MSc Thesis

From lignin to marine biofuel

A market potential and GHG assessment of the most suitable conversion routes in Brazil and Scandinavia.

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Executive summary

Introduction

The shipping sector generates large quantities of greenhouse gas (GHG) emissions; in 2012, it emitted roughly 2.5% of the global GHG emissions. This is projected to increase with 50 to 250% by 2050 for the "business-as-usual" scenario. To help mitigate climate change, the CO_2 emission target for 2050 for the shipping sector should be between -78% and –94% compared to 2005 emissions (taking the EU target path as a reference). Marine drop-in biofuels from lignin could be a promising solution to reduce the GHG emissions from the shipping industry. Large quantities of marine biofuels are demanded to meet the large marine biofuel market. Additionally, biofuels should have lower life cycle GHG emission than the currently used fuels, in order to lead to a reduction in GHG emissions of the sector. To the best of our knowledge, no previous studies focused on the supply market or GHG emissions of lignin conversion to marine biofuel. Therefore, this thesis aims to assess the lignin supply market and the biofuel potential from lignin on a global scale, both for the current situation as for the expected situation in ten years. The ten year period is considered a realistic timeframe for the commercialisation of this process. Furthermore, this thesis aims to assess the GHG emissions resulting from the lignin conversion processes (the direct emissions) and the GHG emissions in the life cycle of other products that are caused by introducing the lignin conversion (the indirect emissions). These GHG emissions were only assessed for two most suitable case studies, with respect to technical and economic aspects. Brazil and Scandinavia were the chosen locations, because they have an intensive biomass industry and GoodFuels has connections and projects in these regions. The most suitable conversion routes to produce marine biofuels from lignin in Brazil and in Scandinavia had to be determined first.

This research answers the following research questions:

1. What does the current global lignin supply market look like and what is the current global marine biofuel potential? How is this expected to evolve over the next ten years?
2. What is the most suitable conversion route available for marine biofuel production from lignin?
3. How much direct GHG emissions (in g CO_2-eq/marine biofuel) are produced with the most promising lignin-to-marine biofuel conversion routes in Brazil and in Scandinavia?
4. How much indirect GHG emissions (in g CO_2-eq/MJ marine biofuel) are produced with the most promising lignin-to-marine biofuel conversion routes in Brazil and in Scandinavia?

This project will contribute to the knowledge on producing marine biofuels from lignin, which could support the biofuel industry in commercialising the marine biofuel production from lignin and thereby help reduce the GHG emissions from the shipping sector. An Excel tool was built to easily calculate new results if future developments or insights should change the variables. This research was performed in cooperation with GoodFuels, a company that is active in sales, marketing, trading and development of truly sustainable fuels.

Methods

The applied methods are shortly described per research question.

1) To assess the lignin supply market, both now and in ten years, literature research was performed on the quantity of lignin, location, feedstock type and separation process for the lignin streams. Also, the current use of the lignin, the location of some of the larger individual lignin sources and the expected change in the production and separation processes of lignin within ten years was investigated. Combining this information provided a picture of the lignin supply market. The biofuel potential was calculated from the quantity of lignin available and the calculated yield of biofuel per tonne of lignin (for research question 3).

2) The most suitable conversion route was determined through literature research and a multi criteria analysis (MCA). A MCA was performed on the main conversion technologies (e.g. pyrolysis or hydrothermal liquefaction), based on the criteria and weights presented in Table 1. The most suitable isolation process and upgrading process were subsequently determined based on the literature research. The optimal feedstock lignin was determined based on quantity, sulphur content and location. A lignin source, providing the most suitable lignin, was appointed in each of the two geographies (Brazil and Scandinavia), based on quantity and location.

Table 1: The criteria and weights that were considered for the MCA.

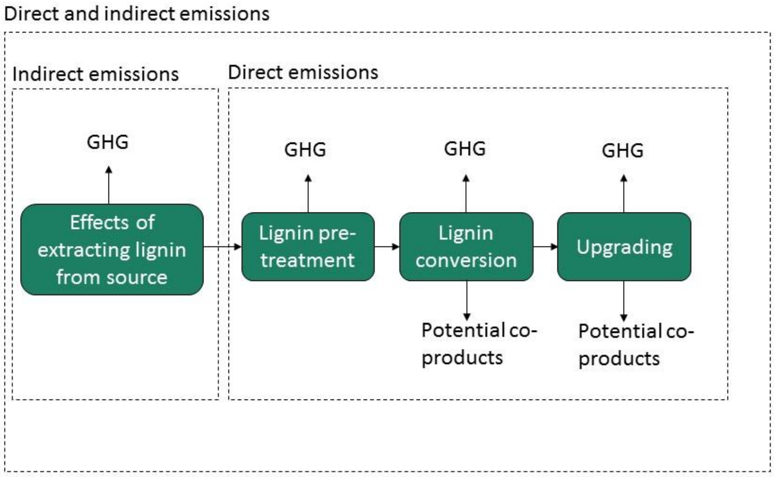
Criterion	Weight
App. costs	0,46
Market status	0,26
Quality biofuel	0,16

Bio-crude yield	0,09
Valuable by-products	0,04

3) For research questions 3 and 4, the same methods applied. The direct and indirect GHG emissions were assessed for the two optimal conversion routes, through a life cycle GHG assessment, following the ISO14040 guidelines. A base case configuration was made for both conversion routes, including the process assumptions, e.g. use of the by-products, source of hydrogen and source of electricity. The goal of this life cycle assessment (LCA) is to assess the direct and indirect GHG emissions that are associated with the conversion of lignin into a drop-in marine biofuel, and to assess the reduction compared to the currently used fuel. This research regards the environmental consequences of the future change in lignin use, so a consequential LCA was performed. The system boundaries of the LCA are presented in Figure 1. The only environmental impact that was considered were the GHG emissions. The functional unit is **g CO_2-eq/ MJ marine biofuel**, and the minimum required properties for the biofuel were defined as follows:
    1. Sulphur content (0.1 wt.%)
    2. Oxygen content (effective H/C ratio of 1.4)
    3. Carbon number (effective H/C ratio of 1.4)
    4. Water content (<1 wt.%)

An Excel tool was created to assess the in- and outputs of the processes. Mass and energy balances of the complete conversion routes were created to test the conservation of mass and energy in the calculation. The GHG emissions of each of the conversion routes were calculated with the relevant CO2-eq emission factors. The uncertainty and sensitivity of the results was analysed through a Monte Carlo simulation.

Figure 1: The system boundaries for the LCA



Results

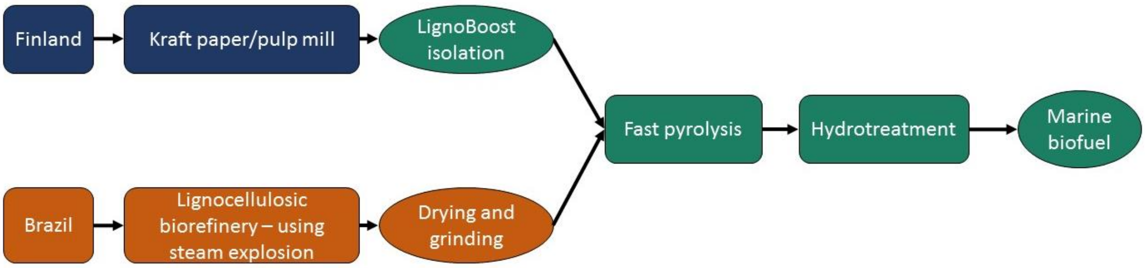
1) The total available lignin is currently approximately 50 – 70 Mt of lignin from paper/pulp mills (mostly Kraft lignin) and 0.16 Mt of lignin from lignocellulosic biorefineries (mostly steam explosion (SE) lignin). The yield of stabilised biofuel per tonne of Kraft lignin was calculated to be 0.25 t (dry oil) and for steam explosion lignin it was 0.29 t (dry oil). Therefore the current potential of biofuel is approximately **12.6 – 17.6 Mt of biofuel per year.** In ten years, the lignin production is projected to expand to 62.5-87.5 Mt from paper/pulp mills and 10.65 Mt of lignin from lignocellulosic biorefineries, the biofuel potential will also increase. Assuming the same yields, the future biofuel potential is estimated at **18.7 – 25.0 Mt of biofuel per year.**

The current marine fuel consumption was estimated between 250 and 325 Mt/yr. Taking the median of both the biofuel production and total fuel consumption and assuming that one tonne of biofuel can replace one tonne of fossil fuel, the current potential market share of the biofuels is roughly **5.2%** of total maritime fuel consumption. The shipping emissions are expected to have increased with 50-250% from 2012 to 2050. It is assumed that the fuel consumption will increase accordingly. Assuming a conservative 25% increase of the 2012 value up to 2026 (ten years), the potential share of biofuels in ten years is **6.0%.**

2) Figure 2 shows the two optimal conversion routes that were determined for RQ 2. Both Kraft lignin and steam explosion (SE) lignin were determined as suitable feedstock. Therefore, one case-study was performed using Kraft lignin from a paper/pulp mill and one using steam explosion lignin from a lignocellulosic biorefinery. There are no lignocellulosic biorefineries in Scandinavia yet, so the Scandinavian case-study was performed on Kraft lignin from a Scandinavian paper/pulp mill. For Brazil, a case study was created on steam explosion lignin from a Brazilian biorefinery. The MCA showed that the

pyrolysis related conversion technologies are currently the most suitable technologies, with fast pyrolysis rating highest. Pyrolysis oils are of very low quality and require upgrading to stabilise them, before they can be used as a fuel. Low severity hydrotreatment was considered more suitable than hydroprocessing or hydrocracking to upgrade the bio-oil to a biofuel. Kraft lignin was isolated from the Kraft mill waste stream (black liquor) with the LignoBoost isolation method. SE lignin is already separated in the lignicellulsoic biorefinery and only requires pre-treatment.

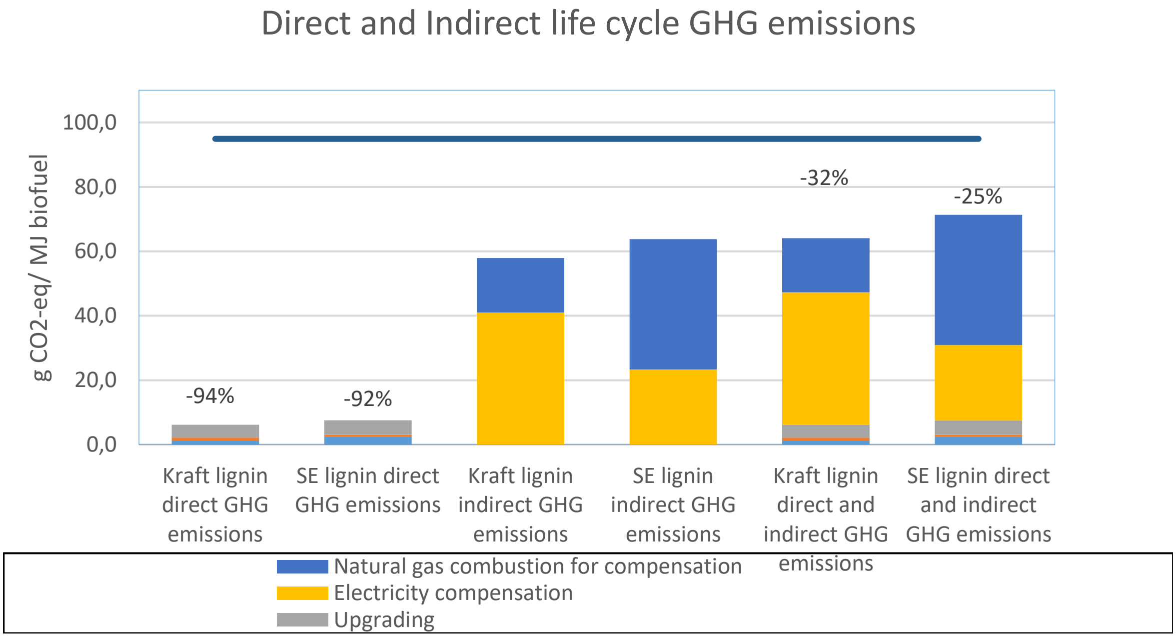
Figure 2: A graphic representation of the two most suitable conversion routes. An LCA will be performed to assess the direct and indirect GHG emissions associated with these routes.



3) The direct and indirect GHG emissions were calculated for both optimal conversion routes. This lead to the results presented in Figure 3. The direct GHG emissions from the conversion of lignin is for both routes a very small part of the overall emissions, 6.2 g CO2-eq/MJ for Kraft lignin and 7.6 g CO2-eq/MJ for SE lingin. Most of the GHG emissions are indirect emissions, from the compensation of the extracted lignin in the Kraft mill or lignocellulosic biorefinery, amounting 57.9 g CO2-eq for Kraft lignin and 63.7 g CO2-eq/MJ for SE lignin. A 32% reduction is achieved from using biofuels from Kraft lignin instead of fossil fuels. For the biofuel from SE lignin conversion, 25% reduction is achieved.

The current amount of CO2-eq emissions that could potentially be mitigated from the use of biofuel from lignin is between 15.8 and 22.0 Mt per year. In ten years, this might increase to roughly between 22.4 and 29.0 Mt CO2-eq/year of mitigated GHG emissions from the use of biofuel from lignin. Since the overall emissions of the shipping industry are 961 Mt CO2-eq (in 2012), currently roughly between 1.6% and 2.3% of the overall shipping emissions could be mitigated. This percentage is projected to increase to between 1.9% and 2.4% ten years from now.

Figure 3: The direct, indirect and overall GHG emissions of marine biofuels produced from SE lignin and Kraft lignin conversion.



Discussion and Conclusion

The overall GHG emission reduction of using biofuels in ships compared to fossil fuel is approximately 32% for Kraft lignin conversion and 25% for SE lignin conversion. A current overall GHG emission reduction potential of 15.6 and 21.9 Mt was calculated from the results of this thesis. In ten years, this potential is expected to increase to roughly between 22.4 and 29.0 Mt GHG emissions per year. This means that approximately between 1.6 and 2.3% of the overall shipping emissions could potentially be mitigated today and between 1.9 and 2.4% in ten years.

From these numbers, it can be concluded that producing marine biofuels does mitigate GHG emissions in the shipping industry, though the reduction is not very large. It was concluded that other configurations of the optimal conversion routes should be considered to increase the GHG emission mitigations, e.g. by replacing natural gas with bark. One configuration that assumed use of the excess biochar to replace fossil coals in coal-fired power plants and one configuration that assumed the use renewable electricity were assessed. Both configurations caused a large increase in GHG emission savings for the Kraft lignin conversion route. For the SE lignin conversion route the increase in emission savings was smaller. More alternative configurations should be studied to find the optimal configuration that yields the highest emission reduction. The results are very sensitive to the emission factors of natural gas and electricity, reducing these could achieve large GHG emission reductions. Natural gas and electricity are also the two products that cause the large indirect GHG emissions. Both conversion routes have a high uncertainty, which should be reduced by improving the quality of the input data to obtain more robust and reliable results.

Before fast pyrolysis of lignin can be commercially used to produce biofuels and decrease the GHG emissions of the shipping sector, there are some barriers to overcome. Fast pyrolysis of lignin has so far proven to be difficult, because the lignin tends to melt and agglomerate in the pyrolysis reactor, causing clogging. Furthermore, it should be assessed if the conversion route is cost-effective and can compete with fossil fuels. This should be researched in future studies.

It can be concluded that the use of biofuels from lignin could be effective in mitigating emissions, but even if the GHG emission savings are increased and the technical barriers are overcome, the quantity of biofuels is not sufficient to realise a large reduction in the GHG emissions of the shipping industry. Therefore, marine biofuels from lignin could be important to reduce the GHG emissions from the shipping industry, but additional measures should also be researched and implemented.

Acronyms and abbreviations

ALCA	Attributional life cycle analysis
CLCA	Consequential life cycle analysis
CO2-eq	Carbon dioxide equivalent
DMA	Distillate Marine Fuel A
dt	Dry metric tonne
ECA	Emission Control Areas
EEDI	Energy Efficiency Design Index
EU	European Union
FP	Fast pyrolysis
GHG	Greenhouse gas
H2SO4	Sulphuric acid
Heff/C	Effective hydrogen to carbon ratio
HFO	Heavy Fuel Oil
HHV	Higher Heating Value
HTL	Hydrothermal liquefaction
IEA	International Energy Agency
IMO	International Maritime Organisation
IPCC	International Panel on Climate Change
ISO	International Standard Organisation
Kt	kilotonne
kWh	Kilowatthour
LCA	Life cycle Analysis
LCI	Life Cycle Inventory
LCIA	Life Cycle Impact Assessment
LHV	Lower Heating Value
MARPOL	International Convention for the Prevention of Pollution from Ships
MCA	Multi Criteria Analysis
Mpa	MegaPascal
Mt	Megatonne
MWe	Megawatt electricity
NaOH	Sodium hydroxide
Nox	Nitrogen Oxides
RED	Renewable Energy Directive
RFS	Renewable Fuel Standard
RMA	Residual Marine Fuel A
RQ	Research question
SE	Steam explosion
SEEMP	Ship Energy Efficiency Management Plan
SOx	Sulphur oxides
Wt.%	Weight percentage

Table of Content

1 Introduction

This thesis was carried out as part of the master's programme Energy Science at the Utrecht University. It was conducted at GoodFuels, as part of their Good Innovations programme, for the time period of 25.5 weeks.

1.1 Context

The main anthropogenic activity affecting the amount and rate of climate change is greenhouse gas (GHG) emissions from burning fossil fuels (EPA, n.d.). Maritime transport generates large quantities of GHG emissions due to the large volumes that are transported globally, even though it is a relatively efficient type of transport per amount of volume transported (IRENA, 2015; OECD/ITF, 2016). In 2012, the total GHG emissions from shipping amounted 961 million tonne CO_2-eq, which accounted for 2.5% of the global GHG emissions (OECD/ITF, 2016). Despite the two market-based energy efficiency measures that have been introduced by the International Maritime Organisation (IMO) in 2011, the GHG emissions are projected to increase with 50 to 250% by 2050 for the "business-as-usual" scenario, as the demand for transport will increase (IMO, 2014; Cames et al., 2015; IRENA, 2015). The CO_2 emissions from shipping may by that time have risen to 17% of global CO_2 emissions (Cames et al., 2015). To help mitigate climate change, the amount of GHG emissions should decrease substantially. Cames et al. (2015) concluded that, taking the EU target path as a reference, the CO_2 emission target for 2050 for the shipping sector should be between -78% and –94% compared to 2005 emissions. The decrease in emissions would need to be even higher if non-CO_2 emissions are also taken into account.

Besides GHG emissions, air pollution caused by maritime transport is also an environmental issue. The share of sulphur emissions caused by the maritime sector is 5-10% of all anthropogenic sulphur emissions, according to different estimations (OECD/ITF, 2016). The International Convention for the Prevention of Pollution from Ships (MARPOL) has set limits for the SOx and NOx emissions from ships and appointed special SOx Emission Control Areas (ECAs) (Moirangthem, 2016). Besides the ECAs, an additional global cap will be introduced in 2020, limiting the sulphur content of marine fuels to 0.5% in all waters outside the ECAs (ICS, 2015). The EU has already set an additional limit of 0.1% Wt.% SOx in harbour regions since 2010. NOx emissions limits are also set, including NOx Emission Control Areas (Moirangthem, 2016), but these emissions are not directly related to the fuel type and therefore not relevant for this study.
There are several ways to reduce the GHG and sulphur emissions of the shipping industry, e.g. using biofuels, wind energy, photovoltaics, tidal energy or hydrogen fuels cells, but due to technical and economic barriers, there has not been a commercially viable solution yet (Cames et al., 2015; IRENA, 2015). Replacing the fossil fuels with biofuels is likely to play an important role in the future marine fuel mix, especially since the heavy transport modes, like ship transport, are not suitable to run on electricity (IEA, 2011; IRENA, 2015). Research has shown that biofuels can be considered a sustainable fuel for the transport sector in terms of decreasing the carbon emissions and improving local air quality, e.g. by decreasing sulphur emissions (Ecofys, 2012; Ragauskas et al., 2014). Schuitmaker (2016) even concluded that the 2-degree target could only be achieved if a number of abatement options are implemented, including a 25% share of biofuels in the shipping sector by 2050. The IEA Roadmap for Biofuels for Transport (2011) envisions the share of biofuels to increase to 27% of the world transport fuel, a steep increase from the 2% share it has today.

First-generation biofuels raise some concerns regarding their sustainability, especially regarding the sourcing of feedstocks, including the impact it may have on biodiversity, land use and competition with food crops. For example, the rising food prices are partly due to the increase in the production of these fuels (Naik et al., 2010). However, lignocellulosic biomass, or "second-generation biomass" now offers potential to be converted to more sustainable biofuels (Naik et al., 2010). Second-generation biofuels from plant biomass are mostly produced from lignocellulosic materials that are not used for food production, and therefore have less direct negative implications on the food market. Second-generation biomass in one of the most abundant and underutilized biological resources on the planet, and is seen as a promising source for fuels and raw materials (Naik et al., 2010).

Lignin is an example of an abundant feedstock that is present in plants and that can be used to produce second-generation biofuels. Lignin is a part of the cell wall of biomass and available in large quantities from multiple sources, for instance as a by-product of paper and pulp mills and lignocellulosic biorefineries. It is currently mostly used as a boiler fuel, but the profitability of the lignocellulosic industry could be improved if the lignin is used for other purposes (de Wild et al., 2014). In contrast to the lignocellulosic industry, which has several opportunities to become more efficient and emit less GHG (like using forest residues or more efficient process equipment), the marine industry is limited to only a few options to reduce their emissions. Producing biofuels from lignin could potentially play a large role in making the marine transport sector more sustainable, while improving the business-case of the lignocellulosic biomass industry.

1.2 Scientific background

The use of marine biofuels, or biofuels in general, has several advantages over fossil fuels. The combustion of biofuels is considered carbon neutral, because the emitted CO_2 was relatively recently taken up by the biomass and therefore causes no net increase in CO_2 content in the atmosphere (as long as the feedstock is re-grown to balance the carbon stock) (E. Johnson, 2009). On the other hand, combustion of fossil fuels releases CO_2 into the atmosphere that was sequestered for a long time, which does cause an increase of CO_2 in the atmosphere. The sulphur content of biofuels depends highly on the feedstock, but is generally very little to zero. Replacing fossil fuels with biofuels can achieve a strong GHG reduction and can reduce the sulphur emissions that influence the local air quality. Furthermore, biofuels are generally better biodegradable, thus reducing the environmental damage in case of spillage (Ecofys, 2012). Therefore, as long as the sustainability of the biofuels is accounted for, biofuels are considered a sustainable alternative to fossil fuels (Ecofys, 2012)

Several types of marine biofuels currently exist, e.g. biomethanol, bioLNG and biodiesel. Some can easily be used in the shipping sector, like biodiesel, while others require more modifications to the ships infrastructure or engine, e.g. bioLNG (Ecofys, 2012). Drop-in biofuels are liquid hydrocarbons that are functionally equivalent to petroleum fuels and are compatible with current existing petroleum infrastructure (Karatzos et al., 2014). They can thus be blended with fossil fuels and they require less investments to the supply chain. Drop-in biofuels are seen as the most promising option in the short term (Ecofys, 2012). Ideally, they should be non-corrosive, non-reactive and non-hydrophilic, just like petroleum fuels, to reduce the risk of rust and corrosion of the engines and storage facilities. Other important properties are miscibility with the petroleum fuels, good storability, usability in existing engines and of course the fuel must be compatible with fuel performance indicators (IEA-AMF, 2013; IRENA, 2015; Karatzos et al., 2014). The biofuels could be blended with bunker parties or aboard of the vessel, this is still a matter of discussion (Ecofys, 2012). There is not much practical experience with using biofuels in ships, but biofuels seem technically compatible with marine engines, so integration should be possible (Ecofys, 2012). The biofuels can be of low quality because of the strong engines that currently mostly run on residual marine fuel (RMA).

The quality of biofuels is, among other things, dependent on the feedstock material. The complex structure of lignin makes it environmentally, technically and economically difficult to convert it to a high quality fuel (Strassberger et al., 2014), but it could be a good feedstock to produce low quality biofuels for the marine industry. 15 to 40 percent of the dry weight of woody biomass consists of lignin, making it the most abundant aromatic polymer on earth and the second must abundant organic polymer (second to cellulose) (Haghdan et al., 2016). Due to these large quantities, it has the potential to become a very important source for liquid transportation biofuels (Haghdan et al., 2016; Ragauskas et al., 2014). However, apart from a few markets and uses for lignin that date back decades, so far lignin has not been converted into a viable, commercially relevant, sustainable feedstock (Ragauskas et al., 2014). Research has been done on the potential of using lignin to produce chemical products, like aromatic chemicals, additives, resins and coating materials (Haghdan et al., 2016). However, though promising, little progress has been made on the required technologies (Strassberger et al., 2014). Furthermore, to upgrade the lignin to high quality chemicals many processing steps are needed, requiring large amounts of hydrogen. This increases the GHG emissions and costs associated with the valorisation of lignin (Strassberger et al., 2014). However, using lignin to produce a low quality marine biofuel would require less processing steps and hydrogen inputs. Biofuels from lignin conversion can be blended in different ratios with the fossil fuel, supporting the use in any ship, with little, or only small changes to the engine (IEA-AMF, 2013; IRENA, 2015). Furthermore, lignin is available all over the world, it shows potential for the production of large quantities of drop-in biofuels, and it is currently only used for heat and electricity production, for which other alternatives exist (e.g. using forest residues).

GoodFuels is a company that is active in the sales, marketing, trading and development of truly sustainable fuels. They believe that using biofuels is one of the few options that the marine industry has to significantly reduce its carbon footprint. Therefore, GoodFuels is interested developing a sustainable supply chain for low quality biofuels that are good enough for the large engines used in the marine industry, and that will help achieve great GHG emission reductions. These low-quality biofuels require less upgrading processes and will thus have lower conversion costs. This project aims to contribute to the research performed by GoodFuels on this topic.

1.3 Research gap

Studies on the general availability of lignin exist, but a more detailed overview of the different lignin streams and methods to isolate lignin could not be found. Such an overview would be useful for the industry aiming to valorise the lignin. Many studies exist on the technical or economic aspects of lignin conversion to oil or chemicals, but they do not include the GHG emissions, nor the upgrading to a transportation fuel (Gosselink, 2011; Noureldin et al., 2014; Pandey & Kim, 2011; Riaz et al., 2016). Other articles do assess lignin conversion to transportation fuels, but they do not address the GHG emissions that would be involved (Azadi et al., 2013; Kang et al., 2013; Singh et al., 2014; Joffres et al., 2013; Ramirez et al., 2015; Lee et al., 2016; Nguyen, 2014; Jones et al., 2013; Mu et al., 2013). There are studies that perform a GHG assessment, but on whole lignocellulosic biomass conversion to more valuable and technically challenging products, such as aromatics, gasoline or jet fuels (Hsu, 2012; Iribarren et al., 2012; Tews et al., 2014; Zhang et al., 2005). Lignin conversion is different from biomass conversion and marine biofuel as it requires less upgrading than aromatics, gasoline or jet fuels. Tews & Elliott (2014) performed a GHG assessment on low severity stabilisation of bio-oils, which were also derived from lignocellulosic biomass. No articles have been found that focus specifically on the production of bio-oil from lignin to be used as a drop-in fuel for the marine industry. Therefore, this research will focus specifically on the supply market and GHG emissions from the production of marine biofuels from lignin.

