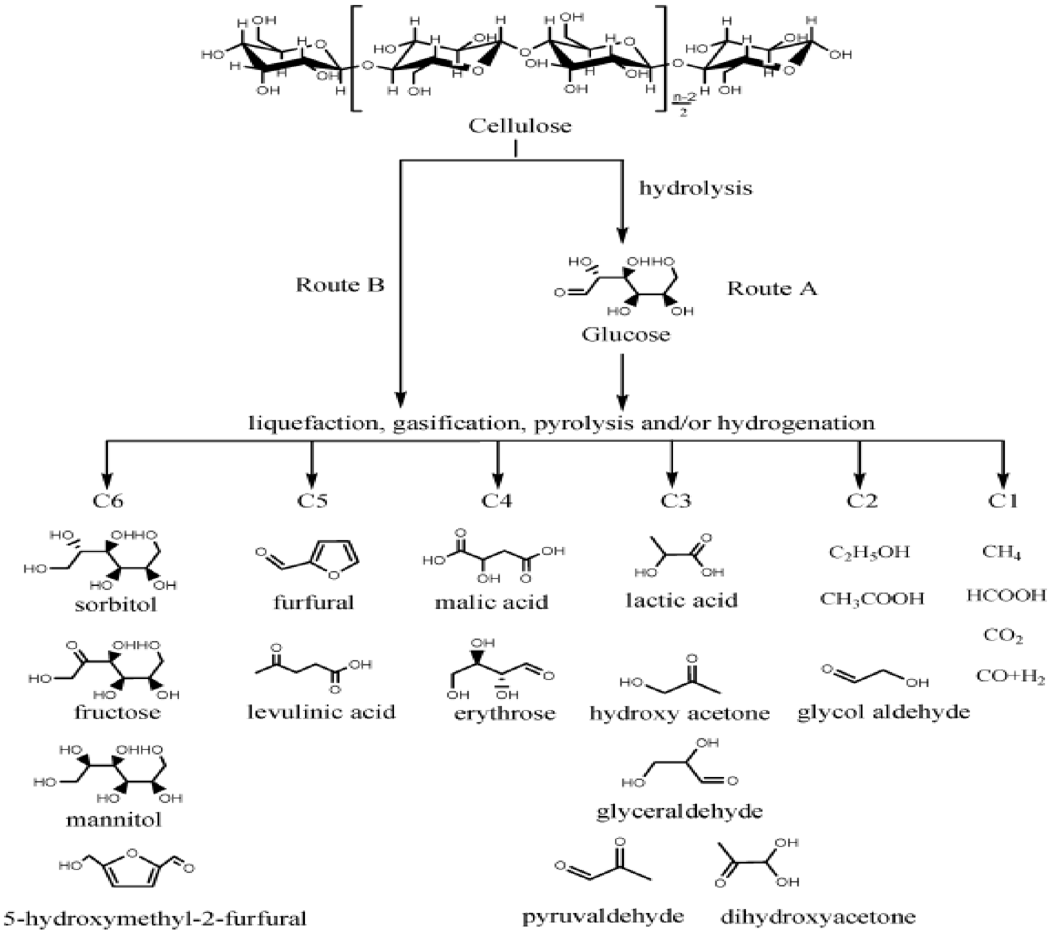


Figure 5 Potential chemicals and fuels from the catalytic conversion of cellulose through different routes (adapted from [24]**)**

Lignin content in lignocellulosic biomass is usually least abundant compared to the other main components, about 15-25% on a dry weight basis (wt%). But, depending upon the source of biomass, lignin content could go further up to 40 wt% of total dry biomass. [25]

In Figure 6, the pyrolysis of lignin results in the formation of phenolic group compounds. These are the main products of the pyrolysis of lignin because lignin consists of a tridimensional network of the phenolic compounds p-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol. Also, vanillin has great importance in the industry since it is found in food, cosmetic and pharmaceutical markets.

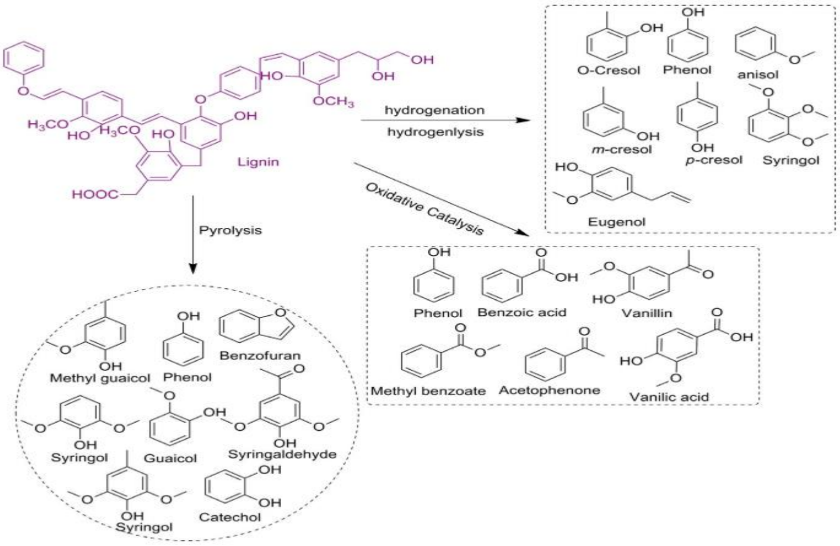


Figure 6 Potential products from the catalytic conversion of lignin through different routes. (adapted from [25]**)**

Lastly, hemicellulose is the largest source of furfural and acetic acid, which can be obtained through reactions of depolymerization, rearrangement, and dehydration. Their reaction pathways are presented in Figure 7.

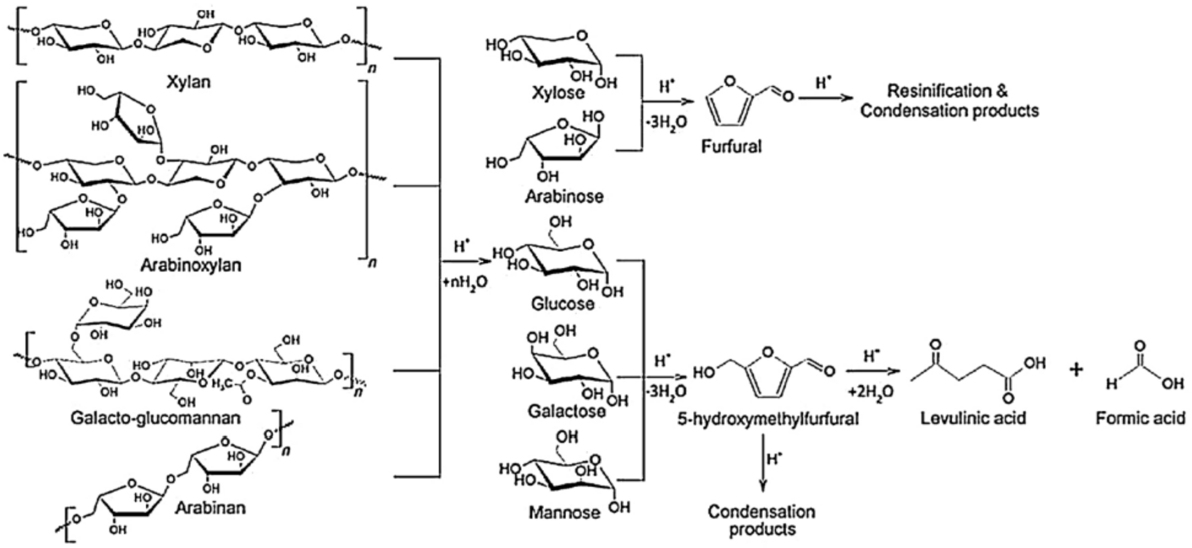


Figure 7 **Potential products from the catalytic conversion of hemicellulose through different routes. (adapted from** [26]**)**

3 Methodology

This chapter proceeds with the application of Life Cycle Assessment (LCA) principles following the ISO 14040/44 rules. [27], [28] It also describes the life cycle assessment methodology, in which all phases of the LCA procedure were formulated with relevant aspects for the study. Furthermore, the methods used to provide an LCA study use specific factors supplied by the *SimaPro* software are described.

Finally, an outline of how to conduct a life cycle assessment and how to apply LCIA methods is performed.

3.1 Life Cycle Assessment

The LCA technique of a product identifies and evaluates inputs, outputs to determine the possible environmental impacts associated with all stages of the product's life, from the extraction of raw materials, through the production stages, distribution and use to its final destination. [29] The focus is on prioritizing improvements in products/processes and also on a comparison between products for internal use. [30] The ISO14040 accounts for LCA principles and framework, while the ISO14044 accounts for requirements and guidelines.

According to ISO 14040, Figure 8, the LCA study proceeds through 4 steps: the goal and scope definition, Life Cycle Inventory Analysis (LCI), Life Cycle Impact Assessment (LCIA) and interpretation of the results.

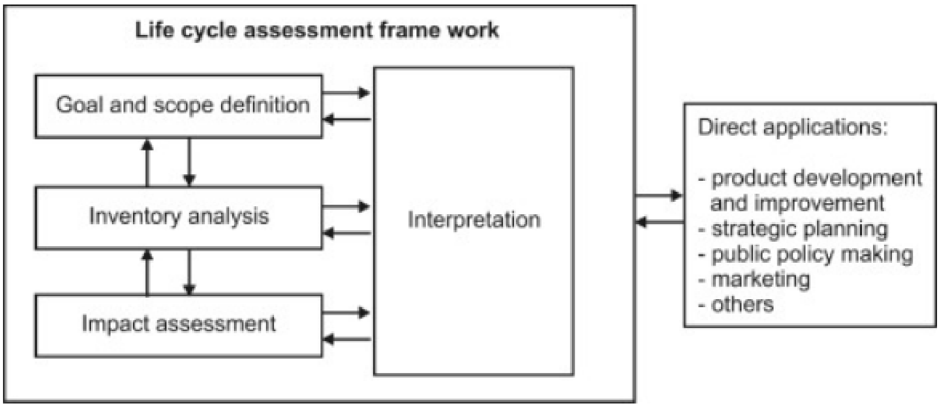


Figure 8 Stages of an LCA study according to the ISO 14040 standard. (adapted from [22]**)**

3.1.1 Goal and Scope Definition

In this step, the plan of the LCA study is defined as precisely and unambiguous as possible. The defined intentions are:

- definition of the specific purpose of the study, aim and objectives for conducting LCA; intended audience;
- description of the functional unit (FU);
- definition of the system boundaries; assumptions and limitations if any used;
- identification of the allocation procedures;
- the studied impact categories and LCIA models used and identification of data quality requirements.

Functional units are quantified descriptions of a representative element of the system being studied. It is the reference unit for the product system from which all inputs and outputs are calculated. Also, reviewed studies used units of bioenergy in J or kWh as the functional unit and recorded LCA results for the "amount of biofuel produced in kg". [31], [32]

The system boundaries included in LCA studies control what processes will be considered for computing environmental impacts.[32] Its "cradle to grave" or "cradle to gate" approach according to *International Standard ISO 14040* and *International Standard ISO 14044,* allow verification of the contribution of the life cycle stages to the environmental load, as it is shown in Figure 9.

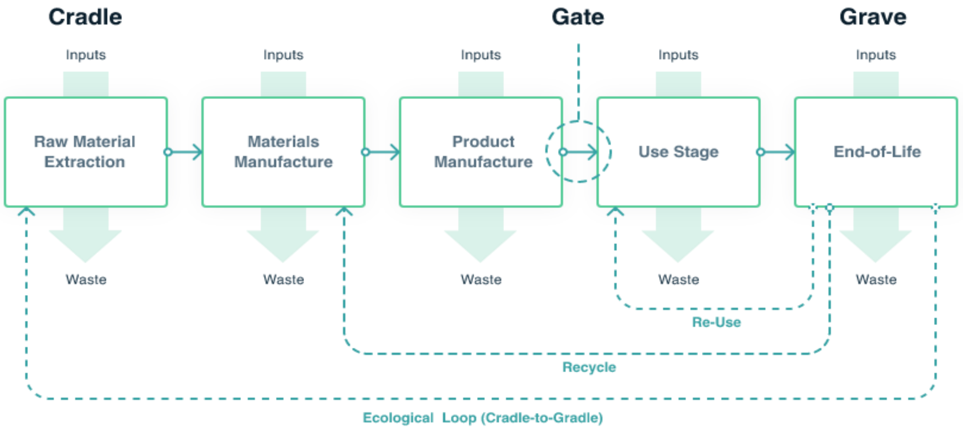


Figure 9 Generic life cycle of a product/ process. (adapted from [25])

A "Cradle to Grave" analysis includes the complete life cycle; a "Cradle to Gate" analysis embraces the materials and product manufacture; a "Gate to Gate" analysis only includes one process and a "Gate to Grave" analysis considers the use stage and end-of-life stages.

Assumptions and limitations include any decisions made through the study that may influence the final results.

3.1.2 Life Cycle Inventory Analysis

In the inventory analysis phase, there is the collection of data and the calculation procedure for the quantification of inputs/outputs of the studied system. LCI is based on a unit process. A unit process corresponds to the smallest element considered in LCI, where environmental inputs and outputs must be quantified. [33], [34] This includes raw materials, energy and physical inputs; products, co-products and waste generation; emissions to land, water and air.

3.1.2.1 Cut-off criteria

Sometimes, the good´s production or its disposal process may be difficult to quantify, therefore, a cut-off procedure can be a solution. The cut-off is the key to the proposition that the system is theoretically infinitely large. This means that non-relevant life cycle stages, specific processes or products, activity types and elementary flows can be omitted.

When cut-off is allowed, it becomes difficult to assure reliable criteria or evaluate the error. The assumption of negligible contribution to mass or cost usually works but can also lead to large errors. Optionally, the estimation of missing parts through the manufacturing process of similar products or by economic input-output tables can be done. [34]

For example, recycled paper only carries the impact of wastepaper collection and the process of turning wastepaper into recycled paper. It is free from any burden of forestry and processing activities necessary for the primary production of paper. Another example is producers of waste do not receive any credit for recycling/reuse of products resulting from any waste treatment. The heat from the incineration of municipal solid waste can be used to heat houses and therefore has value. [35]

3.1.2.2 Allocation procedures

In the case of processes with more than one product, an allocation problem arises. According to ISO directions, allocation procedures correspond to the partitioning of the input/output flows of a unit process to the product under study. To deal with multifunctional processes, like multi-output and input processes and open-loop recycling, the solution chosen for the allocation process has a direct impact on the results of an LCI. [31]

For example, if a certain process needs gasoline (for transportation or any other purpose), the unit responsible for the impact is the refinery that produces this fuel. Simultaneously, other fuels are produced (diesel, heavy oils, etc.), with associated releases of CO_2. Thus, an allocation problem emerges: how much CO_2 emission produced in the process is attributed to gasoline. To overcome this situation, several solutions are proposed, such as splitting the process unit into 2 or more, or expanding the system.

After appropriate cut-off and allocation steps, the final inventory outcomes can be obtained.

3.1.3 Life Cycle Impact Assessment

The Life Cycle Impact Assessment (LCIA) involves the understanding and evaluation of the potential environmental impacts of a product system through its life cycle. This phase proceeds through 4 sub-steps. It includes:

- the selection of impact categories and classification
- characterization
- normalization
- weighting

Furthermore, there are LCIA methods that classify emissions into impact categories and then convert them into common units to allow comparison between them as described in Chapter 3.2 on page 18. The LCIA procedure is explained below.

3.1.3.1 Selection of impact categories and classification

The selection of impact categories and classification, a mandatory step for ISO14044, corresponds to the assignment of material/energy inputs and outputs to the relevant impact category. Impact categories and corresponding indicators can be divided between midpoint and endpoint levels along the cause-effect chain. [34] The midpoint category corresponds to single environmental problems like climate change, for example. Endpoint indicators show the environmental impact on higher aggregation levels, such as human health or damage to ecosystems, as exemplified in Figure 10. Converting midpoint to endpoint levels simplifies the interpretation of the results, although it introduces some uncertainty in the results.

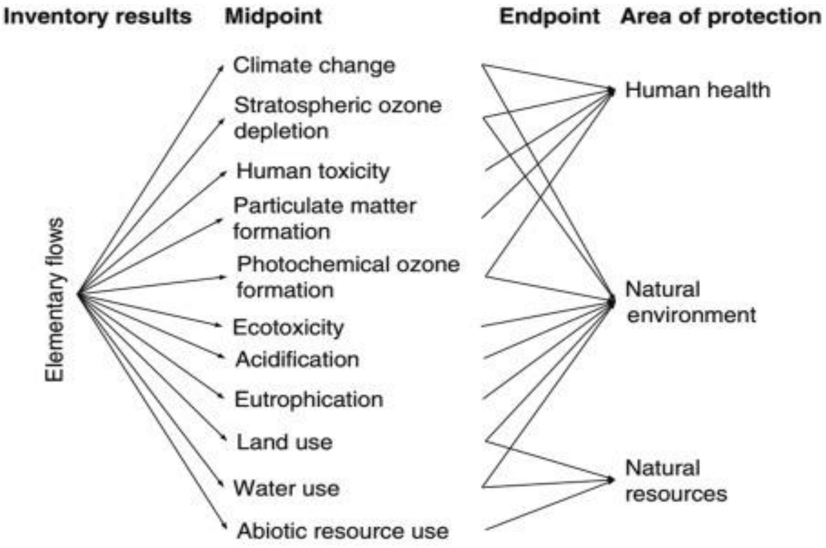


Figure 10 Framework of midpoint impact categories. (adapted from [37]**)**

3.1.3.2 Characterization

The characterization, a mandatory step as well, involves the calculation of the contribution of each input/output to their respective impact categories (at a specific unit), and also, the aggregation of the contributions within each category.

Characterization factors are substance or resource specific. They represent the impact intensity of a substance relative to a common reference substance for an impact category and are used to calculate the impact category indicators. [33]

The following sub-steps in LCIA are optional steps, as specified by *ISO 14040*.

3.1.3.3 Normalization

The normalization step accounts for the multiplication of the results by normalization factors to calculate their contribution to the impact categories, relative to a reference. In other words, it compares the category result to a reference and reflects how significant the impacts are relative to a reference unit, which supports consistency control.

There is still another optional step, grouping. It consists of grouping and ranking impact categories based on indicator results and value choice.

3.1.3.4 Weighting

Weighting, the final LCIA sub-step, consists in determining which impact category is the most damaging and in what intensity in relation to the others. It involves the conversion of normalized or indicator results into an aggregated score based on weighting factors which are derived from value choice. The different weighting factors of each impact category characterise the relative importance of the categories to the environment. [1] These factors are subjective and may vary according to the geographic location based on socioeconomic criteria.

In the weighting phase, the final aim is to obtain a unique result. The results can be used in a highly formalized way to yield "eco points" or "eco indicators", which are preferred solutions for the rapid, automatic weighting of impact assessment results. It is also important to note that according to ISO 14040/44, weighting product comparisons can only be used in companies' internal decisions and are not allowed to be published worldwide.

3.1.4 Life Cycle Interpretation

This stage involves the assessment of the results provided by the LCI and LCIA, relating this to the defined goal and scope. The outcomes of the studied process/ product are evaluated, including the identification of significant issues (conclusions and limitations) in order to give recommendations and possible decisions.

3.2 LCIA methods

Life Cycle Impact Assessment (LCIA) is a very complex step, so methodologies have been developed to simplify and optimize the LCIA process. The LCIA step within an LCA study is the most critical step, as it deals with an exhaustive amount of data that are represented in the inventory analysis results. The impact assessment methods use models for quantifying the causal relationships between the material/energy inputs and emissions and each impact category being assessed.

Several LCIA methodologies were developed over the past years. They may differ in the impact categories covered, selection of indicators and localization. The main methodologies include: CML 2002; Ecological Scarcity Method (Ecopoints 2006); EDIP2003; EPS 2015; IMPACT 2002+; ReCiPe; TRACI and Product Environmental Footprint (PEF).

The methodology CML was proposed by a group of scientists in CML (Center of Environmental Science of Leiden University) which include a set of impact categories and characterization methods for the impact assessment phase. In the Ecological Scarcity method (or Ecopoints method), “eco-factors” are responsible for weighting environmental impacts, including pollutant emissions and resource consumption.

EDIP 2003 methodology attempts to include exposure in the characterization stage, assessing 19 of the main-global impact categories. The EPS 2015 method (Environmental Priority Strategies in product design) has an indicator unit, ELU (Environmental Load Unit), which includes characterization, normalization, and weighting. It is a tool for the internal development process of a product in a company, supporting the choice of the product concept that causes less environmental impacts. This method has been suffering updates since 1996. The method IMPACT 2002+ (IMPact Assessment of Chemicals Toxics) was proposed by the Swiss Federal Institute of Technology including a feasible implementation of a combined midpoint/damage approach, connecting all types of life cycle inventory results via 14 midpoint categories to four damage categories.

The ReCiPe 2016 is an updated and extended version of ReCiPe 2008, which includes both midpoint and endpoint impact categories, available in several perspectives, as it is detailed further ahead in Chapter 3.2.1, page 19.

TRACI (Tool for the Reduction and Assessment of Chemical and other environmental Impacts) is a program developed by U.S Environmental Protection Agency available for many impact categories specifically for US use.

Finally, the PEF method was introduced by the European Commission, being the method currently used in Europe. More details about this methodology are explained in Chapter 3.2.2, page 20.

The methodologies ReCiPe and Product Environmental Footprint (PEF) will be studied in more detail as the results are obtained based on these methods because they are based on European data used in studies that occur in Europe.

3.2.1 ReCiPe

ReCiPe is the successor of the methods Eco-indicator 99 and CML-IA. This method was developed to overcome the uncertainty of results in the impact categories at a midpoint level. The approach of ReCiPe has both midpoint (problem-oriented) and endpoint (damage oriented) impact categories. The midpoint characterization factors are multiplied by damage factors, to obtain the endpoint characterization values. [38]

This method gathers 18 impact categories at the midpoint level. At the endpoint level, the midpoint categories are multiplied by damage factors and aggregated into three endpoint categories: Human health; Ecosystems; Resource surplus costs. The endpoint categories can be normalized, weighted, and aggregated into a single score.