1.4 Problem definition

Marine biofuels from lignin could be a promising solution to reduce the GHG emissions from the shipping industry. A marine biofuel should be available in large quantities to be able to serve the large marine biofuel market. Additionally, it should have lower life cycle GHG emission than the currently used fuels, in order to lead to a reduction in GHG emissions of the sector. Therefore, this thesis aims to assess the lignin supply market and the biofuel potential from lignin on a global scale, both for the current situation as for the expected situation in ten years. The timeframe of ten years was chosen because it is thought to be a realistic timeframe for the commercialisation of this process. Furthermore, this study aims to assess the GHG emissions resulting from the lignin conversion processes (the direct emissions) and the GHG emissions in the life cycle of other products that are caused by introducing the lignin conversion (the indirect emissions). Due to time constraints, these GHG emissions were only assessed for two most suitable case studies, with respect to technical and economic aspects. Brazil and Scandinavia were the chosen locations, because they have an intensive biomass industry and GoodFuels has connections and projects in these regions. The most suitable conversion routes to produce marine biofuels from lignin in Brazil and in Scandinavia had to be determined first.

The current research gap with respect to the production of biofuels from lignin and the potential for reductions of future GHG-emissions in the marine transport sector lead to the following research questions:

1. What does the current global lignin supply market look like and what is the current global marine biofuel potential? How is this expected to evolve over the next ten years?
2. What is the most suitable conversion route available for marine biofuel production from lignin?
3. How much direct GHG emissions (in g CO_2-eq/marine biofuel) are produced with the most promising lignin-to-marine biofuel conversion routes in Brazil and in Scandinavia?
4. How much indirect GHG emissions (in g CO_2-eq/MJ marine biofuel) are produced with the most promising lignin-to-marine biofuel conversion routes in Brazil and in Scandinavia?

This project will contribute to the knowledge on producing marine biofuels from lignin. The understanding of the potentials for lignin valorisation to marine biofuels could help policy makers in their decision-making process, and can provide a starting point for interested companies. In the end, this could support the biofuel industry in commercialising the marine biofuel production from lignin and thus help reduce the GHG emissions from this sector. The analysis of the data in the Excel tool will make it easy to calculate new results if future developments or insights should change the variables.

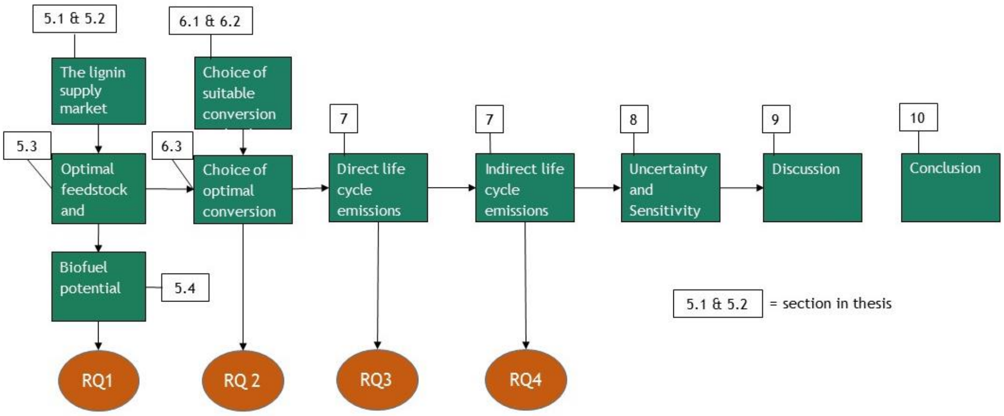
1.5 Thesis outline

This section presents an overview of the structure of the thesis.

- Chapter one: Introduces the problem, discusses previous research on the topic and states the problem definition.
- Chapter two: Provides general background information on the most important concepts that are used in this thesis.
- Chapter three: Introduces the lignin to biofuel processes that were considered for the research.
- Chapter four: Presents the methodologies that are used to answer the research questions.
- Chapters five to eight present the results. To get a good overview of the structure of this part of the research, and the relations between the different sections, this is presented in Figure 4.
    - Chapter five: Shows the results of the market analysis and answers the first research question. It starts with an explanation of the lignin supply market and the different lignin sources.
    - Chapter six: In this chapter the most suitable conversion route was determined and answers the second research question.
    - Chapter 7: Presents the results to the LCA and the uncertainty and sensitivity analysis. In this chapter the GHG emission reduction potential of the two conversion routes are determined.
    - Chapter 8: Presents the GHG emission reduction that would be achieved if the char was used to replace coal in a coal-fired power plant and if renewable electricity was used.

- Chapter 9: Discusses the results and their limitations. It also provides recommendations for future research.
- Chapter 10: Presents the conclusions of the research.
- Appendix 1: Explains what lignin is.
- Appendix 2: Describes the main lignin isolation techniques
- Appendix 3: Describes the main conversion technologies that exist.
- Appendix 4: Describes the main upgrading processes that can be used.
- Appendix 5: Describes the input data for the uncertainty and sensitivity analysis. It presents an overview of the parameters that were assessed and the probability density function and standard deviation that was given to them.

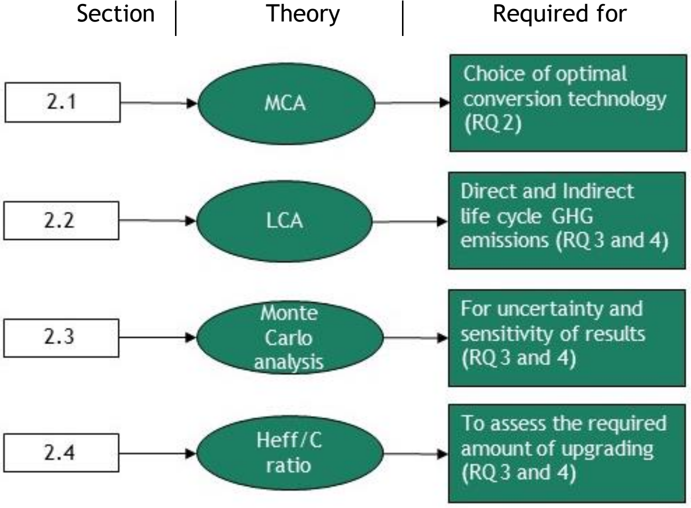
Figure 4: The outline of the results and discussion/conclusion part of this thesis.



2 Theoretical background

In this chapter, the most important concepts used in this thesis are explained. Figure 5 below provides an overview of the concepts that are explained and also shows where the explained concept is used.

Figure 5: The explained theories in this chapter and the part of the thesis that this explanation provides the background information for.



2.1 Multi Criteria Analysis

Following Brinkman (2015) a Multi Criteria Analysis (MCA) will consist of the following six steps:

Step 1. Establish the decision context

First the aim of the MCA must clearly be stated. Various technologies exist to convert lignin to a biofuel. Which one of these technologies is the most suitable technology has to determined, so that a LCA of this technology can be performed.

Step 2. Identify the options and criteria and construct effect table

In this step, the different option that are assessed by the MCA have to be determined. There are many criteria that are important for the conversion technology, and they are dependent on many factors. Only the most relevant criteria should be considered here. The criterion scales have to be defined, both for the qualitative and the quantitative criteria. The results for each of the technologies can be presented in an effect table.

Step 3. Standardize scores for each criterion

The scores have to be standardised between 0 and 1, to be able to compare them. Several standardisation methods exist, so first the appropriate method has to be determined for each criterion. These results can be presented in a standardised effects table.

Step 4. Assign weights of the criteria

Not all criteria should have the same influence on the final result, some are more important than others. Therefore, a weighing method is applied. The order of importance of the criteria is first determined, then the weight of each criteria is calculated. This can be done using the calculations of equation 1 below (obtained from Brinkman, 2015). This way a non-linear distribution of weights is obtained that reflects the importance of each of the criteria.

$$\begin{aligned} W1 &= \frac{1}{5*J} \\ W2 &= \frac{1}{5*J} + \frac{1}{5*(J-1)} \\ W3 &= \frac{1}{5*J} + \frac{1}{5*(J-1)} + \frac{1}{5*(J-2)} \end{aligned} \tag{1}$$

Etc.

J = the number of criteria. W1 is the lowest weight and W5 is the highest weight.

Step 5. Calculate final score for each alternative and determine ranking

The final scores can be calculated by multiplying the weight of each criteria by the standardisation value. These results are presented in a weighted summation table. The overall results for each of the technologies can subsequently be calculated by adding the scores for each criterion. From these values the highest, best scoring end thus most suitable technology could be selected.

Step 6. Perform sensitivity analysis on scores and weights

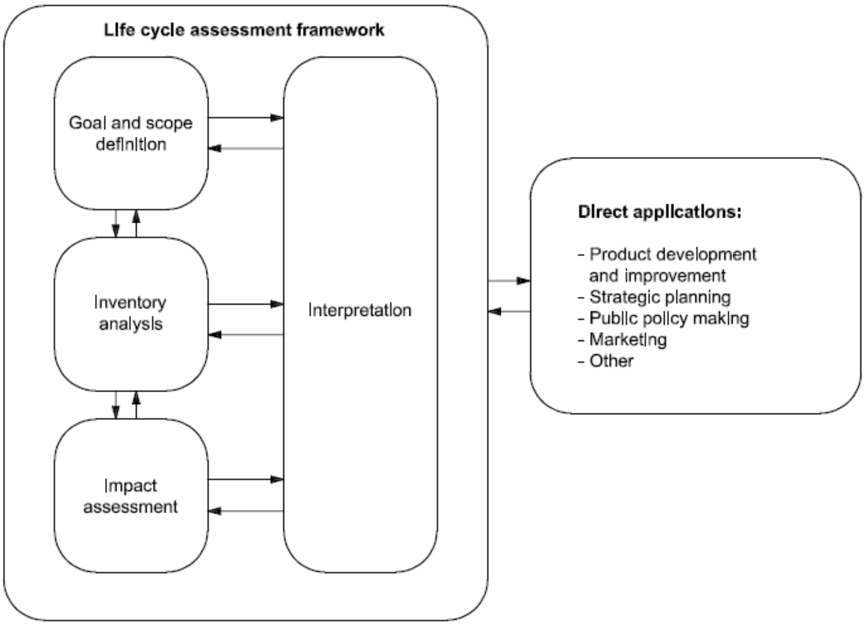
A sensitivity analysis can be performed on the results.

2.2 Life Cycle Analysis

A Life Cycle Analysis (LCA) can be performed to identify the GHG emissions over the life cycle of a product. These results could be used for different purposes, including: identifying opportunities to improve their environmental performance, informing decision-makers, selecting relevant indicators of environmental performance, or for marketing purposes (ISO, 2006).

This LCA was performed following the ISO 14040 guidelines and was therefore divided into the four steps: Goal and scope definition, inventory analysis, impact assessment and interpretation, as can be seen in Figure 6 (ISO, 2006). Each of these steps is described below.

Figure 6: The different steps of an LCA as defined by ISO 14040 (ISO, 2006)



Goal and Scope definition

In the goal and scope definition, the goal of the LCA, the production system, the functional unit, the boundaries, the allocation procedures and impact categories are described (ISO, 2006a).

LCA's can be categorized into attributional LCA's (ALCA) and consequential LCA's (CLCA). An ALCA considers the environmental impacts based on the history of the product. It takes into account the occurring processes and in- and outputs during the life-cycle of a product, also called the direct emissions (Benali et al., 2016). A CLCA studies the environmental consequences of possible (future) changes between alternative product systems (ISO, 2006). In other words, it describes the potential environmental consequences that occur due to a change in the process, not limited to the cradle-to-grave boundaries of a product. That means that, besides the emissions that occur directly from the life cycle of the product (the direct emissions) also the change in emissions that is caused in the life cycle of other products (the indirect emissions) are included (Benali et al., 2016). It requires reliable assumptions to be made for forecasting, modelling and quantifying impacts to avoid large uncertainties (Benali et al., 2016).

A LCA generally takes several environmental impacts into account (e.g. GHG emissions, eutrophication, human health, resource depletion) to get a more complete picture of the environmental impact over the life cycle of a product. However, single issue method for the LCA can also be used. This considers only the impact on one environmental issue, e.g. the GHG emissions, while other issues are excluded.

The allocation method that is used for a LCA can significantly influence the results, and should be considered with care. The energy allocation method is based on the energetic values of the useful outputs. This allocation method is often used for fuels since they are used for their energy content. This method is often preferred by the European Commission since it is easy to apply, predictable over time, minimises counterproductive incentives and the results are usually easy to compare with other substitution methods (*Renewable Energy Directive*, 2009). Another important allocation method is the displacement method, also called the system boundary expansion method. This method represents the actual emissions of producing several products from a pathway. For this method, the emissions that are displaced by non-fuel products are subtracted from the overall emissions of the biofuel production cycle. The method was adopted as the default method in dealing with biofuel co-products in transportation LCA models. A downside of this method is that it requires conducting LCAs of the non-fuel products that are displaced and it can create distorted results if a large part of the products is non-fuel (Wang et al., 2011). Other possibilities are mass allocation, where the impact is allocated to each output based on mass, and economic allocation, where the impact is allocated based on economic value. Mass allocation is often used for consumer products. Economic allocation normalizes all products to a common basis, their economic values, regardless of the purpose of their use. But for future products it is difficult to estimate their price, this is very uncertain (Wang et al., 2011).

Life Cycle Inventory Analysis (LCI)

During this stage the data is collected and the required calculations are performed to quantify the relevant inputs and outputs of a product system (ISO, 2006). All the processes and their inputs and outputs within scope have to be assessed.

Life Cycle Impact Assessment (LCIA)

The impact assessment phase of LCA aims to evaluate the significance of potential environmental impacts. The overall GHG emissions will be calculated based on the results of the LCI (ISO, 2006). The CO_2-eq footprint can be calculated by multiplying the obtained emissions by their emission factor. This should be done in a transparent way, clearly stating the assumptions that were used.

Characterization factors are used to convert GHG emissions into CO_2-eq emissions. To obtain the mass value in CO_2-eq, the emission of each GHG is multiplied by its characterisation factor (in kg CO_2-eq/kg GHG). The characterisation factors account for the radiative efficiency of the GHGs and for their lifetimes in the atmosphere. These characterisation factors were determined by the IPCC (Stocker et al., 2013). Their contribution to the Global Warming Potential (GWP) over a 100-year time frame was used. This is the time frame most commonly used for carbon footprint studies (Gnansounou et al., 2009). These characterisation values are presented in Table 2.

Table 2: The Global Warming Potentials over a 100-year timeframe of the three main Greenhouse gases that are considered in this research (IPCC, 2014).

GHG	GWP
CO_2	1
CH4	28
N2O	265

Interpretation

During this stage the results of the Goal and Scope, LCI and LCIA will be interpreted. This interpretation will lead to conclusions, but also the limitations of the LCA will be explained and recommendation will be provided (ISO, 2006). This also includes an uncertainty and sensitivity analysis.

2.3 Monte Carlo analysis

A Monte Carlo Analysis is a statistical technique for stochastic model calculations and for the analysis of error propagation (Refsgaard et al., 2007). This way the impact of the uncertainty of the key influential parameters can be assessed. A Monte Carlo analysis can also be used to perform a sensitivity analysis on the input data that can be influenced by adjusting the process. A sensitivity analysis can determine the criteria/parameters that have the largest influence on the results and that therefore should be considered with care.

For the Monte Carlo uncertainty analysis, first the key parameters should be identified. Subsequently, for each of these parameters the preferred probability density function (PDF) can be identified, as well as the associated range of values or the standard deviation (STD). This should be done according to IPCC guidelines. If only one or a few values were found, expert judgement is required to choose the most appropriate PDF and uncertainty ranges. The IPCC states that if the decision is based on expert judgement, a normal distribution should be assumed, but a uniform or triangular distribution could also be used. The triangular distribution can be used when experts provide a most likely value, together with a minimum and a maximum value, with each value excluding 2.5% of the population (IPCC, 2001, chapter 6). If only a lower and upper limit are provided it was recommended to use a uniform distribution (IPCC, 2001, chapter 6). The sensitivity analysis was included in the Monte Carlo analysis performed in the @Risk program. In the Monte Carlo analysis, random values of the uncertain input parameters are selected based on their probability density functions (PDF), and used in the CO2 life cycle emission calculations.

2.4 Effective H/C ratio

The H/C ratio of a fuel is an indicator for the length of the carbon chains, as well as for the amount of impurities. The length of the carbon chains influences the viscosity, while the amount of impurities influences the heating value of the fuel. The highest possible H/C ratio is 4, when a carbon atom is bonded with four hydrogen atoms (methane). If the carbon chain lengthens, the H/C ratio lowers, since some carbon atoms are attached to other carbon atoms instead of hydrogen atoms. The H/C ratio also lowers with increasing amounts of impurities, because these replace hydrogen in the fuel. Therefore, this ratio is a good indicator for the quality of the fuel (Karatzos et al., 2014).

The oxygen content and other impurities in the biofuel influence the effective H/C ratio of the fuel during combustion, because they react with hydrogen during combustion to form gases that do not contribute any energy to the system. For example, oxygen reacts with 2 hydrogen atoms to form a water molecule. Therefore, the simple H/C ratio of fossil fuels (that do not contain oxygen) must be corrected for the impurities to obtain a comparable “effective” H/C ratio for biofuels. This is done by subtracting the hydrogen molecules that are needed to form water and other gases from the total hydrogen content. It is assumed that the heterogeneous impurities, the chlorine, nitrogen, sulphur and oxygen, are removed as

HCl, NH3, H2S and H2O respectively (Jechura, 2016). The equation to calculate the Heff/C ratio from the elemental composition of a fuel is obtained from (Karatzos et al., 2014) and is presented here (equation 2).

$$H_{eff}/_{C} = \frac{n(H) - 2n(O) - 2n(S) - 3n(N) - n(CL)}{n(C)} \qquad (2)$$

n=number of atoms of each element.

3 Lignin to biofuel

In the previous chapter the theories that were used for this thesis were explained. The processes are presented in Figure 7. In this chapter, the processes that were assessed for the most suitable conversion routes are presented. It starts with the sources of lignin and the isolation techniques that exist. Next the main conversion technologies that exist were described, followed by the main upgrading technologies. The chapter ends with a description of the marine fossil fuels that are currently used and that the biofuel replaces or is blended with. A short explanation of lignin itself can be found in appendix 1.

Figure 7: The processes of the lignin to biofuel conversion route that were assessed for this thesis.

3.1 Lignin sources and isolation techniques

Isolated lignin is produced at two sources: paper/pulp mills and lignocellulosic biorefineries. Both use different isolation techniques, and within each source also different techniques exist.

Paper/pulp mills

At paper/pulp mills, different pulping processes can be used to separate the cellulose, hemicellulose and lignin in the biomass. The pulping process that is used affects the characteristics of the lignin. The different pulping techniques are listed here, and all four are shortly described in Appendix 2.

1. sulphite cooking process
2. Kraft cooking process
3. alkaline pulping process
4. solvent pulping process.

The Kraft pulping process was most relevant for this thesis, therefore also the isolation techniques are discussed that exist to isolate the lignin from the waste stream of the Kraft mill (the black liquor). The lignin can be isolated from the black liquor waste stream through several methods. The main methods are listed below and were also described in appendix 2. The LignoBoost isolation technique was the most relevant for this thesis and is therefore also described in section 3.1.1.

1. Acid precipitation through sulphuric acid
2. CO_2 precipitation (LignoBoost)
3. Sequential liquid lignin recovery and purification (SLRP)
4. Ultrafiltration
5. Electrolysis
6. Electrodialysis

Lignocellulosic biorefineries

At lignocellulosic biorefineries different methods exist to isolate the lignin from the rest of the biomass. The most commonly used methods are:

1. steam explosion
2. dilute acid pre-treatment
3. alkaline hydrolysis pre-treatment.

All three methods were described in Appendix 2, but only the Steam Explosion technology was relevant for this thesis and was described here.

3.1.1 Kraft paper/pulp mill and LignoBoost

The Kraft pulping process is the dominant pulping method in the world and comprises several steps, both chemical and mechanical. It uses sodium hydroxide and sodium sulphite to separate the different biomass components. Kraft lignin generally contains less than 1 or 2% sulphur, despite the high sulphur environment of the Kraft process. Kraft lignin has a lower molar mass. It can be isolated from the black liquor in a Kraft paper/pulp mill (Laurichesse & Avérous, 2014).

The LignoBoost process uses CO_2 to decrease the pH of the black liquor, but only to around 9.5 or 10.5 (from an original pH of 12-14). The lignin then precipitates and is washed and filtered. CO_2 is consumed during the process and converted to carbonate salts. This method is generally regarded as an economical and efficient isolation process (Fatehi & Chen, 2016). In this process, the black liquor is extracted from the evaporators and is acidified by using CO_2. At this lower pH, the lignin precipitates in a precipitation tank, and additionally H2S gas can be generated. The precipitated lignin slurry is subsequently mixed with an acidic filtrate, followed by a washing stage. This generates small, uncrosslinked lignin precipitates. It is then crushed and dried to form a lignin powder (Fatehi & Chen, 2016). Figure 8 shows a block schedule of the LignoBoost processes, while some important parameters are presented in Table 3. NaOH and H2SO4 are required for the process. H2SO4 is needed to wash the lignin cake, NaOH is needed to neutralize the recycled stream from the lignin isolation process to the evaporators.

Figure 8: A block schedule of the LignoBoost isolation processes (obtained from Fatehi & Chen, 2016)

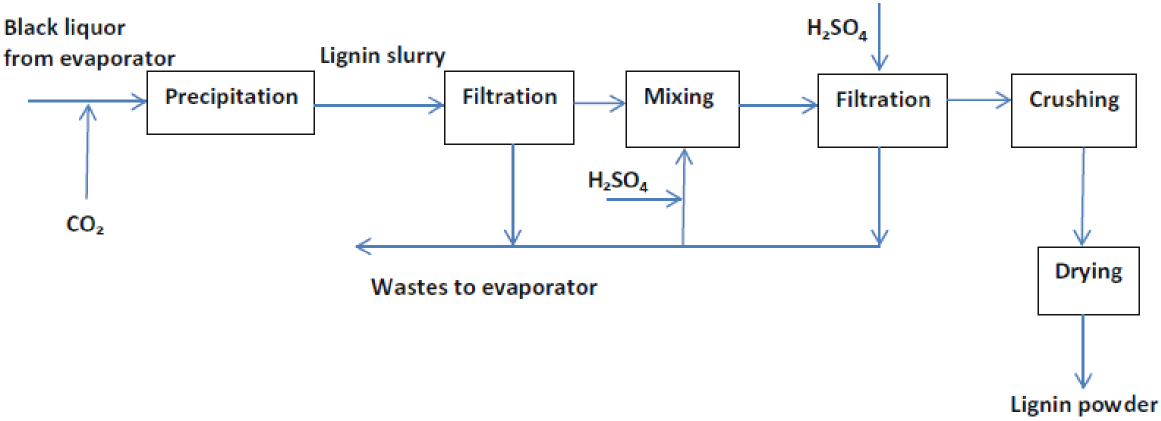


Table 3: Some important parameters of the lignoboost process, as presented by Benali et al. (2016).

Operating parameters and costs	LignoBoost™ process [17, 18]
CO_2 consumption (t/t)	0.15–0.25
O_2 consumption (t/t)	0
Incremental NaOH (t/t)	0.05–0.08
Water (t/t)	2.00–2.50
H_2SO_4 (t/t)	0.09–0.25
Precipitation yield (%)	70.00
Precipitation reactor pressure (kPa)	101.33
Precipitation reactor temperature (°C)	60–70
Lignin ash content (%, w/w)	0.02–1.00
Lignin sulphur content (%, w/w)	1.30–3.40
Chemical costs[a] ($/t of lignin)	100–150

3.1.2 Lignocellulosic biorefinery – Steam Explosion

Steam Explosion (SE) treatment is the most commonly used method for treatment in lignocellulosic biorefineries (Kumar et al., 2009). During the SE treatment, the biomass is impregnated with steam at 200°C or higher and under high pressure. At these high temperatures, water acts as an acid (Kumar et al., 2009). A rapid pressure drop liberates the fibres of the biomass and releases the three biomass components (Lange et al., 2015). The lignin can be obtained by extraction of the fibrous material with an aqueous or alkali solvent, or by fermenting the sugars to ethanol and leaving the lignin behind in the fermentation broth (Bruinincx et al., 2016). Lignin that is released after SE have a lower molecular weight and higher solubility in organic solvents than Kraft lignin (Lange et al., 2015). They contain only little carbohydrates and wood extractive impurities and resemble the native lignin more than any other technical lignin (Bruinincx et al., 2016), but SE lignin from softwood will be more modified and less reactive than those from hardwood (Shevchenko et al., 1999). This lignin is completely or almost completely sulphur free (Bruinincx et al., 2016). Other advantages of this pre-treatment method are the possibility to recover the high pressure steam and use it as an energy source for other processes more downstream, and the fact that is does not require any chemicals (Gerbrandt et al., 2016).

3.2 Conversion technologies

Different conversion technologies to produce marine biofuel from lignin exist. A description of the main existing technologies was presented in Appendix 3. This section shows only the relevant background information on the conversion technology that was part of the most suitable conversion route, fast pyrolysis. The technologies that were included were:

1. Pyrolysis
    - Fast pyrolysis
    - Fast pyrolysis with staged condensation
    - Slow pyrolysis
    - Catalytic pyrolysis
2. Hydrothermal liquefaction (HTL)
3. Solvolysis
4. Catalytic hydroconversion
5. Gasification with Fischer-Tropsch synthesis

Fast pyrolysis

The technology of pyrolysis has been developed for over 30 years (Zhou et al., 2016). It can be described as the thermal conversion of biomass occurring in the absence of oxygen, producing gas, pyrolysis oil and charcoal (Blin et al., 2007). The amount of each product is dependent on the pyrolysis method, the characteristics of the biomass, and the reaction parameters (Blin et al., 2007). Several pyrolysis types exist, but only fast pyrolysis is relevant for this research.

With fast pyrolysis, the lignin is very quickly converted to mostly vapours and aerosols, together with some charcoal and gas. A homogenous liquid is obtained after cooling and condensation. This liquid has around half the heating value of conventional oils (Bridgwater, 2012). To obtain high oil yields, a moderate pyrolysis temperature is required (around 500°C), with high heating rates (10^3 - 10^5 °C/s), short vapour residence times to minimise secondary reactions (< 2s) and fast quenching of the vapours to generate the bio-oil (Bridgwater, 2012; Lu et al., 2009). To obtain such a high heat transfer rate, the total interface surface of the biomass should be large, so the biomass should be ground to particles generally smaller than 3 mm. The biomass should be pre-dried to a water content of less than 10% to minimise the water content in the oil. Also the char should rapidly be removed to minimise vapour cracking (Bridgwater, 2012). The yield of bio-oil from fast pyrolysis could be as much as 75% on a dry-feed basis. The produced char and gases could be used for the processes, leaving ash and flue gas as the only wastes (Bridgwater, 2012). Typical yields for biomass feedstock are 65-70% liquid bio-oil (dry feed basis), 15-20% char (a black charcoal-like powder), and non-condensable gases (Moirangthem, 2016). For lignin pyrolysis lower oil yields have been reported; 40-60% oil, 30-40% char and 8-20% gas (de Wild et al., 2014; Joffres et al., 2013). All the lignin types are degraded in the same way, but the yields may vary (Pandey & Kim, 2011). Fast pyrolysis oils are used in boilers to generate heat and power, but direct use in marine engines is not possible without modifications to the engine. Raw pyrolysis oils have a high viscosity, high acidity and low thermal stability, causing issues on the operation of engines in the long term (Chong & Bridgwater, 2016). Therefore, some upgrading is required. Different reactor types exist, this is further explained in Appendix 3.

Lignin must enter the fast pyrolysis reactor as fine, dry particles. Therefore, it is often first pre-treated to avoid yield losses and reduce the heat requirements. The pre-treatment comprises of mechanical grinding and drying of the feedstock (Wright et al., 2010). Grinding is important to increase the surface area of the biomass and thus ensure its fast and homogeneous heating. This step is energy consuming and expensive (Wright et al., 2010). The particle size should be reduced to a maximum 5 mm, though usually a particle size of 2 or 3 mm is preferred (Ringer et al., 2014; Wright et al., 2010; Zaimes et al., 2015). Drying is important because the moisture takes up much of the process heat and reduces the pyrolysis performance and yield. The feedstock must be dried to a moisture content of less than 10% to ensure that the moisture content of the produced bio-oil remains below 30%, which is the moisture content at which phase separation start occurring (Wright et al., 2010). Less moisture in the feedstock means less moisture in the bio-oil and thus higher stability and higher heating value. However, since drying is an energy intensive process, the feedstock is generally not dried to a moisture content of 0%, but a moisture content of 7% or 8% is considered sufficient (Ringer et al., 2006; Tews et al., 2014; Wright et al., 2010; Zaimes et al., 2015).

3.3 Upgrading processes

Bio-oils, especially those produced from pyrolysis, can contain impurities like sulphur, nitrogen, oxygen and chlorine. This can cause the bio-oils to be corrosive, viscous and highly oxygenated with a low H/C ratio, making them difficult to store, transport and refine. Therefore, they require upgrading to remove the impurities and stabilise the oil. This can be done through hydroprocessing (hydrocracking or hydrotreatment) or catalytic cracking (Brown et al., 2013). Only hydrotreatment is presented here, because this is part of the optimal conversion route, but more information on other types of upgrading can be found in Appendix 4.

Hydrotreatment

Catalysts are required for the hydrotreatment process, but which one is most suitable is hard to determine. In general, two types of catalysts exist, sulphide catalysts and transition metal catalysts. Of both types, different catalysts have been developed and tested, and both are found to have advantages and disadvantages. Sulphided catalysts are extensively studied and cheap, but they can cause sulphur leaching, induce severe coking and they are intolerant to water, which is a problem considering the general moisture content of lignin derived bio-oils. Transition metal catalysts are better reusable, show higher reactivity and require lower temperatures. However these catalysts are not usable in presence of sulphur, which means Kraft lignin ought to be desulphurised before upgrading, and they are expensive (Mu et al., 2013). The complexity of choosing the right catalyst and assessing the exact hydrodeoxygenation reactions that it induces are beyond the scope of this research.

Generally, hydrodeoxygenation processes may cause 6 types of reactions to occur, as presented by Bu et al. (2012):

1. Water separation;
2. Dehydration reaction due to the condensation polymerization reactions, producing water;
3. Decarboxylation reaction. Removing a carboxyl group, producing H2O;
4. Hydrogenation reaction, where the unsaturated components are saturated before the C-O bonds are cleaved (producing water);
5. Hydrogenolysis reaction, breaking up the C-O bonds and releasing the oxygen in the form of water without saturating the aromatic ring;
6. Hydrocracking reaction involving the breakdown of long carbon chains into smaller molecules.

The H/C ratio is related to the oxygen content, and the main role of the hydrotreatment is to remove oxygen from the lignin derived pyrolysis oil. Therefore the hydrogen requirement will be directly proportional to the oxygen content of the oil (Han et al., 2013). Besides removing oxygen, hydrotreatment is also used to remove any chlorine, sulphur and/or nitrogen impurities (Karatzos et al., 2014). Hydrogenation and hydrogenolysis reactions occur substantially to remove the oxygen atoms. Of these two reactions the hydrogenolysis reaction is preferred, since it requires less hydrogen input (Bu et al., 2012).

Some hydrocarbon gases were measured from hydrotreatment of pyrolytic lignin at the University of Waterloo (Elliott, 2007). Runnebaum et al. (2012) also observed the formation of methane during hydrogenolysis reactions. These hydrocarbon gases were the result of hydrocracking and were in this research also assumed to be produced. But due to the low severity of the process conditions, only minor cracking occurs.

Lignin pyrolysis oil contains mostly unsaturated olefins and aromatics, such as phenols (Lou et al., 2015). Lignin derived phenols show low reactivity in the upgrading process, but some upgrading does occur. How much is dependent on the composition of the oil, the catalyst and the process conditions (Bu et al., 2012). It is difficult to estimate the hydrogen requirements for the hydrogenation processes (where the unsaturated bonds are saturated before the oxygen atom is removed), though it is assumed to be small compared to hydrogen requirements for the removal of oxygen from the oil (Han et al., 2013).

3.4 Marine fuel quality

The biofuel will be replacing fossil marine fuel. The biofuel should be compatible with these fossil fuels, so that they can be blended and make use of the same infrastructure. Three main types of marine fossil fuels are currently in use: Distillate Marine Fuel A (DMA), Residual Marine Fuel A (RMA) and Intermediate Fuel Oil (IFO) (Moirangthem, 2016). Especially residual fuels are of very low quality, but in the large marine engines almost any fuel can be used, as long as the regulations regarding the sulphur limits are met. The sulphur content is considered to be an important fuel property, since it affects the air quality, and several legislations are in place that aim to reduce the current and future sulphur emissions of the vessels. These are the only legal restrictions to the quality of the marine fuel. Table 4 shows the sulphur limits of the fuels within and outside of the ECA’s, up to 2020 (Moirangthem, 2016). This could be achieved through fuels that are low in sulphur (e.g. biofuels), or through alternative measures like scrubbers (Moirangthem, 2016). Table 5 shows the fuel standards as defined by ISO for RMA and DMA (Lin, 2013).

Table 4: The sulphur limits as set by MARPOL for within the ECAs and outside of the ECAs (global) (Moirangthem, 2016)

Date	Sulphur limit in fuel (% m/m)	
	SOx ECAs	SOx global
2000	1.5%	4.5%
2010	1.0%	
2012		3.5%
2015	0.1%	
2020[1]		0.5%

Table 5: The ISO8217 fuel standards for Residual Marine Fuel and for Distillate Marine Fuel.

Fuel parameter	Unit	ISO8217 RMA	ISO8217 DMA
Cetane number, min	-	20	40
Sulfur, max	ppmw	45,000	15,000
Density (at 15 °C)	kg/m^3	920 max	890 max
Flash point, min	°C	60.0	60.0
Carbon residue, max	wt.%	2.5	0.3
Kinematic viscosity (at 40 °C)	mm^2/s	10.0 max	2.0 to 6.0
Heating value	MJ/kg	40	42
Water content, max	ppm	3,000	-
Acid number, max	mg KOH/g	2.5	0.5

Ideally, a blend should also meet the same minimum requirements as currently used fossil fuels to ensure a sufficient quality (see Table 5). However, since not all the properties of the bio-oils that were produced by the different technologies from lignin are known and it is possible that the strong vessel engines can also run on a blend of fossil fuels with lower quality bio-oils, only the most important properties are considered in this research to determine the most suitable conversion route.

4 Methods

This chapter describes the methods that were used to obtain the results. In section 4.1. the methods to obtain information on the lignin supply market and the marine biofuel potential are explained. Section 4.2. regards the methods to determine the most suitable conversion routes. Section 4.3 describes how the direct and indirect emissions of the base cases were obtained through a LCA. Section 4.4 describes the alternative cases that were assessed with the LCA and section 4.5 describes the data collection methods.

4.1 The lignin supply market and marine biofuel potential

To assess **the lignin supply market**, both now and in the future, literature research was performed. In order to get a comprehensive view of the supply market, the following information was gathered:

1. The quantity of lignin, location, feedstock type and separation process for the lignin streams. The quantity of lignin is needed to assess the amount of biofuels that can potentially be produced. The location is required since this research focusses on Brazil and Scandinavia. The feedstock type and separation process provide information on the structure and composition of the lignin, which influences the bio-oil yield.
2. The current use of the lignin from each of the general sources. This is needed to assess the substitution effects in a later stage of the research.
3. The location of some of the larger individual lignin sources, also required to assess the substitution effects in a later stage.
4. The expected change in the production and separation processes of lignin within ten years.

By combining the above-mentioned information, a clear picture of the current and future lignin supply market was drawn. Based on this picture the most suitable lignins to focus on during this research were determined. This was done based on quantity, sulphur content and location. Also, a specific locality was

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[1] An alternative date for this limit could be 2025, this is to be determined by a review by the IMO in 2018. However, regardless of this review, this limit will be maintained by the EU in 2020 in EU waters (Moirangthem, 2016).

appointed for the most suitable lignin in each of the two appointed geographies (Brazil and Scandinavia), that would be the focus of this research. This decision was based on quantity and location.

To assess the **biofuel potential** from lignin conversion, first the different technologies and upgrading processes that exist to convert lignin into biofuel were assessed. After choosing the most suitable technology the average conversion yield from lignin to a marine biofuel of sufficient quality was calculated.

4.2 Determining the most suitable conversion technology

The most suitable conversion route was determined through a multi criteria analysis (MCA), so that an LCA could be performed on the optimal conversion route for both locations (Brazil and Scandinavia). First an early stage screening was performed to create a list of possible suitable lignin isolation techniques, conversion technologies and upgrading processes. This was based on scientific literature and expert judgement from people working in the field of biofuels. Each of the assessed conversion technologies and upgrading processes was shortly described (appendix 3 and 4). The most suitable technology was determined through a multi criteria analysis, as explained below. The most suitable isolation process and upgrading process were subsequently determined based on the literature research.

4.2.1 Multi Criteria Analysis

The yield and costs of each technology can vary somewhat per source of lignin. For example, if the lignin is obtained in a liquid waste stream (e.g. Kraft lignin from a paper pulp mill), hydrothermal liquefaction (HTL) has the advantage that it doesn't require pre-drying of the feedstock. On the other hand, a dry lignin feedstock might be less suitable for HTL, since the lignin has to be hydrated first. However, though these differences exist they are thought to be minor compared to other important criteria (e.g. market status and yield). Therefore, the most suitable technology was determined without regard of the characteristics of the lignin feedstock that will be used. Furthermore, the MCA focusses on the general technology and does not assess the differences within them. For example, the general process of catalytic pyrolysis is assessed, and not each catalyst separately, even though they could have an effect on the criteria. Therefore, this MCA is not a detailed analysis of the conversion routes, but should be regarded as a rough assessment.

As stated before, this research aims to find a conversion route for the production of biofuel of the marine industry, hence the biofuel will be competing with low quality, low cost fossil fuels. The most suitable technology can produce the largest amount of just-good-enough biofuel for the lowest costs in the near future. Therefore, the costs, market status, quality and quantity of the technologies are assessed. Valuable by-products could improve the business case of the technology and are therefore also assessed. The processes as assessed here do not include any downstream upgrading processes yet (e.g. hydrotreatment). This data is obtained from scientific literature.

The yields were represented on a quantitative scale by ratio (with an absolute zero point). The quality and approximate costs were qualitatively assessed, using a scale from -- (lowest quality/costs) to ++ (highest quality/costs). The valuable by-products are simply listed per technology. The market status is categorised from the research phase (lowest market status), and increases in maturity to pilot scale, demonstration scale and finally commercial scale.

Standardised scores were assigned to each criterion. The lowest possible bio-crude yield is 0 kg biofuel/ kg lignin, and the largest value is 1 kg biofuel/ kg lignin. The yields were simply standardised between these values, so they maintained the same value. When a range of values was found, the highest, most optimistic range was chosen. The relative values (-- to ++) were standardised using linear interval standardisation, where the lowest value equals zero and the highest equals 1 and the other values are linearly divided with equal intervals (Brinkman, 2015). This is also applied for the market status, where the highest score is for the commercial technologies and the research phase receives 0 points. The weights were assigned based on expert knowledge and following equation 1 (section 2.1). The assessed criteria and their respective weights are presented in Table 6.

Table 6: The criterion that were considered for the MCA and their assigned weights.

Criterion	Weight
App. costs	0,46
Market status	0,26
Quality biofuel	0,16
Bio-crude yield	0,09
Valuable by-products	0,04

4.3 Life cycle GHG assessment

In this section, the LCA methodology that was applied to assess the direct and indirect GHG emissions of the lignin conversion to a marine biofuel for the two optimal conversion routes is explained. Some theoretical background information on LCA's was provided in section 2.2.

The first sections (4.3.1 until 4.3.6.) explain the methodology regarding the goal and scope definition of the LCA. They explain the type of LCA that is used to achieve the goal, the system boundaries, the functional unit, the required characteristics for the produced marine biofuel, the allocation method and the use of higher or lower heating values. Sections 4.3.7 is related to the LCI and regards the method used for the inventory analysis of each life cycle stage. Section 4.3.8 describes the methods used for the LCIA and section 4.3.9 regards the uncertainty and sensitivity analysis that was performed on the results.

4.3.1 Goal

The goal of this LCA is to assess the direct and indirect GHG emissions that are associated with the conversion of lignin into a drop-in marine biofuel and to assess the change in GHG emissions compared to the current situation. This research regards the environmental consequences of the future change in lignin use, so a consequential LCA was performed. This includes the impact of replacing the lignin with a different fuel to produce the heat and electricity that used to be produced from the lignin.

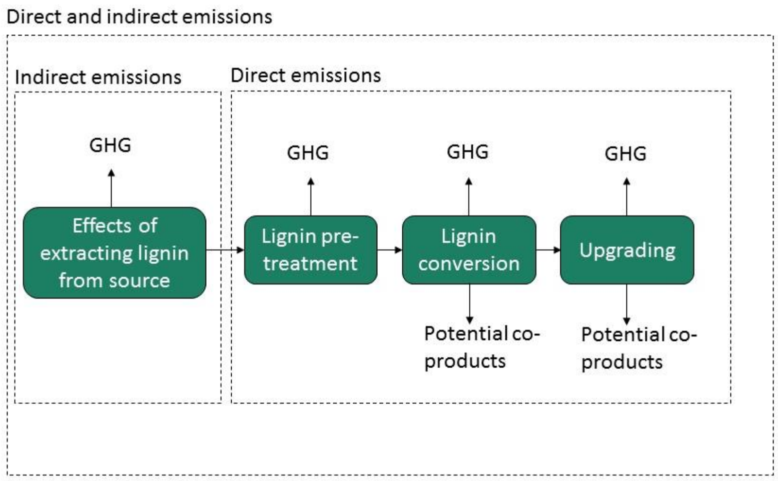
This research performs a single issue LCA, only looking at the GHG emissions. This is considered the most important issue, since the biggest aim of using biofuels in ships is to reduce these emissions. The shipping industry is one of the largest GHG emitting industries, accounting for approximately 2.8% of global GHG emissions (IRENA, 2015). The GHG emissions that are considered in this research are CO_2, CH_4 and N_2O, since these are the most abundant GHGs in the atmosphere, together responsible for the largest part of the increased radiative forcing (Stocker et al., 2013). However, the values obtained from the EcoInvent database include all direct GHGs.

4.3.2 System boundaries

The system boundaries that apply to the LCA that was conducted during this research are shown in Figure 9. The direct emissions are displayed in the inner right system boundary, while the inner left system boundary contains the indirect emissions. These system boundaries apply to both of the most suitable conversion routes that were assessed. Any co-products that are produced will also be included in the LCA. The lignin pre-treatment regards the processes that are required to obtain a lignin that is suitable for the conversion technology, so this includes isolation from the black liquor and drying and grinding of a lignin sludge.

The consequential effects of removing the lignin from the source were included, but the other GHG emissions of the source were all allocated to their main product, and not to lignin. Those emissions fall outside of these system boundaries.

Figure 9: The system boundaries of the LCA that was performed for this research. The inner-right system boundary comprises all the process of the life cycle of the biofuel, from entering the conversion plant to combustion on a vessel. These processes emit the direct GHG emissions. The inner-left system boundary comprises the process that emits the indirect GHG emissions.



4.3.3 Functional unit

The functional unit that is used to express the amount GHGs associated with the conversion of lignin to marine biofuel is **g CO_2-eq/ MJ marine biofuel**. This represents the amount of GHGs per MJ of final product and allows for easy comparison with other fuels because it is not engine or vessel dependent. The functional unit is chosen such that the results are not dependent on combustion characteristics of the fuel, or vehicle fuel use efficiency (as would be the case for g GHG/tkm for example) because these parameters have not been assessed yet, and would also be more difficult to compare with other fuels. The definition of marine biofuel that is used for thesis is presented in the next section (section 4.3.4)

Before the results were obtained in the correct functional unit, the intermediate results were calculated in CO_2-eq emissions/ dt lignin. This was more convenient because the energetic value of the biofuel could only be determined at the end. These values were later divided by the number of MJ of stabilised biofuel produced from one dt lignin to obtain the emissions in the correct functional unit.

4.3.4 Marine biofuel quality

Considering the legislation on te sulphur content of marine fuels, the optimum conversion route must lead to a bio-oil with a sulphur content of max. 0.1%. This ensures that the biofuel is allowed in all open waters around the world, according to the strictest legislation that is currently planned for the future. The oxygen content and carbon number were identified as the most basic properties to be met by Karatzos et al. (2014) and were therefore also considered. A high oxygen content in biofuels reduces the heating value of the oil (Zhou et al, 2016), thus either causing less power to be generated or more fuel to be required to generate the same amount of power as fossil fuels would (Ecofys, 2012). Furthermore, the oxygen can react with the equipment and pipelines (Karatzos et al., 2014), plus a low oxygen content can improve the stability of the bio-oil and its miscibility with fossil fuels (Zhou et al., 2016). The oxygen content and carbon number are reflected by the hydrogen to carbon (H/C) ratio, with oxygen and long condensed carbon chains both lowering H/C ratio. Impurities, like a high sulphur content, also influence the H/C ratio, making this ratio also good indicator for the quality of the fuel (Karatzos et al., 2014). The general H/C ratio of lignin is 0.6, that of heavy crude oil is 1.4 and the H/C ratio of diesel is 2.0 (Karatzos et al., 2014). Since this research is looking at biofuels to be used in marine vessels we will assume an effective H/C ratio (so corrected for the impurities) of 1.4 will be sufficient for the biofuel that is produced from the lignin, since the large low to medium speed vessels now often run on residual marine fuel.

Another important parameter is water content. Too much water can take up energy during combustion, and leads to destabilisation or even phase separation of the biofuel during storage (Karatzos et al., 2014). To obtain a stable biofuel with a sufficiently high heating value that resembles that of fossil fuels, the acceptable water content of the produced biofuel will be assumed to <1 wt.%.

So, in short, the minimum required properties for the biofuel produced from lignin, that will be assessed for this research are:

1. Sulphur content (0.1 wt.%)
2. Oxygen content (effective H/C ratio of 1.4)
3. Carbon number (effective H/C ratio of 1.4)
4. Water content (<1 wt.%)

4.3.5 Allocation method

The greenhouse gases that are emitted during the conversion process had to be allocated to all the valuable outputs. The conversion process produced bio-oil, non-condensable gases and char. If the char and gas were used to produce internal process heat, they were not considered valuable outputs and all the GHG emissions were allocated to the biofuel. If the char or gases were used outside of the system boundaries of the LCA of biofuel, the system expansion allocation method was used, so that all the changes in the actual effects of changing the situation are represented in the results. This means that the displaced emissions of using the char or gas were included in the overall life cycle emissions of the biofuel.

4.3.6 Higher and lower heating values

The higher heating value, or the gross heating value, of a product is the amount of heat produced from complete combustion of a unit of fuel, including the heat from condensing of the water vapour. The lower, or net, heating value is the amount of heat produced from complete combustion of a unit fuel, but without the heat released from condensing of the water vapour. Since the heat for condensation of the water vapour cannot be made useful for the processes, the calculations were performed on a LHV basis. Generally, the lower heating values were obtained from the literature.

Sometimes the LHV of a fuel was not found in the literature. In these cases, the general equation developed by Channiwala and Parikh (2002) for solid, liquid and gaseous fuels was used, see equation 3.

$$HHV = 0.3491C + 1{,}1783\mathrm{H} + 0{,}1005\mathrm{S} - 0{,}1034\mathrm{O} - 0{,}0151\mathrm{N} - 0{,}0211\mathrm{A} \tag{3}$$

C, O, S, N and A are the carbon, oxygen, sulphur, nitrogen and ash content of the material respectively, expressed in mass percentages of dry basis (Channiwala & Parikh, 2002)

This HHV could then be converted to LHV using equation number 4 (obtained from Nieuwlaar et al., 2014). This equation subtracts the latent heat of vaporisation of water vapour formed by combustion from the HHV.

$$LHV = HHV - h * 2.442 * 8.936 \qquad (4)$$

Where: h= mass fraction of hydrogen in the fuel.
2.442= heat of evaporation of water (in MJ/kg).
8.936= mass of water created per unit mass of hydrogen (in kg $H2O$/ kg H).

4.3.7 Life Cycle Inventory

After the goal and scope definition, a Life Cycle Inventory Analysis (LCI) is performed on both of the suitable conversion routes. The data was collected through interviews with experts in the field and scientific literature. Different articles often use different values for the in- and outputs of the processes, in which case the most suitable value or an average was chosen. Energy calculations were done on a LHV basis, as explained in section 4.3.6. Mass and energy balances of the complete conversion routes were created, to ensure the same amount of mass and energy was going into the system as was leaving the system.

The optimal conversion routes are a general description of the main technologies that were used. Now, first the exact cases had to be defined, that describe all the included sub-processes and energy and material flows. The base cases as considered in this research was chosen from a few different cases that were found in the literature. They are simple cases, that assume external electricity and hydrogen production. This can provide a basic result that can in the future form the basis for the calculation of GHG emissions of different scenarios, where the number of included processes can be extended. The flow charts of the two cases can be found in figure 10 (Kraft lignin conversion) and 11 (SE lignin conversion). For convenience, the conversion route was subdivided into the following stages:

1. Lignin isolation
   Comprises the in- and outputs related to the isolation of the lignin from the waste stream.
2. Indirect effects
   Extracting lignin from a Kraft mill or lignocellulosic biorefinery caused a change in their energy balance. These indirect effects were described in this section.
3. Pretreatment
   Comprises the in- and outputs of the necessary grinding, drying and feed handling of the lignin before it is suitable to be converted in the fast pyrolysis reactor.
4. Fast Pyrolysis
   This step assesses the in- and outputs from converting the lignin into the three pyrolysis products: gas, oil and char. This step includes the quenching of the pyrolysis vapours to obtain the bio-oil.
5. Hydrotreater
   During this process the hydrogen is added to the bio-oil to create a more stable and more suitable marine fuel.
6. Char combustor
   The char was separated from the bio-oil and gas, and was combusted here to provide process heat.

Each of these stages, and all the included processes, were discussed in this section for each of the conversion routes. The fast pyrolysis and upgrading stage was the same for both routes.

Figure 10: A flow chart of the material and energy flows considered for the conversion of Kraft lignin to marine biofuel.

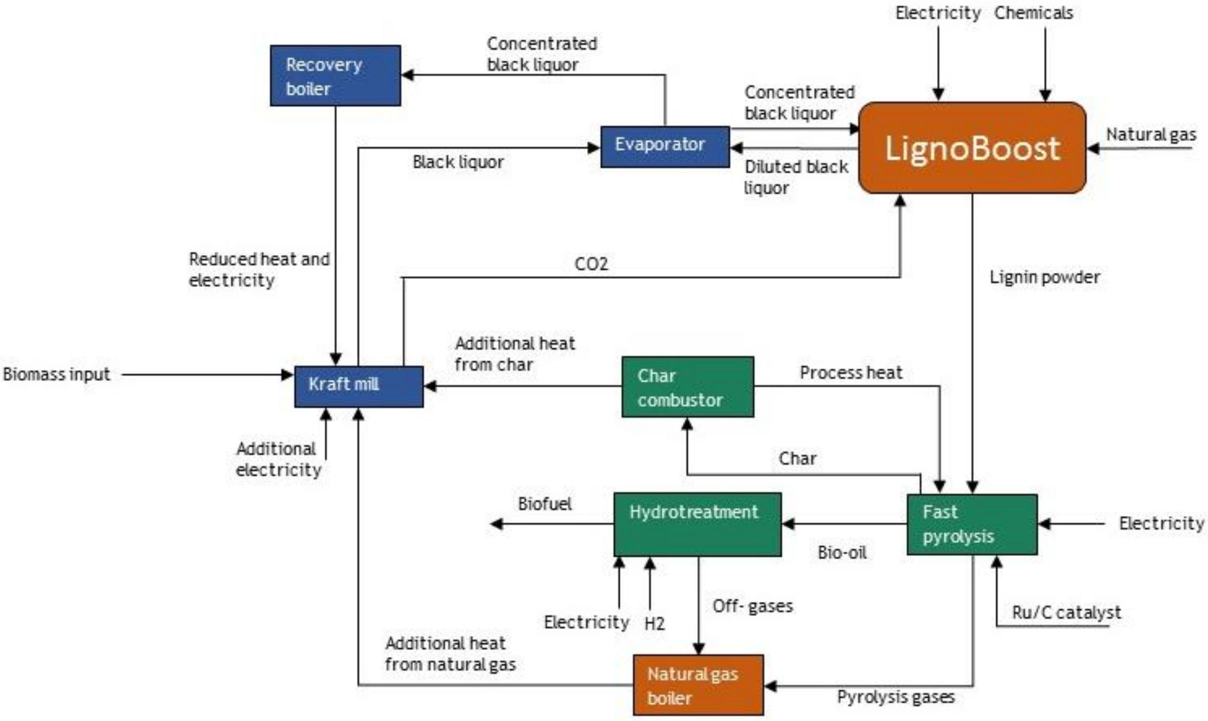
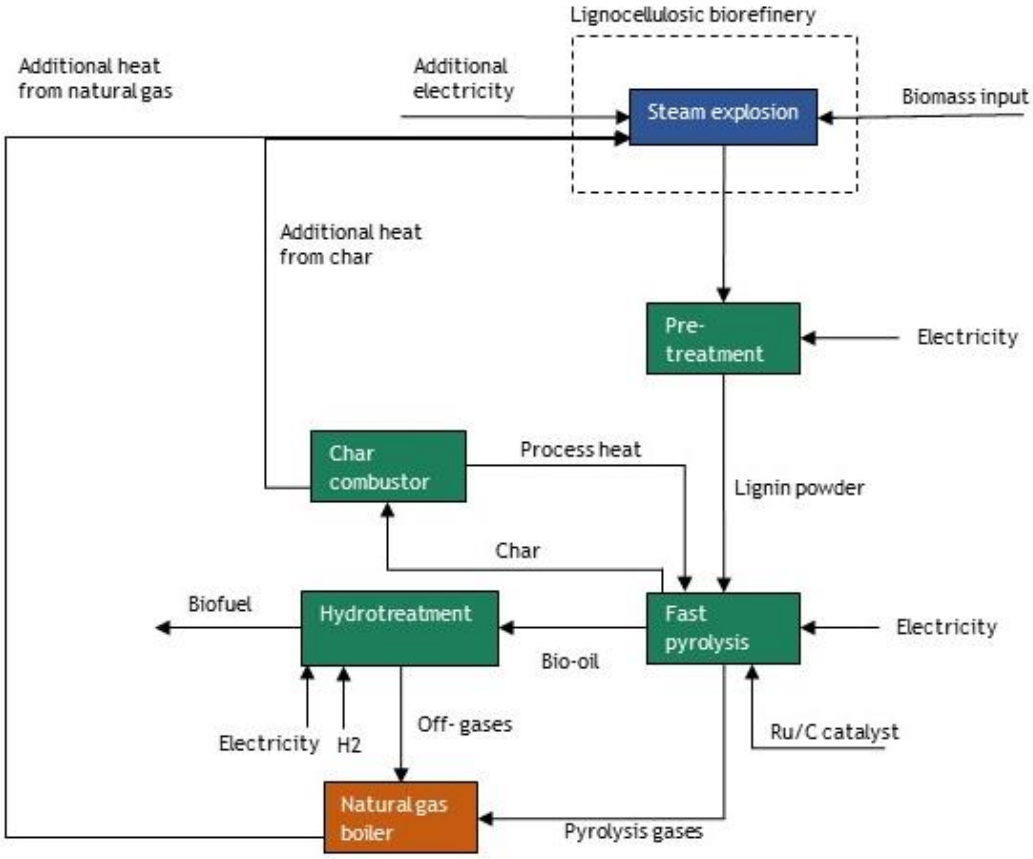


Figure 11: A flow chart of the material and energy flows considered for the conversion of SE lignin from a lignocellulosic biorefinery to marine biofuel.