3.2.1.1 Classification and Characterisation

The several impact categories used in the ReCiPe methodology are briefly described in Table A. 1 in Annexes (page 65). ReCiPe provides characterisation factors that are representative of the global scale instead of the European scale while maintaining the possibility for a number of impact categories to implement characterisation factors at a country and continental scale.

3.2.1.2 Normalisation and Weighting

When using ReCiPe, weighting is performed at the damage category level, i.e., endpoint level. At this point, the midpoint categories are multiplied by damage factors and aggregated. The 3 end-point level categories are described below in Table 1.

Table 1 Description of ReCiPe Endpoint categories.

Endpoint category	Description
Human health	The categories included are ozone depletion; Human toxicity; Photochemical oxidant formation; Ionizing radiation; Particulate matter formation; Terrestrial acidification; Human Health is expressed as the number of years of life lost and the number of years lived disabled. The unit is years.
Ecosystems	The categories included are climate change; Terrestrial ecotoxicity; Agricultural land occupation; Urban land occupation; Natural land transformation; Marine ecotoxicity; Marine eutrophication; Freshwater eutrophication and Freshwater ecotoxicity. Ecosystems are expressed as the loss of species over a certain area, during a certain time in years.
Resource surplus costs	The categories included are fossil fuel depletion; Minerals depletion and freshwater depletion. Resources surplus costs are expressed as the surplus costs of future resource production over an infinitive timeframe (assuming constant annual production), considering a 3% discount rate.

3.2.1.3 Impact assessment methods

When using ReCiPe, there are 3 different perspectives. For each one of them, there is a specific weighting set ready to use.

Distinctive ethical attitudes are used to investigate alternative model routes for decision-making. Each model contains factors according to 3 different cultural perceptions: Individualist, Hierarchist and Egalitarian.

- Individualist: based on short-term interest, optimistic that technology can avoid many problems in future.
- Hierarchist: consensus model, as often encountered in scientific models, is often considered to be the default model. It is based on the most common policy principles with regard to others.
- Egalitarian: long-term based on precautionary principle thinking.

The difference between these perspectives is represented through a set of choices on issues like time or expectations that proper management or future technology development can avoid future damages. [39]

The hierarchist version of ReCiPe with average weighting is chosen as default. In general, value choices made in the hierarchist version are scientifically and politically accepted regarding the time frame (100-year time horizon) and plausibility of impact mechanisms. It includes all exposure routes for all chemicals, in which at least one specie has to be tested for ecotoxicity.

Hence, the type of indicators and perspective should be chosen according to each particular case. The hierarchist version of ReCiPe with average weighting is chosen as default because the value choices made in this version are scientifically and politically accepted.

3.2.2 Product Environmental Footprint (PEF)

The Product Environmental Footprint (PEF) methodology was established by the European Commission to harmonize and improve the quality of sustainability information shared with consumers and thus inciting the consumption and production of sustainable products within the European Market. Its goal is to provide “a common way of measuring the environmental performance of any product throughout its life cycle”.

Like the LCA, the PEF takes a life cycle perspective but follows further product category-specific requirements and standardised specifications which create higher comparability of the results. It applies a cradle-to-gate approach, which takes into account raw materials, manufacturing, packaging, distribution, and product end-of-life.

The Environmental Footprint (EF) database is designed to support the use of PEF category rules and Organisation Environmental Footprint (OEF) sector rules, used in *SimaPro* software.

3.2.2.1 Classification and Characterisation

When applying PEF, in characterisation, all compounds are categorised in each impact category by characterisation factors. These factors represent the influence of the compounds on the category in question. Each step of the product lifecycle is assessed through 16 environmental criteria. (Table A. 2 in Annexes, page 65)

Concerning the product’s total impact for the environmental impact category, the quantity of the compound is multiplied by its characterisation factor and the harmonised impacts of all the compounds in each category are summed. Then, the significance of the impact can be assessed using normalisation. There are impact categories that are assessed by different methods. [40]

The global normalization set for the reference year 2010 is part of the EF method.[38]

3.2.2.2 Normalisation and Weighting

The PEF method also includes the weighting of the environmental impact assessment. These factors are set for the reference year 2010 of an average EU citizen. When the impact categories are compared or summed up to a single environmental impact score, the normalised results are multiplied by the weighting factors that define the relative importance of the impact categories.[8]

3.3 SimaPro

This sub-chapter presents a simple overview of SimaPro software. It is demonstrated in a general way, how to use it and its applications. The introduction of a new project in *SimaPro* is presented along with some brief explanations of each step procedure.

SimaPro software is a powerful tool to drive sustainable change. Built on robust life cycle thinking of products/ services, *SimaPro* is recommended for product designers, decision-makers and sustainability experts. The *SimaPro* suite of tools includes several methodologies, projects with all the inputs/outputs used and possible scenarios for waste treatment. Most of these processes always have 2 versions (cut-off and APOS), and when possible, for different countries or regions.

After gathering all the information about materials, processes, energy used, transportation and end-of-life conditions, depending on the type of analysis done, it is already possible to introduce this data into *SimaPro*.

When the programme is opened, several projects are displayed, already existing in the *SimaPro* libraries. A new project is then created by clicking on "new" to which we give the desired name. The Life Cycle Assessment (LCA) project is divided into 5 chapters, visible on the left side: "Objetivo e âmbito", "Inventário", "Avaliação de impacto", "Interpretação" e por fim "Dados gerais".

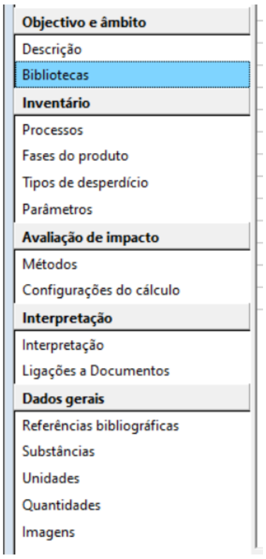


Figure 11 Division of the LCA in *SimaPro*.

Within the topic Objetivo e âmbito", in the subtopic "Bibliotecas", the first step is to select the libraries that will be part of the database of the new project created.

Following the procedure, in "Inventário" is placed all the necessary data to obtain an LCA. All the information regarding the chosen libraries is gathered in this chapter, divided by "Processos", "Fases do produto" and "Tipos de desperdicio".

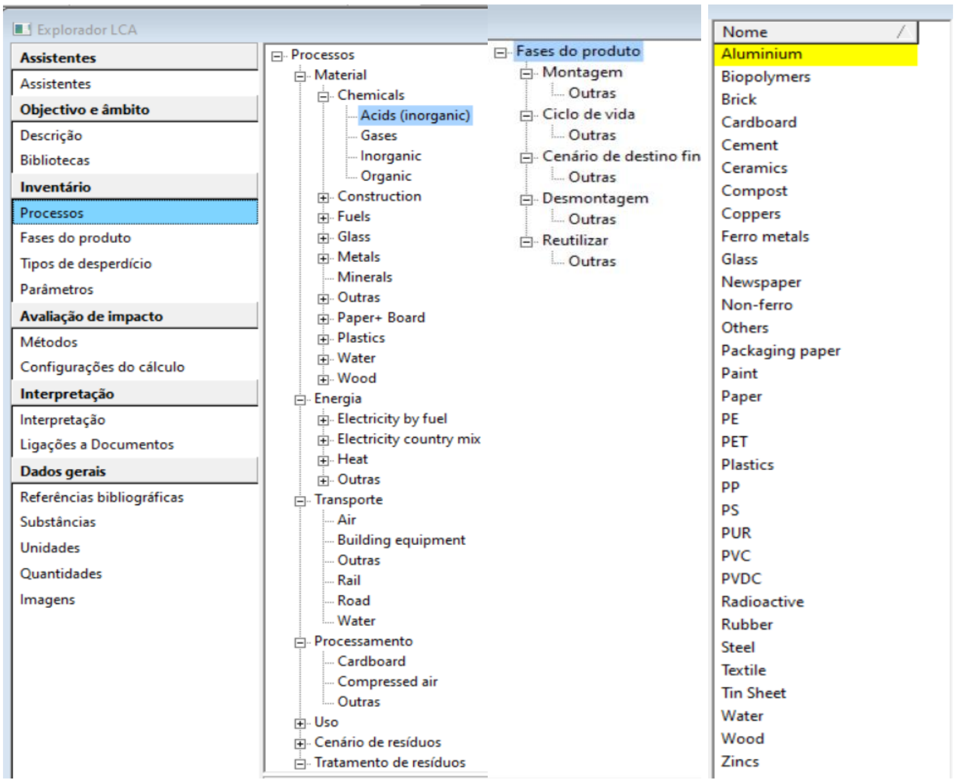
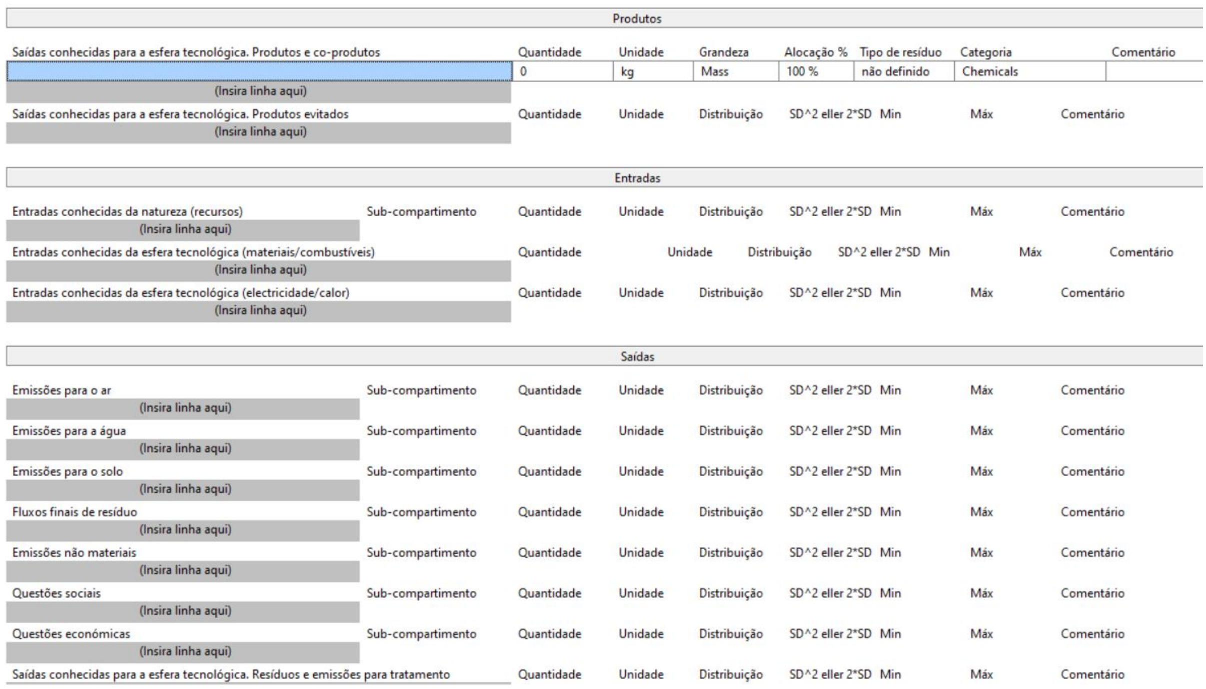


Figure 12 Subtopics of the Topic "Processos" in *SimaPro*.

According to the type of product to be studied, in "Processos" a new production process is introduced. So, a product life cycle model with all environmental inputs and outputs is built up. Conforming to the type of product, the new process is defined in the most suitable category. For example, if the objective is to study the impact of a chemical compound, the new process is edited in "Materials, Chemicals, chemical class of the compound".

Once the new process has been selected, the data gathered in the inventory is entered as the panel shown below.



Produtos

Saídas conhecidas para a esfera tecnológica. Produtos e co-produtos	Quantidade	Unidade	Grandeza	Alocação %	Tipo de resíduo	Categoria	Comentário
	0	kg	Mass	100 %	não definido	Chemicals	
(Insira linha aqui)							

Saídas conhecidas para a esfera tecnológica. Produtos evitados — Quantidade — Unidade — Distribuição — SD^2 eller 2*SD — Min — Máx — Comentário
(Insira linha aqui)

Entradas

Entradas conhecidas da natureza (recursos) — Sub-compartimento — Quantidade — Unidade — Distribuição — SD^2 eller 2*SD — Min — Máx — Comentário
(Insira linha aqui)
Entradas conhecidas da esfera tecnológica (materiais/combustíveis) — Quantidade — Unidade — Distribuição — SD^2 eller 2*SD — Min — Máx — Comentário
(Insira linha aqui)
Entradas conhecidas da esfera tecnológica (electricidade/calor) — Quantidade — Unidade — Distribuição — SD^2 eller 2*SD — Min — Máx — Comentário
(Insira linha aqui)

Saídas

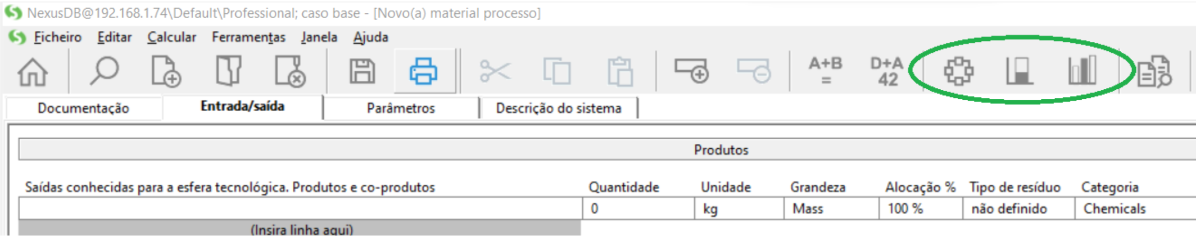
Emissões para o ar — Sub-compartimento — Quantidade — Unidade — Distribuição — SD^2 eller 2*SD — Min — Máx — Comentário
(Insira linha aqui)
Emissões para a água — Sub-compartimento — Quantidade — Unidade — Distribuição — SD^2 eller 2*SD — Min — Máx — Comentário
(Insira linha aqui)
Emissões para o solo — Sub-compartimento — Quantidade — Unidade — Distribuição — SD^2 eller 2*SD — Min — Máx — Comentário
(Insira linha aqui)
Fluxos finais de resíduo — Sub-compartimento — Quantidade — Unidade — Distribuição — SD^2 eller 2*SD — Min — Máx — Comentário
(Insira linha aqui)
Emissões não materiais — Sub-compartimento — Quantidade — Unidade — Distribuição — SD^2 eller 2*SD — Min — Máx — Comentário
(Insira linha aqui)
Questões sociais — Sub-compartimento — Quantidade — Unidade — Distribuição — SD^2 eller 2*SD — Min — Máx — Comentário
(Insira linha aqui)
Questões económicas — Sub-compartimento — Quantidade — Unidade — Distribuição — SD^2 eller 2*SD — Min — Máx — Comentário
(Insira linha aqui)
Saídas conhecidas para a esfera tecnológica. Resíduos e emissões para tratamento — Quantidade — Unidade — Distribuição — SD^2 eller 2*SD — Min — Máx — Comentário

Figure 13 Inclusion of inventory data to create a new process in *SimaPro.*

Starting by discriminating the known outputs for the technological sphere (products), the quantity, the unit of measurement and its allocation are selected.

Regarding the process inputs, the procedure is the same as the previous one. In this phase, the inputs are differentiated (known inputs from nature - resources, from the technological sphere – materials/ fuels and electricity/ heat), where these constituents entered can be selected from the *SimaPro* database or defined by the user. The same happens with the outputs - emissions. It is also possible to add entries on economic and social issues such as the working hours of an educated worker. Finally, if the waste or emissions for treatment are within the system boundaries, they can also be defined. If one of the study goals corresponds to evaluating the final impact of the substitution of the new product by others, this analysis can be done by adding in “Produtos evitados” the product replaced along with its quantity and unit. In such a manner, the credits referring to the replaced product will have a non-negative impact, as it is being avoided.

Subsequently, after the process is defined, it is possible to evaluate their impact environmentally. By clicking on the icons at the top, circled, various types of analysis are possible.



Saídas conhecidas para a esfera tecnológica. Produtos e co-produtos	Quantidade	Unidade	Grandeza	Alocação %	Tipo de resíduo	Categoria
	0	kg	Mass	100 %	não definido	Chemicals
(Insira linha aqui)						

Figure 14 Analysis tools of *SimaPro*.

The icons represented correspond to the process network, which show all the steps of the process, including the contributions of each one, an analysis of the process and a comparison of the selected process and another one. The last two tasks should include the selection of a method, in a way to evaluate a process according to the norms of the method. If the method is not chosen, the analysis will only present the inventory used in the process. It is also possible to define the functional unit, in order to obtain the results based on it.

The results always include the impact evaluation, the inventory, the contribution of each process, some verifications and a general description of the process, given in tables or in charts for further analysis. It is important to mention that when the results have a negative value means a positive impact, i.e., the lower the impact value, the better the results. When the value is zero it means that there is no impact, above that, there is impact on the environment, and below that score there is none.

4 Liquefaction process

Liquefaction is one of the most important technologies to produce bio-oils. In this chapter, the transformation of biomass into liquid products will be analysed. These products correspond to potential intermediates to produce fuels and chemicals. The types of liquefaction processes will be discussed, including the process of manufacturing liquefied biomass.

It also includes a brief description of the liquefaction process, the procedure applied and the mass balance for the conditions under study (BATCH and continuous) of the liquified biomass from Eucalyptus and paper sludges.

4.1 Acid liquefaction

In the context of the project under study, liquefaction corresponds to the complete conversion of biomass into liquid fuels. Biomass decomposition generates small, unstable and reactive fragments that can repolymerize into different compounds. During the liquefaction process, several reactions occur, such as solvolysis, depolymerization, decarboxylation and hydrogenation.[19]

Additionally, in liquefaction, the biomass does not need to be dried, but the reaction requires the presence of a catalyst. It has the function of favouring the kinetics of the reaction, thus reducing the necessary reaction temperature and the solvent used must delay the repolymerization reactions of the monomers of the biomass.

The liquefaction process can be classified into direct and indirect liquefaction.

In direct liquefaction, the process takes place in 2 steps: the conversion of biomass into synthesis gas by the gasification process and a catalytic reaction between the gas formed and the catalyst. The first phase of the procedure occurs in the partial presence of O2/air at high temperatures (>1000ºC), while in the second phase, the operating temperatures are lower (230-340ºC), allowing the formation of olefins and gasoline or diesel and derivatives.

Within the direct liquefaction process it is possible to distinguish several steps, namely, the solvolysis reaction, which occurs between the biomass and the solvent; the depolymerization of the main components of the biomass (cellulose, hemicellulose and lignin); the chemical and thermal decomposition of monomers and smaller molecules, providing molecular rearrangements through the breaking of bonds and decarboxylation reactions; and, still, the degradation reaction of oxygenated compounds in the presence of hydrogen. [19]

The indirect liquefaction follows part of the previous process. It consists of converting biomass into liquid fuels without the gasification step.

4.2 Description of ENERGREEN Project

The process of biomass liquefaction, developed by the ALFAGreen project from the *SECIL company*, is described as the conversion of biomass from different sources into biofuel through a liquefaction process, whose purpose is to replace the petroleum coke today consumed in the clinker kiln.

Figure 15 presents a block diagram with the main steps of the biomass liquefaction process used in the ALFAGreen project. Figure 16 shows the equipment and installations used in this process, namely a boiler, a biomass feed hopper, a worm drive, a reactor, and a solvent tank. The pilot plant operates in semi-continuous mode.

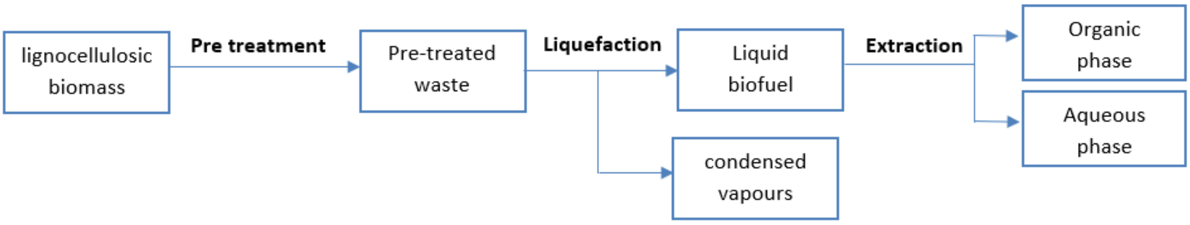


Figure 15 Sequential scheme of the implementation of the biomass liquefaction process.

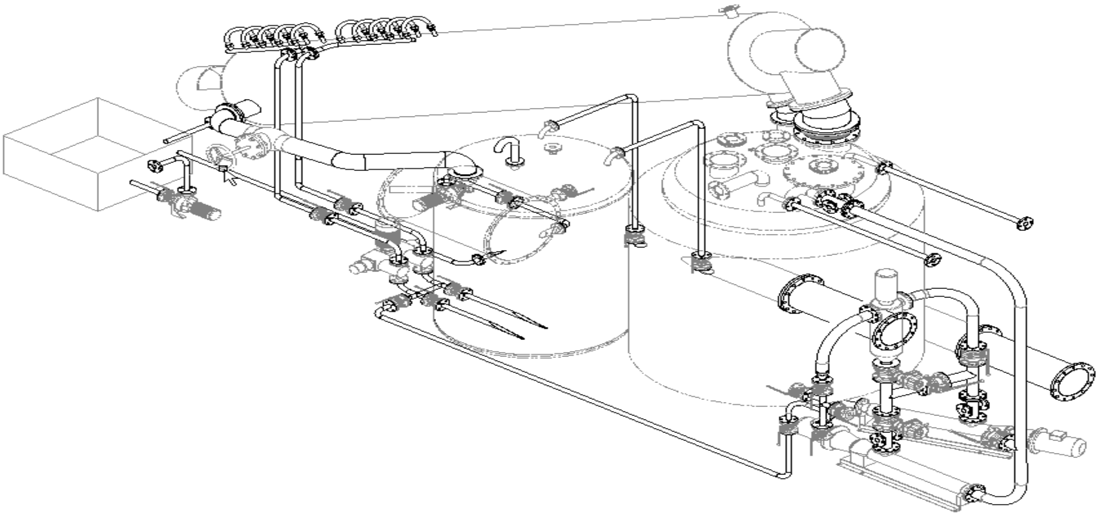


Figure 16 ALFAGreen process facility.