Lignin isolation

Kraft lignin isolation

It was assumed that roughly half of the total lignin in the black liquor stream was removed with the LignoBoost process, translating to 300 kg of lignin per tonne of pulp produced. Removing this quantity of lignin was found not to have a significant effect on the burning properties of the black liquor, besides obviously a lower LHV. This means that the black liquor could still be burned by currently operating recovery boilers after lignin removal, though less energy was produced (Manninen, 2010).

The LignoBoost process consumed electricity that is assumed to be obtained from the national grid. Furthermore, CO_2 was consumed in the precipitation reactor and it was recycled back to the evaporator and the recovery boiler. It reacts with Na at the recovery boiler, leading to an increase of Na2CO3 in the smelt stream (Benali et al., 2016). This CO_2 can be subtracted from the GHG emissions, though only if it is CO_2 that would otherwise be emitted. For this research the CO_2 is assumed to be obtained from a CO_2 emitting process (e.g. from the lime kiln) and was thus accounted for as negative emissions (Manninen, 2010).

Steam Explosion lignin isolation

The lignin from the lignocellulosic biorefinery does not require any additional isolation processes.

Indirect effects

Kraft lignin indirect effects

It is important to realise that the lignin isolation affects the Kraft paper/pulp mill significantly, since it used the lignin to generate the required process heat and electricity. Less lignin will be available for combustion in the recovery boiler, causing the recovery boiler to produce less steam and electricity (Benali et al., 2016). For the base case scenario, the heat production of the mill is maintained the same as without lignin isolation. The reduction in electricity production is substituted by electricity from the national grid, since it regards either electricity that used to be supplied to the grid - this will simply not be supplied and will need to be compensated by the other suppliers, or it regards electricity that is needed by the mill - this can be consumed from the national grid. The additional energy that is required by the evaporators to evaporate the water from the diluted black liquor stream is assumed to be obtained from the combustion of natural gas. Possible other possibilities would have been char or forest residues like bark. Natural gas was chosen because it is a relatively easy and cheap option (Karatzos et al., 2014). Recovered sodium from the electrostatic precipitator and bleaching plant (make-up sodium) are considered sufficient to compensate for the process losses. However, sodium hydroxide required for neutralizing the recycled stream from the lignin process to the existing evaporators is included in the LCA inventory. Furthermore, it is assumed that the waste water treatment plant (WWTP) installed at the Kraft pulp mill has adequate capacity for treating the incremental effluent streams and that the capacity of the mill's existing evaporator system is sufficient to concentrate the spent and filtrate streams, which are recycled from the lignin recovery process and mixed with the weak black liquor. The transportation distance for chemicals and consumables transferred to the mill gate is 200 km (Benali et al., 2016; Manninen, 2010).

Steam explosion lignin indirect effects

The lignin used to be combusted in the lignocellulosic biorefinery to generate heat and electricity. If the lignin is extracted and used to produce marine biofuel, the biorefinery will have to substitute for the removed lignin, just like the Kraft mill. Just like for the Kraft mill, it is assumed for the base case scenario that the reduced heat production is compensated for by natural gas combustion, since this is generally the easiest and cheapest option (Karatzos et al., 2014). The reduced electricity production is compensated for by purchasing electricity from the grid. Since around 45% of the Brazilian primary energy requirement is met by renewable energy sources it is more sustainable to purchase electricity from the grid than to produce it from natural gas (IEA, 2013). The boiler is assumed to be less efficient for lignin as for natural gas. The efficiency for lignin is 85%, while the efficiency for natural gas assumed to be 95%. The assumed energy consumption for ethanol production from lignocellulosic biomass is 3.8 GJ of steam and 792 MJ of electricity (Scott et al., 2008). This research will assume the same ratio of heat to electricity. The biorefinery is assumed to have a boiler producing heat in the form of steam for the processes and for electricity production. Electricity is produced from the steam with an assumed efficiency of 80%.

Pre-treatment process

Kraft lignin pre-treatment

It was assumed that the fast pyrolysis plant was located next to the Kraft paper/pulp mill, so that no additional transport was required. The grinding and drying of the lignin was already included in the LignoBoost process.

Steam explosion lignin pre-treatment

Lignin must enter the fast pyrolysis reactor as fine, dry particles. Therefore, the moist steam explosion lignin sludge was first pre-treated to avoid yield losses and reduce the heat requirements. The pre-treatment comprised of mechanical grinding and drying. This research aimed for a **particle size of 2 mm** and a **moisture content of 7%**. Heat from the char combustor was used for the drying process.

Fast Pyrolysis

The fast pyrolysis stage was the same for the Kraft lignin conversion as for the SE lignin conversion. There is a number of process variables that could be varied with fast pyrolysis, e.g. temperature and reactor design. The base case process chain assumed the conversion of 2000 dry tonne of lignin/day, however processed in 4 fast pyrolysis reactors of 500 dry tonne/day. This was based on reactor sizes found in literature, and due to concerns about the scalability of the current reactor pyrolysis designs (Tews et al., 2014; Wright et al., 2010). The heat required for the pyrolysis was provided by a char combustor. The excess heat produced by the char combustor was send to the Kraft mill or lignocellulosic biorefinery to partly compensate for the reduced heat and electricity production caused by the extraction of lignin. The pyrolysis gases were combusted in a gas-fired boiler to produce process heat. It was assumed that all the biogenic methane in the pyrolysis gas was stoichiometrically combusted according to reaction number 5, so that only CO_2 was emitted. This was biogenic CO2, and can be considered carbon neutral, as explained in section 1.2. (E. Johnson, 2009). This scenario assumed that the hydrogen was imported.

$$CH_4 + 2(O_2 + 3.76\,N_2) \rightarrow\ CO_2 + 2H_2O + 7.52N_2{}^{2} \qquad (5)$$

A fluidised bed reactor at a temperature of 520°C and a residence time of 1-2 seconds was assumed. The reactor was heated with hot sand. The pyrolysis vapours, char and sand exited the reactor. The char, ash and sand were separated by the cyclones and sent to the char boiler, where the char was combusted to provide process heat for the fast pyrolysis reactor and Kraft mill or lignocellulosic biorefinery, and the sand was re-heated. The pyrolysis vapours were quenched in the cooling tower to a temperature of 35 degrees at atmospheric pressure. Part of the non-condensable gases was used as fluidising medium in the reactor (Tews & Elliott, 2014).

Upgrading

Process conditions

Low severity hydroprocessing, under low pressure and temperature, was thought to be sufficient in order to merely stabilise the bio-oil (Tews & Elliott, 2014). Low severity hydroprocessing was performed at a single stage hydroprocessing reactor, at lower temperature and pressure than more severe hydroprocessing. The hydroprocessing conditions were obtained from Tews & Elliott (2014), who researched the low severity upgrading of biomass derived fast pyrolysis oils. They used a fixed-bed, continuous-flow reactor, packed with catalyst and combined the bio-oil with compressed hydrogen and pressurised the mixture to 10 MPa. This was led over the catalyst bed a rate of 0.50 volume of oil per volume of catalyst bed per hour, at a temperature of 85°C. The temperature of the raw bio-oil was already almost the right temperature, so no additional heat input was assumed (Tews & Elliott, 2014). The hydroprocessing was assumed to take place in a hydrogen-rich environment, containing around 5 wt.% of hydrogen (Wright et al., 2010). After the upgrading process, 90% of the hydrogen in the off-gas was assumed to be recovered by a pressure swing adsorption (PSA) system and re-used in the hydroprocessing reactor (Tews & Elliott, 2014). The same catalyst as used by Tews and Elliot (2014), was also assumed for this research. This is a Ru/C catalyst that has experimentally been shown to create a sufficiently stable bio-oil from biomass derived fast pyrolysis oils (Tews & Elliott, 2014).

Process reactions

The inventory analysis for the hydrotreatment stage was a little more complex than for the other stages and based on the composition of the lignin derived fast pyrolysis oil. This composition was obtained from scientific literature. From this composition, the amount of hydrogen that was required to obtain a Heff/C ratio of 1.4 was calculated, as well as the composition of the flue gases.

For convenience of the calculations, the amount of hydrocarbon gases that were the result of cracking, was assumed to be only related to the amount of bio-oil input, and not to the extent of the hydrotreatment. This was done, because calculation of the exact quantity of these gases is very complex, and fell out of the scope of this research. It was assumed that these gases were substituted by 1 hydrogen atom.

Due to the complexity of estimating the hydrogen requirements for the hydrogenation processes, the base case scenario assumed that no saturation of the components occurred. Thus, no hydrogen input for the saturation of the aromatics and olefins was included.

The results of this hydrotreatment step was a stabilised bio-oil with a high moisture content. Before the oil was suitable as a fuel, the water had to be removed. This was assumed to be done through a simple decantation step, which was not assumed to emit significant GHGs. This step was therefore not included in the LCA.

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[2] (The Engineering Toolbox, n.d.)

Upgrading

The following assumptions were made for the assessment of the upgrading stage. These assumptions were further explained in the text.

1. Selectivity of H atoms is the same for each of the impurities.
2. The following products were formed from the impurities:
    - O → H2O (l)
    - N → NH3 (g)
    - S → H2S (g)
    - Cl → HCL (g)
3. Hydrocarbon gases were substituted by 1 hydrogen atom.
4. All water formed during hydrotreatment was in liquid phase.
5. The gases that were formed were not soluble in water, they were all removed from the biofuel.
6. There was enough time for the required processes to take place.

The number of C, H and O atoms that were removed from the bio-oil by formation of the hydrocarbon gases are not related to the amount of upgrading. Therefore, they were subtracted from the total number of C, H and O atoms in the pyrolysis oil before calculation of the quantity of heterogeneous impurities that had to be removed to obtain the required Heff/C ratio of 1.4. The chlorine, nitrogen, sulphur and oxygen, were removed as HCl, NH3, H2S and H2O respectively (Jechura, 2016) and the selectivity of H atoms was assumed to be the same for each of the impurities.

To calculate the H consumption and impurities removal, first the required H in the biofuel was calculated:

$$H = 1.4 * C \qquad (6)$$

$$\text{So: } H = 1.4 * (C_{in\ bio-oil} - C_{in\ hydrocarbon\ gases}) \qquad (7)$$

Next the hydrogen content of the fast pyrolysis oil and the H required for the substitution of the hydrocarbon gases were subtracted from this required H, and the H emitted through the hydrocarbon gases was added. This resulted in the H that was consumed by substitution of the heterogeneous impurities to obtain a H/C ratio of 1.4. Note that this was not the H consumed to obtain an effective H/C ratio of 1.4, since the amount of impurities left in the biofuel was not known yet. The exact amount of hydrogen consumption for an Heff/C ratio of 1.4 was later obtained using the Solver function in Excel.

The fraction of impurities that was removed, was calculated by dividing the H consumption by the total amount of impurities in the pyrolysis oil. When the percentage of impurities that had to be removed with the input of hydrogen was known, the absolute amount of removed impurities could be calculated for each impurity. This was done by taking the product of this percentage and the moles of impurity present in the bio-oil. Since it was known that O → H2O (l), N → NH3 (g), S → H2S (g) and Cl → HCL (g), the mole impurity that was removed equalled the mole gas formed. It also equalled the mole hydrogen consumed by substitution, assuming each atom of impurity was substituted by one H atom. The moles of hydrogen atoms needed for formation of the gases was calculated by taking the product of the amount of each gas (in mole) and the amount of H atoms in that gas. For each of the produced gases, the HHV was obtained from literature[3] and the HHV of the overall gas was calculated. Part of the water that was produced as a result of the deoxygenation reactions would exit the oil as a gas. However, since the gases were separated at a temperature of 60°C and a pressure of still 100 bar, the vapour pressure of the water was so small that for this research it was assumed negligible. Some of the gases were actually soluble in water, but it was assumed that they were all removed from the biofuel in the gas phase. It was assumed that there was enough time for the required reactions to occur.

The hydrotreatment took place in a hydrogen-rich environment, containing 5 wt.% of hydrogen (Wright et al., 2010). Therefore, the actual hydrogen input/dt of lignin was calculated using equation 8.

$$0.05 * bio - oil\ yield + H\ consumption\ for\ biofuel\ upgrading \qquad (8)$$

After the upgrading process, 90% of the hydrogen in the off-gas was assumed to be recovered by a pressure swing adsorption (PSA) system and re-used in the hydroprocessing reactor (Tews & Elliott, 2014). This was calculated using equation number 9, the other 10% was lost and exits the reactor with the off-gases.

$$0.05 * bio - oil\ yield * 0.9 \qquad (9)$$

By subtracting the weight of the removed impurities, except for the oxygen since this remains in the oil in the form of water, and hydrocarbon gases from the original weight of the bio-oil, and adding the weight of the substitution H atoms, the weight of the upgraded biofuel was obtained. This weight, divided by 100, was also the yield of upgraded biofuel per unit of bio-oil. The moisture content of the biofuel was calculated by dividing the weight of the water by the weight of the biofuel on a wet basis.

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[3] ("Fuel Gases And Heating Values," n.d.)

To calculate the amount of hydrogen required for the upgrading for the scenarios presented in this report, first the Solver function in Excel was used for the optimal Heff ratio. The Heff ratio was the requested results, and the prerequisites were that it should be >1.4, while the S content of the stabilised oil should be >0.1 Wt.%. The H/eff ratio was calculated with equation number 2, presented in section 2.4. With the optimal Heff/C ratio, the overall hydrogen consumption comprised the hydrogen used for:
Substitution of impurities + Formation of gas from impurities + Substitution of hydrocarbon gases + Lost in waste stream (not recovered by PSA) – hydrogen emitted with hydrocarbon gases.

Char combustor

A char combustor was included in the scenario to provide process heat. The char was obtained from the fast pyrolysis reactor, and the combustion heat was partly used for the fast pyrolysis process, partly for the drying of the lignin and partly for the Kraft mill or lignocellulosic biorefinery. Stoichiometric combustion was assumed. The useful heat efficiency of the char combustor was assumed to 84%, meaning that 16% of the generated heat was lost. This efficiency was calculated from Tews et al. (2014).

4.3.8 Life cycle Inventory Assessment

In the Life Cycle Impact Assessment (LCIA) stage of the LCA, the GHG emissions were calculated for each of the relevant in- and outputs that were listed in the LCI. They were converted to the correct functional unit, CO_2-eq/MJ biofuel, and added to obtain the overall GHG that were associated with the process. The same structure was used as in the LCI. Thus, the results were first calculated per life-cycle stage and presented in CO_2-eq/dt of lignin. The individual results were merged and converted to the proper functional unit in the end. The CO_2-eq emission factors for electricity was obtained from the EcoInvent database in SimaPro. For the electricity, the emissions of the national grid, low voltage are used. This includes electricity production and imports, and losses during transmission. The natural gas combustion emission factor was obtained from IPCC (2006) guidelines, the default values were used. Added to this were the natural gas emissions for distribution network as obtained from the EcoInvent database, including leakages. The hydrogen emission factor was also obtained from EcoInvent, from which the values for hydrogen at the European market were chosen.

4.3.9 Uncertainty and Sensitivity Analysis

For the LCA, the uncertainty and sensitivity of the results was analysed through a Monte Carlo simulation. The @Risk7.5 program in Excel was used to perform the analysis.

The key parameters were identified and for each of these parameters the preferred probability density function (PDF) was determined, as well as the associated range of values or the standard deviation (STD). This was done according to IPCC guidelines. Since for most of the assessed parameters, only one or a few values were found, expert judgement was required to choose the most appropriate PDF and uncertainty ranges. The sensitivity analysis was also performed in the Monte Carlo analysis in the @Risk program. 50.000 Iterations were used to calculate the probability of the final answer, as this provides a strong base for the stochastic calculations.

4.4 Alternative configurations

After the direct and indirect GHG emissions of the base case scenario were obtained, 2 other alternative configurations were assessed. These used the same assumption and methods as the base case, only process characteristic was be changed. The two alternative configuration are presented below.

1. Using renewable electricity instead of electricity from the national grid.
   Electricity from photovoltaic solar panels was assumed, the emission factor was obtained from the EcoInvent database. The same value was used for both conversion routes (a Finnish emission factor). It was assumed that all the electricity was obtained from these panels, also for the indirect effects.
2. Co-combusting the excess char in a nearby coal-fired power plant.
   Transport and combustion emissions were considered. A nearby coal-fired power plant was chosen for both of the conversion routes. The emission factors were obtained from the EcoINvent database. It was assumed that 20% of the coal would be replaced by char and that this does not influence the efficiency of the power plant.

4.5 Data collection methods

4.5.1 Literature research

To gather information for this research, a literature research was performed. The sources used to obtain the required data were company websites and (online) scientific and non-scientific articles.

4.5.2 SimaPro

For some inputs, e.g. electricity from national grid, natural gas and diesel, the associated emissions were obtained through the EcoInvent 3 database. This database was accessed through the LCA software

SimaPro8 V8.0. If the database did not contain the exact required information, comparable data was extracted.

Results

5 The lignin supply market

The lignin producers can roughly be subdivided into lignocellulosic biorefineries and paper/pulp mills, where the lignocellulosic biomass is fractionated and lignin remains as a by-product (de Wild et al., 2014). The supply of lignin from both lignin sources is discussed in this section.

5.1 Paper/pulp mills

In 2010, the paper/pulp industry produced ca. 50-70 Mt lignin (Laurichesse & Avérous, 2014; Lora, 2008; Strassberger et al., 2014). The vast majority of this lignin, between 40 and 55 Mt, is Kraft lignin, released within the black liquor waste stream from the Kraft pulping process (Bruinincx et al., 2016; Gosselink, 2011). Lignin is also produced by the other pulping processes: organosolv, soda and sulphite pulping (Hanlon et al., 1998). The majority of the lignin (>95%) is combusted for electricity and heat production, only a small part of the lignin is currently used for commercial applications (Laurichesse & Avérous, 2014; Li et al., 2015).

The global production of paper and paperboard amounts currently approximately 400 Mt. The production volumes are still growing, especially due to increasing consumption in China and other parts of Asia. It is estimated that the global production will increase to 500 Mt in 2025 (Finnish Forest Industries, 2013). This means that also the global lignin production from paper/pulp mills will increase. A quick calculation learns that if the annual global pulp production increases from 400 to 500 Mt, the annual global lignin production will roughly increase from 50-70 Mt to 62.5-87.5 Mt (current lignin production times the $^5/_4$ increase in production). Assuming the share of Kraft lignin to be 80% (roughly the current share), the future Kraft lignin production will be between 50 and 70 Mt.

Many paper/pulp mills exist in the world, too many to list here. For this thesis, only the large mills in Scandinavia and Brazil are shown here, since only the lignin conversion routes in these regions are assessed. Table 7 shows the largest paper/pulp mills in these regions and the amount of pulp produced by them, as well as the feedstock, production process and electricity self-sufficiency (where found). Also a few large new paper/pulp mills and expansions of current mills are planned (Table 8). It is obvious that the Kraft process is the most used pulping process.

Table 7: The largest existing paper/pulp mills in Scandinavia and Brazil.

Current Paper/Pulp mills in Scandinavia and Brazil			Total Pulp production	Feedstock	pulping process	Electricity self-sufficiency
Country	Cooperation	City	Mt/yr.			%
Finland	Metsa Fibre	Joutseno	0.69	Softwood	Kraft	173
		Kemi	0.53	Softwood and hardwood	Kraft	151
		Rauma	0.65	Softwood	Kraft	145
		Aanekoski	0.53	Softwood and hardwood	Kraft	129
	UPM Pulp	Lappeenranta	0.74	Softwood and hardwood	kraft	>100% self-sufficient. Additional surplus sold to grid
		Kouvola	0.7	Softwood and hardwood	kraft	>100% self-sufficient. Additional surplus sold to grid
		Pietarsaari	0.8	Softwood and hardwood	kraft	>100% self-sufficient. Additional surplus used for paper production
Sweden	Sodra Cell	Monsteras	0.7-0.8		kraft	
	Stora Enso	Borlange	0.8		Integrated mechanical pulp	
	SCA	Sundsvall	0.8		Integrated mechanical pulp	
	Metsä Board Sverige	Husum	0.7-0.8		Kraft	
	BillerudKorsnäs Skog och Industri AB	Gävle	0.7-0.8		Kraft	
	Domsjo	Örnsköldsvik	0.255	Softwood	lignosulfonates	
Brazil	Suzano pulp and paper	Mucuri, Bahia	1.74	hardwood (eucalyptus)	Kraft	
		Imperatriz, Maranhao	1.5	hardwood (eucalyptus)	Kraft	
		Suzano, Soa Paolo	0.63	hardwood (eucalyptus)	Kraft	
		Limeira, Sao Paolo	0.65	hardwood (eucalyptus)	Kraft	
	Fibria	Barra do Riacho, Espírito Santo	2.3	hardwood (eucalyptus)	kraft	self-sufficient, producing 170MWh
		Jacarei, sao paolo	1.1	hardwood (eucalyptus)	kraft	Self-sufficient in electricity, with over 80% from renewable natural resources
		The Três Lagoas, Mato Grosso do Sul State	1.3	hardwood (eucalyptus)	kraft	self-sufficient in energy, using biomass from eucalyptus and black liquor used in the industrial process
	Eldorado Brasil	The Três Lagoas, Mato Grosso do Sul State	1.7	hardwood (eucalyptus)	kraft	Production capacity of 20 MW/h. 95 MW is used in pulp production, 50 MW is supplied to companies that produce inputs (White Martins and AkzoNobel), surplus is sold to grid.
	Cenibra	Belo Oriente, Minas Gerais	1.2	hardwood (eucalyptus)	Kraft	
	Veracel	Eunapolis, Bahia	1.1	hardwood (eucalyptus)	Kraft	>100% self-sufficient, surplus (ca. 35% of total electricity) sold to grid
	Bahia Specialty celulose	Camaçari Industrial Complex, Bahia	0.485	hardwood (eucalyptus)	Kraft	
	Orsa International	Mogi-Guaçu, São Paulo	0.4	hardwood (eucalyptus)	Kraft	

Current Paper/Pulp mills in Scandinavia and Brazil			Total Pulp production	Feedstock	pulping process	Electricity self-sufficiency
Country	Cooperation	City	Mt/yr.			%
		Luiz Antonio, São Paulo	0.41	hardwood (eucalyptus)	Kraft	
	CMPC	Guaiba, Brazil	1.75	hardwood (eucalyptus)	Kraft	>100% self sufficient

Table 8: The largest planned paper/pulp mills in Scandinavia and Brazil.

Future Paper/Pulp mills in Scandinavia and Brazil				Total Pulp production	Feedstock	pulping process	Electricity self sufficiency
Country	Cooperation	City	Planned start of operations	Mt/yr.			%
Finland	Metsa Fibre	Aanekoski	end 2017	1.3	Softwood and hardwood	Kraft	240
	Finnpulp	Kuopio	2021	1.2	Softwood	Kraft	(1TWh) Surplus to grid
Sweden	Sodra cell	Värö	end 2016	0.7	softwood	Kraft	
Brazil	Klabin	Ortigueira, Paraná	2017	1.5	hardwood and softwood	Kraft	270 MW, of which 150 MW supplied to grid
	Eldorado Brasil	The Três Lagoas, Mato Grosso do Sul State	(2017?)	3.5	hardwood (eucalyptus)	Kraft	>100% self-sufficient, additional surplus supplied to companies that produce inputs (White Martins and AkzoNobel) and sold to grid.

5.2 Lignocellulosic biorefineries

A biorefinery is defined as a refinery that produces gaseous or liquid biofuels, chemicals or other products that are usually produced at traditional refineries, using agricultural or forestry biomass (first, second or third generation) as feedstock (Bajpai, 2013). The production of chemicals from biomass started already in the first half of the 20th century and is important for biorefineries because of the high value of the chemicals in combination with low material demands.

The ethanol production from second generation lignocellulosic biomass in so called lignocellulosic biorefineries has only recently started commercializing, so not many exist yet. In the US, the four first commercial scale lignocellulosic ethanol facilities became operational in 2014 (RFA, 2015), three of them are still operational today. Furthermore, one facility exists in Brazil and one in Italy. As can be seen in Table 9, the total current ethanol production from lignocellulosic biorefineries amounts 394 million liters per year. Generally, it can be assumed that per kg of ethanol, 0.5 kg of lignin is produced (Bruinincx et al., 2016). Therefore 0.399 kg of lignin is produced per liter of ethanol, assuming a density of 0.789 g/mL (Nutrientsreview.com, n.d.). The estimated amount of produced lignin per lignocellulosic biorefinery, as well as the total global production, can also be found in Table 9. The overall amount of lignin currently produced at lignocellulosic biorefineries is 157 Kt, or 0.157 Mt. Thus, it can be concluded that the total amount of lignin produced by these biorefineries is at present still much less than at the paper pulp mills.

Table 9: The lignocellulosic biorefineries, their cellulosic ethanol production and pre-treatment method.

Company	Location	Total ethanol production (million litres/yr.)	Total lignin production (kt/yr)	Pre-treatment process
Beta Renewables	Crescentino, Italy	75[4]	29.9	Steam explosion[5]
GranBio	Sao Miguel dos campos, Alagoas, Brazil	82[6]	32.7	Steam explosion[3]
POET-DSM	Emmetsburg, IA, USA	76[7]	30.2	Dilute sulphuric acid / Steam[8]
Quad County Corn Processors	Galva, Ida County, Iowa, USA	8[9]	3.0	Ammonia / Steam[10]
DuPont	Nevada, IA, USA	114[11]	45.3	Ammonia / Steam[12]
Raízen Energia	Costa Pinto, Piracicava, Brazil	40[13]	16.0	Sulphuric acid / steam[14]
Total	**global**	**394**	**157**	

The market for cellulosic ethanol is expected to grow significantly in the future, partly driven by government imposed renewable fuel mandates. In 2015, 34 individual countries plus the European Union had these mandates in place (Seay & You, 2016). An important example is the United States Energy Information and Security Act (EISA), requiring at least 60.6 billion liters of lignocellulosic biofuels by 2022, a steep increase from the circa 200 million liters they are currently commercially producing. Furthermore, the Renewable Energy Directive of the European Commission requires 10% of all transportation fuels to be renewable by 2020 and India aims to increase the ethanol usage in gasoline from the current 5% to 20% by 2017 (Seay & You, 2016). China set the goal to produce 300 million tonne of cellulosic and non-grain ethanol by 2020 (USDA Foreign Agricultural Service, 2015).