4.2.1 Pre-treatment

The first step of the generation of biomass liquefaction corresponds to the pre-treatment of the initial mixture, known as swelling. In swelling, the mixture, which has different types of biomasses, is sprayed with a solvent, 2-ethyl hexanol (2EH), which will increase the volume of the cells and consequently, break the cellulosic and lignocellulosic membranes, facilitating the access of the catalyst to all components of the residue.

This phase of the procedure takes place in an endless screw, responsible for transporting the reaction mixture into the reactor. It also has a hollow conveyor on the outside, where the gases (mostly steam) coming from the reactor circulate in counter current, leading to a pre-heating of the mixture.

4.2.2 Liquefaction

Inside the reactor, liquefaction processing of the pre-treated biomass takes place, at a temperature between 130° and 250°C in the presence of stirring. An acid catalyst (p-toluene sulfonic acid) is used in amounts between 0.01% and 3.0% (m/m) of dry biomass, and a solvent in amounts between 0% and 50% of the number of lignocellulosic materials.

In an early stage, diethylene (DEG) or 2-ethyl hexanol is used as a solvent, but then the liquefied itself behaves as the solvent. Acid liquefaction promotes the depolymerization of the major components of biomass (hemicellulose, cellulose, and lignin) and subsequently, the chemical decomposition of its monomers, followed by new molecular arrangements through bond breaking, dehydration and decarboxylation. The repolymerisation can also occur, to a certain degree.

For better use of the heat coming from the reactor, it has an external jacket, where the gases from liquefaction, mainly steam, circulate. There is a half-pipe welded on the outside of the reactor and hollow on the inside, which allows the passage of these gases. The release of steam, which depends on the moisture content of the biomass residues, is used to preheat the feed in the endless screw.

After the end of the reaction, the residue that is not yet liquefied is fed back to the reactor, while the liquid phase is injected into the endless screw, to do the swelling of the residue that was later added. When the liquefied residue reaches the desired conversion, the next step is taken.

4.2.3 Extraction

Next, in extraction, the obtained liquefied biomass is mixed with water, the condensates are separated through a liquid-vapour equilibrium (and subsequent condensation) and the aqueous and organic phases (which contain the hydrophobic compounds) are obtained.

From the organic phase, it is possible to recover the solvent and reach the biofuel, which has a low energy density with a high calorific value, with valid applications being able to be used in a furnace or boiler.

4.3 Mass Balance – Calculation strategy

To calculate the mass balances of the liquefied biomass production, data provided by the company Secil was used. Different operating conditions (BATCH and continuous) from Eucalyptus residues and paper industry sludges were taken into account.

4.3.1 BATCH process

4.3.1.1 Liquified biomass from eucalyptus

The biomass liquefaction process starts by introducing the biomass from the eucalyptus source, represented by stream 1, the solvent 2-ethyl hexanol (stream 2), and the p-toluene sulfonic acid catalyst (stream 3) into the auger, preceded by a mixer, according to Figure 17.

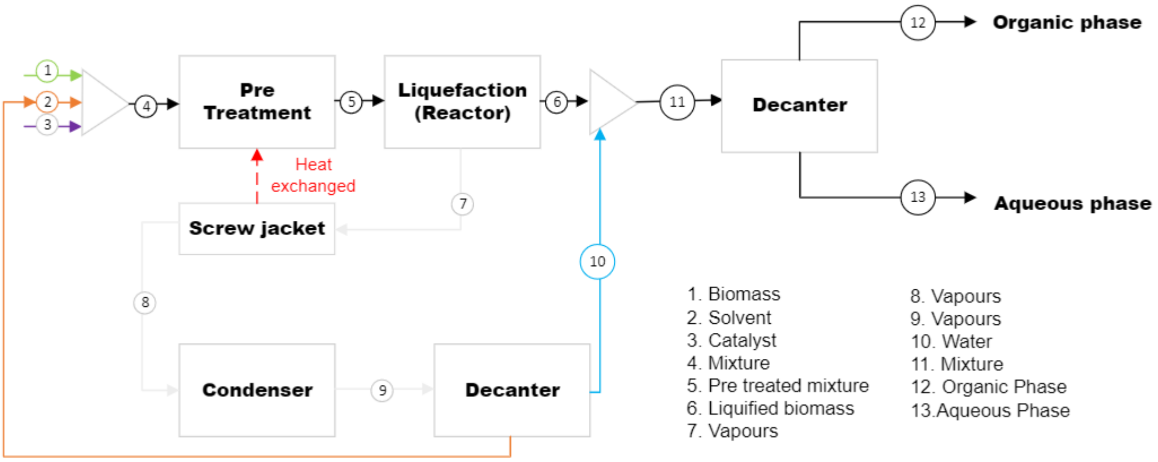


Figure 17 Block Diagram of the biomass liquefaction process.

Assuming a volume of biomass entering the facilities of 1m^3, with a density of 400 kg/m^3, the total biomass mass is 400kg. 70% of the total biomass corresponds to dry biomass, 280 kg, while 30% refers to the moisture present in the total biomass, 120 kg. Additionally, 10% of the dry biomass corresponds to ash (28 kg).

Initially, the reactor is filled with 180 kg of solvent, which is pre-heated and recirculated to spray the biomass circulating through the screw, where it undergoes a swelling process. Here, the volume of the cells increases, followed by the breakdown of the cellulosic and lignocellulosic membranes. The screw transports the mixture into the reactor (stream 5).

Additionally, the p-toluene sulfonic acid catalyst introduced into the auger through stream 3 is calculated from equation (1) [41]:

$$Q_{catalalyst} = 0.015 \times (Q_{dry\ biomass} + Q_{solvent}) \tag{1}$$

Thus, the quantity of catalyst present is 6.9 kg.

In the reactor, the liquefaction of the mixture takes place. Considering the processing of 586.9 kg of the reaction mixture, the final product after the reaction corresponds to the liquefied biomass, with an output of 286.9 kg, represented by stream 6. This is correspondent to a conversion of about 90% of the dry biomass. The liquefied biomass, collected in stream 6, consists of ash, solvent and dry biomass.

At this stage of the process, the liquefied biomass can be used as fuel directly in the boiler or sent to the extraction stage (stream 11).

After the liquefaction reaction in the reactor, vapours consisting of water and solvent are released in stream 7, forming an azeotrope in the proportion 0.6:0.4 ($x_{2EH} = 0.6;\ x_{H_2O} = 0.4$).

In stream 7, it is assumed that the total amount of water present in the biomass is released, dragging with it 240 kg of solvent. This azeotropic mixture passes through the screw sleeve, exchanging heat and heating up the mixture in the endless screw. Then, the azeotropic mixture passes through a condenser (stream 8), and a decanter (stream 9), where the two constituents of the azeotrope are separated. The solvent undergoes a makeup, where it is reintroduced into the mixer before the endless screw, stream 2. Stream 10 corresponds to condensed water directed to a mixer, where it will participate in the extraction process.

Currently, the process finishes after obtaining the liquefied biomass, as the purpose is to apply the liquefied product as an upgraded fuel. The liquified biomass can later undergo an extraction process, which is currently not being operated.

In Table 2 the input and output values of the process are resumed.

Table 2 Values of mass balance in BATCH process using biomass from Eucalyptus.

Inputs of the process (kg)		
Stream 1	total biomass	400
	dry biomass	280
	H_2O in biomass	120
Stream 2	2-ethyl hexanol	180
Stream 3	catalyst	6.9
Outputs of the process (kg/h)		
Stream 6	liquified biomass	286.9
Stream 10	condensed H_2O	120

4.3.1.2 Liquified biomass from paper sludges

A potential source of biomass is sludge from the paper mill. The total biomass has 70% of humidity and 30% of dry biomass, according to an indication by the company Secil.

Although the biomass liquefaction process is the same regardless of the biomass source, the quantities of the present compounds will vary. Therefore, the values used in biomass liquefaction from sludges from the paper mill in a BATCH mode, are detailed in Table 3.

Table 3 Values of mass balance in BATCH process using biomass from sludges.

Inputs of the process (kg)		
Stream 1	total biomass	800
	dry biomass	240
	H_2O in biomass	560
Stream 2	2-ethyl hexanol	840
Stream 3	catalyst	16

Outputs of the process (kg)		
Stream 6	liquified biomass	256
Stream 10	condensed H_2O	560

4.3.2 Continuous process

4.3.2.1 Liquified biomass from eucalyptus

Considering the block diagram of the liquefaction system in Figure 17, now, the conditions analysed refers to a process that operates on the basis of continuous flow.

In a steady state, 515 kg/h of Eucalyptus biomass enter the process (stream 1), with 361 kg/h of dry biomass (70% of the total biomass) and 155 kg/h of water existing in the biomass (30% of the total biomass). Simultaneously, 2.7 kg/h of solvent (stream 2) and 0.4 kg/h of catalyst (stream 3) are added to the endless screw, where the pre-treatment occurs.

The value of 2-ethyl hexanol is obtained from the difference between the solvent in the reaction and the solvent recovered from the azeotrope formed in stream 7 according to equations (2) and (3):

$$(2\mathrm{EH}_{\text{in reaction}} - 2\mathrm{EH}_{\text{azeotrope}}) \times \rho_{2\mathrm{EH}} \tag{2}$$

$$2\mathrm{EH}_{\text{azeotrope}} = q_{\text{condensed } \mathrm{H_2O}} \times \frac{0.6}{0.4} \tag{3}$$

Every 14 hours, under stationary conditions, it is necessary to add 5 kg of catalyst, which corresponds to 0.4 kg every hour.

The reaction proceeds and the final product leaves through stream 6, 35 kg/h of liquefied biomass. The bio-oil is collected and can be used directly in the kiln/boiler. In 35 kg of liquefied biomass, there is 2 kg of 2-EH, 0.4 kg of p toluene sulfonic acid and 32 kg of biomass, approximately.

In stream 7, the mixture with an azeotrope with 0.6 of 2 ethyl-hexanol and 0.4 of water provided from the biomass passes through the screw sleeve, exchanging heat and heating up the mixture at the pre-treatment. After condensation and decantation of the mixture, the solvent is reintroduced into the mixer before the endless screw and 155 l/h of water are collected. It is assumed that the total amount of water present in the biomass is released.

Currently, the extraction procedure is not considered (from stream 11), so the condensate water is saved.

Table 4 Values of mass balance in continuous process using biomass from Eucalyptus.

Inputs of the process (kg/h)		
stream 1	total biomass	515
	dry biomass	361
	H_2O in biomass	155
stream 2	2-ethyl hexanol	2.7
stream 3	catalyst	0.36
Outputs of the process (kg/h)		

stream 6	liquified biomass	35
Stream 10	condensed H_2O	155

4.3.2.2 Liquified biomass from paper sludge

In a continuous process, the values used when the biomass derives from sludges are in Table 5.

Table 5 Values of mass balance in continuous process using biomass from sludges.

Inputs of the process (kg/h)		
stream 1	total biomass	1200
	dry biomass	360
	H_2O in biomass	840
stream 2	2-ethyl hexanol	24.8
stream 3	catalyst	2.7
Outputs of the process (kg/h)		
stream 6	liquified biomass	402.6
Stream 10	condensed H_2O	840

5 Life Cycle Assessment of liquefied biomass

The procedure for the study of the production of bio-oil through a Life Cycle Assessment (LCA) analysis, as well as its results will be presented in this chapter. Additionally, the procedure to introduce the process data and perform the impact analysis in *SimaPro* software is demonstrated.

5.1 Goal and Scope of the study

The purpose of this study is to investigate the environmental impacts of the substitution of petcoke by liquefied biomass derived from eucalyptus' forest residues and sludges from the paper industry. The effects of this substitution are accounted for the environmental credits from petcoke substitution.

This LCA attempts to assess the industrial production of liquefied biomass, which includes the environmental impacts of manufacturing and the transport of feedstock. The intended audience of this study corresponds to the company Secil since they want to know the advantages of replacing petroleum coke. Additionally, the European Regional Development Fund is also interested in the LCA results because intends to invest in a smarter, greener, more connected and more social Europe.

5.1.1 Functional Unit

In this study, the functional unit (FU) selected is the use of 1 GJ of liquefied biomass. This type of functional unit is apt for comparing energy-based end products such as gasoline and diesel.

5.1.2 System Boundaries

In the liquefaction process, the LCA system boundary framework involves the collection of feedstocks, transportation of feedstock, pre-treatment, and manufacturing process. This means that the boundary of the investigated system is defined from cradle to gate, as illustrated in Figure 18.

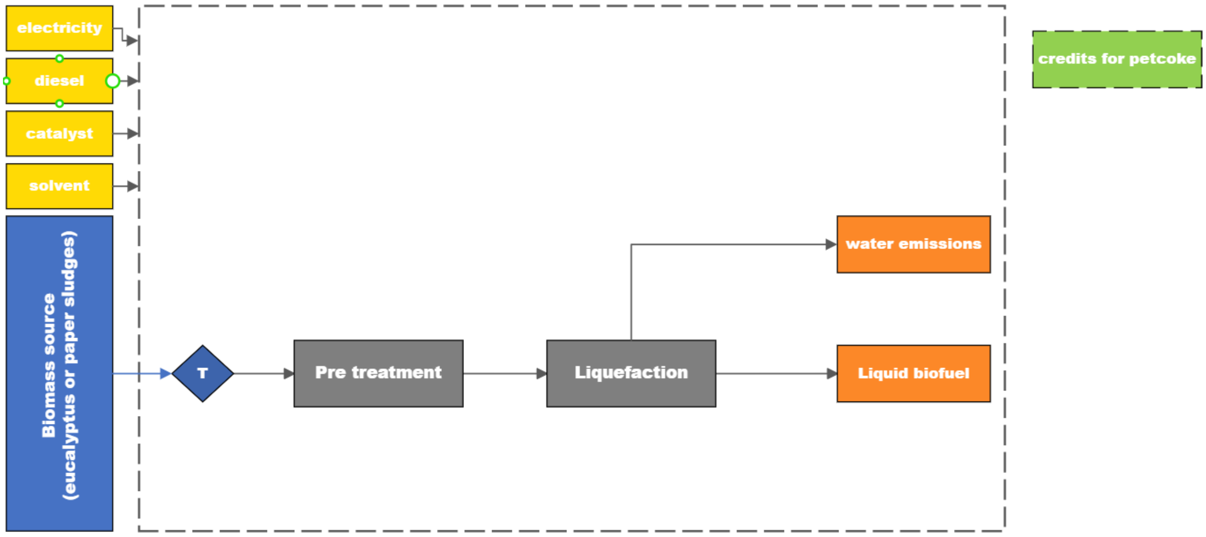


Figure 18 Cradle to gate system boundaries to produce bio-oil.

5.1.3 Geographical boundaries

The production of liquefied biomass is based in Portugal. Thus, the Ecoinvent V3 database was used for the background data assuming the Portuguese context whenever possible. For example, the input electricity is modelled for the Portuguese context, but, for the rest of inputs, since there is no Portuguese data available, for diesel, transport and cyclohexanol, they were based on European markets.

5.1.4 Allocation Procedures

The allocation approach chosen, existing in the *SimaPro* database, was the “cut-off system model”. In this type of modelling, the full burden of waste by-products is allocated to the primary user of a product (the first waste producer). This means that when a product is part of a second life cycle through recycling or reuse, it will be “burden-free”, except for the recycling process.

5.1.5 Assumptions and limitations

Some assumptions and limitations were considered in this study. They are listed below.

- The infrastructure was not included in the assessment;
- Long-term emissions were excluded;
- The distance travelled by biomass to the facility is the same in all cases;
- The electricity remains the same in all cases;
- The solvent 2-ethyl hexanol is not available in the Ecoinvent V3 Database, hence several approaches were tested to model this component, which are described in sections 5.1.6.1 (page 35) and 5.2.1.3 (page 48).

5.1.6 Modelling software and impact assessment methods

The LCA software used for modelling the liquefied biomass production was *SimaPro*. The software quantifies environmental impacts, enabling more organisation to improve products and systems, measure progress, and report sustainability efforts.

Additionally, the methods chosen in software were PEF and ReCiPe, since the study being considered occurs in Europe. Their databases present values considering European statistics.

5.1.6.1 Data application in *SimaPro*

In *SimaPro* software, it was defined the inputs and outputs of the process. The inputs included the raw materials, fuels, heat or electricity known from the technological sphere. The outputs were defined as the final product, in particular the liquefied biomass, and possible emissions.

As an example, the data presented in this subchapter are related to the mass balance of the BATCH process, where the source of biomass was Eucalyptus (Chapter 4.3.1, page 28). The rest of the cases followed the same methodology, with their values shown in Table 7 on page 37.

Based on the mass balance calculated in Chapter 4.3.1.1, on page 28, the final product should have 286.9 kg. The emissions to water considered were 120 l of wastewater since condensate water proceeds for treatment.

To introduce the inputs in *SimaPro* it was necessary to specify the biomass feedstock, the solvent, the catalyst, the fuel used, the biomass transport and the electricity used, as it is shown in Figure B 1 in Annex B (page 70).

The biomass source is the forest residues of Eucalyptus. These forest residues are a waste product of logging operations and contain non-tradable parts of felled trees, like small twigs and leaves, which are left to decompose or burn on the forest floor. As such, this raw material carries no environmental burden associated with the extracted wood, so it wasn’t introduced as an input in *SimaPro*, but the transport from the forest to the pilot installation was considered.

It was considered that the 400 kg of biomass were transferred over 79.8 km from Figueira da Foz to Pataias, where the pilot installation is assembled. This transport was made by a lorry with a capacity between 7.5-16 metric tons, considered in Europe. As well, it corresponds to 31.92 tkm, which means the transportation of 0.004 tonnes over 79.8 kilometres.

As there is no existing life-cycle impact data in *SimaPro* libraries for the solvent or the catalyst, the environmental impacts of these were estimated.

Toluene sulfonic acid, the catalyst, is synthesised from a reaction between toluene and sulfuric acid with a molar ratio of 1:1.

$$\mathrm{C_6H_5CH_3 + H_2SO_4 \longrightarrow C_7H_8O_3S + \ H_2O} \qquad (4)$$

Using this equation as a basis, the environmental impacts of toluene sulfonic acid were modelled with *SimaPro* (Figure B 2 in Annex B (page 71)) as explained in [42]. The values introduced correspond to their respective molar masses, considering a yield of the reaction of 100%. The specific amount used was 6.9 kg.

In the absence of the solvent 2-ethyl hexanol in the *SimaPro* database, an s-proxy approach was considered. An s-proxy is a chemical component that can be chosen to substitute a certain component that is not available in the database but has a similar chemical structure and molecular weight. Substances that have approximately the same chemical structure and molar mass as the considered substance can be assumed as a substitute.[42] Hexane, heptane and cyclohexanol were considered for the case. Since it is intended to compare their environmental impact, the functional unit in this case corresponds to 1 kg of each solvent (Figure 19).

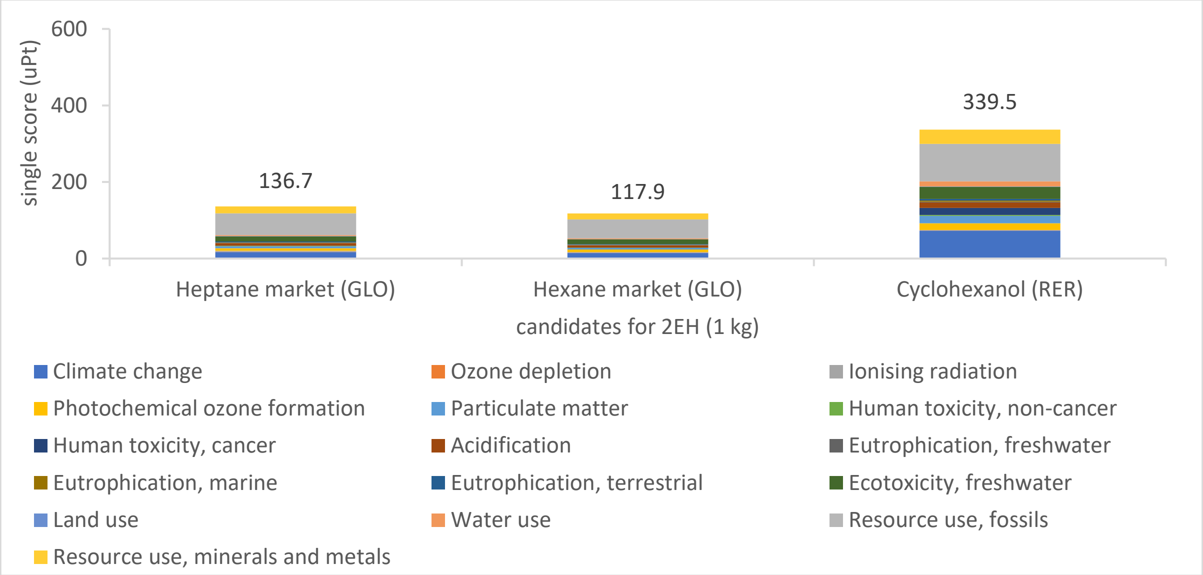
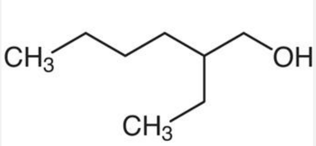
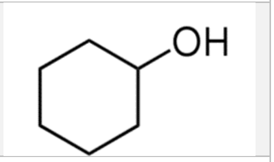


Figure 19 Comparison of the environmental impact of different candidates to replace 2EH. GLO: Global, RER: Europe.