However, it remains to be seen whether these targets will actually be achieved. The target for lignocellulosic biofuels in the EISA for 2015 was 3 billion liters, while, as stated before, the current production is only around 200 million liters. Also China faces difficulties as industry experts expect the cellulosic ethanol produced in China by 2020 to be around 10 million tonnes instead of 300 (USDA Foreign Agricultural Service, 2015). Furthermore, a lignocellulosic biorefinery that started in 2014 has recently filed for bankruptcy (Abengoa in Kansas), and another one, built in 2012, never started production (INEOS BioEnergy Centre in Florida) (Rapier, 2016). On the other hand the market is expanding, since several new lignocellulosic biorefineries are currently being built to start production in the near future, (see Table 10) and plans for the development of more projects are in the making (Lane, 2015).

The currently planned biorefineries, excluding China, cause an increase of 163 Kt in the annual lignin production in the world by 2019 (see Table 10). Since the market only recently started commercialising and still faces technical and economic difficulties, its future development is still uncertain (Rapier, 2016). For this report, we will assume a linear increase in production from 2019 to 2025, thus another increase of 326 Kt. The 10 million tonnes of lignocellulosic ethanol that will be produced in China by 2020 according to industry experts, which signifies a lignin production of roughly 5 million tonnes (again assuming 0.5 kg lignin per kg of lignocellulosic ethanol). Assuming once more a linear increase in production leads to another 5 million tonnes increase between 2020 and 2025. A linear increase is a conservative estimation, but since biorefineries are currently closing down and growth is still much less than was estimated before, an exponential growth is probably too much. Therefore, an overall increase of roughly 10,489 Mt is expected until 2025. By adding the current production, the total annual lignin production from lignocellulosic biorefineries in 2025 is calculated to be around 10.646 Mt. A small majority of this lignin will be isolated through the steam explosion process.

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[4] (BetaRenewables, n.d.-a)
[5] (Biochemtech, 2013)
[6] (BetaRenewables, n.d.-b)
[7] (Poet-DSM, n.d.)
[8] (D. L. Jones, 2010)
[9] (Rosen, 2015)
[10] (D. Johnson, 2015)
[11] (DuPont, n.d.)
[12] (Provine et al., 2014)
[13] (Lane, 2014b)
[14] (Iogen Corporation, n.d.)

Table 10: The currently planned lignocellulosic biorefineries

Company	Location	Ethanol production (million litres/yr.)	Lignin production (kt/yr)	Pre-treatment process	Planned start of production
Biochemtex	Clinton, NC, USA	75[15]	29,9	Steam explosion (Proesa technology) [13]	2018[13]
Energochemica with Biochemtech	Strazske, Slovak Republic	69[16]	27,5	Steam explosion (Proesa technology) [14]	2017[17]
M&G Group with Guozhen group	Fuyang (Anhui Province), China	251[18]	100,0	Steam explosion (Proesa technology)[16]	Construction is expected to start in 2016[16]
Maabjerg Energy Centre	Maabjerg, Denmark	77[19]	30,7	Steam explosion (Inbicon technology)[17]	2018[17]
DuPont	Pelagonia, Macedonia	100[15]	39,9	Ammonia/ steam[15]	2018[15]
Bluefire	Lancaster, California	15[20]	6,0	Sulphuric acid hydrolysis[18]	Unknown
Bluefire	Fulton, Mississippi	72[18]	28,7	Sulphuric acid hydrolysis[18]	Unknown
Total	**Global**	**659**	**263**		

5.3 Optimal feedstock and feedstock source

The overall lignin supply currently amounts roughly 50-70 Mt of lignin. The lignin produced by lignocellulosic biorefineries currently amounts only 0.16 Mt (or 0.22-0.31% of the total), so it can be concluded that almost all of the lignin is released at paper/pulp mills. Since most paper pulp mills use the Kraft cooking process, the majority of the lignin is Kraft lignin, released as part of the black liquor.

The numbers show that although the lignin released at the lignocellulosic biorefineries possibly increases to 10.6 Mt in the next ten years, the production will remain much smaller than the lignin released by the paper/pulp industry. It should be noted that the lignin produced at biorefineries is a rough estimation, because it is still uncertain how the lignocellulosic ethanol market will evolve. The paper/pulp industry on the other hand is a very mature industry, that is more predictable. Furthermore, most of the lignin released by lignocellulosic biorefineries is expected in China, while paper/pulp mills can be found all over the world.

Based on this information, it is clear that Kraft lignin is now, and will remain, the largest source of feedstock and it is reliable and widespread. The downside is that Kraft lignin contains sulphur, though processes exist to desulphurise the lignin in order to produce sulphur-free biofuels. However, the amount of steam explosion lignin will also be substantial in the future, and they have the benefit of being sulphur-free. Therefore, both Kraft lignin and steam explosion lignin are chosen as the most suitable feedstocks for marine biofuel production, so they were both assessed.

5.4 The biofuel potential

The current biofuel potential from lignin was calculated from the current available lignin assessed in sections 5.1 and 5.2, and the stabilised biofuel yield as calculated in chapter 7. The total available lignin is currently approximately 50 – 70 Mt of lignin from paper/pulp mills and 0.16 Mt of lignin from lignocellulosic biorefineries. The yield of stabilised biofuel per tonne of Kraft lignin was calculated to be 0.25 t (dry oil) and for steam explosion lignin it was 0.29 t (dry oil). Therefore, the current potential of biofuel is approximately **12.6 – 17.6 Mt of biofuel per year.**

If in ten years the lignin production has expanded to 62.5-87.5 Mt from paper/pulp mills and 10.646 Mt of lignin from lignocellulosic biorefineries, the biofuel potential will also increase. The future biofuel potential is estimated at **18.7 – 25.0 Mt of biofuel per year.**

To calculate the potential share of biofuel in the maritime fuel market, it was assumed that one tonne of biofuel can replace one tonne of fossil fuel. The heating values of the fuels are approximately similar; The LHV of the biofuel from Kraft lignin was calculated to be 41.35 MJ/kg and that of steam explosion lignin was approximately 38.46 MJ/kg, while the LHV of residual marine fuel, currently often used in the large vessels in the maritime industry, is 40 MJ/kg. The current maritime fuel consumption was estimated

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[15] (BetaRenewables, n.d.-c)
[16] (BetaRenewables, n.d.-d)
[17] (Lane, 2014a)
[18] (Biochemtex, n.d.)
[19] (MEC, 2015)
[20] (Bluefire, n.d.)

between 250 and 325 Mt/yr. (average between 2007 and 2012) (IRENA, 2015). Taking the median of both the biofuel production and total fuel consumption, the current potential market share of the biofuels is roughly **5.2%** of total maritime fuel consumption. The shipping emissions are expected to have increased with 50-250% from 2012 to 2050. It is assumed that the fuel consumption will increase accordingly. Assuming a conservative 25% increase of the 2012 value up to 2026 (ten years), the potential share of biofuels in ten years is **6.0%.**

6 Choice of conversion route

In order to select the optimal conversion route, first the most suitable conversion technology had to be determined. This was done through a multi criteria assessment (MCA), presented in section 6.1. Secondly, the most suitable upgrading process was decided on in section 6.2. The most suitable isolation process was determined in section 6.3. Finally, the optimal feedstock, conversion technology and upgrading process were combined in section 6.4, resulting in the optimal conversion route.

6.1 Most suitable conversion technology

In this section the results of the MCA that was performed to find the most suitable conversion technology are presented.

6.1.1 Effects table

The results of the assessment are shown in the effects table (Table 11). The yields presented were obtained from scientific literature. The large ranges for some of the technologies are due to different catalyst or solvents used. The quality of the bio-oil is assessed for each technology relative to the rest. The worst quality bio-oil is obtained from fast pyrolysis and the best quality from gasification Fischer-Tropsch. Pyrolysis produces three valuable by-products, char, ash and gas. Gas can be burned to dry the biomass and char and ash can be used as soil fertilisers or fuels (Bridgwater, 2012; Dickerson & Soria, 2013). Hydrothermal liquefaction produces only char as a valuable by-product, and gasification Fischer-Tropsch produces heat and electricity from cooling the Fischer-Tropsch reactors and from burning the off-gas. The approximate costs of the processes are assessed relative to each other and based on the costs found in literature. Fast pyrolysis, though producing the worst quality of bio-oil, is also the cheapest process due to low capital costs. Catalytic pyrolysis is more expensive, since most of the catalysts that have been researched now are still expensive and/or required in very large quantities (Dickerson & Soria, 2013). However, this technology has the possibility to become a cheap option in the future, since catalysts could potentially substantially lower the required process conditions (Karatzos et al., 2014). Slow pyrolysis requires substantially more energy due to the large residence time, and is therefore also more expensive than fast pyrolysis (Jahirul, Rasul, Chowdhury, & Ashwath, 2012) and fast pyrolysis with staged condensation is more expensive since additional condensers are required. Hydrothermal liquefaction, solvolysis and catalytic hydroconversion require very high pressures, plus the use of materials that can withstand these high pressures, and are therefore more expensive. The separation and reuse of the solvent and catalysts also add to the costs (Lee et al., 2016). Gasification Fischer-Tropsch is the most expensive technology with very high investment costs, since it comprises several processes: gasification, gas cleaning and Fischer-Tropsch synthesis (Karatzos et al., 2014). Since none of the technologies are beyond the research phase yet for lignin (IEA, n.d.), the market status presented in the table applies to lignocellulosic biomass. This is assumed to be an indicator for the time needed before the technology could be applied to lignin.

Table 11: The effects table for the MCA to decide on the most suitable conversion route to produce marine biofuel from lignin.

	Bio-crude yield	Quality biofuel	Valuable by-products	App. Costs	Market status
Conversion technology	Kg fuel/kg biomass				
Fast pyrolysis	0,4-0,6	--	char, ash and gas	--	commercial
Fast pyrolysis staged condensation	0,235	+	char, ash and gas	-	research phase
Slow pyrolysis	0,33 (for biomass)	-	char, ash and gas	-	commercial
Catalytic pyrolysis	0,749	+	char, ash and gas	+	commercial
Hydrothermal liquefaction	0,69	+/-	char	+	demonstration scale
Solvolysis	0,35-0,85	+	char	+	research phase
Catalytic hydroconversion	0,49-071	+	char	+	research phase
Gasification Fischer-Tropsch	0,53	++	heat and electricity from cooling of FT reactors and off-gas	++	commercial scale

6.1.2 Standardised effects table

Next all the values were standardised so that they could be compared. The standardised effects table is presented in Table 12.

Table 12: The standardised effects table

	Bio-crude yield	Quality biofuel	Valuable by-products	App. Costs	Market status
Fast pyrolysis	0,60	0	0,75	1	1
Fast pyrolysis staged condensation	0,24	0,75	0,75	0,75	0
Slow pyrolysis	0,33	0,25	0,75	0,75	1
Catalytic pyrolysis	0,75	0,75	0,75	0,25	1
Hydrothermal liquefaction	0,69	0,5	0,25	0,25	0,67
Solvolysis	0,85	0,75	0,25	0,25	0
Catalytic hydroconversion	0,71	0,75	0,25	0,25	0
Gasification Fischer-Tropsch	0,53	1	1	0	1

6.1.3 Weighing

The cost of the bio-oil is considered the most important criteria. The technology must yield the oil at a reasonable price, otherwise there will not be a market for it, regardless of the quality or quantity. The second important aspect is the market status, since it could take long for a technology to reach a commercial scale from the research stage, while the aim is to use the conversion route as soon as possible. The third important criterion is the quality of the oil. The oil must be good enough to be used with the current infrastructure and current engines, without requiring too much expensive and unsustainable upgrading. On the other hand, the oil does not have to be of really good quality, like aviation fuel, therefore it is not the most important criterion. The forth important criterion is the bio-oil yield, because it is important sufficient amounts of oil are produced from a conversion plant. Least important are the valuable by-product. They could help the business case of the bio-oil, but the value of the by-products is assumed to be small compared to the value of the oil. Multiplying the weights by the standardisation value results in a weighted summation table (Table 13). The first row displays the weight that is assigned to the criterion. These weights were calculated using equation number 1 in section 2.1. The pyrolysis related technologies obtained higher scores than the other technologies, with fast pyrolysis and fast pyrolysis with staged condensation obtaining the highest scores.

Table 13: The weighted summation table, showing the final score of each conversion technology.

	Bio-crude yield	Quality biofuel	Valuable by-products	App. Costs	Market status	Total score
Weight	0,09	0,16	0,04	0,46	0,26	1
Fast pyrolysis	0,05	0,00	0,04	0,46	0,26	0,68
Fast pyrolysis staged condensation	0,02	0,12	0,03	0,34	0,06	0,62
Slow pyrolysis	0,03	0,04	0,03	0,34	0,26	0,58
Catalytic pyrolysis (catalytic cracking)	0,07	0,12	0,01	0,11	0,26	0,52
Hydrothermal liquefaction	0,06	0,08	0,01	0,11	0,19	0,43
Solvolysis	0,08	0,12	0,01	0,11	0,06	0,47
Catalytic hydroconversion	0,06	0,12	0,01	0,11	0,06	0,45
Gasification Fischer-Tropsch	0,05	0,16	0,00	0,00	0,26	0,43

6.1.4 Conclusions

From the weighted summation table, it becomes clear that the pyrolysis related conversion technologies are currently the most suitable technologies. Fast pyrolysis rates highest, followed by fast pyrolysis with staged condensation. These processes comprise the same processes. The only difference is the condensation part, which is thought not to contribute significantly to the GHG emissions. Therefore, only fast pyrolysis was analysed with a LCA.

6.2 Most suitable upgrading process

For this research hydrotreatment was considered most suitable.

In order to stabilise the bio-oil, so that it can be used as a marine biofuel, the bio-oil as produced through fast pyrolysis must be upgraded. Upgrading of the biofuels can be done through hydroprocessing and through catalytic cracking. Catalytic cracking yields fuels with very low LHV, due to a low H/C ratio, the coking problem is much more severe than with hydroprocessing, and their capability to deoxygenate phenolics is limited (Mu et al., 2013). Furthermore, marine vessels have large engines that can combust very low quality fuels with long carbon chains. Therefore, cracking of the carbon chains is assumed not to be required, making hydrocracking an unnecessary process. Therefore, catalytic cracking is not considered suitable for the purpose of this research.

Hydrotreatment, however, is required to increase the stability and remove any impurities (Karatzos et al., 2014). Additionally, hydroprocessing yields alkanes and aromatics that are more suitable for fuel blending (Brown et al., 2013). Hydrotreatment under low severity conditions was assumed to be sufficient. It removes the chlorine, nitrogen, sulphur and oxygen impurities (as HCl, NH3, H2S and H2O respectively) under atmospheric or slightly increased pressure, with minimal cracking of the molecules (Jechura, 2016). It is a cheaper route than hydrotreatment with high pressures and it is already commercialised. However, a high amount of coking can occur and the resulting oils are still of relatively poor quality (Xiu & Shahbazi, 2012).Since the produced fuel will be used in large ship engines, the quality does not need to be high and low severity hydrotreatment is considered the most suitable upgrading process and is used for the conversion route assessed in this thesis.

6.3 Most suitable isolation processes

Before the lignin is available to produce marine biofuels, it has to be separated from the rest of the biomass. In section 5.3 it was determined that the lignin assumed for the Scandinavian case study was isolated through the Kraft pulping method, while for the lignin in the Brazilian case-study steam explosion was assumed.

Kraft lignin is released from the Kraft mill in the black liquor waste stream, and needs to be isolated from this stream before it can be pyrolyzed. A description of the main isolation processes is presented in appendix 2. For this project, the CO_2 precipitation, or LignoBoost, method is used to isolate Kraft lignin from the paper/pulp mill. This was chosen based on a literature research. The methods requiring the use of membranes are not considered, because of the challenges it still faces (appendix 2) and the fact that they are not commercialized yet. The SLPR and acid precipitation through sulphuric acid method are excluded because they require more severe process conditions and result in a higher sulphur content of the lignin. Additionally, the SLPR method is also not commercialized yet. Thus, the CO_2 precipitation method is chosen. It consumes CO_2, results in a lower sulphur content of the lignin and a high precipitation yield (Benali et al., 2016).

The steam explosion lignin is released in lignin-rich, moist sludge. Since they contain only little carbohydrates and wood extractive impurities, it is assumed that no additional isolation processes are required. (Bruinincx et al., 2016).

6.4 Optimal conversion route

In section 5.3, it was determined that both Kraft lignin and steam explosion (SE) lignin were suitable feedstocks. Therefore, one case-study was performed using Kraft lignin from a paper/pulp mill and one using steam explosion lignin from a lignocellulosic biorefinery. Since also two locations were determined, for each location a case-study of a different lignin was performed. There are no lignocellulosic biorefineries in Scandinavia yet, so the Scandinavian case-study was performed on Kraft lignin from a Scandinavian paper/pulp mill. For Brazil, a case study was created on steam explosion lignin from a Brazilian biorefinery. Fast pyrolysis was determined as the most suitable conversion technology, and hydrotreatment the most suitable upgrading technique.

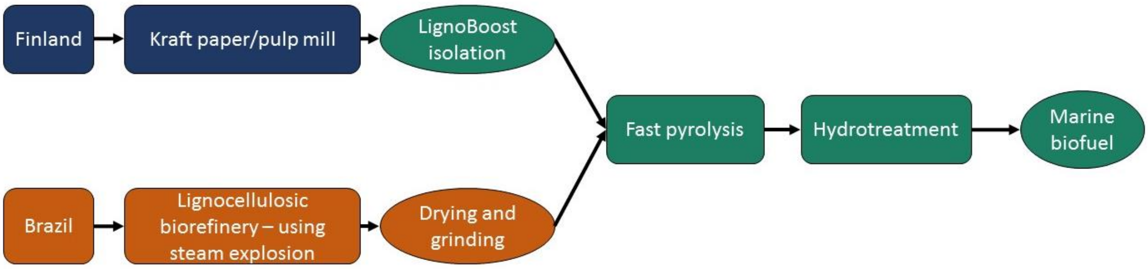
For the Scandinavian area, the Rauma pulp mill in Finland, owned by Metsa Fibre, was selected as case-study. This specific mill could be a suitable place for a lignin conversion plant, since it is a large paper/pulp mill, using only softwood as a feedstock. As explained before, softwood contains more lignin than hardwood. The mill produces more electricity than it needs, which is supplied to the grid. Furthermore, its location near a port is beneficial for the shipping of the produced fuels. For the Brazilian case, the GranBio biorefinery in Sao Miguel dos campos was selected, since it produces more ethanol and thus more lignin and is located closer to the ocean than the other biorefinery in Brazil.

The optimal conversion route comprises the most suitable feedstock, conversion technology and upgrading process. By combining the information from chapter 5 and 6, the 2 optimal conversion routes were obtained. They are presented in Figure 12, and shortly described below.

1. Kraft lignin extracted from the black liquor waste stream from the Rauma pulp mill in Finland, converted to biofuel for the marine industry through fast pyrolysis and upgraded through hydrotreatment.

2. Steam explosion lignin from the GranBio biorefinery in Sao Miguel dos campos, converted to biofuel for the marine industry through fast pyrolysis and upgraded through hydrotreatment.

Figure 12: A graphic representation of the two most suitable conversion routes. An LCA will be performed to assess the direct and indirect GHG emissions associated with these routes.



7 Life cycle GHG assessment

The goal of this LCA was to assess the GHG emissions that are associated with the conversion of lignin into a drop-in marine biofuel and to assess the reduction compared to the currently used fuel. This provides insight into the sustainability of using waste lignin as a feedstock to produce marine biofuels. The LCA was performed on the base case scenarios, the two most suitable conversion routes, that were determined in section 6.4. First a life cycle inventory assessment (LCI) was performed, assessing all the relevant in- and outputs of the lignin to marine biofuel life cycle. This was followed by a life cycle impact assessment, where the GHG emissions were calculated for each of the relevant in- and outputs that were listed in the LCI. As mentioned before, only the LCA for the fast pyrolysis without fractional condensation is presented here, since the GHG emissions for fast pyrolysis with or without fractional condensation would be the same.

First a Life Cycle Inventory Analysis (LCI) is performed on each of the routes. The LCI starts with a mass and energy balance of the complete conversion route, followed by a more detailed description of the life cycle inventory per life cycle stage. After the LCI, a life cycle impact assessment (LCIA) was performed. During this assessment, the in- and outputs were converted to GHG emissions. The results are interpreted in the last stage of the LCA.

7.1 Life cycle inventory of Kraft lignin fast pyrolysis

In this section, each of the life cycle stages was discussed individually. First the mass and energy balances are presented, followed by the LCI of the direct effects of lignin conversion. In the last part the indirect effects were assessed.

7.1.1 Mass and energy balance Kraft lignin

Here, the mass and energy balances of the overall life cycle of the base case scenario of the Kraft lignin to marine biofuel is presented, showing all the in- and outputs. A more detailed description of the relevant in- and outputs is presented per life cycle stage in 7.1.2 (for the direct emissions) and 7.1.3 (for the indirect emissions).

Mass balance Kraft lignin	IN			OUT		
Process	Product	t/dt lignin[21]	Source	Product	t/dt lignin	Destination
LignoBoost isolation (Inc. drying and grinding)	Black liquor	5,0[22]	Pulp mill	Ground and dried lignin	1,1	FP
	NaOH	0,065-0,13[23]	Market	Concentrated black liquor (incl. chemicals)	2,4[24]	Recovery boilers
	H2SO4	0,2	Market	Moisture from black liquor	2,0[25]	Out
	CO_2	0,2	Lime kiln	Flue gas from natural gas combustion	1,95E-02[26]	Out
	Natural gas	1,95E-02	Market			
FP	Pre-treated lignin	1,1	processed	Pyrolysis vapours	0,5[27]	Quenching
	Recycle gas	0,5	Quenching	Char for process heat[28]	0,1[29]	Char combustor
	Catalyst Ru/C	2,91E-05[30]	Market	Recycle gas[31]	0,5	Quenching
		0,0		Char for additional steam production	0,4[32]	Char combustor
				Catalyst Ru/C	2,91E-05	Out
Quenching	Pyrolysis vapours	0,5	Processed	Recycle gas	0,5	FP
	Recycle gas	0,5	FP	NCG	0,1	Out
				Biocrude	0,4	Hydrotreater
Hydrotreater	Bio-oil	0,4	Quenching	Stabilised bio-oil	0,4[33]	Market
	Hydrogen	1,79E-02[34]	Market	Off gas production	3,79E-02[35]	Out
	Recycled hydrogen	1,60E-02	Hydrotreater	Recycle hydrogen	1,60E-02	hydrotreater
Char combustor	Combustion air	6,6	Out	Ash	1,59E-03[36]	Market
	Char	0,1	FP	Flue gas	7,2	Out

Mass balance Kraft lignin	IN (tonne/dt)	OUT (tonne/dt)	Change %
LignoBoost isolation (Inc. drying and grinding)	5,53	5,53	100%
FP	1,53	1,53	100%
Quenching	0,99	0,99	100%
Hydrotreating	0,44	0,44	100%
Char combustor	7,16	7,16	100%

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[21] "Dry" lignin is the lignin after the drying pre-treatment step. It was assumed to have a moisture content of 7%.

[22] Assuming that the black liquor is extracted from the evaporators at 40% lignin, of which 50% is removed.

[23] Obtained from (Manninen, 2010). For the calculations the value of 0.10 t/dt lignin was used.

[24] All inputs minus moisture evaporated from the black liquor in the evaporators.

[25] Manninen (2010)

[26] Containing CO_2, H2O and N2 (stoichiometric combustion, note that the N2 and O2 from the combustion air and is not included in the mass balance)

[27] Containing the non-condensable gases and the oil phase. The yields of the products are obtained from (Kosa et al., 2011) and corrected for the 7% moisture that remained in the dry lignin.

[28] The overall char yield is obtained from Kosa et al. (2011) and corrected for lignin with a moisture content of 7%. The energy content of the char was calculated from the energy balance, and was assumed to equal the energy input of the fast pyrolysis reactor minus the energy output except for the char. The LHV in MJ/kg was calculated by dividing the energy of the char with the weight of the char. The process heat required by the FP reactor (obtained from Tews et al. (2014) was divided by the LHV of char to obtain the amount of char required to produce that heat.

[29] Calculated from the heat requirements of the process.

[30] Assuming a lifetime of one year, though this assumption is quite uncertain (Tews et al., 2014)

[31] Used to fluidise the reactor bed, calculated from (Tews et al., 2014)

[32] Overall weight of char minus weight of char for process heat, includes ash.

[33] The stabilised bio-oil has a moisture content of 33%. In practice it is likely that the water should be removed before the bio-oil can be used. This will influence the bio-oil output in mass (to 0.25t) but not in energetic value since the calculated LHV is on a dry oil basis.

[34] This includes the hydrogen consumed by the biocrude and the hydrogen that is lost because only 90% of the hydrogen in the off gases can be separated.

[35] The amount of off gas is dependent on the amount of upgrading. It comprises the gases formed by the removal of the impurities with hydrogen, the hydrocarbon gases from the cracking of the carbon chains and the hydrogen that was not recycled by the PSA.

[36] The ash is already present in the lignin and the value is obtained from (Tomani, 2013). The ash content in the char combustor is relative to the amount of char.

Energy Balance Kraft lignin (LHV)	IN			OUT		
Process	Product	value MJ/dt lignin	Source	Product	value MJ/dt lignin	Destination
LignoBoost isolation (Inc. drying and grinding)	Black liquor	27333,3[37]	Pulp mill	Ground and dried lignin	24400,0	FP
	Electricity	200,0	Grid	Kinetic energy and heat losses	2180,0[38]	Out
	Heat for drying	1080,0	Lime kiln	Concentrated black liquor (incl. chemicals)	2933,3[39]	Recovery boilers
	Natural gas	900,0	Market			
FP	Pre-treated lignin	24400,0	Dryer	Pyrolysis vapours	11512,6[40]	Quenching
	Electricity	73,4[41]	Grid	Char for process heat	2751,3	Char combustor
	Heat	2306,7[42]	Char	Char for additional steam production	10909,3	Char combustor
	Recycle gas	5377,8[43]	Quenching	Heat loss and kinetic energy	1606,9[44]	Out
				Recycle gas	5377,8	Quenching
Quenching	Pyrolysis vapours	11512,6	FP	Recycle gas	5377,8	FP
	Recycle gas	5377,8	FP	NCG	1510,2[45]	Out
				Biocrude	10002,3[46]	Hydrotreater
Hydrotreater	Biocrude	10002,3	Quenching	Stabilised bio-oil	10290,8[47]	Market
	Hydrogen	2152,2	Hydrogen plant	Off gas production	1221,4[48]	Out
	Electricity	10,5	Grid	Recycled hydrogen	1924,4	Hydrotreater
	Recycled hydrogen	1924,4	Hydrotreater	Heat loss	1943,6[49]	Out
Char combustor	Char for process heat	2751,3	FP	Heat loss	2207,0[50]	Out
				Useful process heat	2306,7	Pre-treatment

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[37] Calculated from Manninen (2010). Taking the heat and electricity produced by recovery boiler in a Kraft paper/pulp mill (5412 MJ/t pulp), dividing by efficiency recovery boiler (69%), dividing by amount of lignin isolated from black liquor per tonne pulp (0.3 tonne).