Despite the good results of hexane and heptane, these cannot be the solvent selected for the process. This happens because, as seen before, the liquefaction reaction may reach 160°C, and these solvents have a boiling point of 98.42°C and 69°C, respectively, leading to their evaporation, which will prevent the reaction from proceeding. Therefore, cyclohexanol with a boiling point of 161.8°C is the most suitable solvent as it meets all the necessary criteria, seen in Table 6.

Table 6 Comparison of 2-ethylhexanol and cyclohexanol.

	2-ethyl hexanol	**cyclohexanol**
		
Chemical Formula	$C_8H_{18}O$	$C_6H_{12}O$
Boiling Point (°C)	184.7	161.8
Molar Mass (g/mol)	130.2	100.2
Density (kg/m3)	833	962

To describe the fuel used in the boiler, it was defined as an input already present in the *SimaPro* databases, the diesel in the European market. The quantity of fuel administrated is 5 l, but since its density is approximately 1 kg/l, it was considered an input value of 5 kg, calculated by the equation 5.

$$\rho_{fuel} = \frac{m\ (kg)}{v\ (l)} \Leftrightarrow m_{fuel} = 1\,\frac{kg}{l} \times 5\ l \tag{5}$$

Finally, the electricity considered was of medium voltage in Portugal, which included the endless screw, agitator and transport pumps. The value introduced was 12 kWh.

It is important to refer that the transport of reagents to the pilot facility was not considered. That includes the distance and fuel (or another similar) in their dislocation.

In Table 7 are gathered all the data introduced in *SimaPro* for all cases of bio-oil production (from Eucalyptus and paper sludges in BATCH and continuous mode.

Table 7 Data introduced in *SimaPro* for the liquefied biomass from Eucalyptus and paper sludges, BATCH and continuous mode.

Inputs in *SimaPro*	**Eucalyptus BATCH**	**Paper Sludges BATCH**	**Eucalyptus Continuous**	**Paper Sludges Continuous**
Solvent (kg)	180	840	2.7	24.8
Catalyst (kg)	6.9	16.2	0.36	2.7
fuel (kg)	5	5	5	5
Transport (tkm)	31.92	63.84	31.92	63.84
electricity (kWh)	12	12	12	12
Outputs in *SimaPro*				
liquefied biomass (kg)	286.9	256.2	35	402.6
condensed water (l)	120	560	155	840

5.1.6.2 Lower Calorific Value – Calculation strategy

The lower calorific value (LCV) or lower heating value (LHV) was calculated to assess the effectiveness of liquefied biomass as a fuel. The LCV corresponds to the amount of energy per unit mass released in the oxidation of a given fuel. Its calculation allows it to compare the LCVs of fuel and biomass liquefied to check if the biomass liquefied can substitute fuel.

Knowing the LCV and the proportion of each compound of liquefied biomass, the LCV of liquefied biomass is the sum of every component present in it. In Table 8, are presented their LCV values, where the solvent corresponds to 2EH, despite being the cyclohexanol used in *SimaPro* to reach conclusions.

Table 8 Values of LCV.

catalyst	19.3	GJ/t
dry biomass (Eucalyptus)	18.5	GJ/t
dry biomass (sludges) [43]	12.3	GJ/t
solvent	37.5	GJ/t

The percentage of solvent is between 13 and 14%, the catalyst is 9%, and the percentage of biomass is 85%, through 148 tests. The methodology for all cases is presented in equation (6):

$$\%solvent \times LCV_{solvent} + \%catalyst \times LCV_{catalyst} + \%dry\ biomass \times LCV_{dry\ biomass} \tag{6}$$

For one test where the solvent is 2-ethyl hexanol, the equation applied is:

$$0.139 \times 37.5 + 0.009 \times 19.3 + 0.851 \times 18.5 \tag{7}$$

The final values of each study correspond to the average of all studies and the quantities of mass of each fuel to produce 1 GJ of energy were obtained through their LCV, as described in Table 9. The mass value is obtained from the inverse of the LCV.

Table 9 Mass of fuel to obtain 1 GJ of energy in BATCH mode.

Case Study	LCV liquefied biomass (GJ/ton)	Mass (kg) to 1GJ
Bio-oil Eucalyptus	21.06	47.49
Bio-oil Paper Sludges	15.71	63.65
Petcoke [44]	31.3	31.95

According to Table 9, it is necessary 47.49 kg of bio-oil from Eucalyptus to produce 1 GJ of energy. For the rest of the cases next presented, the procedure applied was similar.

5.2 Life Cycle Impact Assessment Results

In this subchapter, a comparison of both Life Cycle Impact Assessment (LCIA) methods and tools will be made. The results obtained with *SimaPro* will be considered and, for each case study, the methodologies used will be analysed. They will be compared in terms of the characterization of impacts, the normalized values, the weighting factors used and the single score. Additionally, several sensitivity analyses are going to be made in order to obtain the best conditions for the biofuel produced. The Life Cycle Assessment (LCA) results will be presented concerning the functional unit defined as 1 GJ of liquefied biomass.

5.2.1 BATCH process

In an attempt to obtain the LCA result of liquefied biomass from the BATCH process, the known inputs and outputs were introduced in *SimaPro* software, as described previously. ReCiPe and Product Environmental Footprint (PEF) methodologies allowed us to discover the main impacts on the environment.

5.2.1.1 ReCiPe Methodology

Opening with the ReCiPe MidPoint 2016 with a hierarchic perspective method, the evaluation of 1 GJ of biomass liquefied starts with the characterization indicator. The characterization at the midpoint level has 18 impact categories with their respective unit and characterisation factor.

Therefore, in Figure 20 the bio-oil obtained in batch conditions from Eucalyptus and from paper sludges will be compared, without taking into account the petcoke replacement credits.

In the first instance, of all impact categories under analysis, the major impact seems to be global warming, terrestrial ecotoxicity and fossil resource scarcity categories. Since every impact has its own unit, it is impossible to compare them. In other words, in the characterization step, it is only possible to reach conclusions within an impact category since the unit is the same.

In all impact categories, the most expressive case is the liquified biomass derived from paper sludges. This happens mainly due to the quantity of solvent used (cyclohexanol), which is relatively higher than the one used in the bio-oil derived from Eucalyptus. Also, to produce 1 GJ of energy, a larger amount of bio-oil is needed, since its LHV is lower.

Cyclohexanol ($C_6H_{11}OH$), a secondary alcohol, is produced in a large scale, as precursor to nylon, by the oxidation of cyclohexane in air, typically using cobalt catalysts, according to equation 8:

$$C_6H_{12} + \frac{1}{2}O_2 \rightarrow C_6H_{11}OH \qquad (8)$$

It also has many industrial applications such as solvent for rubber, oils, esters and ethers and can be used in the preparation of adipic acid and cyclohexanone.

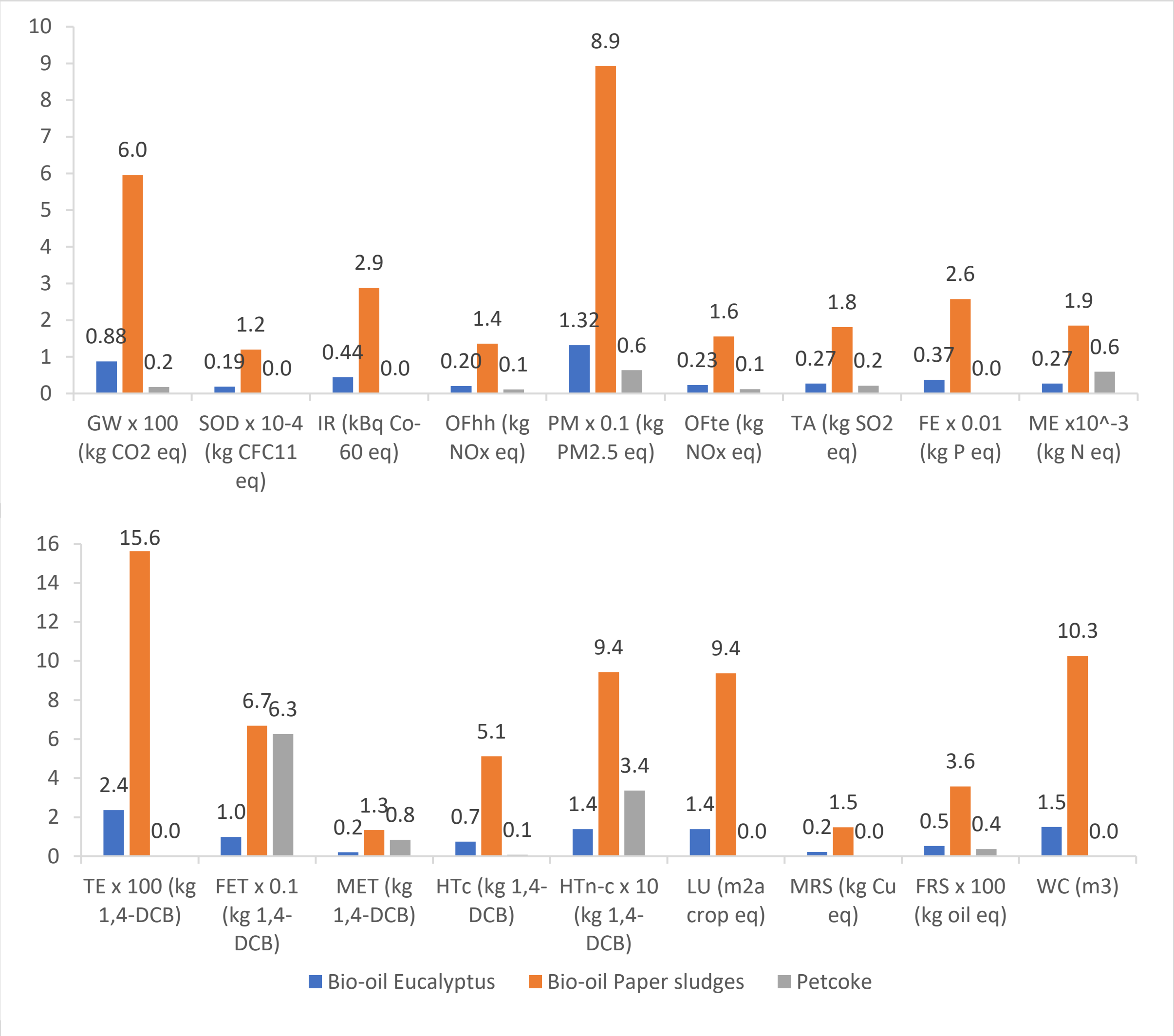


Figure 20 Comparison of the characterisation values of impact categories of liquefied biomass with ReCiPe method. GW: global warming, SOD: stratospheric ozone depletion, IR: ionizing radiation, OFhh: Ozone formation - Human health, PM: fine particulate matter formation, OFte: Ozone formation, terrestrial ecosystem, TA: terrestrial acidification, FE: freshwater eutrophication, ME: marine eutrophication, TE: terrestrial ecotoxicity, FET: freshwater ecotoxicity, MET: marine ecotoxicity, HTc: human carcinogenic toxicity, HTn-c: human non-carcinogenic toxicity, LU: land use, MRS: mineral resource scarcity, FRS: fossil resource scarcity; WC: water consumption.

Knowing some of the backgrounds of this solvent and after analysing the results, the impact global warming category is mostly caused by the emissions to the atmosphere, where cyclohexanol and transportation are the main contributors to these results. The results in the particulate matter formation category are caused by the reaction of producing cyclohexanol, since most particles in the atmosphere are the result of complex reactions of chemicals, which are pollutants emitted from power plants, industries and automobiles.

The second sub step corresponds to the normalization. The normalization of the indicator results allows calculating its magnitude about reference information, in this case, the average citizen scores for the year 2010. The reference situation corresponds to an average citizen score per impact category. In Figure 21 it is shown these results for the BATCH mode excluding the credits of the substitution of petcoke.

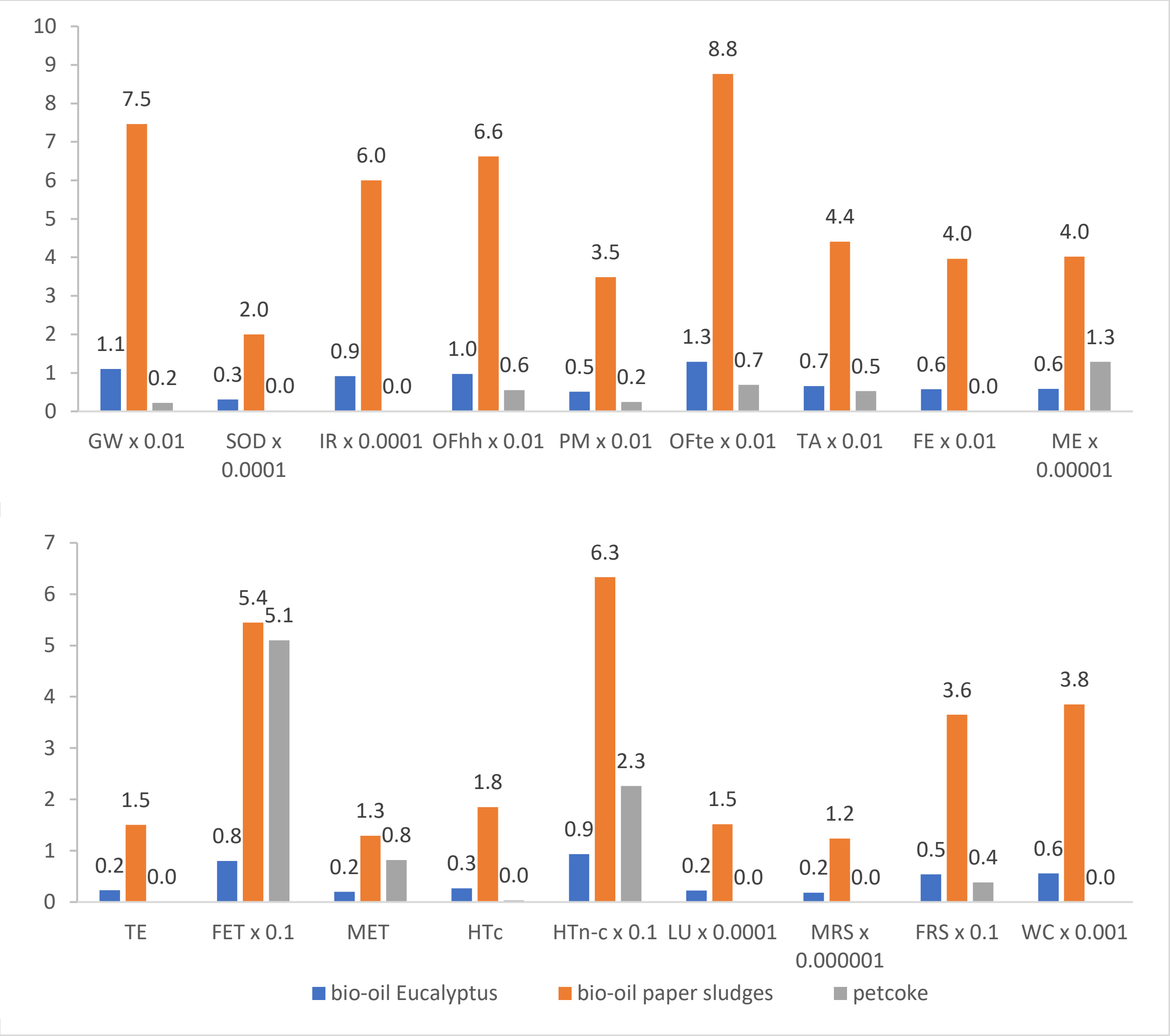


Figure 21 Comparison of the normalization values of impact categories of liquefied biomass with ReCiPe method. GW: global warming, SOD: stratospheric ozone depletion, IR: ionizing radiation, OFhh: Ozone formation - Human health, PM: fine particulate matter formation, OFte: Ozone formation, terrestrial ecosystem, TA: terrestrial acidification, FE: freshwater eutrophication, ME: marine eutrophication, TE: terrestrial ecotoxicity, FET: freshwater ecotoxicity, MET: marine ecotoxicity, HTc: human carcinogenic toxicity, HTn-c: human non-carcinogenic toxicity, LU: land use, MRS: mineral resource scarcity, FRS: fossil resource scarcity; WC: water consumption.

Based on the reference global normalization factors for the reference year 2010, the most expressive impact categories for the liquefaction of biomass cases are human carcinogenic toxicity followed by terrestrial ecotoxicity and marine ecotoxicity.

Once again, cyclohexanol was the main responsible for this score. These impact categories present these results because the emission of chemicals through all life cycle stages of cyclohexanol causes toxic impacts on human beings and/or ecosystems. The environmental fate of emitted toxic chemicals, human and ecosystem exposure to the increased environmental concentrations of cyclohexanol are evaluated in these impact categories.

The cyclohexanol compound is a hazardous substance since it causes short-term effects like nausea, vomiting and dizziness or causes chronic health effects in human. Since all these consequences are taken into account, the results obtained are justified.

In the petcoke case, the impact categories with the highest score are marine ecotoxicity, fresh ecotoxicity and human non-carcinogenic toxicity. Petroleum coke use may cause water quality hazards and potential exposure to toxic substances. If this fuel is released into the aquatic environment, it may incorporate sediments or float on the surface. Additionally, it is chemically inert, so it doesn't vaporize into the atmosphere or react in the presence of water or light. In relation to the potential human non-carcinogenic toxicity category, inhalation and skin contact were assessed to be the most likely exposure routes to humans, whereas petcoke was not found to be carcinogenic through these vias.

Comparing the cases of biomass liquefaction with the petcoke, it is notorious that the impact of the second is lower in most of the categories, except in the categories of marine eutrophication, freshwater, marine and human non-carcinogenic toxicity. Such results can be justified by the amount of fuel used to satisfy 1 GJ of energy, which is lower for the petcoke case. Despite this information, for the category of freshwater ecotoxicity, the highest punctuation is from petroleum coke. As said before, it can be justified by the potential water quality hazards.

Considering the ReCiPe Midpoint version, the stage of weighting doesn't belong to the procedure but in the ReCiPe Endpoint version, the weighting exists.

5.2.1.2 PEF Methodology

The environmental impact of the liquified biomass was also evaluated using the PEF methodology. The premises introduced in *SimaPro* were the same as the previous ones and in Table 9, on page 38, it is the data needed to produce 1 GJ of energy.

The first indicator to be analysed is characterisation, Figure 22. In the graphic it is represented impact categories, including their subcategories, with their own unit. These impact categories are climate change, human toxicity cancer and non-cancer and freshwater ecotoxicity.

Once again, the production of bio-oil from biomass derived from Eucalyptus and sludge from the paper industry is evaluated, not counting the credits for replacing petcoke.

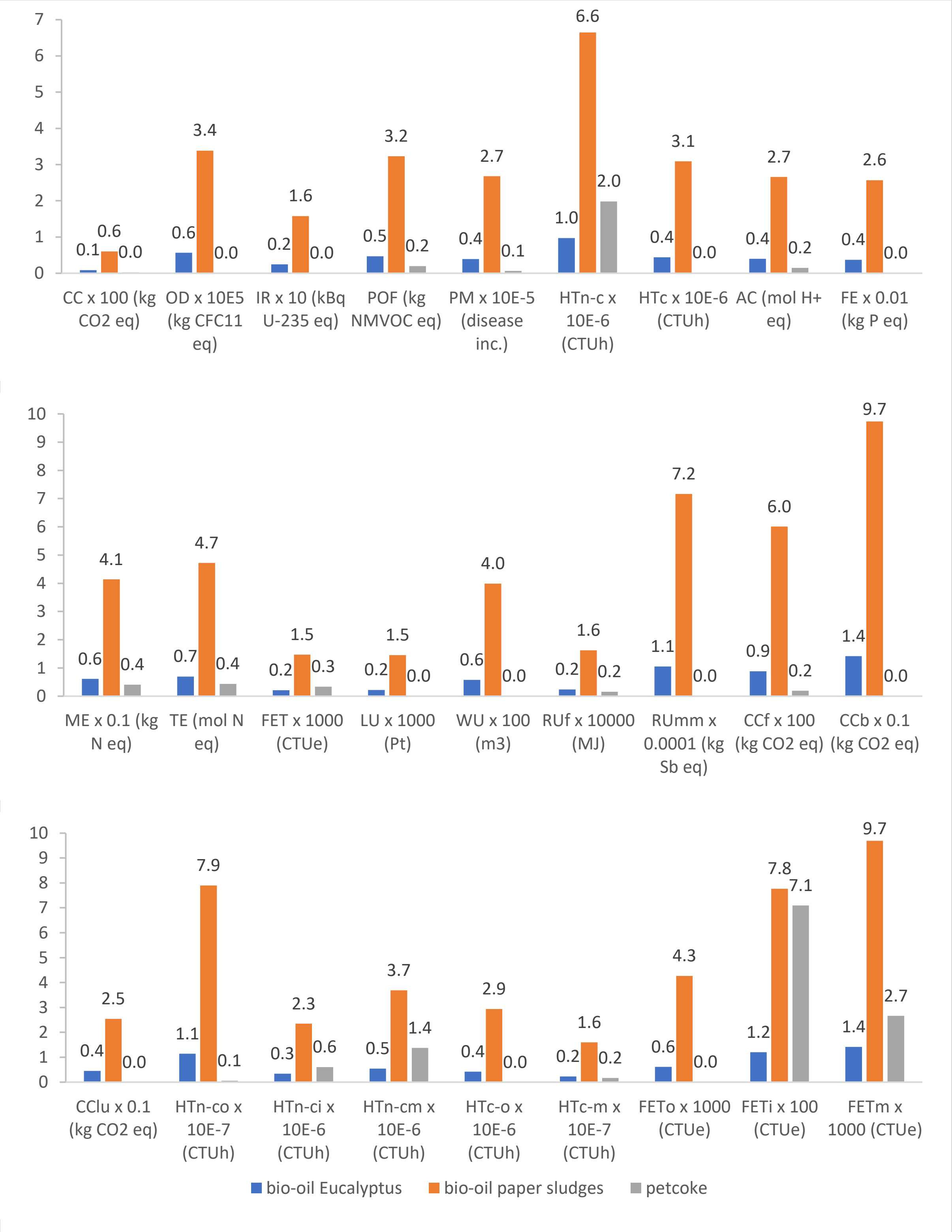


Figure 22 Comparison of the characterisation values of impact categories of liquefied biomass with PEF method. CC: climate change, OD: ozone depletion, IR: ionising radiation, POF: photochemical ozone formation, PM: particulate matter, HTn-c: human toxicity non-cancer, HTc: human toxicity cancer, AC: acidification, FE: freshwater eutrophication, ME: marine eutrophication, TE: terrestrial eutrophic, FET: freshwater ecotoxicity, LU: land use, WU: water use, RUf: resource use – fossils, RUmm: resource use – minerals and metals, CCf: climate change – fossil, CCb: climate change – biogenic, CClu: climate change – land use and change, HTn-co: human toxicity non cancer – organics, HTn-ci: human toxicity non cancer – inorganics, HTn-cm: human toxicity non cancer – metals, HTc-o: human toxicity cancer – organics, HTc-m: human toxicity cancer – metals, FETo: freshwater ecotoxicity – organics, FETi: freshwater ecotoxicity – inorganics, FETm: freshwater ecotoxicity – metals.

Recalling the idea that in the characterization the impact categories cannot be compared with each other, inside every category, the bio-oil from paper sludges usually has the highest score, except for the freshwater ecotoxicity (inorganic), where petcoke is the highest.

Like in ReCiPe method results, the main responsible for these outcomes is the quantity of solvent used, which is relatively higher than the one used in the bio-oil derived from Eucalyptus. Also, to produce 1 GJ of energy, a larger amount of bio-oil is needed, since its LHV is lower.

Since the reference analysis base isn't the same for all categories, these values have to be normalized. In PEF, the global normalization is set for the reference year 2010. Furthermore, the impact categories are reduced to 16 categories because the indicators of climate change, human toxicity - cancer and non-cancer and ecotoxicity of freshwater gather all their contributors to that effect. Next, Figure 23 presents the normalised impact categories for 1 GJ.

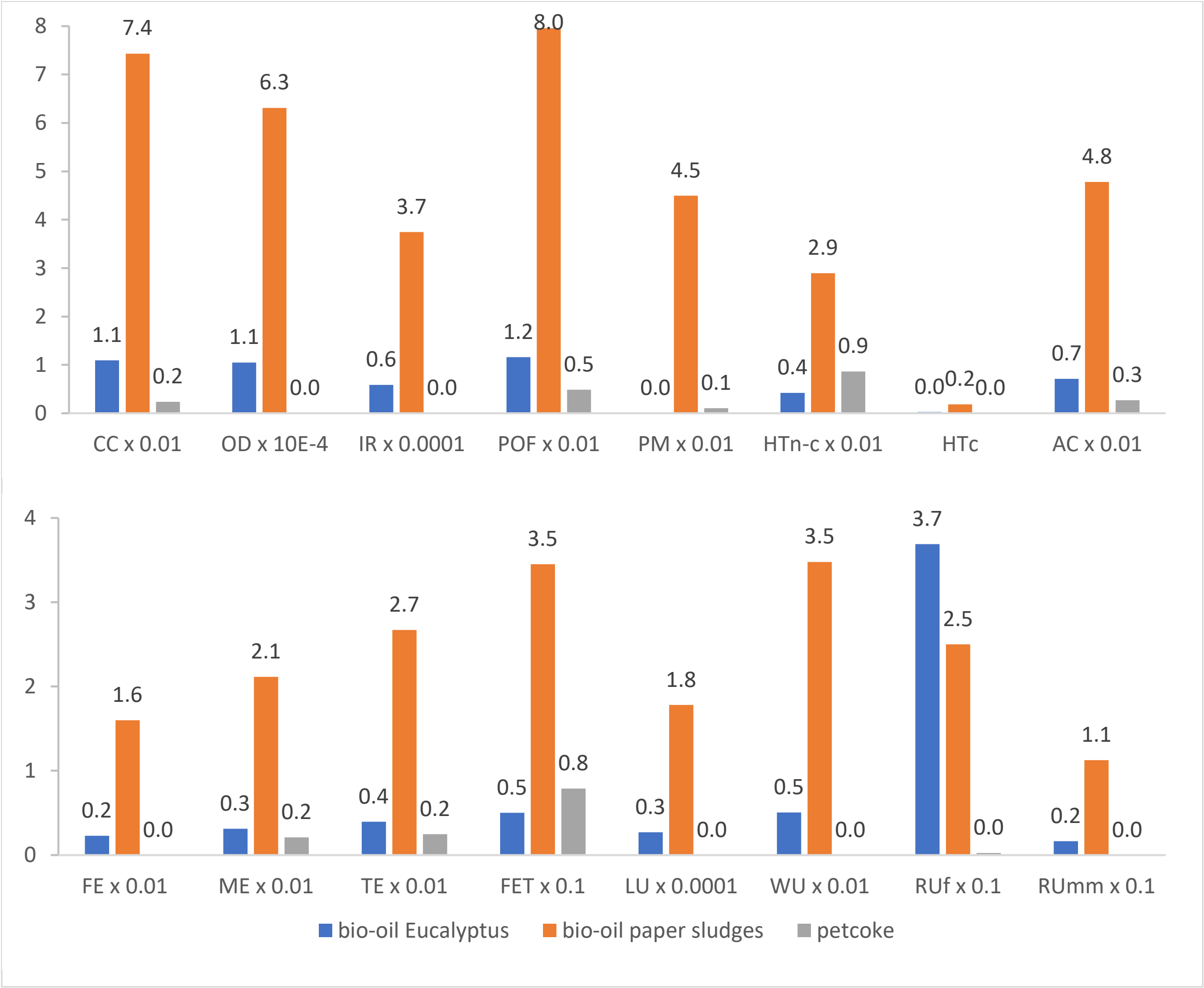


Figure 23 Comparison of the normalization values of impact categories of liquefied biomass with PEF method. CC: climate change, OD: ozone depletion, IR: ionising radiation, POF: photochemical ozone formation, PM: particulate matter, HTn-c: human toxicity non-cancer, HTc: human toxicity cancer, AC: acidification, FE: freshwater eutrophication, ME: marine eutrophication, TE: terrestrial eutrophic, FET: freshwater ecotoxicity, LU: land use, WU: water use, RUf: resource use – fossils, RUmm: resource use – minerals and metals.

The categories with the highest impact are ecotoxicity (freshwater), use of fossil resources and human toxicity (cancer). It confirms the release of chemicals in the water, causing hazardous impacts. Another impact with a considerable influence is the use of fossil resources. Either bio-oil or cyclohexanol uses fossil resources in their path like in the generation of electricity, fuel used in transport or in industrial plants. Finally, the potential of cancerogenic effects should be considered, as it is caused by the intake or exposure of toxic substances related to cancer, used in bio-oil and in petcoke. The chemical and petroleum industries provide an increased risk of developing several different cancer types.

Proceeding with the analysis of the bio-oil life cycle, in the next optional step, weighting, weights or values are assigned relative to the different impact categories based on their perceived importance or relevance (Figure 24).

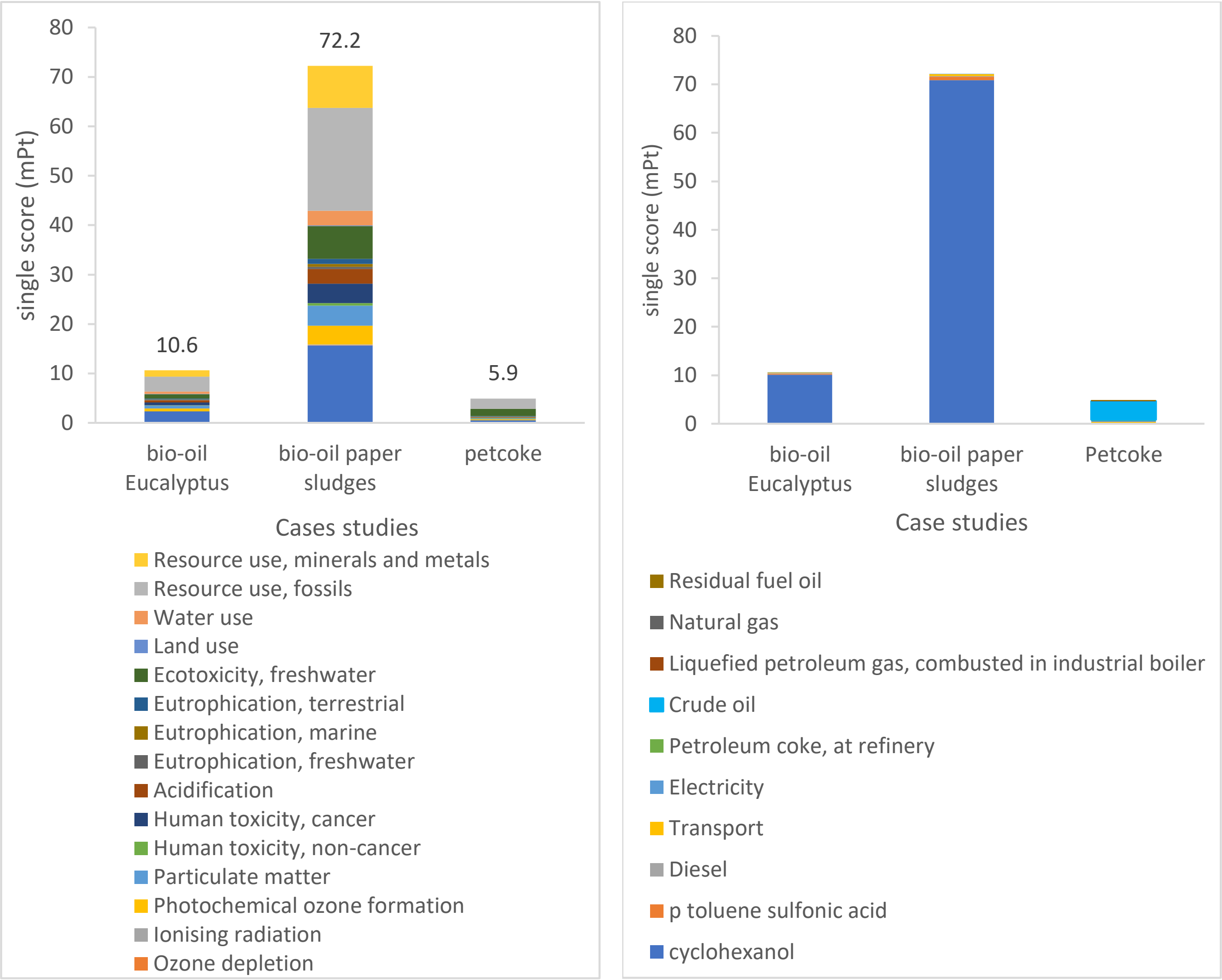


Figure 24 Comparison of the weighting values of impact categories of liquefied biomass with PEF method divided by impact categories and contribution of processes without the petcoke credits.

When analysing the results as single score, in both cases of bio-oil, cyclohexanol is the biggest cause of impact, which confirms the previous results. Once again, climate change, the use of fossil resources and the ecotoxicity of freshwater are the greatest impacts, which corroborate the conclusions made in the normalisation sub step. An explicit disadvantage corresponds to the use of a greater amount of biofuel to equal the efficiency of fossil fuel, which translates in a lower impact of petcoke. Still, it has more advantages when compared to petcoke.

As aforementioned, one of the applications of the bio-oil is to replace the petroleum coke used in the cement line. In order to obtain the environmental impact of this substitution, it was necessary to introduce in the *SimaPro* software, how much quantity of petcoke could be replaced.

For this to happen, the petcoke replaced was calculated using the following equation:

$$m_{liq.biomass\ to\ replace\ pet\ coke} = m_{liq.\ biomass} \times {LHV_{liq.biomass}}/{LHV_{pet\ coke}} \tag{9}$$

The LCV of heavy fuel oil is approximately 41 GJ/ton [44] and the LCV of coke is 31,3 GJ/ton. [45]

As an example, for the case of the liquefied biomass from Eucalyptus source in BATCH mode, the final mass of liquefied biomass obtained is 286.9 kg. According to equation 9 it is possible to know the mass of petcoke substituted:

$$m_{liq.biomass\ to\ replace\ pet\ coke}(kg) = 286.9 \times {21.06}/{31.3} = 193 \tag{10}$$

The same procedure was applied for the other case, presented in Table 10.

Table 10 Mass of petcoke substituted.

Case Study	LHV liquefied biomass (GJ/ton)	Petcoke replaced (kg)	Mass (kg) to 1GJ	Total environmental impact (mPt)
Eucalyptus	21.06	193	47.49	1.25
Paper Sludges	15.71	129	63.65	8.49
Petcoke [44]	31.3			

According to these data, the following analyses will include the credits of the substitution of petcoke. Taking into account the information available in Table 10, it is represented in Figure 25 this case by applying the PEF methodology, in single score results to obtain 1 GJ of energy.

When considering petcoke replacement credits, the total impact of both cases decreases but it is still considerable. This evidence may be justified with the greater amounts of bio-oil necessary to produce 1 GJ, justified by the same reasons mentioned above.

As matter of fact, in *SimaPro* software, the positive results on the numerical scale translate into a negative impact on the environment. The greater the amount of petcoke replaced, the smaller the impact will be because it is being substituted by a biofuel (liquefied biomass) with a lower impact than petcoke. This implies that the petcoke replaced will not have a prejudicial impact on the environment.

It is also possible to affirm that the impact of the bio-oil from paper industries is higher, therefore the cyclohexanol solvent. It is used more mass of bio-oil from paper sludges to produce 1 GJ and consequently, the amount of petcoke replaced is lower.

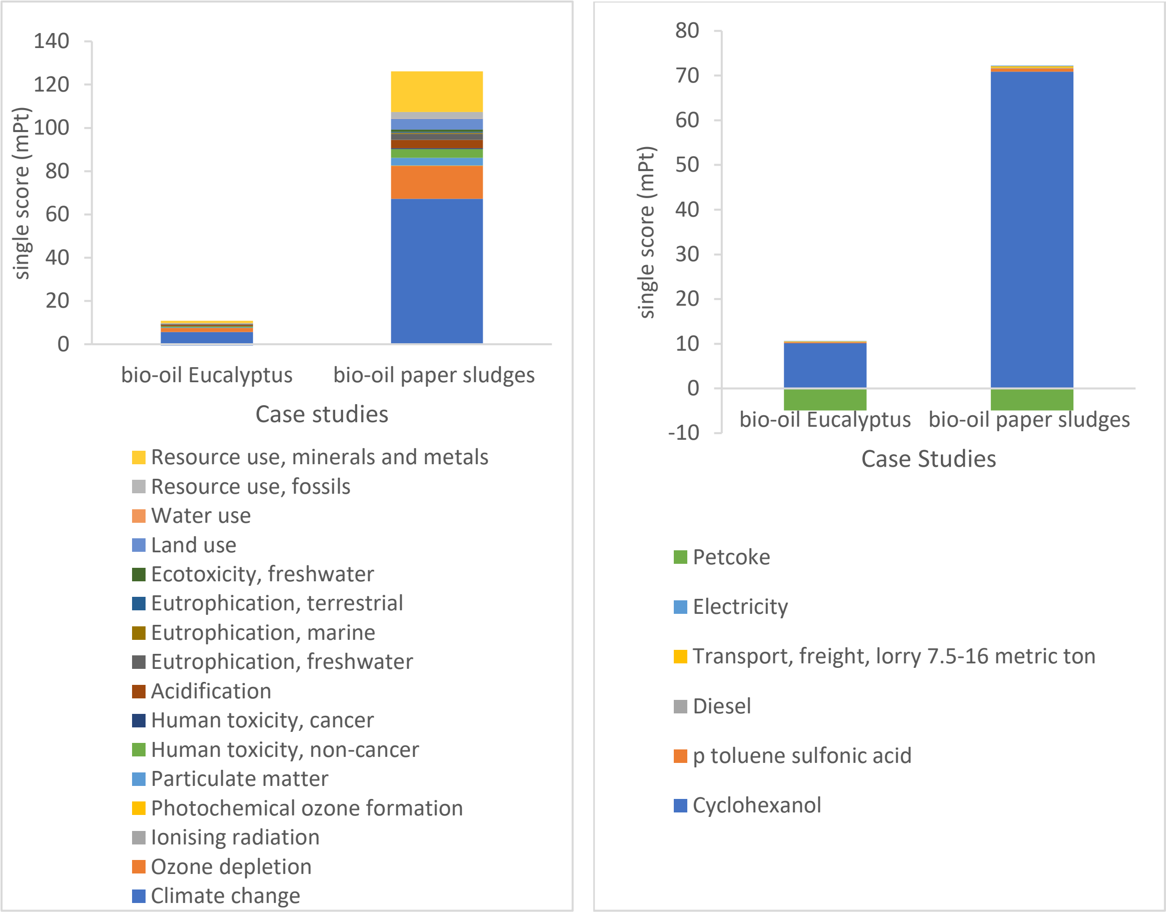


Figure 25 Comparison of the weighting values of impact categories of liquefied biomass with PEF method divided by impact categories and contribution of processes with the petcoke credits.

Finally, the impact categories that stand out the most are the use of fossil resources, climate change and the use of minerals and metals resources for both cases. These results are due to the manufacturing process of cyclohexanol, which uses minerals, metals and fossil resources, and consequently will release prejudicial compounds to the environment that contribute to climate change, as seen previously.

After a discussion of the results, they seem to be in agreement with the ReCiPe results. Although the ReCiPe method is indicated in this study, the PEF method was recently developed with its completion expected by the end of 2024. For this reason, ReCiPe is no longer used in Europe.

Thus, the following analyses presented will be based only on the PEF method and will include the credits of replacing petcoke with biofuel, since one of the objectives under study is to evaluate the impact of this substitution.

5.2.1.3 Introduction of 2-ethyl hexanol in *SimaPro* software

Of all the studies done, most of the impacts were due to cyclohexanol, which was intended to replace 2-ethyl hexanol (2-EH). So, to obtain a more realistic result, the data related to the production of 2-ethyl hexanol was introduced in *SimaPro* software.

In a first approach, it was planned to study the industrial production of 2EH in 4 steps, starting with an aldolization of butyraldehyde and subsequent dehydration, separation of the aldolization solution, hydrogenation of unsaturated 2-ethyl-2-hexenal as an intermediate product, and finally, fractionation of 2-ethyl hexanol. [46]Unfortunately, the butyraldehyde compound didn´t exist in the software, so, other methods to produce 2EH were sought.

Based on the synthesis of 2-ethyl hexanol via butanol (BuOH), the same procedure applied to the catalyst was used, which corresponds to the use of an equation as a basis and the respective molar masses. [47] The synthesis of 2-ethyl hexanol via butanol through the Guerbet reaction starts with a dehydrogenation of butanol followed by aldol condensation and hydrogenation of the unsaturated condensation product. In order to realize this reaction a bifunctional catalyst, characterized by a dehydrogenating/hydrogenating metal species and a basic component, is required. Homogeneous catalysts at 120°C based on phosphine complexes of different transition metals (Rh, Ru, Ir, Pt, Pd, and Au) were used in the Guerbet self-condensation of BuOH.

$$C_4H_{10}O \leftrightharpoons C_4H_8O + H_2 \tag{11}$$

$$C_4H_8O \rightarrow C_8H_{14}O + H_2O \tag{12}$$

$$C_8H_{14}O \rightarrow C_8H_{18}O \tag{13}$$

It is well established that the Guerbet reaction is a more friendly environmental process than the conventional ones up to now applied for the synthesis of 2EH. [48]

Based on stoichiometric reaction and molar masses, the reagents and catalyst used and energy were introduced as inputs. Table 11 and Figure B 3 in Annex B (page 70) show the *SimaPro* inputs and outputs conditions.

Table 11 Inputs and outputs of 2-ethyl hexanol in *SimaPro*.

Inputs in *SimaPro* (2-EH)	
0.00058 g	Palladium
74.12 g	1-butanol
0.7 MJ	heat from steam
Outputs in *SimaPro* (2-EH)	
130.23 g	2-ethylhexanol
2 g	hydrogen (air emission)
18 g	wastewater (water emission)

With the intention of verifying the relation between both solvents, it was made a comparison with 1 kg of 2-ethyl hexanol and 1 kg of cyclohexanol, supported by the PEF methodology. Their single scores allow easier comparison between them, as shown in Figure 26.