[38] Obtained by adding the electricity and heat input from natural gas and from the lime kiln.

[39] Black liquor energy input minus the lignin energy output.

[40] Assuming LHV heavy oil phase of 28.37 MJ/kg (calculated from HHV obtained by (Kosa et al., 2011), LHV watery oil phase of 4.01 MJ/kg (calculated from HHV obtained by (Kosa et al., 2011), LHV non condensable gas of 11.80 MJ/kg (calculated from the composition of the gas obtained from (Wright et al., 2010) times the LHV of each gas obtained from ("Fuel Gases And Heating Values," n.d.).

[41] Obtained from Tews et al. (2014).

[42] Obtained from Tews et al. (2014).

[43] The amount of recycled non-condensable gases times their LHV (calculated as explained in footnote #**Fout! Bladwijzer niet gedefinieerd.**)

[44] The electricity input plus the heat required, as obtained from (Tews et al., 2014).

[45] The yield obtained from (Kosa et al., 2011) times the LHV (calculated as explained in footnote #**Fout! Bladwijzer niet gedefinieerd.**)

[46] Calculated from the watery oil phase and the heavy oil phase yields, times their respective LHV value as calculated from the HHV obtained from (Kosa et al., 2011).

[47] The HHV of the stabilised biofuel was obtained on a dry basis using the formula from (Channiwala & Parikh, 2002). From this value the LHV was calculated and this was converted to the LHV on a wet basis through the following equation: LHV*(1-fraction of moisture of wet fuel). This moisture comprises the moisture that was already in the biocrude and the moisture that was formed during the hydrotreatment.

[48] The amount of off gas times the LHV of the off gas, which was calculated from the HHV. The HHV was calculated by taking the product of the fraction of each gas in the off gas times it respective HHV. The HHVs were obtained from (Waldheim, L. Nilsson, 2001).

[49] The heat loss is obtained from (Tews & Elliott, 2014) and scaled to the amount of hydrogen input, to relate it to the amount of upgrading.

[50] The useful heat efficiency of the char combustor is 0.84 (calculated from Tews & Elliott, 2014). The required heat is also obtained from (Tews & Elliott, 2014)

Energy balance Kraft lignin (LHV)	IN (MJ/dt)	OUT (MJ/dt)	Change in %
LignoBoost isolation (Inc. drying and grinding)	29513,33	29513,33	100%
FP	32157,93	32157,93	100%
Quenching	16890,38	16890,38	100%
Hydrotreating	14089,38	15380,21	92%[51]
Char combustor	13660,64	13660,08	100%

7.1.2 LCI of the direct effects for Kraft lignin

LCI lignin isolation stage Kraft lignin

Table 14: The LCI for the LignoBoost lignin isolation process

LignoBoost inputs /dt lignin			
Product	Input	Unit	Comment
Electricity	200.00	MJ	From national grid. Used for the LignoBoost process.
CO_2	0.220	t	For acidification in the precipitation reactor
Chemicals	0.065-0.13 and 0.19	t, for NaOH and H2SO4 respectively.	NaOH and H2SO4, including production and transport of 200 km. H2SO4 for washing of the lignin cake, NaOH for neutralizing the recycled stream from the lignin isolation process to the evaporators
Natural gas	900	MJ	Incremental steam production evaporators

The electricity consumption of the LignoBoost process was 55.556 kWh/tonne of isolated lignin (Manninen, 2010). This electricity is obtained from the national grid. The CO_2 consumption of the LignoBoost process is 0.15 to 0.25 tonnes/tonne of isolated lignin (Benali et al., 2016). For this research the value of 0.22 tonne/ tonne of lignin, as used by Manninen (2010), was assumed. It was also assumed that it is obtained from a CO_2 emitting process (e.g. from the lime kiln) and could thus be accounted for as negative emissions (Manninen, 2010). The heat required for the drying of the lignin (0.324 GJ/t lignin) was also obtained from the flue gases of the lime kiln. The lime kiln was assumed to produce more than sufficient heat and CO_2, and the dried lignin is assumed to contain 7% moisture. The energy consumption of the evaporators amounts 450 MJ/t H2O. The washing of the removed lignin with acidified water lead to an increase in water going through the evaporators of approximately 2 M^3/tonne of lignin. Therefore the additional energy requirement is 900 MJ/tonne lignin (Manninen, 2010). For the base case scenario, this energy requirement was included and it was assumed that this energy was obtained from the combustion of natural gas. The incremental NaOH and H2SO4 consumption was 0.05-0.13 and 0.09-0.25 t/t of lignin respectively (Benali et al., 2016; Manninen, 2010). For this research the same values as Manninen (2010) were used, of between 0.065-0.13 and 0.19 for NaOH and H2SO4 respectively. The composition of the isolated Kraft lignin was presented in Table 15. The recovery boiler produced less steam and electricity, but this was discussed in section 7.1.3 as an indirect effect.

Table 15: The approximate composition of Kraft lignin isolated through the Lignoboost process (obtained from (Tomani, 2013)

Lignin		Composition (wt.%)						HHV
Type	**Isolation process**	**C**	**H**	**O**	**N**	**S**	**Ash**	**MJ/kg**
softwood/hardwood	Kraft pulping, lignoboost	63-66	5,7-6,2	26-27,5	0,1-0,2	2-3	0,2-1,4	25-27

LCI pre-treatment Kraft lignin

No pre-treatment required (see base case scenario).

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[51] The in- and outputs of the hydrotreatment stage are not completely balanced. This is because many of the values are based on values from different scientific sources and various large assumptions were made. The values are still used, since a 8% change was considered minor. However, it does show that there are some uncertainties associated with the values, as explained in the discussion session.

LCI fast pyrolysis stage Kraft lignin

Table 16: The relevant in- and outputs of the fast pyrolysis stage.

Fast pyrolysis in- and outputs /dt lignin				
Product	**IN**	**OUT**	**Unit**	**Source/destination**
Electricity	73,44		MJ	National grid
Ru/C catalyst	2,91E-05		t	Market
Bio-oil		0,4	t	Hydrotreater
Char for FP process heat		0,1	t	Char combustor
NCG for Kraft mill process heat		0,13	t	Gas fired boiler
Of which CH4		3,47E-04	t	Gas fired boiler
CO		6,51E-02	t	Gas fired boiler
CO2		5,37E-02	t	Gas fired boiler
H2		5,83E-03	t	Gas fired boiler
NH3		1,20E-04	t	Gas fired boiler
C2H6		1,41E-03	t	Gas fired boiler
C3H8		1,51E-03	t	Gas fired boiler
Excess char for Kraft mill process heat		0,44	t	Char combustor

The fast pyrolysis requires 73.4 MJ electricity input per dry tonne of lignin, as well as 2306.7 MJ/dt of heat[52]. The heat is supplied internally by the char combustor and the electricity is obtained from the national grid (Tews et al., 2014). The assumed yield of the fast pyrolysis products was obtained from Kosa et al. (2011) for the fast pyrolysis of CO_2 precipitated Kraft lignin from softwood, and presented in Table 17. Kosa et al (2011) and Ben & Ragauskas (2011) both found liquid consisting of two separate phases as a results of lignin pyrolysis; a heavy organic oil phase and a light watery liquid phase. The watery phase consists of app. 80% water and can therefore not be used for fuel applications. The heavy oil phase has a moisture content between 0.2 and 0.78 wt.%. For the base case scenario, the median value was assumed (0.49%). The major other components in the watery phase are methanol, catechol and acetic acid[53] (Ben & Ragauskas, 2011). For the base case scenario, it was assumed that the two phases are collected together and send to the hydrotreater as one oil. The elemental compositions and heating values of each of the pyrolysis products can be found in Table 17. The HHV of the gas phase was calculated based on the composition of the gas obtained by Wright et al. (2010) for corn stover (see Table 19). All of the char was transported to the char combustor, but since there was more char than required for the process heat, the excess char was combusted to provide heat for the Kraft mill, compensating for the extracted lignin. The gas phase was also assumed to be combusted to provide process heat for Kraft mill. The char combustion for the Kraft mill was part of the indirect effects, and assessed in section 7.1.3.

Table 17: The yield, composition and heating values of the fast pyrolysis products.

Fast pyrolysis products (Kraft lignin)		Composition (wt.%)					Heating values	
Product	**Yield (Wt.%)[54]**	**C**	**H**	**O**	**N**	**S**	**HHV (MJ/kg)**	**LHV[55] (MJ/kg)**
Watery oil phase	5.6	8,27	2,25	10,09	0	0	4,50	**4,01**
Heavy oil phase	32	69,1	6,7	23	0	1,2	29,83[56]	**28,37**
Pyrolysis gas phase	11.91	See Table 19					12.96[57]	**11,80**
Char[58]	50.50	77,70	3,46	17,73	1,08	0,03	28,14[59]	**25,16**

Table 18: The composition of the watery oil phase, the values are for softwood Kraft pyrolysis, obtained from Ben and Ragauskas (2011).

Composition (wt.%), assuming only these three products				
Methanol	Catechol	Acetic acid	water	Total
15,09	1,60	3,92	79,39	100,0[60]

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[52] The values of both electricity and heat are from the pyrolysis of forest residue

[53] Values obtained from the pyrolysis of softwood Kraft lignin.

[54] The yields of the products are obtained from (Kosa et al., 2011).

[55] The LHV of the products are calculated from the HHVs.

[56] For the fast pyrolysis of CO_2 precipitated softwood Kraft lignin, obtained from Kosa et al. (2011).

[57] The composition of the pyrolysis gas was obtained from Wright et al. (2010) and the HHV was calculated from this composition using the HHV of the different gases that make up the overall pyrolysis gas.

[58] The char yield includes the ash content of 0.8 wt.% of dry lignin (Tomani, 2013).

[59] Calculated to balance out the energy balance. The value is similar (though a little lower) than the values obtained through the equation of Channiwala & Parikh (2002) (29.3 MJ/kg) and from the literature (31.8 MJ/kg, Pakdel et al., 1992).

[60] The total presented by Ben & Ragauskas (2011) added up to a total of 79.39, indicating that other unknown components together made up more than 20% of the watery oil phase. For convenience it was assumed that only methanol, catechol and acetic acid were present and their wt.% was increased to form a total of 100%.

Table 19: The composition of the fast pyrolysis gas from corn stover pyrolysis, as obtained from Wright et al. (2010).

Gas composition from FP (wt.% of dry feed)						
CH4	CO	CO_2	H2	NH3	C2H6	C3H8
0,04%	6,56%	5,42%	0,59%	0,01%	0,14%	0,15%

LCI upgrading stage Kraft lignin

Table 20: The relevant in- and outputs of the hydrotreatment stage.

Relevant in- and outputs of hydrotreating stage per dt lignin				
Product	IN	OUT	Unit	Source/destination
Hydrogen	0,018		t	Market
Electricity	10,47		MJ	National grid
Stabilised bio-oil (wet basis)		0,38	t	Market
Stabilised bio-oil (dry basis)		0.25	t	Market
Off-gas		0,04	t	Gas-fired boiler

During the hydrotreatment stage hydrogen was added to the bio-oil to stabilise the bio-oil and improve its quality. This caused impurities and small hydrocarbons to be removed from the bio-oil and replaced with hydrogen atoms, which reduced the weight of the oil and thus the yield. The calculated yield of stabilised bio-oil with an Heff/C ratio of 1.4 was 0.38 t/dt lignin on a wet basis, with a moisture content of 35%. After removal of the water, 0.25 t of stabilised bio-oil/dt of lignin was left. Furthermore, 0.04 t of off-gas was produced. This off-gas was send to a gas-fire boiler together with the NCG to provide process heat for the Kraft mill. This was further discussed with the indirect effects, in section 7.1.3.

The electricity input during the hydrotreatment stage was assumed to be related to the bio-oil input and amounts 25.9 MJ/t bio-oil, or 10.47 MJ/dt lignin (Tews & Elliott, 2014). 48.52 kg of hydrogen/t bio-oil, or 17 kg/dt lignin, was required for the upgrading of the biofuel to a Heff/C ratio of 1.40. The actual input of hydrogen was calculated at 98.52 kg/t bio-oil to maintain a hydrogen rich environment. That meant the waste stream still contained 18 kg H /dt lignin, of which 10% (so 1.8 kg/dt lignin) was lost and exited the system with the off gas, while the other 90% was recycled. The rest of the off-gas comprised the gases produced from removal of the impurities and the hydrocarbon gases. The overall LHV of the off-gas was 32,20 MJ/kg. The exact composition of the off-gas can be found in Table 22 for the Kraft lignin upgrading.

As can be seen in Table 21, all the heteroatoms in the bio-oil had to be removed to obtain a Heff/C ratio of 1.4. Since there were no heteroatoms left in the stabilised biofuel, the LHV is quite high, similar to the LHV of marine distillate fuel. Also, the fuel contains no sulphur, so it meets the requirements set out in the regulations.

Table 21: The composition of the stabilised bio-oil, calculated from the hydrogen inputs and gas outputs.

Stabilised bio-oil after upgrading of bio-oil from Kraft lignin		**Composition (wt.%) of stabilised bio-oil**							
Product	Yield dry basis (Wt.% of dry lignin)	C	H	O	N	S	HHV dry basis (MJ/kg)	LHV[61] dry basis (MJ/kg)	Heff/C ratio
Stabilised bio-oil	25%	89,47%	10,53%	0,00%	0,00%	0,00%	43,64	41,35	1.40

Table 22: The composition of the off-gas produced at the hydrotreater.

Source	Gas	Quantity (t/dt lignin)
Gas from removing impurities during hydrodeoxygenation	H2S	4,4E-03
Gas from hydrocracking	CO_2	1,2E-02
	CH4	1,0E-02
	Ethane (C2H6)	3,2E-03
	Propane (C3H8)	2,9E-03
	Butane (C4H10)	3,0E-03
Hydrogen losses from hydrotreater	H2	1,8E-03
Total	**Overall off-gas**	**3,8E-02**

LCI char combustor Kraft lignin

Part of the char was combusted for process heat for the fast pyrolysis reactor and the feedstock drying, the rest was combusted to provide heat for the Kraft paper/pulp mill to compensate for the removed lignin. The efficiency of the char combustor was 84% (Tews & Elliott, 2014). To obtain sufficient heat for the FP process, 0.22 t/dt of char was combusted. The in- and outputs of the char combustor, from combustion of all the char, are presented in Table 23. The relative composition of this flue gas was

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[61] The LHV of the products are calculated from the HHVs.

obtained from Jones and Zhu (2009), who modelled this for the char from wheat straw lignin from an ethanol biorefinery. For the Kraft lignin scenario, the sulphur content of the char was corrected using the ratio of sulphur that ends up in the bio-oil versus the sulphur that ends up in the char (Jensen et al., 2014).

Table 23: The relevant in- and outputs of the char combustor.

Char combustor in- and outputs				
Product	**IN**	**OUT**	**Unit**	**Source/destination**
Ash		1,59E-03	t	Market
Flue gas		7,2	t	Atmosphere
Of which CO_2		1,4	t	
CO		1,7E-03	t	
water		0,3	t	
Nitrogen		5,2	t	
Oxygen		0,2	t	
NO2		2,8E-05	t	
SO_2		5,0E-03	t	
H2		1,5E-05	t	

7.1.3 LCI of the indirect effects for Kraft lignin

Reduced heat and electricity production Kraft mill

Since the recovery boiler of the Kraft mill produces less steam and electricity, this must be compensated for. A recovery boiler efficiency of 69% and a back-pressure construction factory (the produced electricity divided by the produced heat) of 0.22 were assumed. Furthermore, the initial dry solids content of the black liquor was assumed to be 40%, roughly 50% of the original lignin is isolated (which translates to 0.3 tonne of lignin per tonne of produced pulp) and the lignin had an energy content of 24.4 (LHV). In this scenario, the fuel required to produce the heat and electricity production reduction in the recovery boiler per tonne of dry isolated lignin amount 13.8 GJ and 3.0 GJ, respectively (calculated from Manninen, 2010). Table 24 shows the relevant data for the indirect effects.

Char

There are several possible ways to compensate for the lost energy (e.g. char combustion, bark combustion, natural gas). For the base case scenario, the heat was as much as possible compensated for by burning the excess char in the char combustor. The char produced 9146 MJ of heat, which was not enough to compensate for all the heat losses.

Off-gases

The off-gases comprises the following gases:
1. Non-condensable gases: 0.13 t/dt, LHV 11.80 MJ/kg
2. Off-gas from hydrotreater: 0.038 t/dt, LHV 32.20 MJ/kg

For the base case scenario, it was assumed that these gases were used as fuel to replace natural gas at the pulp mill to produce heat to compensate for the lignin losses. The pulp mill was assumed to be located near the fast pyrolysis reactor; therefore, no emissions were assumed for transport of the gases. The heating value of both gases together is 2731.7 MJ/dt lignin. It was assumed that the efficiency for combustion of natural gas and these off-gases was the same, so 2731.7 MJ/dt lignin of natural gas can be replaced.

Natural gas and electricity from the grid

The rest of the heat was compensated for by combusting natural gas in a boiler with an efficiency of 95%. The electricity was obtained from the national grid. The output of flue gases from the char combustor is included in Table 23. Table 24 shows the relevant data for the char and off-gas combustion for process heat, as well as the natural gas and electricity input that was still required. From this table, it can be seen that another 2166.8 MJ of natural gas are required, together with 3040.0 MJ of electricity.

Table 24: The relevant data for the calculation of the required natural gas and electricity to compensate for the heat and electricity losses in the Kraft mill. Also, the excess char and the off-gases from the FP reactor and the hydrotreater are combusted to provide heat for the Kraft mill.

Excess char combustion for compensation of removed lignin		
Boiler efficiency lignin	69%	
Reduced heat production	13800,0	MJ/dt lignin
Reduced electricity production	3040	MJ/dt lignin
Efficiency boiler for char combustion	84%	
Excess char	10909,4	MJ/dt lignin
Incremental heat produced from char	9146,5	MJ/dt lignin
Combustion of off-gases for compensation of removed lignin		
Off-gas hydrotreater	0,04	t/dt lignin
Non-condensable gases from fast pyrolysis	0,13	t/dt lignin
LHV off-gas hydrotreater	32,2	MJ/kg
LHV non-condensable gases	11,8	MJ/kg
Overall energy gases	2731,7	MJ/dt lignin
Efficiency boiler for natural gas combustion	95%	
Heat produced from off-gases	2595,1	MJ/dt lignin
Required natural gas and electricity for compensation of removed lignin		
Efficiency boiler for natural gas combustion	95%	
Required natural gas for heat production	2166.8	MJ/dt lignin
Required electricity from grid	3040,0	MJ/dt lignin

7.2 Life cycle impact assessment Kraft lignin fast pyrolysis

Also the LCIA is subdivided into the direct emissions and the indirect emissions. The emissions are presented per kg CO_2-eq/dt lignin, and in the correct functional unit g CO_2-eq/MJ of biofuel.

7.2.1 LCIA Direct emissions Kraft lignin

Table 25: The life-cycle GHG emissions of the fast pyrolysis process per life-cycle stage

Total emission without consequential effects		
Life-cycle stage	GHG emissions (kg CO2-eq/dt lignin	g CO2-eq/ MJ Biofuel
Lignin isolation	13,5	1,3
Fast pyrolysis	10,4	1,0
Upgrading	39,7	3,9
Char combustor	0,00	0,00
Total	**63,5**	**6,2**

Table 25 shows all the GHG emissions of each life-cycle stage of the fast pyrolysis process in the correct functional unit. The direct GHG emissions from Kraft lignin conversion to marine biofuel are 6,2 g CO2-eq/MJ biofuel.

The emissions per life-cycle stage are presented in Table 26, Table 27 and Table 28. The LignoBoost process chemicals have a very large impact on the carbon footprint. The electricity and natural gas also have a large impact. However, most of these emissions were offset by the CO2, whose emissions were negative because they were consumed from a fossil fuel source. The emission factors of the chemicals were obtained from the EcoInvent database, but in literature very different values for this impact were found, that would have a large effect on the results. This is further discussed in the discussion chapter.

For the fast pyrolysis process, the only in- or output that contributed to the greenhouse gas emissions were those of the electricity that was used and the catalyst. The EcoInvent database does not contain the lifecycle GHG emissions of a Ru/C catalyst. Therefore, a zeolite product from the EcoInvent database (“zeolite, powder, at plant/RER U”) is used as a proxy. The actual hydrotreating catalysts may have a very different GHG impact than that approximated with zeolite. The pyrolysis gases were assumed to be combusted for process heat, so that the only emitted GHG was CO_2. These CO2 emissions were biogenic and considered carbon neutral, so they did not attribute to global warming. An overview of the emissions can be found in Table 27.

The only emissions of greenhouse gases during the upgrading stage are from the production of the hydrogen and the electricity. The off gases are, just like at the fast pyrolysis stage, are biogenic, so considered carbon neutral. The char combustor does not emit any GHGs. The flue gases contain a large amount of CO_2; however, they are considered carbon neutral due to their biogenic nature.

Table 26: The GHG emissions from the LignoBoost isolation process.

LignoBoost lignin isolation process	
Product	**Kg CO_2-eq/dry tonne lignin**
Electricity	27,8[62]
NaOH and H2SO4	133,6[63]
CO_2	-220,0[64]
Natural gas	72,1
total	**657,7**

Table 27: The GHG emissions from fast pyrolysis.

Fast pyrolysis, relevant in- and outputs (kg CO_2-eq/dt lignin)	
Product	**Kg CO_2-eq/dry tonne lignin**
Electricity	10,21
Ru/C catalyst	0,15[65]
Total	**10.36**

Table 28: The GHG emissions from the upgrading stage.

Upgrading, relevant in- and outputs (kg CO_2-eq/dt lignin)	
Product	**Kg CO_2-eq/dry tonne lignin**
Hydrogen	38,21[66]
Electricity	1,46
Total	**39,67**

7.2.2 LCIA indirect emissions Kraft lignin

Reduced heat and electricity production Kraft mill

To produce the reduced heat and electricity, 13.8 GJ of heat and 3.0 GJ of electricity is required per dt lignin. The heat is produced from combustion of the char, off-gases and natural gas, the electricity is obtained from the national grid. The emissions from char and off-gas combustion are biogenic, so this combustion is considered carbon neutral. The combustion of the natural gas produces 174[67] kg CO2-eq/dt lignin. The emissions from the Finnish electricity grid for the required electricity are 423 kg CO2-eq/dt lignin. The overall emissions from the compensation of the reduced heat and electricity production in the Kraft mill are thus 596 kg CO_2-eq/dt lignin. This translates to **57.9 g CO2-eq/MJ** biofuel, converted to the correct functional unit.

7.2.3 Total emissions Kraft lignin fast pyrolysis

Adding the direct and indirect emissions of the conversion of Kraft lignin to marine biofuel yields the following results (Figure 13: Showing the direct and the indirect GHG emissions of Kraft lignin conversion to marine biofuel through fast pyrolysis and subsequent hydrotreatment.Figure 13). The interpretation of the results, together with a comparison with fossil fuels and the results of SE lignin conversion is presented in section 7.5.

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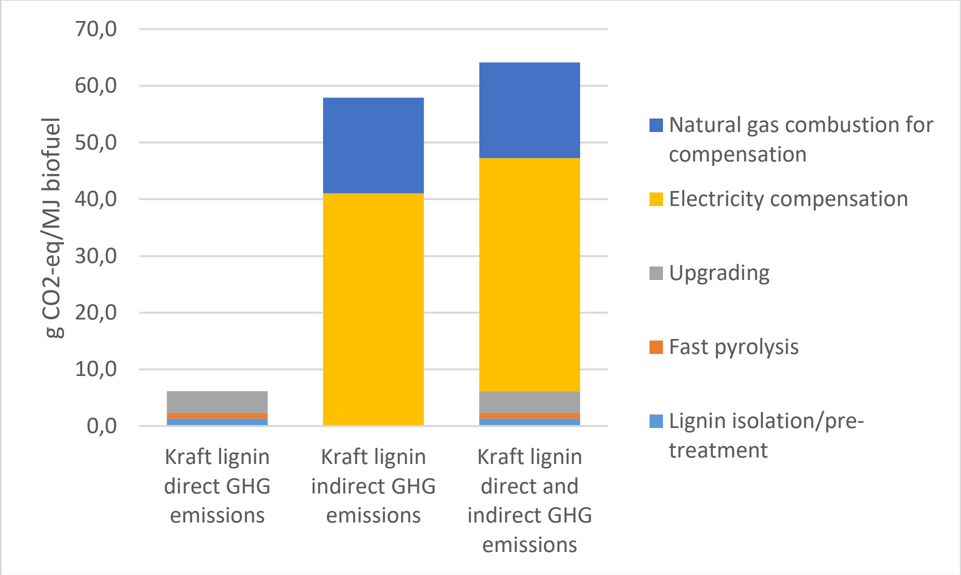
[62] Finland grid, low voltage, incl. import.
[63] Incl. transport of 200 km, value obtained from Manninen et al. (2010).
[64] Consumed during the process.
[65] value for zeolite proxy, obtained from EcoInvent.
[66] General value for hydrogen sold in the european market.
[67] Default value for combustion of natural gas was obtained by IEA (IPCC 2006 guidelines). Life cycle production value was obtained from EcoInvent.

Figure 13: Showing the direct and the indirect GHG emissions of Kraft lignin conversion to marine biofuel through fast pyrolysis and subsequent hydrotreatment.



7.3 Life cycle inventory of steam explosion lignin fast pyrolsysis

7.3.1 Mass and energy balance SE lignin

Here, the mass and energy balances of the overall life cycle of the base case scenario of the steam explosion lignin to marine biofuel were presented, showing all the in- and outputs. A more detailed description of the relevant in- and outputs was presented per life cycle stage in 7.3.2 (for the direct emissions) and 7.3.3 (for the indirect emissions).

Mass balance SE lignin	IN			OUT		
Process	**Product**	**t/dt lignin**[68]	**Source**	**Product**	**t/dt lignin**	**Destination**
Grinding	Wet lignin	1,8	Pulp mill/biorefinery	Ground lignin	1,8	Dryer
Drying	Ground lignin	1,8	Grinder	Pre-treated lignin	1,1[69]	Handling
				Moisture	0,7	Out
FP	Pre-treated lignin	1,1	Pre-treatment	Pyrolysis vapours	0,6	Quenching
	Recycle gas	0,5	Quenching	Char for process heat	0,2	Char combustor
	Catalyst Ru/C	3,82E-05	market	Recycle gas	0,5	Quenching
				Char for compensation of lignin extraction	0,2	Char combustor
				Catalyst Ru/C	3,82E-05	Out
Quenching	Pyrolysis vapours	0,6	FP	Recycle gas	0,5	FP
	Recycle gas	0,5	FP	NCG	0,1	Out
				Biocrude	0,5	Hydrotreater
Hydrotreater	Biocrude	0,5	Quenching	Stabilised bio-oil	0,5	Market
	Hydrogen	2,25E-02	Market	Off gas production	4,33E-02	Out
	Recycled hydrogen	1,87E-02	Hydrotreater	Recycle hydrogen	1,87E-02	hydrotreater
Char combustor	Combustion air	5,51	Out	Ash	5,53E-06	Market
	Char for process heat	0,19	FP	Flue gas	5,96	Out
	Char for compensation of lignin extraction	0,26	Lignocellulosic biorefinery			

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[68] "Dry" lignin is the lignin after the drying pre-treatment step. It was assumed to have a moisture content of 7%.

[69] Assuming no losses during the pre-treatment processes.