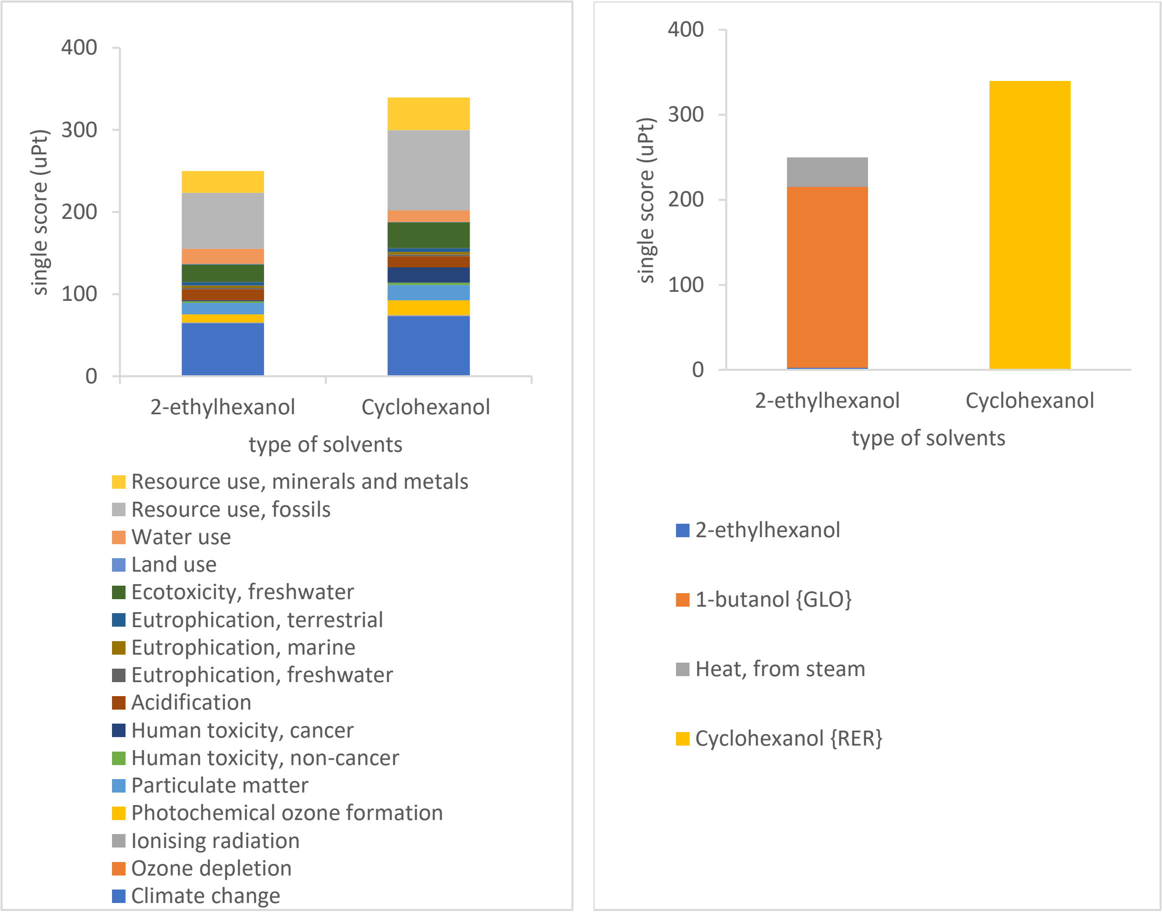


Figure 26 Comparison of the weighting values of both solvents with the PEF method divided by impact categories and contribution of processes.

As expected, the environmental impact caused by cyclohexanol is much greater than 2-EH. The final single score of 2-EH is 250 uPt against 339 uPt.

In both cases, the categories with higher expression correspond to the use of fossil resources, climate change and the use of minerals and metals. These contributions are mainly due to the use of cyclohexanol and butanol in each case because they consume non-renewable resources, present a higher concentration of minerals and emit compounds into the atmosphere causing climate change. It is important to mention that the production of 2EH and consequently its results are an approximation, and therefore present a large uncertainty associated. Since it is the main responsible for the impact the LCA results of bio-oil will also have a great level of uncertainty.

By substituting the cyclohexanol with 2-EH, the quantity of solvent used remained the same, as well as the rest of the inputs. The new results of bio-oil production will be studied, considering 2-EH as the solvent and the replacement of petcoke, as it is shown in Figure 27 and Table 12.

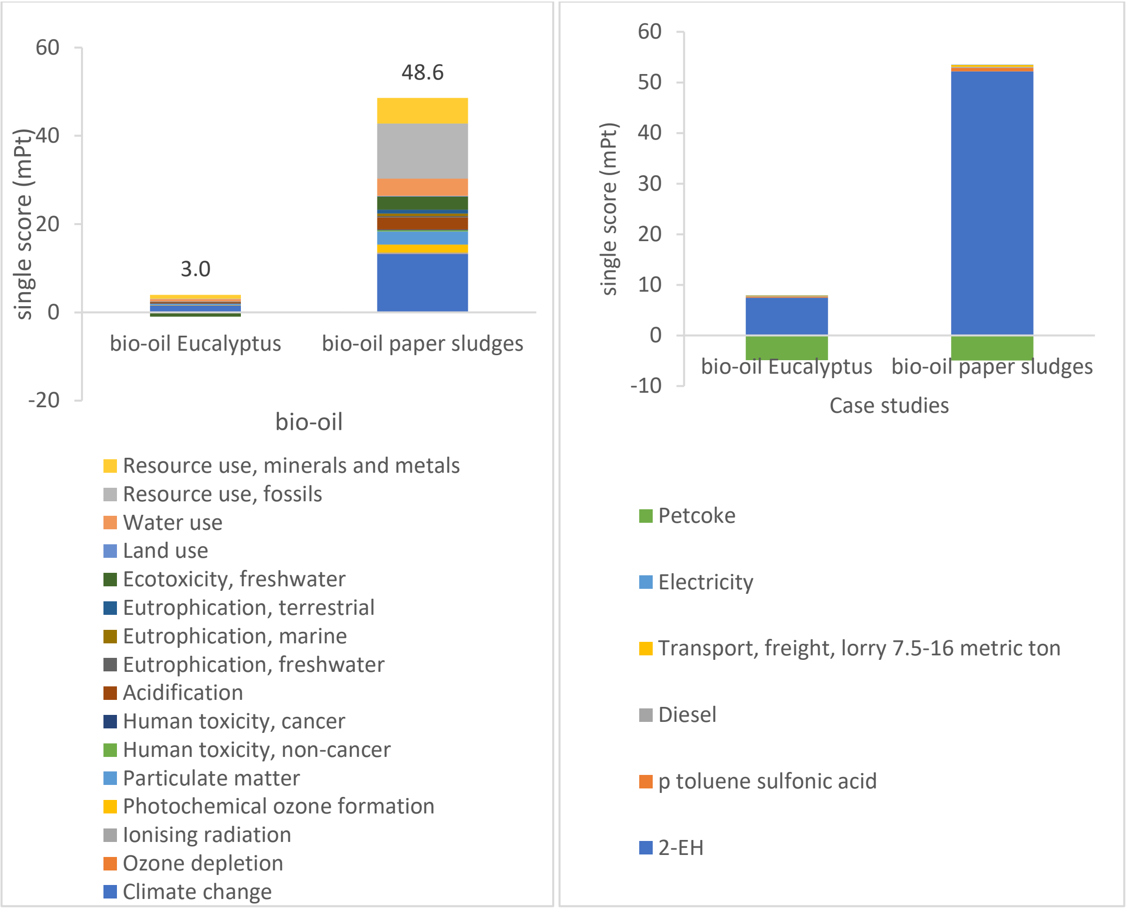


Figure 27 Comparison of the weighting values of impact categories of liquefied biomass with PEF method detailed by impact categories and contribution of processes with the petcoke credits.

Table 12 Data of bio-oil with PEF method (contribution of processes with the petcoke credits).

Case Study	LHV liquefied biomass (GJ/ton)	Petcoke replaced (kg)	Mass (kg) to 1 GJ	Total environmental impact (mPt)
bio-oil Eucalyptus	21.06	193	47.49	3.04
bio-oil paper sludges	15.71	129	63.65	48.61
Petcoke	31.3			

Considering credits for replacing petcoke and the use of 2-EH as the solvent, the environmental impact of the production of bio-oil has decreased, despite its impact still being noticed.

In this case, the main contributor for these impacts is the 2-EH compound, but still has a smaller impact than cyclohexanol. Also, the most important impact categories are the same as before, fossil resources, climate change and the use of minerals and metals.

The impact is still greater for the bio-oil produced from paper sludges because it is necessary a greater amount of bio-oil to produce 1 GJ and a low amount of petcoke is replaced. This implies that the petcoke replaced will not have a prejudicial impact on the environment. Therefore, the greater the amount of petcoke replaced, the smaller the impact will be because it is being substituted by a biofuel (liquefied biomass) with a lower impact than petcoke.

5.2.1.4 Sensitivity analysis – influence of glycerine in the solvent

As previously demonstrated, the solvent used in the liquefaction process is the main contributor to the environmental impact of the bio-oil produced. Hence, new alternatives were searched to substitute 2-ethyl hexanol (2EH). A component that may be part of the solvent is glycerine, which has an influence on the solvent´s behaviour. The use of glycerine together with 2EH improves the homogenization of the medium, makes it possible to increase the process conversion and obtain value-added products with nitrogen. For this reason, the source of glycerine was analysed and its environmental impact was compared with 2EH. In order to compare solvent impact, the functional unit chosen was 1 kg solvent.

In *SimaPro*, it was selected glycerine from the market, glycerine obtained from the treatment of waste cooking oil, purification and an esterification reaction in France and the rest of the world (RoW), glycerine from a biodiesel plant and finally, 2-ethylhexanol. Figure 28 shows the environmental impact of 1 kg of each type of solvent as a single score in uPt with PEF methodology.

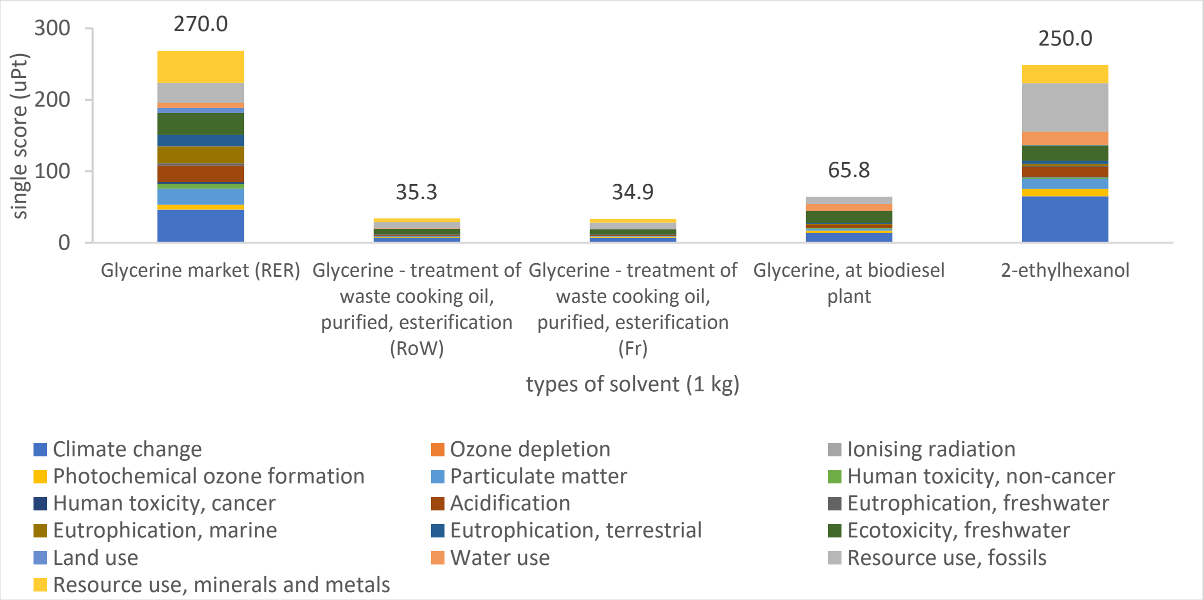


Figure 28 Comparison of the environmental impact of different types of glycerine and 2EH. RoW: rest of the world, Fr: France.

As can be seen, the glycerine from the market has the highest punctuation, which translates into a greater impact on the environment, and unviability for the process. The single score values of glycerine after treatment of waste cooking oil from France and the rest of the world are similar and the lowest. This comparison between France and the rest of the world was made to check if the results changed depending on the geographic location. Since the case study takes place in Portugal, the results from glycerine after treatment of waste cooking oil (RoW) are chosen to proceed with the study. As follows, a comparison of the environmental impact of bio-oil with different proportions of the solvents was done. The mixture of 2-EH and glycerine from the treatment of waste cooking oil are in the ratio of 1:0, 0.75:0.25, 0.50:0.50, 0.25:0.75 and 0:1, respectively. The results of this sensitivity analysis for the Eucalyptus and paper-sludges bio-oil are gathered in the following figures and tables.

Figure B 4 in Annexes (page 72) shows how this data was introduced in *SimaPro*, as an example for one case.

Figure 29 presents the results for biomass liquefaction with eucalyptus and Figure 30 the results with paper sludges. Table 13 and Table 14 display these data, respectively.

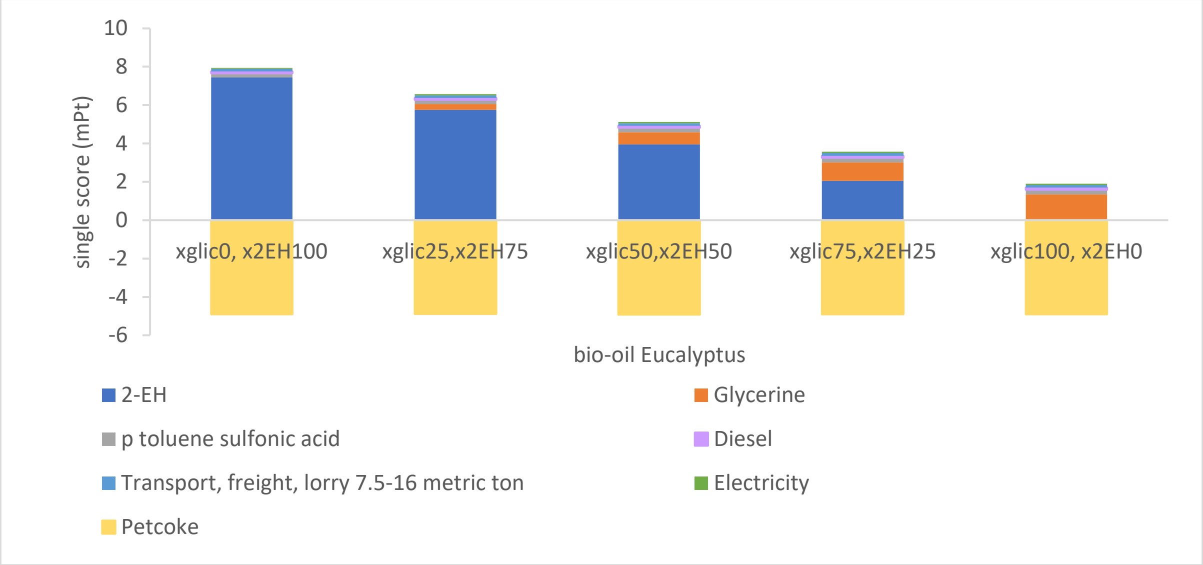


Figure 29 Influence of glycerine in the solvent with petcoke credits (bio-oil Eucalyptus).

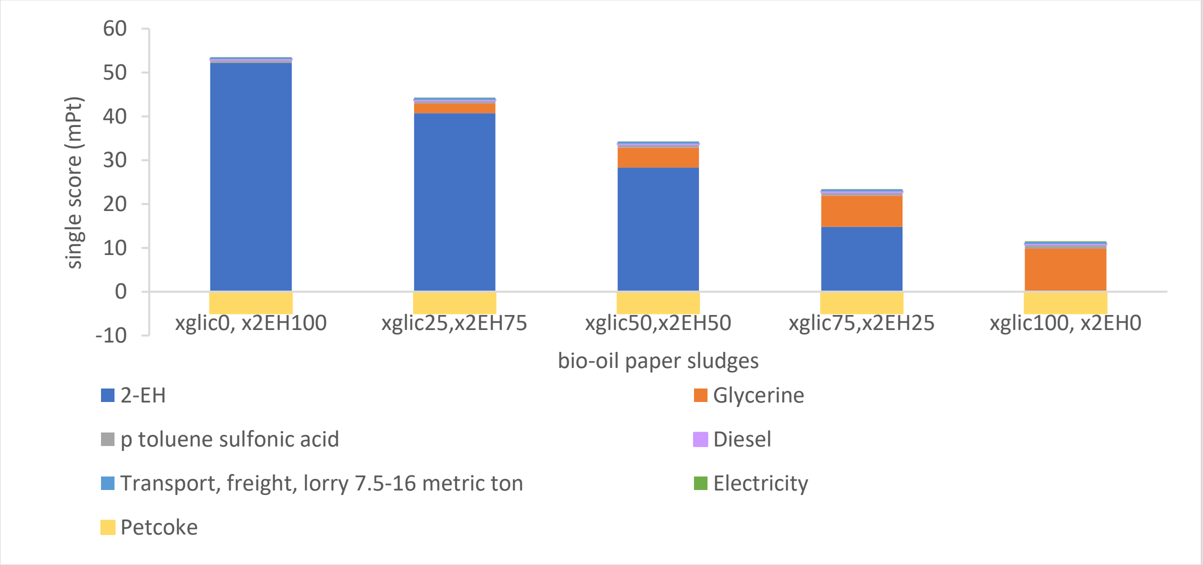


Figure 30 Influence of glycerine in the solvent with petcoke credits (bio-oil paper sludges).

This analysis allows us to confirm the positive impact of glycerine from waste cooking oil after treatment, purification and esterification. In fact, in the presence of glycerine, the impact has an inversely proportional relationship with it, i.e., as the proportion of glycerine increases, the environmental impact decreases.

Table 13 Influence of glycerine from waste cooking oil in the 2EH solvent (bio-oil Eucalyptus).

Solvent	LHV liquefied biomass (GJ/ton)	Petcoke replaced (kg)	Mass (kg) to 1GJ	Total environmental impact (mPt)
2EH	21.06	193	47.49	3.04
xglic25, x2EH75	20.44	187	48.93	1.67
xglic50, x2EH50	19.82	182	50.46	0.2
xglic75, x2EH25	19.20	176	52.10	-1.35
xglic100	18.57	170	53.84	-2.99
petcoke	31.3		31.95	.

Table 14 Influence of glycerine from waste cooking oil in the 2EH solvent (bio-oil Eucalyptus).

solvent	LHV liquefied biomass (GJ/ton)	Petcoke replaced (kg)	Mass (kg) to 1GJ	Total environmental impact (mPt)
2EH	15.71	129	63.65	48.6
xglic25, x2EH75	15.09	124	66.27	39.4
xglic50, x2EH50	14.47	118	69.11	29.4
xglic75, x2EH25	13.85	113	72.21	18.5
xglic100	13.23	108	75.60	6.6
petcoke	31.3	-	31.95	-

Under the same conditions, the impact of the bio-oil from paper industries is consistently higher. Once again, it is used more mass of bio-oil from paper sludges to produce 1 GJ and consequently, the amount of petcoke replaced is lower. Therefore, the greater the amount of petcoke replaced, the smaller the impact.

As said before, in *SimaPro* software, when the results are negative, they represent a positive impact on the environment. Specifically, in this case, because we introduce the credits for petcoke replacement, when the final single score has a negative value, it means that the environmental impact of the bio-oil is lower than the impact of petcoke, and it is beneficial to proceed with the substitution of an operation because it is reducing the impact.

For the case of bio-oil produced from Eucalyptus in BATCH mode, the presence of 75% of glycerine in the solvent seems to be the best option, since it has a reasonable value of LHV and a positive impact on the environment. Although the best score corresponds to the case when there is only glycerine, is not feasible because glycerine has a much higher viscosity than 2EH and therefore adds processing difficulties.

On the contrary, in the case of bio-oil obtained from paper sludges, the replacement of petcoke does not compensate for its impacts, since the impact score of the overall process is still positive, despite being lower. Even though, the best possible scenario corresponds to the case when the solvent is 2EH because it has the best LHV, as for the rest of the options their LCV is too low to be considerable.

5.2.2 Continuous process

By changing the study conditions, the life cycle study outcomes will be evaluated. Based on the values in Table 7 (page 37), the results obtained followed the PEF methodology, and all the conclusions are related to 1 GJ of liquefied biomass as a product.

5.2.2.1 PEF Methodology

Under continuous conditions, the outcomes in the environment are very different when compared to the previous ones. Initially, the credits of petcoke aren't considered, in order to prove the benefits of replacing it, as it is described in Figure 31.

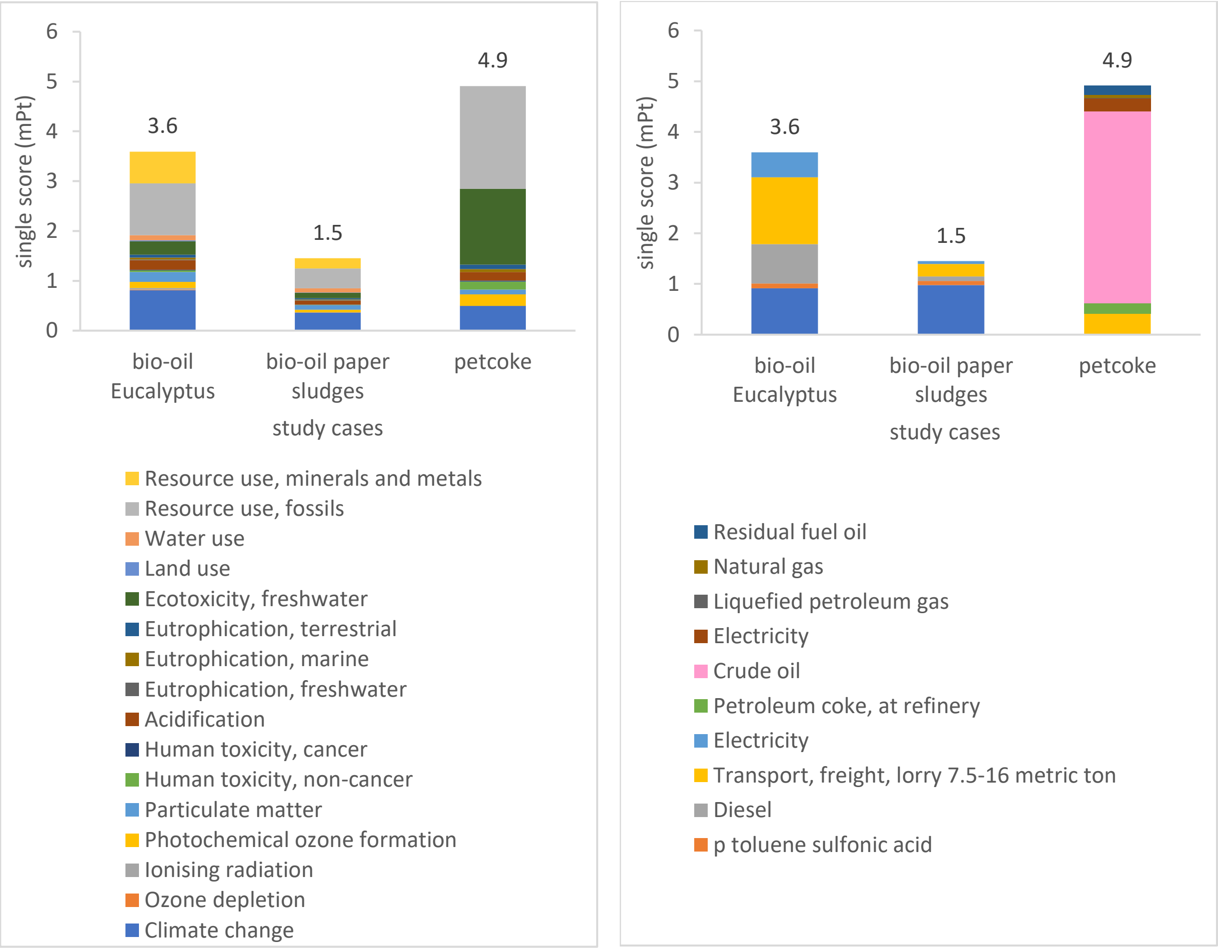


Figure 31 Comparison of the weighting values of impact categories of liquefied biomass with PEF method detailed by impact categories and contribution of processes without the petcoke credits.