Mass balance SE lignin	IN (tonne/dt)	OUT (tonne/dt)	Change %
Pre-treatment	3,64	3,64	100%
FP	1,53	1,52	100%
Quenching	1,08	1,08	100%
Hydrotreating	0,57	0,56	100%
Char combustor	5,96	5,96	100%

Energy Balance SE lignin (LHV)	IN			OUT		
Process	**Product**	**MJ/dt lignin**	**Source**	**Product**	**MJ/dt lignin**	**Destination**
Grinding	Wet lignin	23895,1	Pulp mill/biorefinery	Ground lignin	23895,1	Dryer
	Electricity	193,5	Grid	Kinetic energy and heat losses	193,5	Out
Drying	Ground lignin	23895,1	Grinder	Pre-treated lignin	23895,1	FP
	Electricity for dryer	123,9	Grid	Kinetic energy and heat losses	2845,2[70]	MJ
	Heat for drying	2721,3	Char combustor			
FP	Pre-treated lignin	23895,1	Pre-treatment	Pyrolysis vapours	11305,1	Quenching
	Electricity	95,6	Grid	Char for process heat	5997,1	Char combustor
	Heat	2306,7	Char combustor	Char for compensation of lignin extraction	7756,1	Char combustor
	Recycle gas	4094,2	Quenching	Heat loss and kinetic energy	1629,0	Out
				Recycle gas	4094,2	Quenching
Quenching	Pyrolysis vapours	11305,1	FP	Recycle gas	4094,2	FP
	Recycle gas	4094,2	FP	NCG	893,3	Out
				Biocrude	10411,7	Hydrotreater
Hydrotreater	Biocrude	10411,7	Quenching	Stabilised bio-oil	10938,4	Market
	Hydrogen	2704,6	Hydrogen plant	Off gas production	1396,9	Out
	Electricity	13,6	Grid	Recycled hydrogen	2240,5	Hydrotreater
	Recycled hydrogen	2240,5	Hydrotreater	Heat loss	2442,5	Out
Char combustor	Char for process heat	5997,12	FP	Heat loss	2259,72	Out
	Char for compensation of lignin extraction	7989,81	Lignocellulosic biorefinery	Useful heat for fast pyrolysis process	5027,99	Pre-treatment
				Heat for lignocellulosic biorefinery	6698,65	Lignocellulosic biorefinery

Energy balance SE lignin (LHV)	IN (MJ/dt)	OUT (MJ/dt)	Change %
Pre-treatment	50828,83	50828,83	100%
FP	30391,47	30781,50	99%
Quenching	15399,22	15399,22	100%
Hydrotreating	15370,45	17018,27	90%[71]
Char combustor	13986,93	13986,36	100%

7.3.2 LCI of the direct effects for Kraft lignin

Lignin isolation stage SE lignin

No lignin isolation required (see base case scenario). However, the extracted lignin leads to a decrease in energy generation of the lignocellulosic biorefinery that must be compensated for. This is further discussed in section 7.3.3, as these are indirect GHG emissions.

Pre-treatment stage SE lignin

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[70] Assuming the energy input is released with the moisture.

[71] Just like for the Kraft lignin, the in- and outputs of the hydrotreatment stage are not completely balanced. This is because many of the values are based on values from different scientific sources and various large assumptions were made. The values are still used, however, it does show that there are some uncertainties associated with the values, as explained in the discussion session.

All the relevant in- and outputs and the overall energy consumption in the pre-treatment stage can be found in Table 29. The energy inputs are converted to MJ per dry tonne of lignin. The composition of the lignin can be found in Table 30.Table 30: The composition and heating value of the Steam explosion lignin from Aspen wood (obtained from

Table 29: The relevant inputs during the pre-treatment stage of steam explosion lignin.

Relevant pre-treatment in- and outputs /dt lignin				
Product	**IN**	**OUT**	**Unit**	**Source/destination**
Electricity	317,42		MJ	Grid

The energy requirements for grinding biomass to a particle size of 2 mm as found in the literature vary from 15 kWh/dry t for miscanthus bales to 71.2 kWh/dry t for forest residues (Braimakis et al., 2014; Ringer et al., 2006; Tews et al., 2014; Wright et al., 2010; Zaimes et al., 2015). For this research, the energy requirement of **50 kWh/dry t** as assumed by Ringer et al (2014) is used.

The initial moisture content of the lignin is assumed to be 45% (SB Jones & Zhu, 2009). The theoretical minimum of evaporating water has been determined at 2442 KJ/kg of moisture evaporated at 25°C. However, actual drying usually occurs at temperatures slightly higher than 100°C and has to account for the sensible heat taken up by the biomass and the air used for drying (R. C. Brown & Brown, 2014). Therefore Brown & Brown (2014) have determined the actual energy requirement to be 150% of the theoretical requirements, so 3663 kJ/kg moisture evaporated at 25°C. The actual value is of course dependent on the biomass type, but this difference is assumed to be small since the energy requirement for the evaporation of the water is much higher than for the heating of the water and biomass (2258,67 kJ/kg, 4.188 kJ/kg/°C and ~2.1 kJ/kg/°C resp.) (Farag et al., 2002). Therefore, in this research the rule of **150% of 2442 KJ/kg evaporated moisture** is used for the drying of both lignin types. This energy is obtained in the form of heat, which can be from the excess heat produced during condensation of the pyrolysis vapours or from the waste heat produced from combustion of the chars (Ringer et al., 2006; Tews et al., 2014). The amount of steam required for this heat is 524.4 t/t evaporated moisture (Tews et al., 2014). Furthermore, a dryer requires electricity. A typical rotary dryer uses around **32 KWh/dry t**, which is also the value that is used for this research (Braimakis et al., 2014). The electricity can be obtained from the national grid (scenario one and two) or produced internally from combustion of the chars and non-condensable gases (scenario three). The outputs from this process are the dried feedstock and moist air.

The fast pyrolysis plant is assumed to be located right next to the lignocellulosic biorefinery. Therefore, the additional energy requirements for the transportation of the lignin from the refinery to the fast pyrolysis plant is assumed to be zero.

Table 30: The composition and heating value of the Steam explosion lignin from Aspen wood (obtained from Pakdel et al., 1992)

Lignin		Composition (wt.%)						HHV
Type	**Isolation process**	**C**	**H**	**O**	**N**	**S**	**Ash**	**MJ/kg**
Aspen wood	Steam explosion	58,17	5,98	34,8	0,98	0,07	1,2	25,2

Fast pyrolysis stage SE lignin

Table 31: The relevant in- and outputs of the fast pyrolysis stage

Fast pyrolysis in- and outputs /dt lignin				
Product	**IN**	**OUT**	**Unit**	**Source/destination**
Electricity	95,55		MJ	National grid
Ru/C catalyst	3,82E-05		t	Market
Biocrude		0,53	t	Hydrotreater
Char for process heat FP		0,19	t	Char combustor
NCG		0,10	t	Gas fired boiler
Of which CH_4		2,70E-04	t	
CO		5,05E-02	t	
CO_2		4,18E-02	t	
H_2		4,53E-03	t	
NH_3		9,32E-05	t	
C_2H_6		1,09E-03	t	
C_3H_8		1,17E-03	t	
Char for process heat for lignocellulosic biorefinery		0,26	t	Char combustor

No good composition of the bio-oil obtained from fast pyrolysis of steam explosion lignin could be found. Therefore the composition of lignin from steam explosion of Aspen wood (Table 30, obtained from Pakdel et al.(1992)) was extrapolated to obtain the most probable composition of its oil. Bio-oil obtained from lignin has almost the same composition as the lignin. Small changes were included, based on the changes between the Kraft lignin and its bio-oil. The C composition was used to make the total exactly 100%. The same fast pyrolysis gas composition is assumed as for the Kraft lignin scenario, for lack of reliable data from steam explosion lignin[72]. However, the HHV of the pyrolysis gas was obtained from Pakdel et al. (1992), together with the char composition and heating value. Thus, these values are for pyrolysis of steam exploded Aspen lignin. The energy requirements for the reactor were the same as for the Kraft fast pyrolysis reactor. Table 31: The relevant in- and outputs of the fast pyrolysis stageTable 31 shows the most important in- and outputs of the FP stage for the SE lignin. The process heat is produced from the char, the excess char and the NCG are used to produce heat for the lignocellulosic biorefinery, which affects the indirect effects and is in more detail explained in section 7.3.3.

The elemental compositions and heating values of each of the pyrolysis products can be found in Table 32. Some of the char is transported to the char combustor, and the excess char is sold on the market.

Table 32: The fast pyrolysis products from the fast pyrolysis of SE lignin, their composition and their heating values.

Fast pyrolysis products (SE lignin)		Composition (dry basis, wt.%)					Heating values (dry basis)	
Product	Yield (dry basis)	C	H	O	N	S	HHV (MJ/kg)	LHV (MJ/kg)[73]
Bio-oil phase (~21% pyrolytic water)	38,6	62,39	6,68	29,92	0,98	0,03	26,54	25,09
Pyrolysis gas phase	9,25	See Table 19					9,20[74]	8,98
Char	41,2	77,70	3,46	17,73	1,08	0,03	31,8	31,04

Upgrading stage SE lignin

Table 33: The relevant in- and outputs of the upgrading stage.

Upgrading in- and outputs /dt lignin				
Product	**IN**	**OUT**	**Unit**	**Source/destination**
Hydrogen	0,023		t	Market
Electricity	13,61		MJ	National grid
Stabilised bio oil (wet basis)		0,50	t	Market
Stabilised bio oil (dry basis)		0.29	t	Market
Off-gas		0,04	t	Atmosphere

For the upgrading of the bio-oil from SE lignin, the same assumptions and methods were used as for the upgrading of bio-oil from Kraft lignin. The relevant in- and outputs are presented in Table 33. The composition of the stabilised biofuel that was produced can be found Table 34. The off gas comprises the hydrocarbon gases, the gas from removing the heteroatoms and the hydrogen that could not be recovered by the PSA. The composition of the off-gas can be found in Table 35.

As can be seen in Table 34, not all of the heteroatoms in the bio-oil had to be removed to obtain a Heff/C ratio of 1.4. The fraction of impurities that had to be removed in order to obtain a biofuel with a Heff/C ratio of 1.4 and less than 0.1 wt.% of sulphur.

Table 34: The composition and heating values of the stabilised biofuels.

Stabilised bio-oil after upgrading of bio-oil from SE lignin		Composition (wt.%) of stabilised bio-oil from upgrading							
Product	Yield dry basis (Wt.% of dry lignin)	C	H	O	N	S	HHV dry basis (MJ/kg)	LHV[75] dry basis (MJ/kg)	Heff/C ratio
Stabilised bio-oil	29%	82,89	10,60	6,28	0,22	0,01	40.77	38.46	1.40

Table 35: The composition of the off-gases from the hydrotreatment.

Source	Gas	Quantity (t/dt lignin)
Gas from removing impurities during hydrodeoxygenation	NH3	4,16E-03
	H2S	1,25E-04
Gas from hydrocracking	CO_2	0,00E+00
	CH4	1,44E-02
	Ethane (C2H6)	1,20E-02
	Propane (C3H8)	3,71E-03
	Butane (C4H10)	3,34E-03
Hydrogen losses from hydrotreater	H2	3,44E-03

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[72] The composition of the fast pyrolysis gases from the pyrolysis of corn stover was used, obtained from (Wright et al., 2010).

[73] Calculated from the HHV with the equation from (Channiwala & Parikh, 2002).

[74] Obtained from (Pakdel et al., 1992).

[75] The LHV of the products are calculated from the HHVs.

Total	**Overall off-gas**	**0,04**

Char combustor SE lignin

The efficiency of the char burner is 84% (Tews & Elliott, 2014). The amount of char needed for the process heat is 0.19 t/dt lignin and 0.25 t of char/dt lignin is combusted to partly compensate for the reduced energy production in the lignocellulosic biorefinery. The composition of these flue gases if obtained in the same way as for the Kraft lignin, from Jones & Zhu (2009), only this time there was no need to correct for the sulphur content of the char. The relevant in- and outputs of the char combustion stage can be found in Table 36.

Table 36: The relevant in- and outputs of the char combustion stage for SE lignin.

Char combustor in- and outputs				
Product	**IN**	**OUT**	**Unit**	**Source/destination**
Ash		5,6E-06	t	Market
Flue gas		5,96	t	Atmosphere
Of which CO_2		1,18	t	
CO		1,45E-03	t	
water		0,24	t	
Nitrogen		4,33	t	
Oxygen		0,20	t	
NO2		2,31E-05	t	
SO_2		3,95E-04	t	
H2		1,23E-05	t	

LCI of the indirect effects for SE lignin

Reduced heat and electricity production Lignocellulosic biorefinery

The biorefinery is assumed to have a boiler that produces heat in the form of steam for the processes and for electricity production with an efficiency of 80%. Part of the steam can be used for electricity production in a turbine with 80% efficiency also. The assumed energy consumption for ethanol production from lignocellulosic biomass is 3.8 GJ of steam and 792 MJ of electricity per unit of ethanol (Scott et al., 2008). The boiler efficiency for natural gas is assumed to be 95%. but since the electricity is produced in a second turbine, the amount of lignin or natural gas combusted to produce 792 MJ of electricity is 990 MJ. This research assumed the same ratio of fuel for heat and electricity (3800 to 990 MJ respectively). The amount of lignin that is extracted and must thus be substituted is 23895,1 MJ/dt lignin. This means that the reduced heat production is 15165,1 and the reduced electricity production is 3160,7 MJ. The heat is compensated from by combustion of char in the char combustor and off-gases and natural gas in a gas-fired boiler. The electricity is obtained from the national grid. Table 37 shows the relevant information on the heat from each source.

Char
7989.8 MJ of char was combusted to provide 6698.7 MJ of process heat.

The off-gases
The off-gases comprises the following gases:
1. Non-condensable gases: 0.10 t/dt, LHV 8.98 MJ/kg
2. Off-gas from hydrotreater: 0.04 t/dt, LHV 32.23 MJ/kg

For the base case scenario, it was assumed that these gases were used as fuel. The easiest scenario is that they replace natural gas at the refinery (e.g. at the boiler). The refinery is located near the fast pyrolysis reactor; therefore, no emissions are assumed for transport of the gases. The heating value of both gases together is 2290.2 MJ/dt lignin. Assuming again the same efficiency for the combustion of natural gas and the combustion of these off-gases, 2290.2 MJ/dt lignin of natural gas can be replaced.

Table 37: The amount of heat produced from char and off-gases to compensate for the reduced heat from lignin extraction. The two final rows show the natural gas and electricity requirement to fully compensate for the reduced heat and electricity.

Combustion of char for process heat		
Excess char	7989,8	MJ/dt lignin
Lignin reduction	23895,1	MJ/dt lignin
Boiler efficiency lignin	80%	
Reduced heat production	15165,1	MJ/dt lignin
Reduced electricity production	3160,7	MJ/dt lignin
Heat produced from char for lignocellulosic biorefinery	6698,7	MJ/dt lignin
Combustion of off-gases to replace natural gas		
Off-gas hydrotreater	0,04	t/dt lignin
Non-condensable gases from fast pyrolysis	0,10	t/dt lignin
LHV off-gas hydrotreater	32,2	MJ/kg
LHV non-condensable gases	8,98	MJ/kg
Overall energy gases	2290,2	MJ/dt lignin
Combustion efficiency gas-fired boiler	95%	
Heat produced from off-gases	2175,7	MJ/dt lignin
Required natural gas and electricity for compensation of removed lignin		
Boiler efficiency natural gas	95%	
Natural gas required for heat production	6621,9	MJ/dt lignin
Electricity from grid	3160,7	MJ/dt lignin

7.4 Life cycle impact assessment of Steam explosion lignin fast pyrolysis

Also the LCIA is subdivided into the direct emissions and the indirect emissions. The emissions are presented per kg CO_2-eq/dt lignin, and in the correct functional unit g CO_2-eq/MJ of biofuel.

7.4.1 Direct life-cycle emissions.

Table 38: The emissions per life-cycle stage and the overall emissions, both per dt of lignin and in the correct functional unit.

Total direct GHG emissions of SE lignin conversion to biofuel		
Life-cycle stage	GHG emissions (kg CO_2-eq/dt lignin	GHG emissions (g CO_2-eq/MJ biofuel)
Pre-treatment	25,65	2,3
Fast pyrolysis	7,91	0,7
Upgrading	49,12	4,5
Char combustor	0	0
Total	**82,68**	**7,6**

Table 38 shows all the GHG emissions of each life-cycle stage of the fast pyrolysis process.
The GHG emissions over the whole fast pyrolysis process are presented per life-cycle stage in Table 39, Table 40 and Table 41. Just like with the Kraft lignin, methane is assumed to be combusted and the CO_2 emitted from biomass is considered carbon neutral.

Table 39: The GHG emissions from the pre-treatment stage of the SE lignin.

Pre-treatment, relevant in- and outputs (kg CO_2-eq/dt lignin)	
Product	Kg CO_2-eq/dry tonne lignin
Electricity[76]	25,65

Table 40: The GHG emissions from the fast pyrolysis stage of SE lignin.

Fast pyrolysis, relevant in- and outputs (kg CO_2-eq/dt lignin)	
Product	Kg CO_2-eq/dry tonne lignin
Electricity	7,72
Ru/C catalyst	0,19[77]
Total	**7,91**

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[76] For the carbon intensity of electricity, the value of the Brazilian grid were extracted from EcoInvent for low voltage and including imports.

[77] The value for a zeolite proxy was obtained from EcoInvent. The European values were also used for the Brazilian case.

Table 41: The GHG emissions from the upgrading stage of SE lignin.

Upgrading, relevant in- and outputs (kg CO_2-eq/dt lignin)	
Product	Kg CO_2-eq/dry tonne lignin
Hydrogen	48,02[78]
Electricity	1,10
Total	**49,12**

7.4.2 Indirect GHG emissions

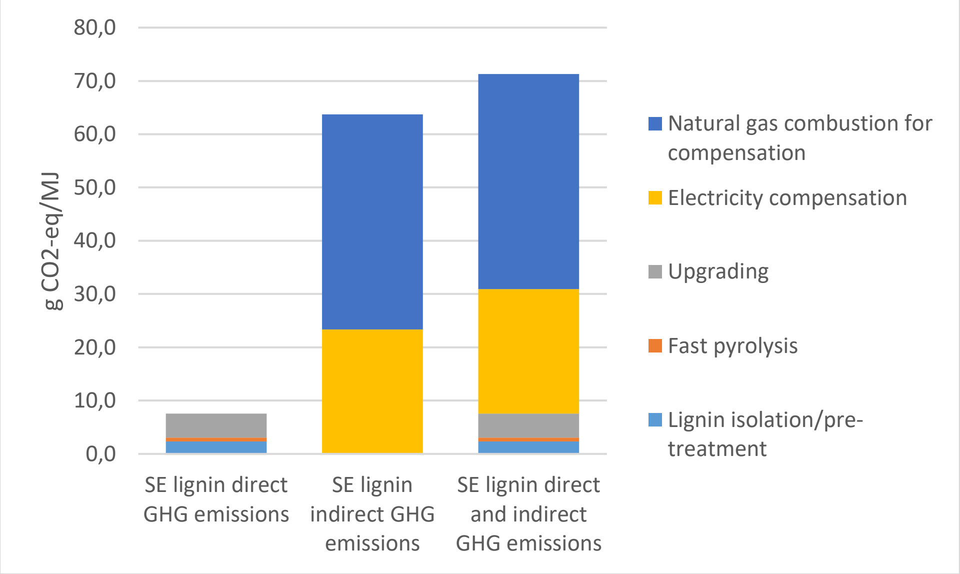
Reduced heat and electricity production lignocellulosic biorefinery

The heat reduction in the lignocellulosic biorefinery was 15165.1 MJ, and the electricity requirement from the grid is 3160.7 MJ. The heat is compensated for by combustion of the char, off-gases and natural gas, the electricity is compensated from the national grid. The emissions from char and off-gas combustion are biogenic, so this combustion is considered carbon neutral. The combustion of the natural gas produces 442[79] kg CO2-eq/dt lignin. The emissions from the Brazilian electricity grid for the required electricity are 255 kg CO2-eq/dt lignin. The overall emissions from the compensation of the reduced heat and electricity production in the Kraft mill are thus 697 kg CO_2-eq/dt lignin. This translates to **63.7 g CO2-eq/MJ** biofuel, converted to the correct functional unit.

7.4.3 Total emissions SE lignin fast pyrolysis

Adding the direct and indirect emissions of the conversion of SE lignin to marine biofuel yields the following results (Figure 13: Showing the direct and the indirect GHG emissions of Kraft lignin conversion to marine biofuel through fast pyrolysis and subsequent hydrotreatment.Figure 14). The interpretation of the results, together with a comparison with fossil fuels and the results of Kraft lignin conversion is presented in section 7.5.

Figure 14: The direct and indirect GHG emissions of SE lignin conversion to marine biofuel through fast pyrolysis



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[78] Based on a general carbon intensity value for hydrogen sold in the European market. These values were also used for the Brazilian case.

[79] Default value for combustion of natural gas was obtained by IEA (IPCC 2006 guidelines). Life cycle production value was obtained from EcoInvent for global liquid hydrogen.

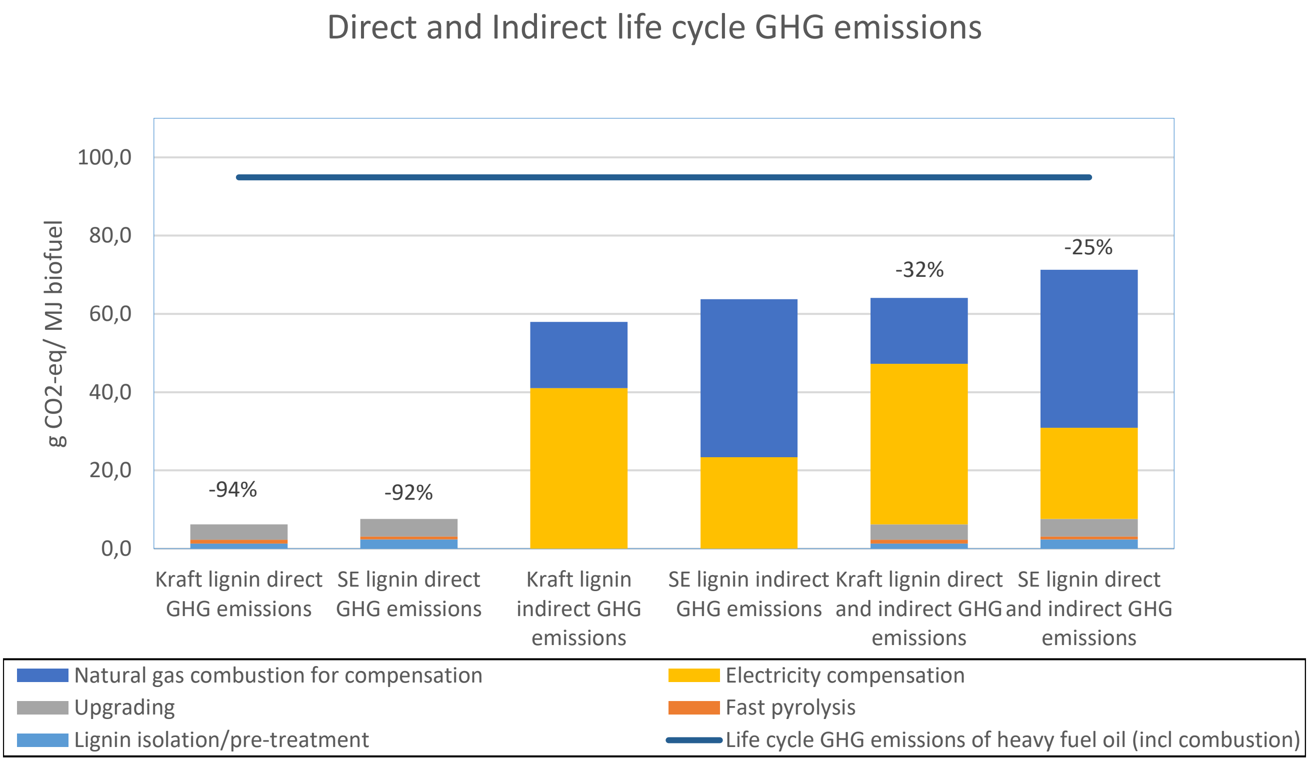
7.5 Interpretation

In this section the results of the LCA of the two conversion routes are discussed. It starts with a discussion of the life cycle GHG emissions of the two biofuels. This is followed by a short discussion of the biofuel quality and the overall mitigation potential. The uncertainty and sensitivity of the results was discussed in the next section, section 7.6.

7.5.1 Life cycle GHG emissions

Figure 15 shows the direct and indirect GHG emissions of Kraft and SE lignin conversion to marine biofuel through fast pyrolysis and subsequent hydrotreatment. The life cycle GHG emissions from the combustion of heavy fuel oil is also included as a reference, to see the potential difference in emissions with the current situation.

Figure 15: The direct, indirect and overall GHG emissions of marine biofuels produced from SE lignin and Kraft lignin conversion.



The emissions from Kraft lignin conversion, including consequential effects, were 32% lower than the life cycle emissions of diesel combusted in a building machine. The overall emissions (comprising the direct and indirect emissions) from producing biofuel from SE lignin were also less than that of HFO; a reduction of 25% was achieved. Therefore, the overall process of fast pyrolysis from lignin to produce a biofuel that replaces HFO in large freight vessels mitigates GHG emissions.

For both conversion routes, the direct life cycle emissions from the actual conversion processes of fast pyrolysis and hydrotreatment only makes a small contribution to the overall life cycle emissions. Also the pre-treatment of SE lignin and the Kraft lignin isolation process have a small contribution. The largest part of the emissions was caused by the indirect effects of lignin conversion; compensating for the reduced heat and electricity losses in the Kraft mill or lignocellulosic biorefinery. The direct life cycle GHG emissions of the biofuel from Kraft lignin were 94% lower than the life-cycle GHG emissions of the HFO, for SE lignin a reduction of 92% was calculated. This shows that if the indirect GHG emission could be reduced, a very large reduction could be possible. The indirect emissions could be reduced by using a less carbon intensive energy source to supply the required heat and electricity, e.g. electricity from solar PV and heat from forest residues.

The emission factor for the electricity grid in Finland was much higher than that for the electricity grid in Brazil. Also the emission factor of the natural gas life cycle was much higher for natural gas in Finland as for Brazil. This also contributes to the difference between the two conversion routes, especially for the indirect effects, where large amounts of natural gas and electricity are required. For both conversion routes, obtaining the required Heff/C ratio required more hydrogen than meeting the sulphur limit.

Therefore, the hydrogen input is quite large and the sulphur content of the stabilised biofuel is much smaller than required. The hydrogen input could thus be smaller if a lower Heff/C ratio was allowed.

7.5.2 Biofuel quality

The composition of the biofuel from Kraft lignin conversion, as calculated for this thesis, has roughly the same LHV as residual marine fuel (41 MJ/kg biofuel vs 40 MJ/kg RMA). It contains no oxygen and sulphur and has the same Heff/C ratio as heavy crude oil, (1.4). The biofuel produced from SE lignin was also of good quality. The LHV was only a little lower than that of RMA (38.46 and 40 respectively). The oxygen content was 6.3 wt.%, the sulphur content is well below the limit 0.01 wt.% and the Heff/C ratio was also 1.4. Both biofuels seem promising as drop-in fuels, though this should be tested on more criteria and on real engines.