Taking into consideration the environmental impacts of bio-oil, the liquefied biomass from Eucalyptus has a higher impact. This is a consequence of the smaller amount of solvent used when comparing the bio-oils proportionally. Since the major contributor is 2EH, by reducing its amount, the impact also decreases. This also suggests that the source type of the biomass has influence on the results.

It is still possible to state that the petcoke has the highest value of impact, even with a low amount of mass needed to produce energy. This indicates that petcoke has an appreciable impact, being advantageous to invest in its replacement.

The use of liquefied biomass should replace petroleum coke since the overall impact on the environment decreases. It allows the reduction of fossil resources (petroleum), promotes the use of biodegradable and ecological products, and contributes to the reduction of the emission of CO_2 to the atmosphere. Therefore, in Figure 32, the next case to be analysed takes into account the credits of the replacement of petcoke.

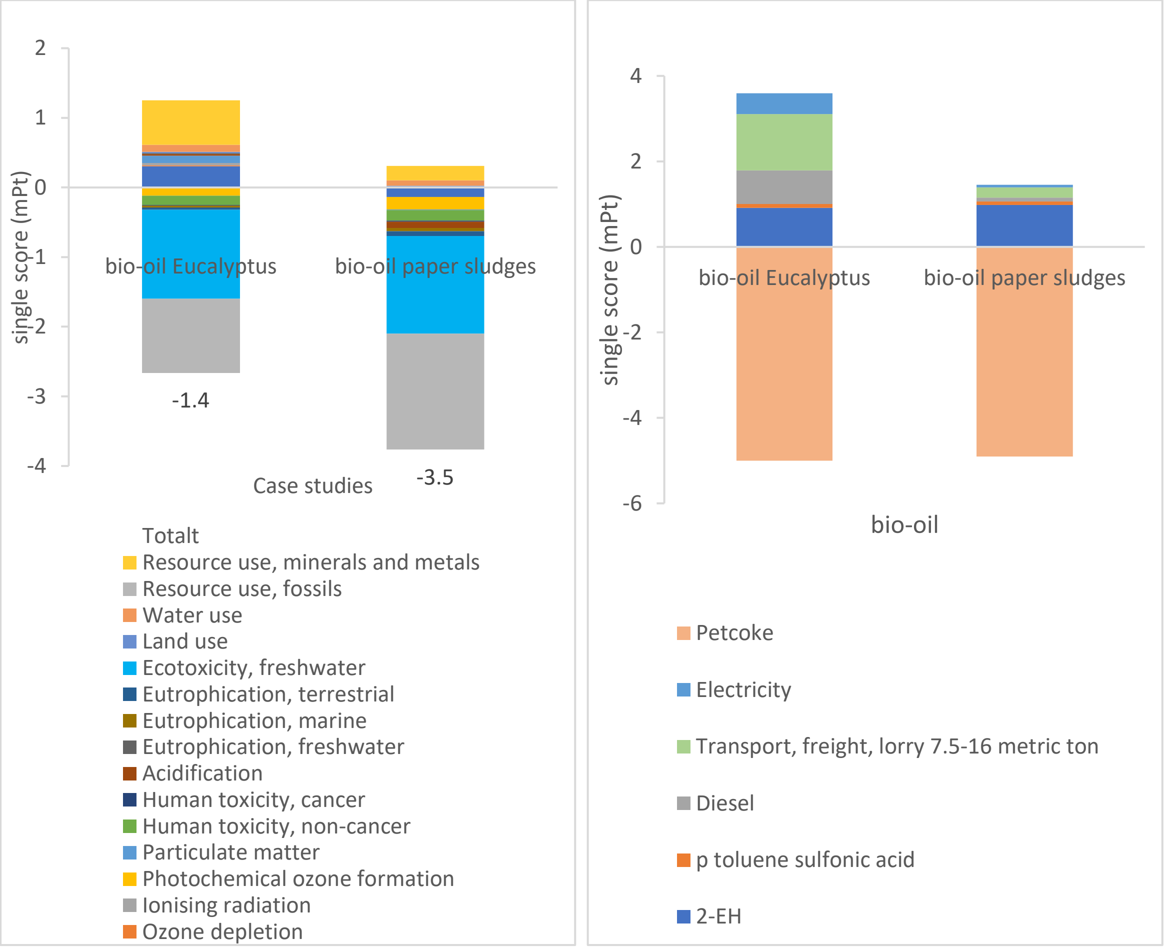


Figure 32 Comparison of the weighting values of impact categories of liquefied biomass with PEF method detailed by impact categories and contribution of processes with the petcoke credits.

As in the previous case, the bio-oil from Eucalyptus has a higher impact. This consequence is the result of a low amount of petcoke replaced. On the contrary, for the bio-oil from paper sludges the petcoke quantity replaced is considerable. Despite its lower impact, its LCV is too low, which corresponds to a need for a higher amount of this biofuel leading to an increased environmental impact.

Under continuous conditions, the biomass from Eucalyptus brings more benefits. Not only has a higher LCV but also has a lower environmental impact when substituting the petroleum coke. Since its value is negative, it means that it is advantageous this procedure.

5.2.2.2 Sensitivity analysis – influence of glycerine

As seen before for the batch conditions, it was favourable the introduction of glycerine in the solvent. Thus, the following analysis attempts to evaluate the influence of glycerine in the bio-oil in continuous mode.

The mixture of 2-EH and glycerine from the treatment of waste cooking oil are in the ratio of 1:0, 0.75:0.25, 0.50:0.50, 0.25:0.75 and 0:1, respectively. The results of this sensitivity analysis for the Eucalyptus and paper-sludges bio-oil are gathered in the following figures and tables (Figure 33, Figure 34 and Table 15,Table 16).

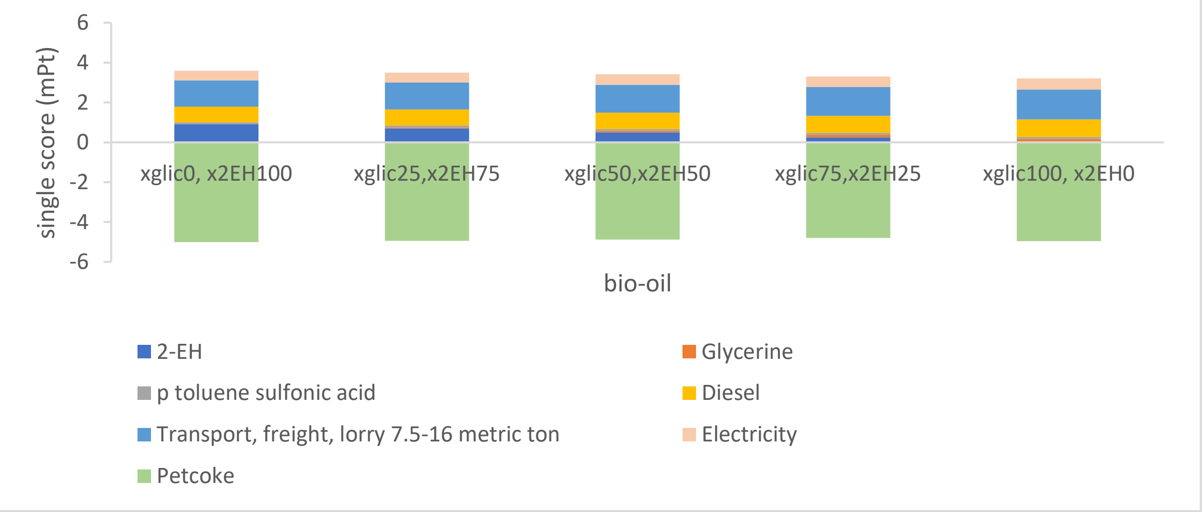


Figure 33 Influence of glycerine in the solvent with petcoke credits (bio-oil Eucalyptus).

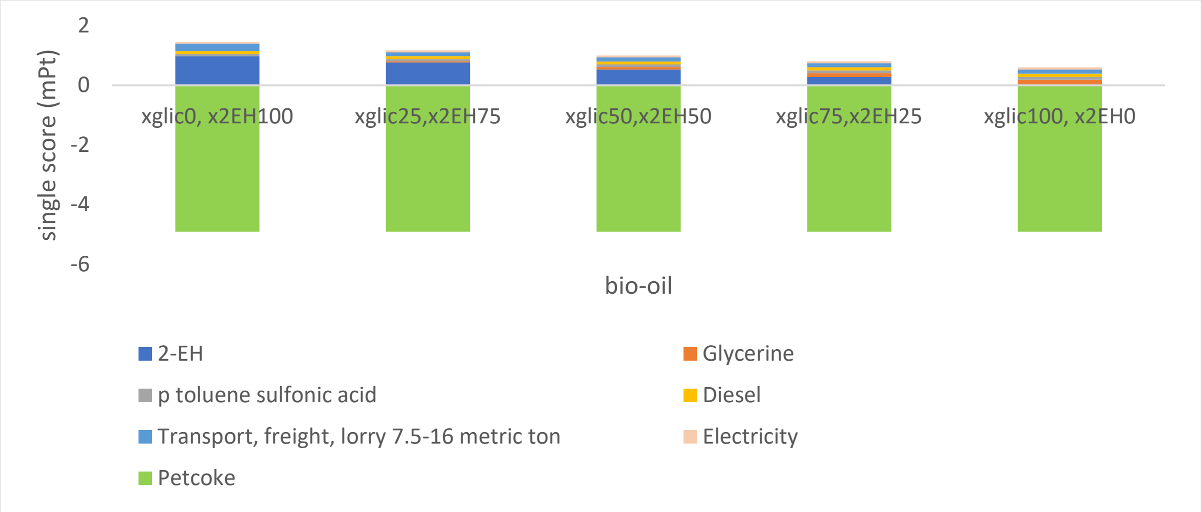


Figure 34 Influence of glycerine in the solvent with petcoke credits (bio-oil paper sludges).

Table 15 Influence of glycerine in the solvent with petcoke credits (bio-oil Eucalyptus).

solvent	LHV liquefied biomass (GJ/ton)	Biomass to replace petcoke (kg)	mass (kg) to produce 1GJ	Total environmental impact (mPt)
2EH	21.06	24	47.49	-1.41
xglic25, x2EH75	20.44	23	48.93	-1.43
xglic50, x2EH50	19.82	22	50.46	-1.46
xglic75, x2EH25	19.20	21	52.10	-1.49
xglic100	18.57	21	53.84	-1.76
petcoke	31.3			

Table 16 Influence of glycerine in the solvent with petcoke credits (bio-oil paper sludges).

solvent	LHV liquefied biomass (GJ/ton)	Biomass to replace petcoke (kg)	mass (kg) to produce 1GJ	Total environmental impact (mPt)
2EH	15.71	202	63.65	-3.45
xglic25, x2EH75	15.09	194	66.27	-3.74
xglic50, x2EH50	14.47	186	69.11	-3.91
xglic75, x2EH25	13.85	178	72.21	-4.10
xglic100	13.23	170	75.60	-4.30
petcoke	31.3			

It is possible to state that as the amount of glycerine increases and the amount of 2-EH decreases, the environmental impact also decreases. This consequence proves that it is beneficial to add glycerine to the solvent, as the overall environmental impact is reduced since the biggest contributor to the environmental impact is 2-EH.

The parameter of transport and 2-EH are the ones with the most expressive impact in Eucalyptus, considering the same premises used in BATCH mode. Additionally, the impact of bio-oil Eucalyptus is the highest even if it is beneficial for the environment. It can be also said that the best possible scenario accounts for 75% of glycerine and 25% of 2-EH, like in BATCH conditions.

For the bio-oil paper sludges, the impact is the lowest, but as said before, the LCV is too low to be considerable, so the best possible case corresponds to the use of 2-EH as solvent.

5.2.3 BATCH vs Continuous processes

From all the results previously discussed, taking into account the credits for the substitution and the best scenarios of each case, was made a comparison between them to evaluate the effect of the conditions (in Table 17).

Table 17 Comparison of the best scenario of bio-oil in BATCH and continuous mode.

	Bio-oil (Eucalyptus)	**Bio-oil (paper sludges)**
LCV (GJ/ton)	20.44	15.71
BATCH mode (mPt)	-1.35	48.6
Continuous mode (mPt)	-1.49	-3.45

The results obtained from continuous mode have a lower impact, associated with other benefits like less labour intensive or less processing and holding time. The overall impact is quite positive since the liquefied biomass production compensates for the bad impact of petroleum coke, principally in the continuous mode.

The impact under BATCH conditions is expected to be greater since initially it is required a greater amount of the components to start the process like the solvent or the catalyst. Furthermore, the liquefied biomass is only counted when the steady state is reached. In initial conditions, there aren´t reunited conditions to obtain the liquefied biomass with the properties needed, so until that stage is reached, the inputs of the process account for the impact. All these factors contribute negatively to the environment since there isn’t yet the bio-oil to compensate for these impacts.

6 Conclusions and future work

The main objective of this work was to evaluate the impact of the liquefied biomass production process. Different situations such as working conditions (BATCH and continuous), source of biomass (Eucalyptus and paper sludges) and presence of glycerine were studied. These sensitivity analyses allowed us to select the best options for the bio-oil.

Based on the analysis carried out, it was concluded that it is advantageous to replace petcoke with liquefied biomass, whatever the source. When replacing petroleum coke, the categories with the biggest saves correspond to the use of fossil resources and water use. Even so, eucalyptus residues are preferred as a source because it has the highest LCV. The best scenario for this type of bio-oil in both BATCH and continuous conditions corresponds to the case where the glycerine is 75% of the solvent. Taking into account the credits for the replacement of petroleum coke, the environmental impact is -1.35 mPt (BATCH) and -1.49 mPt (continuous). For the paper sludges case, the best possible case has a single score of 48.6 mPt for BATCH and a single score of -3.45 mPt in continuous conditions. Once again, it is valued the optimum LCV.

In conclusion, the liquefied biomass produced is a viable option to replace the petcoke in the cement line, despite the higher amounts of fuel needed and the dependence on the biomass, since it is used on a large scale.

During all the work it was noticed that the major impact was due to the solvent, whether cyclohexanol or 2-ethylhexanol. In future work, it is suggested to substitute this solvent with other with low or no impact, for example, as a result of another process. If this hypothetical situation occurs the solvent wouldn't carry any environmental burden associated, since it can be considered a waste product.

It is still suggested to use more different types of biomass sources, since it enables to give a second life to residues/waste, preventing its accumulation; promotes the reduction in the consumption of liquid fuels derived from petroleum, avoiding the emission of compounds harmful to ecosystems and consequently the environmental impact.

The impact of 2-ethyl hexanol obtained was an estimate since there was no data regarding it in *SimaPro*. Thus, to obtain reliable results when this compound is used in an LCA, a more in-depth study and research should be carried out in order to reduce the uncertainty of the results.

Finally, in terms of research, it is important to continue the assessment of the quantification of impacts, consolidating the data used and assumptions used, covering a greater number of organizations and data, including impacts and costs in order to facilitate the comparison of results globally.

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Annexes

Annex A - Impact categories considered for each method

Table A. 1 ReCiPe impact categories and their unit of measurement, with a short description. kg CFC-11 eq: kg equivalent of trichlorofluoromethane; kg 14-DCB eq: kg of 1,4-dichlorobenzene equivalents; kg U235 eq: kg of Uranium-235.

Impact category	Unit	Description
Ozone depletion	kg CFC-11 eq.	Ozone depletion is the gradual thinning of the earth's ozone layer in the upper atmosphere caused by the release of chemical compounds containing gaseous chlorine or bromine from industry and other human activities. This is a problem because it increases the amount of UV radiation that reaches the earth's surface, leading to cases of skin cancer, eye cataracts or genetic and immune system damage. The characterization factor for ozone layer depletion accounts for the destruction of the stratospheric ozone layer by anthropogenic emissions of ozone-depleting substances (ODS).
Human toxicity and ecotoxicity	kg 14-DCB eq.	Emission inventories of different products may contain chemicals, of which many will have the potential to cause toxic impacts on human beings and/or ecosystems.[49] The characterization factor of human toxicity and ecotoxicity accounts for the environmental persistence (fate) and accumulation in the human food chain (exposure), and toxicity (effect) of a chemical. 14-DCB:1,4-dichlorobenzene
Ionizing Radiation	kg U235 eq.	According to World Health Organization, ionizing radiation is radiation with enough energy to remove tightly bound electrons from the orbit of an atom. Some examples are X-ray, IV light, and UV light. Only the energy from ionizing radiation that is imparted to (or absorbed by) the human body can cause harm to health. The characterization factor of ionizing radiation accounts for the level of exposure. U235: Uranium-235

Table A.1 (cont.) ReCiPe impact categories and their unit of measurement, with a short description. kg NMOV: kg of Non-Methane Volatile Organic Compounds; kg PM10 eq: kg of Particulate matter equivalents; kg CO_2 eq: kg of equivalent of carbon dioxide; m^2: square meter.

Photochemical oxidant formation	kg NMVOC	Photochemical oxidants are formed through the concentration of a variety of highly reactive gases in the atmosphere and are often implicated in problems of smog, crop damage and the degradation of monuments. The characterization factor is defined as the marginal change in the 24h-average European concentration of ozone due to a marginal change in emission of substance x. NMVOC: Non-methane volatile organic compounds
Particulate matter formation	kg PM10 eq.	Particulate matter (PM) corresponds to solid particles and liquid droplets in the air. Generally, any type of burning or dust-generating activity is a PM source. PM_{10} includes particles 10 micrometres in diameter and smaller. The ReCiPe characterization factor of particulate matter formation is the intake fraction of PM_{10}.
Climate change	kg CO_2 eq.	The main driver of climate change is the greenhouse effect. Burning fossil fuels, cutting down forests and farming livestock are increasingly influencing the climate and the earth's temperature. The characterization factor of climate change is the global warming potential.
Agricultural and urban land occupation	m^2	The amount of either agricultural land or urban land occupied for a certain time.
Natural land transformation	m^2	The amount of natural land transformed and occupied for a certain time.

Table A. 1 (cont.) ReCiPe impact categories and their unit of measurement, with a short description. kg N eq: kg of equivalent of nitrogen; kg P eq: kg of equivalent of phosphorus; kg Fe eq: kg of equivalent of iron; m3: cubic meter.

Marine eutrophication	kg N eq	Marine eutrophication can be defined as a response of the marine ecosystem to the increased availability of a limiting nutrient in the euphotic zone of marine waters. [50] The characterization factor of marine eutrophication accounts for the environmental persistence (fate) of the emission of N-containing nutrients.
Freshwater eutrophication	kg P eq	Freshwater eutrophication occurs due to the discharge of nutrients into the soil or into freshwaters and the subsequent rise in nutrient levels (namely, phosphorus and nitrogen). A sequence of ecological impacts offset occurs by increasing nutrient emissions into freshwater, thereby increasing nutrient uptake by autotrophic organisms (cyanobacteria and algae) and potential losses to biodiversity. The characterization factor of freshwater eutrophication accounts for the environmental persistence (fate) of the emission of phosphorus (P) - containing nutrients.
Fossil fuel depletion	kg oil eq.	Fossil fuel depletion is the reduction in the future availability of fossil fuels caused by the primary extraction of fossil fuels linked to fuel use, energy use and to produce other inputs. The characterization factor of fossil depletion is the amount of extracted fossil fuel extracted, based on the lower heating value.
Minerals depletion	kg Fe eq.	The depletion of minerals is a decrease in initial reserves and a discrepancy between the norms for the extraction of natural resources and the needs of mankind. The characterization factor for mineral depletion is the decrease in grade.
Freshwater depletion	m^3	Freshwater depletion means a drastic reduction in the total amount of usable water due to human activities and changes in the environment. The factor for freshwater depletion is the amount of freshwater consumption.

Table A. 2 PEF impact categories and their unit of measurement, with a short description. kg CO_2 eq: kg of carbon dioxide equivalents; kg CFC-11 eq: kg equivalent of trichlorofluoromethane; CTUh: Comparative Toxic Unit for humans; kg $PM_{2.5}$ eq: kg of particulate matter with a diameter of less than 2.5 micrometres equivalents; kg U235 eq: kg of Uranium-235.

Impact category	Unit	Description
Climate change	kg CO_2 eq.	Climate change refers to the long-term alteration of temperature and typical weather patterns in one place. The indicator corresponds to Global Warming Potentials with a time horizon of 100 years (GWP_{100}). These values include the carbon feedback for different substances.
Ozone depletion	kg CFC-11 eq.	The description is the same as ReCiPe impact category.
Human toxicity, cancer	CTUh	According to European Commission, this impact category accounts for the adverse health effects on human beings caused by the intake of toxic substances related to cancer. Comparative Toxic Unit for humans (CTUh) expresses the estimated increase in morbidity in the total human population per unit mass of a chemical emitted (cases per kilogramme).
Human toxicity, non-cancer	CTUh	According to European Commission, this impact category accounts for the adverse health effects on human beings caused by the intake of toxic substances as they are related to non-cancer effects that are not caused by respiratory inorganics or ionising radiation.
Particulate matter/ Respiratory inorganics	kg $PM_{2.5}$ eq	It aims at assessing damage to human health from outdoor and indoor emissions of primary and secondary PM $_{2.5}$ in urban and rural areas.
Ionising radiation, human health	kbq U235 eq	The description is the same as ReCiPe impact category.

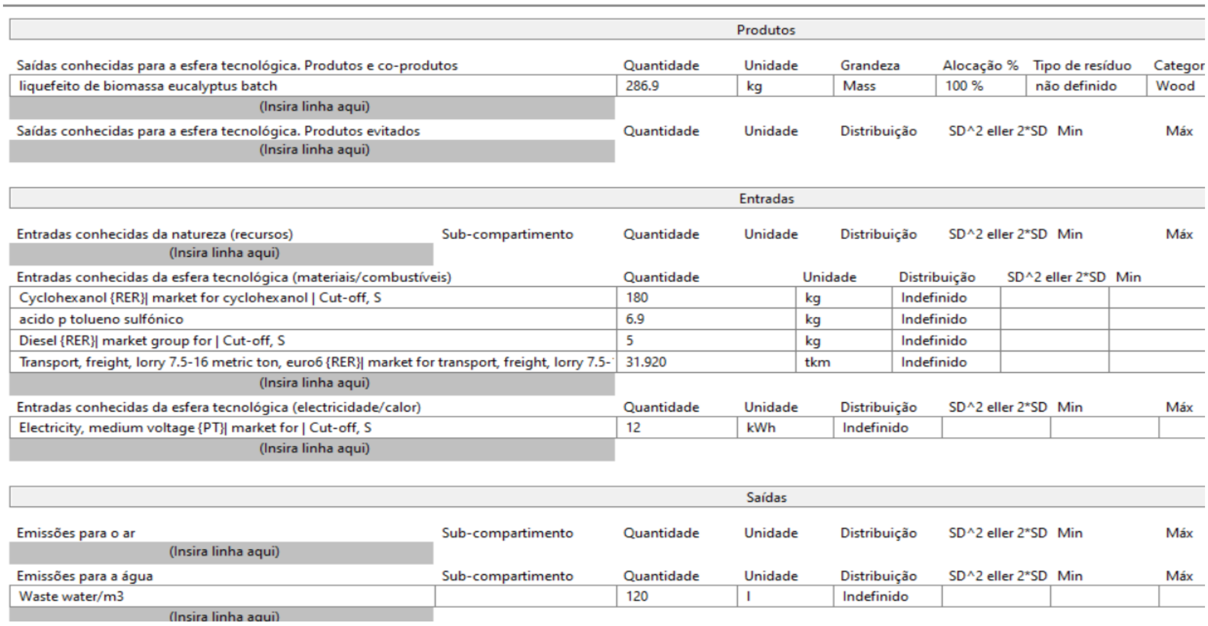
Table A. 2 (cont.) PEF impact categories and their unit of measurement, with a short description. kg NMOV: kg of Non-Methane Volatile Organic Compounds; mol H+ eq: Units of mole of H+ equivalents per kg of product; mol N eq: equivalent of moles of nitrogen; kg P eq: kg equivalent phosphorus; kg N eq: kg equivalent nitrogen; kg C deficit: soil organic carbon deficit in kg.

Photochemical ozone formation, human health	kg NMVOC eq.	Impact category that accounts for the formation of ozone at the ground level of the troposphere caused by photochemical oxidation of Volatile Organic Compounds (VOCs) and carbon monoxide (CO) in the presence of nitrogen oxides (NOx) and sunlight. It is expressed with the potential contribution to photochemical ozone formation.
Acidification	mol H^+ eq.	Impact category that addresses impacts due to acidifying substances in the environment. Emissions of NO_x, NH_3 and SO_x lead to releases of hydrogen ions (H+) when the gases are mineralised. Accumulated Exceedance (AE) characterises the change in critical load exceedance of the sensitive area in terrestrial and main freshwater ecosystems, in which acidifying substances deposit. mol H+ eq corresponds to units of mole of H+ equivalents per kg of product.
Terrestrial eutrophication	mol N eq.	Process of enrichment of soil by nutrients. AE characterises the change in critical load exceedance of the sensitive area, to which eutrophying substances deposit.
Freshwater eutrophication	kg P eq.	P equivalents express the degree to which the emitted nutrients reach the freshwater end compartment (phosphorus considered as limiting factor in freshwater).
Marine eutrophication	kg N eq.	N equivalents express the degree to which the emitted nutrients reach the marine end compartment (nitrogen considered as limiting factor in marine water).
Land use	kg C deficit	A greenhouse gas inventory sector that covers emissions resulting from direct human-induced land use, land-use change and forestry activities. kg C deficit: soil organic carbon deficit in kilograms.

Table A. 2 (cont.) PEF impact categories and their unit of measurement, with a short description. CTUe: Comparative Toxic Units for ecosystem; m3 water eq: equivalent volume of water; kg Sb eq: kg equivalent of antimony.

Ecotoxicity freshwater	CTUe	Ecotoxicity of freshwater attempts to understand the overall pollution to freshwater from air, land (pesticides) and chemicals released in water. [51] CTUe expresses an estimate of the potentially affected fraction of species integrated over time and volume per unit mass of a chemical emitted.
Water scarcity	m^3 water eq.	Water scarcity corresponds to the lack of freshwater resources to meet the standard water demand.
Resource use, energy carriers	kg Sb eq.	Abiotic resource depletion fossil fuels (ADP-fossil); based on lower heating value
Resource use, minerals and metals	kg Sb eq.	Abiotic resource depletion (ADP ultimate reserve). This factor is derived for each extraction of elements, with the depletion of the element antimony as a reference.

Annex B – *SimaPro* Print Screens



Produtos

Saídas conhecidas para a esfera tecnológica. Produtos e co-produtos	Quantidade	Unidade	Grandeza	Alocação %	Tipo de resíduo	Categor
liquefeito de biomassa eucalyptus batch	286.9	kg	Mass	100 %	não definido	Wood
(Insira linha aqui)						

Saídas conhecidas para a esfera tecnológica. Produtos evitados	Quantidade	Unidade	Distribuição	SD^2 eller 2*SD	Min	Máx
(Insira linha aqui)						

Entradas

Entradas conhecidas da natureza (recursos)	Sub-compartimento	Quantidade	Unidade	Distribuição	SD^2 eller 2*SD	Min	Máx
(Insira linha aqui)							

Entradas conhecidas da esfera tecnológica (materiais/combustíveis)	Quantidade	Unidade	Distribuição	SD^2 eller 2*SD	Min
Cyclohexanol {RER}| market for cyclohexanol | Cut-off, S	180	kg	Indefinido		
acido p tolueno sulfónico	6.9	kg	Indefinido		
Diesel {RER}| market group for | Cut-off, S	5	kg	Indefinido		
Transport, freight, lorry 7.5-16 metric ton, euro6 {RER}| market for transport, freight, lorry 7.5-	31.920	tkm	Indefinido		
(Insira linha aqui)					

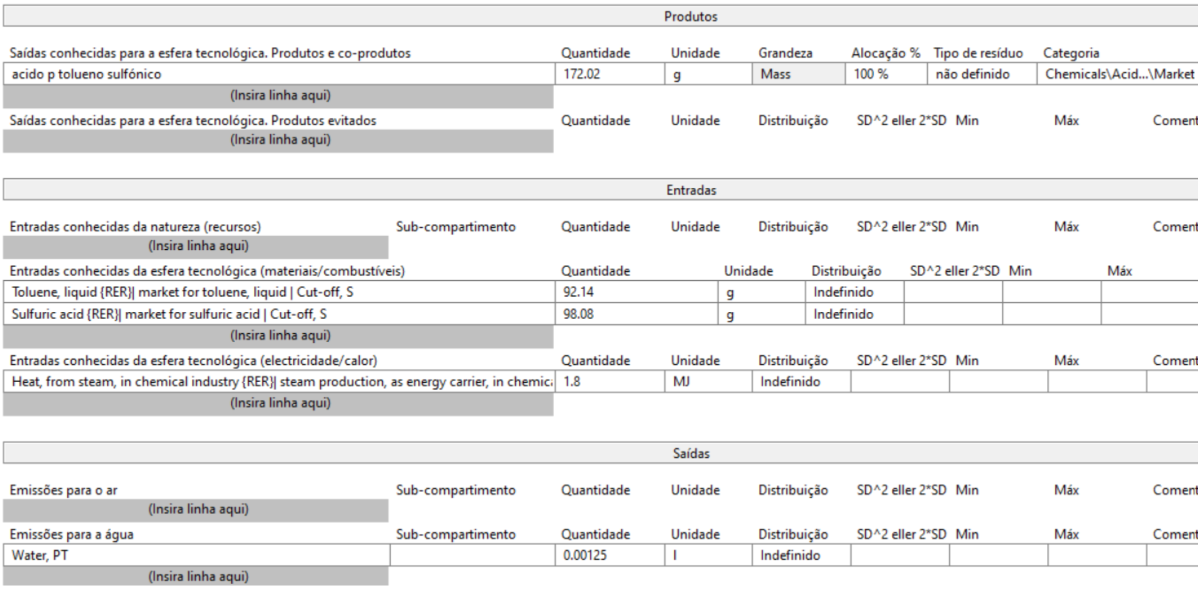
Entradas conhecidas da esfera tecnológica (electricidade/calor)	Quantidade	Unidade	Distribuição	SD^2 eller 2*SD	Min	Máx
Electricity, medium voltage {PT}| market for | Cut-off, S	12	kWh	Indefinido			
(Insira linha aqui)						

Saídas

Emissões para o ar	Sub-compartimento	Quantidade	Unidade	Distribuição	SD^2 eller 2*SD	Min	Máx
(Insira linha aqui)							

Emissões para a água	Sub-compartimento	Quantidade	Unidade	Distribuição	SD^2 eller 2*SD	Min	Máx
Waste water/m3		120	l	Indefinido			
(Insira linha aqui)							

Figure B 1 Inputs/ outputs of bio-oil Eucalyptus (BATCH mode) in *SimaPro* software in Chapter 5.1.6.1, page 35.



Produtos

Saídas conhecidas para a esfera tecnológica. Produtos e co-produtos	Quantidade	Unidade	Grandeza	Alocação %	Tipo de resíduo	Categoria
acido p tolueno sulfónico	172.02	g	Mass	100 %	não definido	Chemicals\Acid...\Market
(Insira linha aqui)						

Saídas conhecidas para a esfera tecnológica. Produtos evitados	Quantidade	Unidade	Distribuição	SD^2 eller 2*SD	Min	Máx	Coment
(Insira linha aqui)							

Entradas

Entradas conhecidas da natureza (recursos)	Sub-compartimento	Quantidade	Unidade	Distribuição	SD^2 eller 2*SD	Min	Máx	Coment
(Insira linha aqui)								

Entradas conhecidas da esfera tecnológica (materiais/combustíveis)	Quantidade	Unidade	Distribuição	SD^2 eller 2*SD	Min	Máx
Toluene, liquid {RER}| market for toluene, liquid | Cut-off, S	92.14	g	Indefinido			
Sulfuric acid {RER}| market for sulfuric acid | Cut-off, S	98.08	g	Indefinido			
(Insira linha aqui)						

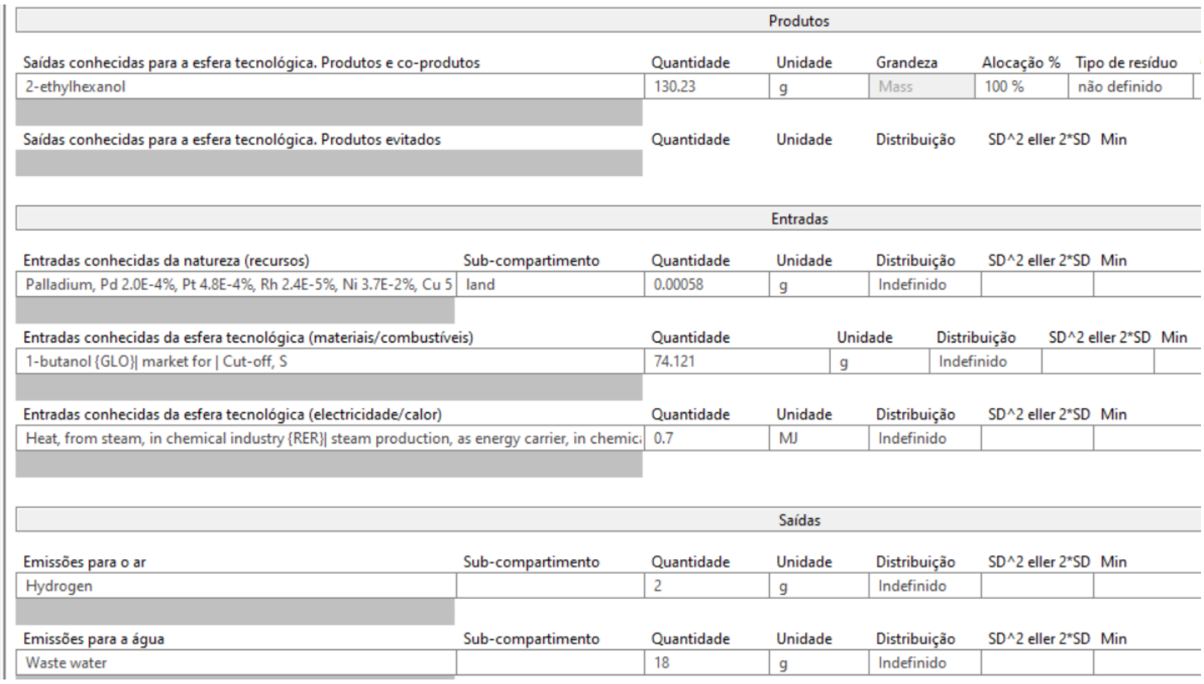
Entradas conhecidas da esfera tecnológica (electricidade/calor)	Quantidade	Unidade	Distribuição	SD^2 eller 2*SD	Min	Máx	Coment
Heat, from steam, in chemical industry {RER}| steam production, as energy carrier, in chemic	1.8	MJ	Indefinido				
(Insira linha aqui)							

Saídas

Emissões para o ar	Sub-compartimento	Quantidade	Unidade	Distribuição	SD^2 eller 2*SD	Min	Máx	Coment
(Insira linha aqui)								

Emissões para a água	Sub-compartimento	Quantidade	Unidade	Distribuição	SD^2 eller 2*SD	Min	Máx	Coment
Water, PT		0.00125	l	Indefinido				
(Insira linha aqui)								

Figure B 2 Inputs/ outputs of p toluene sulfonic acid in *SimaPro* software in Chapter 5.1.6.1, page 35.



Produtos

Saídas conhecidas para a esfera tecnológica. Produtos e co-produtos	Quantidade	Unidade	Grandeza	Alocação %	Tipo de resíduo
2-ethylhexanol	130.23	g	Mass	100 %	não definido

Saídas conhecidas para a esfera tecnológica. Produtos evitados	Quantidade	Unidade	Distribuição	SD^2 eller 2*SD	Min

Entradas

Entradas conhecidas da natureza (recursos)	Sub-compartimento	Quantidade	Unidade	Distribuição	SD^2 eller 2*SD	Min
Palladium, Pd 2.0E-4%, Pt 4.8E-4%, Rh 2.4E-5%, Ni 3.7E-2%, Cu 5	land	0.00058	g	Indefinido		

Entradas conhecidas da esfera tecnológica (materiais/combustíveis)	Quantidade	Unidade	Distribuição	SD^2 eller 2*SD	Min
1-butanol {GLO}| market for | Cut-off, S	74.121	g	Indefinido		

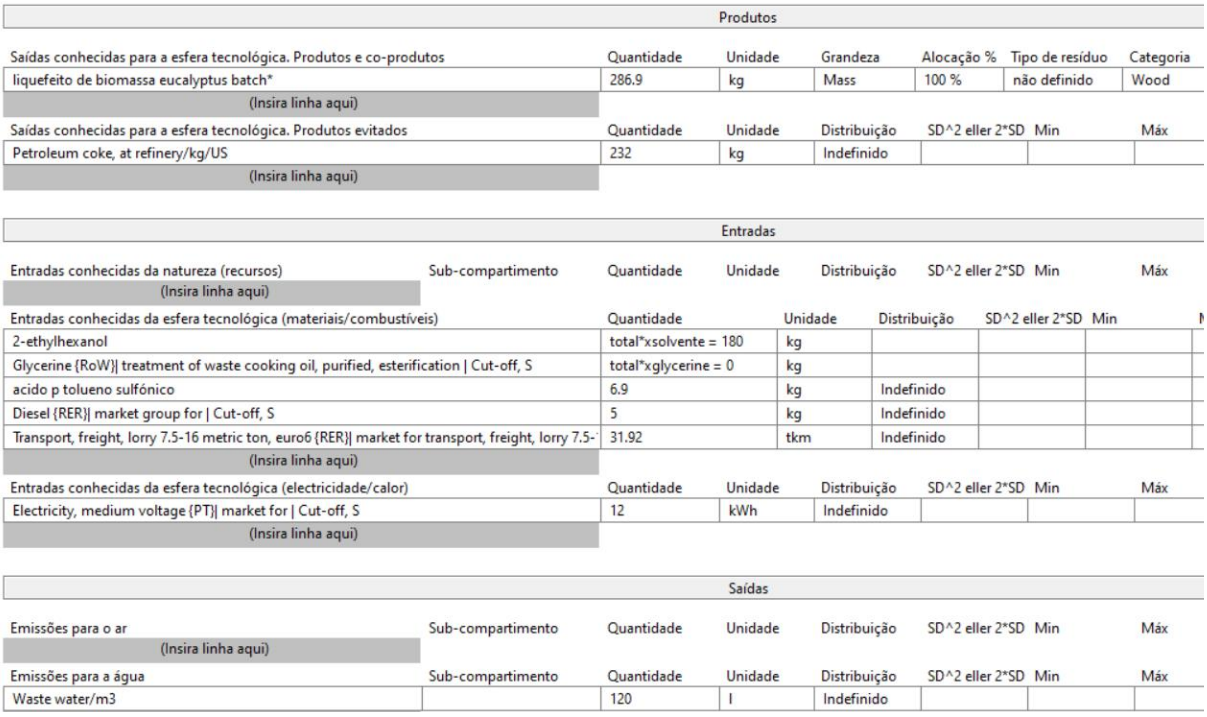
Entradas conhecidas da esfera tecnológica (electricidade/calor)	Quantidade	Unidade	Distribuição	SD^2 eller 2*SD	Min
Heat, from steam, in chemical industry {RER}| steam production, as energy carrier, in chemic	0.7	MJ	Indefinido		

Saídas

Emissões para o ar	Sub-compartimento	Quantidade	Unidade	Distribuição	SD^2 eller 2*SD	Min
Hydrogen		2	g	Indefinido		

Emissões para a água	Sub-compartimento	Quantidade	Unidade	Distribuição	SD^2 eller 2*SD	Min
Waste water		18	g	Indefinido		

Figure B 3 Inputs/ outputs of 2-ethyl hexanol in *SimaPro* software in Chapter 5.2.1.3, page 48.



Produtos

Saídas conhecidas para a esfera tecnológica. Produtos e co-produtos	Quantidade	Unidade	Grandeza	Alocação %	Tipo de resíduo	Categoria
liquefeito de biomassa eucalyptus batch*	286.9	kg	Mass	100 %	não definido	Wood
(Insira linha aqui)						

Saídas conhecidas para a esfera tecnológica. Produtos evitados	Quantidade	Unidade	Distribuição	SD^2 eller 2*SD	Min	Máx
Petroleum coke, at refinery/kg/US	232	kg	Indefinido			
(Insira linha aqui)						

Entradas

Entradas conhecidas da natureza (recursos)	Sub-compartimento	Quantidade	Unidade	Distribuição	SD^2 eller 2*SD	Min	Máx
(Insira linha aqui)							

Entradas conhecidas da esfera tecnológica (materiais/combustíveis)	Quantidade	Unidade	Distribuição	SD^2 eller 2*SD	Min	M
2-ethylhexanol	total*xsolvente = 180	kg				
Glycerine {RoW}| treatment of waste cooking oil, purified, esterification | Cut-off, S	total*xglycerine = 0	kg				
acido p tolueno sulfónico	6.9	kg	Indefinido			
Diesel {RER}| market group for | Cut-off, S	5	kg	Indefinido			
Transport, freight, lorry 7.5-16 metric ton, euro6 {RER}| market for transport, freight, lorry 7.5-	31.92	tkm	Indefinido			
(Insira linha aqui)						

Entradas conhecidas da esfera tecnológica (electricidade/calor)	Quantidade	Unidade	Distribuição	SD^2 eller 2*SD	Min	Máx
Electricity, medium voltage {PT}| market for | Cut-off, S	12	kWh	Indefinido			
(Insira linha aqui)						

Saídas

Emissões para o ar	Sub-compartimento	Quantidade	Unidade	Distribuição	SD^2 eller 2*SD	Min	Máx
(Insira linha aqui)							

Emissões para a água	Sub-compartimento	Quantidade	Unidade	Distribuição	SD^2 eller 2*SD	Min	Máx
Waste water/m3		120	l	Indefinido			

Figure B 4 Inputs/ outputs of bio-oil Eucalyptus xglic0, x2H100 with petcoke credits (BATCH mode) in *SimaPro* software in Chapter 5.2.1.4, page 51.