The biofuel from Kraft lignin has a slightly higher quality because it required the removal of all the heteroatoms to obtain the required Heff/C ratio. However, it consumed a little less hydrogen/ MJ of biofuel during upgrading, partly because Kraft lignin and the bio-oil from Kraft lignin contain less oxygen than bio-oil from SE lignin, and partly because more bio-oil is produced from SE lignin. So, removing all the impurities from the bio-oil from Kraft lignin required less hydrogen than removing only part of the impurities from the bio-oil from SE lignin (see Table 42). Table 43 shows the different yields and heating values of the products of the two conversion routes. There are differences, but these are quite small.

Table 42: The hydrogen consumption in the hydrotreater to produce a biofuel that meets the set requirements.

H consumption during hydrotreatment	Kraft lignin	SE lignin	Unit
Hydrogen consumption (incl losses)	1,74	2,06	g H2/MJ biofuel

Table 43: The yields and LHV of the different fast pyrolysis products.

Yield and LHV of the fast pyrolysis products	Kraft lignin	SE lignin	Kraft lignin	SE lignin
Product	Yield (wt.% of dry lignin)	Yield (wt.% of dry lignin)	LHV (MJ/kg)	LHV (MJ/kg)
Lignin	N/A	N/A	24,4	23,9
Bio-oil (dry)	32,0	38,6	28,4	25,1
Biofuel (dry)	25,1	28,6	41,3	38,5
Char	50,5	41,9	25,5	31,0
Pyrolysis gas	11,9	9,3	11,8	9,0
Off gas hydrotreater	3,79E-02	4,33E-02	32,2	32,2

7.5.3 The overall mitigation potential

As calculated in section 5.4, the global biofuel potential from lignin is currently around 12.6 – 17.6 Mt of biofuel per year. Most of the biofuel potential is from Kraft lignin conversion, which according to this research mitigates approximately 32% of the emissions. Roughly between 12.4 and 17.4 Mt of Kraft biofuel could be produced per year, which means that roughly between 15.7 and 21.9 Mt CO2-eq emissions per year could potentially be mitigated from biofuel from Kraft lignin. The SE lignin mitigates 25% of the emissions and potentially 50 Kt of biofuel per year is available from lignocellulosic biorefineries. This could potentially mitigate roughly 0.05 Mt of CO2-eq emissions per year. So, the current amount of CO2-eq emissions that could potentially be mitigated from the use of biofuel from lignin is between 15.8 and 22.0 Mt

In ten years, this might increase to 18.7 – 25.0 Mt of biofuel per year. The SE lignin biofuel will have increased to 3.1 Mt of biofuel per year, and the Kraft between 15.6 and 21.9 Mt biofuel. Assuming the LHV of the fuels nor the GHG emission reduction will change, that means that roughly 2.8 Mt of CO2-eq could potentially be mitigated by SE biofuels per year. Roughly between 19.6 and 26.2 Mt/year could be mitigated by Kraft lignin biofuels. So, the amount of CO2-eq emissions that could potentially be mitigated from the use of biofuel from lignin in ten years, is between 22.4 and 29.0 Mt CO2-eq/year.

Since the overall emissions of the shipping industry are 961 Mt CO2-eq (in 2012), currently roughly between 1.6% and 2.3% of the overall shipping emissions could be mitigated. The shipping emissions are expected to have increased with 50-250% from 2012 to 2050. Assuming a conservative 25% increase of the 2012 value up to 2026 (ten years), means that by that time approximately 1201 Mt of CO2-eq are emitted by the shipping sector. So, between 1.9% and 2.4% of the emissions could potentially be mitigated by the biofuels ten years from now.

7.6 Uncertainty and Sensitivity analysis

This section presents the uncertainty and sensitivity analysis of the results for the Kraft lignin conversion route and the SE lignin conversion route. The criteria and the uncertainty that was appointed to them is presented in appendix 5, where also a short motivation for the choice of the probability density functions is presented.

7.6.1 Uncertainty analysis

The mean calculated GHG emissions of the Kraft lignin conversion route was 68.59 g CO2-eq/MJ. The uncertainty analysis shows that there is a 90% certainty that the results fall between 47.7 and 92.7 g CO2-eq/MJ (Figure 16). Since the GHG emissions of HFO are 94.9 g CO2-eq/MJ, it is very probable that the emissions of the Kraft conversion are larger than that of HFO, and that at least some GHG emissions are mitigated when HFO is replaced by the biofuel. The uncertainty graph shows that there is approximately a 96% chance that the GHG emissions from Kraft lignin conversion are lower than that of HFO. %. There is a chance of 72.3% that the reduction is more than 20%. A chance of 46.5% that the reduction is more than 30% and a chance of 19.9% that the reduction is more than 40%. The chance of a reduction of more than 50% is only 4.7%. This confirms what was already stated in section 7.5 (interpretation); fast pyrolysis of Kraft lignin from Finland to produce marine biofuels as was researched for this thesis is likely to be effective in mitigating GHG emissions.

The mean calculated GHG emission of SE lignin conversion is 75.6 g CO2-eq/MJ, as can be seen in Figure 17. There is a 90% chance that the emissions are between 57.5 and 94.7 g CO2peq/MJ. That means that there is a 95% chance that the emissions are less than 94.7, which is almost exactly the same amount of GHG emissions as HFO. So, there is a 95% chance of a GHG reduction of more than 0%, a 81.0% chance of reduction of more than 10%, a 52.6% chance of a reduction of more than 20% and a 21.1% chance of a reduction of more than 30%. These numbers confirm what was already clear in the previous section: Biofuels from SE lignin conversion in Brazil could be used to mitigate GHG emissions in the shipping sector.

The results for both conversion routes show a large uncertainty. More robust input data is required to obtain more reliable results. This could be achieved by finding more values, so that an average can be calculated, or by performing a test that specifically assesses these cases. An important uncertainty arises regarding the GHG emissions of the chemicals for the LignoBoost isolation process of Kraft lignin. This is discussed in more detail in the discussion, section 9.2.

Figure 16: The uncertainty analysis of Kraft lignin conversion. The x-axis shows the value of the result in g CO2-eq/MJ and the y-axis shows the fraction of the total iterations that resulted in that value.

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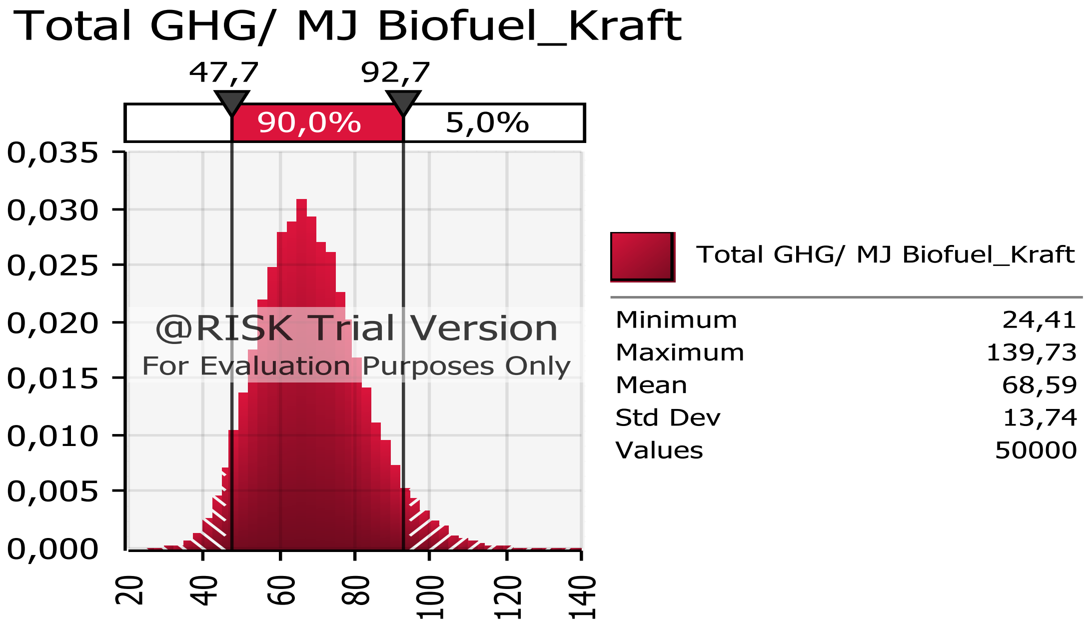
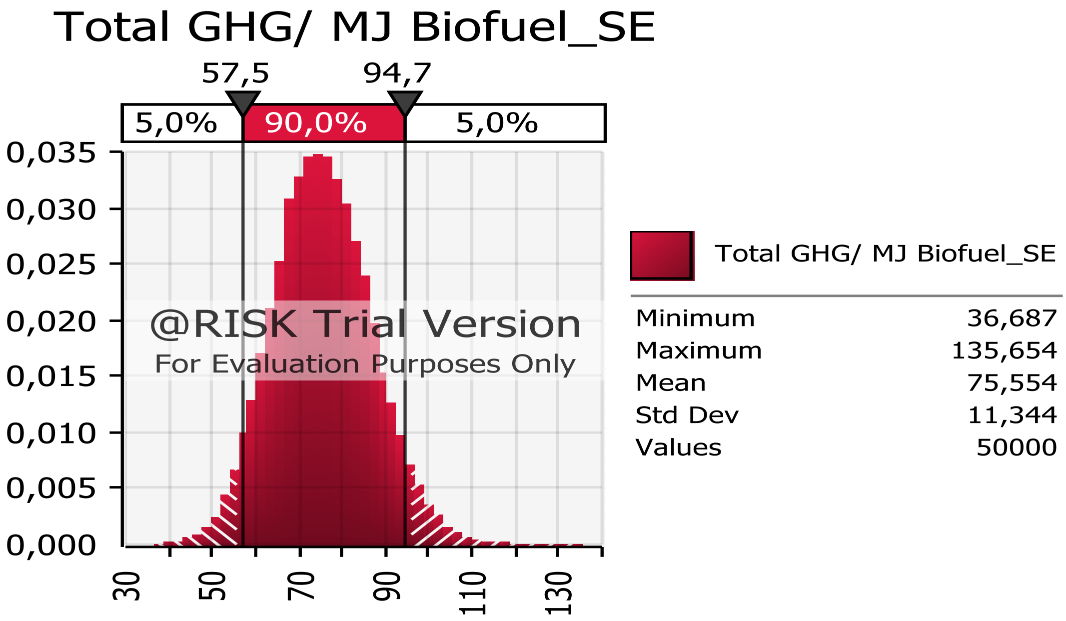


Figure 17: The uncertainty analysis of SE lignin conversion. The x-axis shows the value of the result in g CO2-eq/MJ and the y-axis shows the fraction of the total iterations that resulted in that value.



7.6.2 Sensitivity analysis

A sensitivity analysis was performed on the most important input parameters in the research. This sensitivity analysis addresses the impact of these parameters on the outcome. It shows which parameters have the largest influence, and should thus be chosen with care.

For the Kraft lignin conversion route, the results are most sensitive to the emission factor of the electricity grid of Finland. Electricity is required for almost every life-cycle stage and for the indirect effects. As mentioned before, the electricity emission factor was quite high for Finland. If the emission factor would decrease in the future, e.g. due to increasing production of renewable electricity, or if the Kraft mill were to produce its own electricity, e.g. from solar PV panels or forest residues, this would improve the results significantly. After the electricity emission factor, the results are most sensitive to the bio-oil yield. Increasing the bio-oil yield would decrease the GHG emissions of the biofuel. The yield was obtained for the right lignin type and the right process conditions, but research shows that these values still differ between different articles. More research should be done to assess the yield of LignoBoost Kraft lignin fast pyrolysis. Also, research that aims to increase the bio-oil yield of fast pyrolysis would be important. The third largest effect on the results is from the natural gas emission factor. This is because of the quite large amounts of natural gas that were required, especially for the indirect effects. If in the future, the emission factor of gas increases because it becomes increasingly difficult to extract, this could significantly increase the overall GHG emissions of the process. The natural gas is mainly used for heat production, so finding another, more sustainable, source of heat would be worthwhile. For example, forest residues could be used. The other parameters with a large influence on the results can be found in Figure 18.

As can be seen in Figure 19, the parameter with the largest influence on the result for SE lignin is the natural gas combustion emission factor. Most of the natural gas is used to produce heat to compensate for the extracted lignin in the lignocellulosic biorefinery. Finding an alternative energy source could be worthwhile to reduce the GHG emissions. The second most important parameter is the emission factor of electricity in Brazil. This was quite a low value (much lower than for Finland), but because so much electricity is required, still also for SE lignin conversion, the electricity is responsible for a large share in the overall emissions. So also for this conversion route it is true that changing the electricity source to green electricity would have a large effect on the overall GHG emissions. The third parameter is the LHV of the steam explosion lignin, where a lower value would increase the mitigated emissions. This influences the amount of energy that is extracted from the lignocellulosic biorefinery and that should thus be compensated for using electricity from the grid and natural gas. Though this is not completely realistic, because in reality the LHV of the lignin would also influence the LHV of the bio-oil, and thus the amount of upgrading that is required. So, the effect of the LHV of the lignin might not really be this large, but it does illustrate again the influence of the indirect effects on the results of SE lignin conversion. The other important parameters can be found in Figure 19.

Figure 18: The 10 parameters that have the largest influence on the GHG emissions from Kraft lignin conversion.

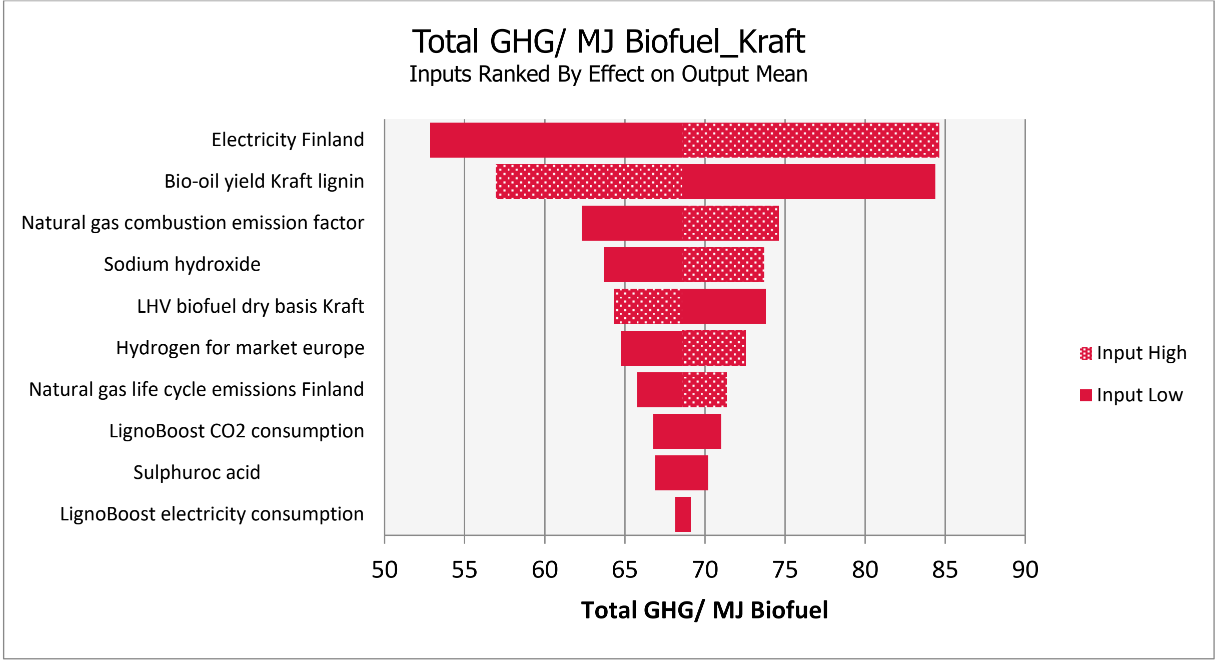
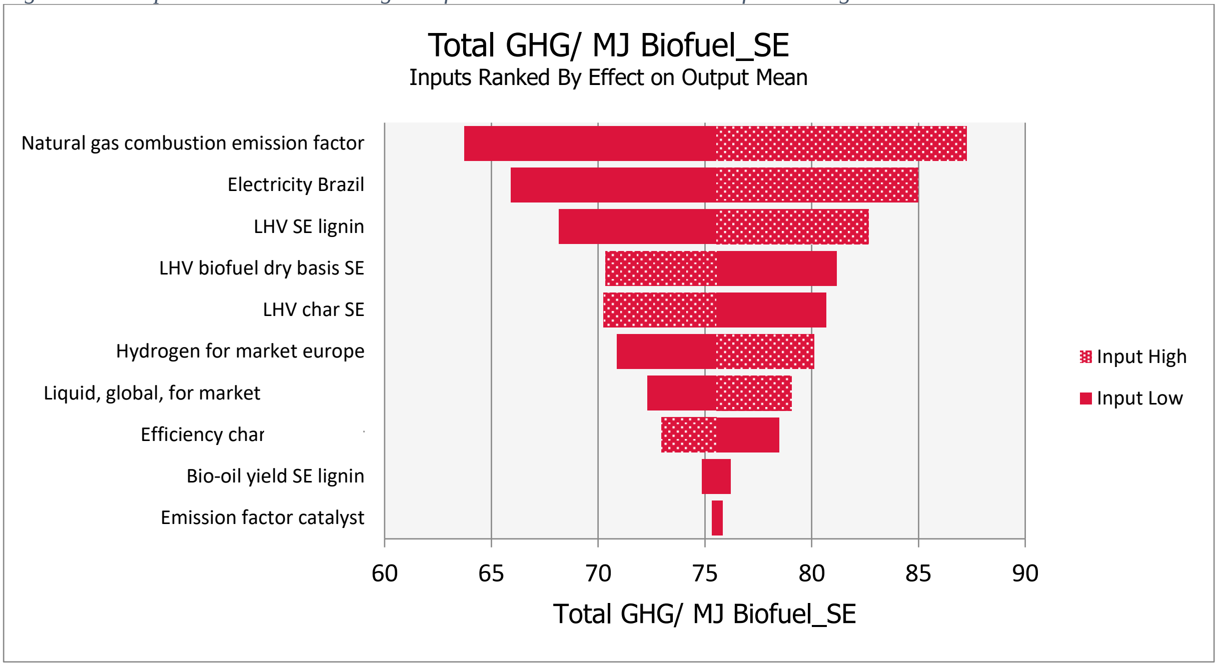


Figure 19: The parameters with the largest influence on the GHG emissions from SE lignin conversion route.



8 LCA of alternative configurations

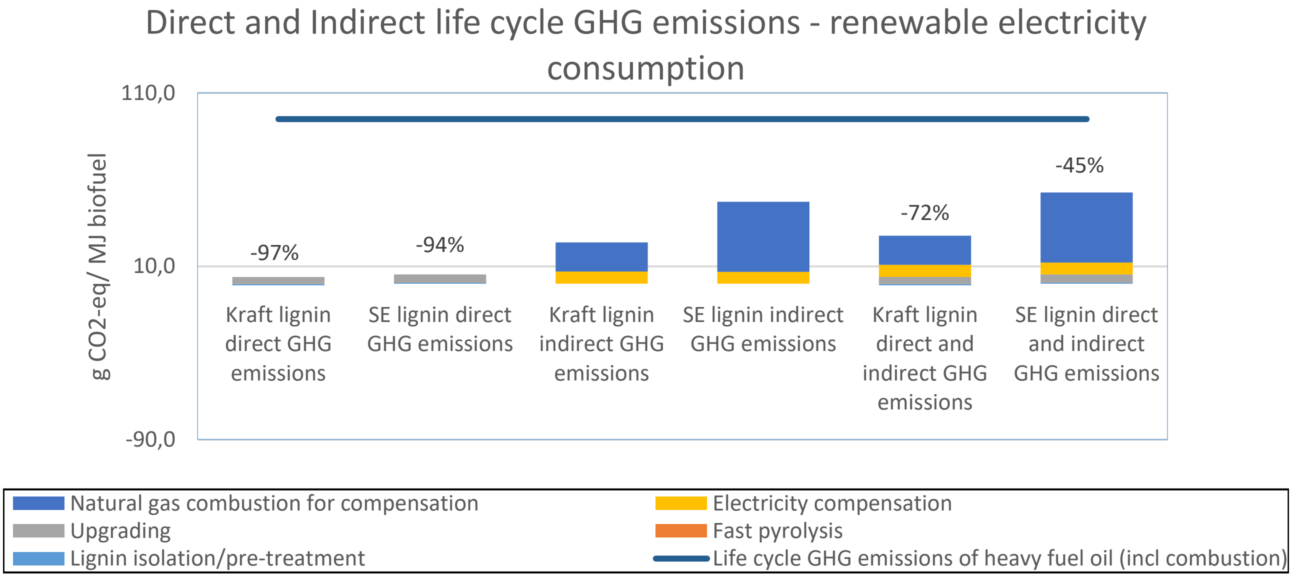
In the previous chapter, the GHG emission of the base case configuration were calculated. If some of the assumption in the configuration were changed, more GHG savings could potentially be achieved. The base case configuration assumed that the required electricity was consumed from the national grid, which especially for the Kraft lignin conversion route had a high emission factor. In section 8.1, the results of renewable electricity consumption, of solar photovoltaic panels, were assessed. In section 8.2, the GHG mitigation potential of co-combusting the excess char in a coal-fired power plant was assessed, instead of combusting it to provide internal process heat.

8.1 Renewable electricity.

In the base case configuration, electricity from the grid was obtained to compensate for the loss in electricity production from lignin combustion and for the electricity required for the processes. Renewable electricity could also be used for this, in order to achieve larger GHG savings. The impact of using renewable electricity is assessed in this section. The results can be found in Figure 20. The impact of using renewable electricity is largest for the Kraft lignin conversion route, which now mitigates 72% of the GHG emissions. Kraft lignin is more sensitive to the new emission factor for electricity, because electricity was responsible for the largest part its emissions. The large amount of excess char in the Kraft conversion route already significantly reduced the natural gas consumption.

The SE lignin conversion route consumed less electricity and more natural gas, therefore the smaller emission factor for electricity does not have a large effect. With renewable electricity consumption, still only 45% of GHG is mitigated.

Figure 20: The GHG emissions of the Kraft and SE lignin conversion to marine biofuel, when solar photovoltaic electricity is used



8.2 Co-combustion of char in coal-fired power plant

For the base case scenario, it was assumed that the char is combusted to provide process heat. In this section, we will assess the GHG emissions if the char is co-combusted in a coal-fired power plant, so it replaces coal.

8.2.1 Char from Kraft lignin

Finland still uses approximately 50 PJ of hard coal per year as fuel for electricity and heat production (StatisticsFinland, 2016). Finland is making an effort towards becoming a fossil-free nation and part of their plan is to, at least in the near future, switch from coal to biomass and forest residues for their electricity and heat production (Andrew Silver, 2016).

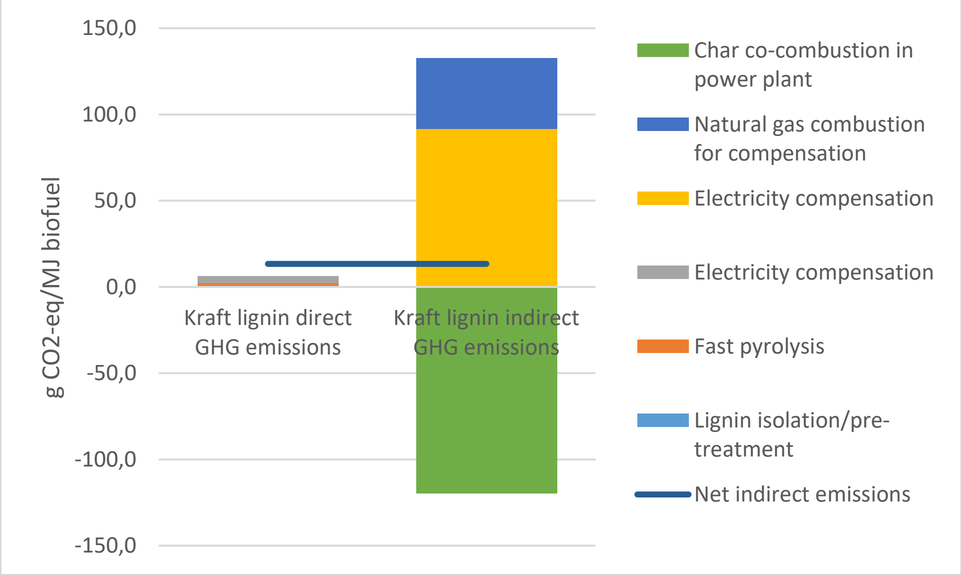
Combustion of biochar is different from combustion of fossil hard coal. For example, biochar usually has a lower energy density, the higher fraction of volatile matter can cause more “flaming combustion” instead of “carbon combustion”, biochar is usually less dense, it contains different types of ash and it has different energy requirements for grinding (Ciolkosz, 2010). These properties can influence the efficiency of the power plant. However, it is assumed that only a small percentage of the coal is replaced by the biochar (<20%), which is assumed to have minor influence on the efficiency of the power plant. Therefore the power plant efficiency is assumed to remain the same as with combustion of only fossil hard coal. The average efficiency of a coal fired power plant in the Nordics was approximately 42% in 2011 (Hussy et al., 2014).

The biochar will have to be transported to a coal-fired power plant. With the fast pyrolysis of approximately 2000 dt of lignin/day as assumed in the base case scenario, roughly 880 t of excess biochar per day is produced. A power plant near to the Metsa Fibre Rauma pulp mill is the Meri-Pori Power Station. It is quite a large power plant, producing 565 MWe from bituminous coal (TVO, n.d.). Assuming the hard coal has a LHV of 25 MJ/kg[80] and the efficiency of the power plant for producing electricity is 42% (general value for the Nordics (Hussy et al., 2014)), then roughly 5649 t of coal is combusted per day. That means that the power plant can easily combust the 900 tonnes of biochar produced per day at the fast pyrolysis plant without having to replace more than 20% of the coal. The transportation distance is approximately 80 km, which is assumed to be transported overland, by trucks. The emissions of the transport are obtained from the EcoInvent database for large lorries (>32 metric ton, Euro 5). These parameters are presented in Table 44. The overall GHG emission that can be mitigated by co-combustion of biochar in a coal-fired power plant are 119.5 g CO2-eq/MJ. The effect of the co-combustion of char on the overall GHG emissions of Kraft lignin conversion can be seen in Figure 21.

Table 44: The mitigated GHG emissions when char is used to replace fossil coal in a coal-fired power plant.

Co-combustion of biochar in coal fired power plant		
Excess char	10909,44	MJ/dt lignin
Assumed change in power plant efficiency	0%	
Emissions mitigated in power plant	1232,77	kg CO2-eq/dt lignin
t char transported/dt	0,44	t/dt
Distance of transport	80	km
Transport	34,82	tkm/dt lignin
Overall mitigated emissions from coal replacement by biochar	1229,81	kg CO2/dt lignin
Overall mitigated emissions from coal replacement by biochar	**119,51**	**g CO2/dt lignin**

Figure 21: The effect of co-combusting the char in a coal-fired power plant.



8.2.2 Char from steam explosion lignin

Brazil has one of the least carbon intensive energy sectors in the world, and not many coal-fired power plants exist. However, the industry still partly relies on imported coking coal, which could be replaced by the biochar produced during fast pyrolysis (IEA, 2013). It is assumed that the coal will be combusted in the port of Maceio, 55 km from the biorefinery. Since 0.25 t/dt lignin of char will be transported, the char transport is 13.75 tkm/dt lignin.

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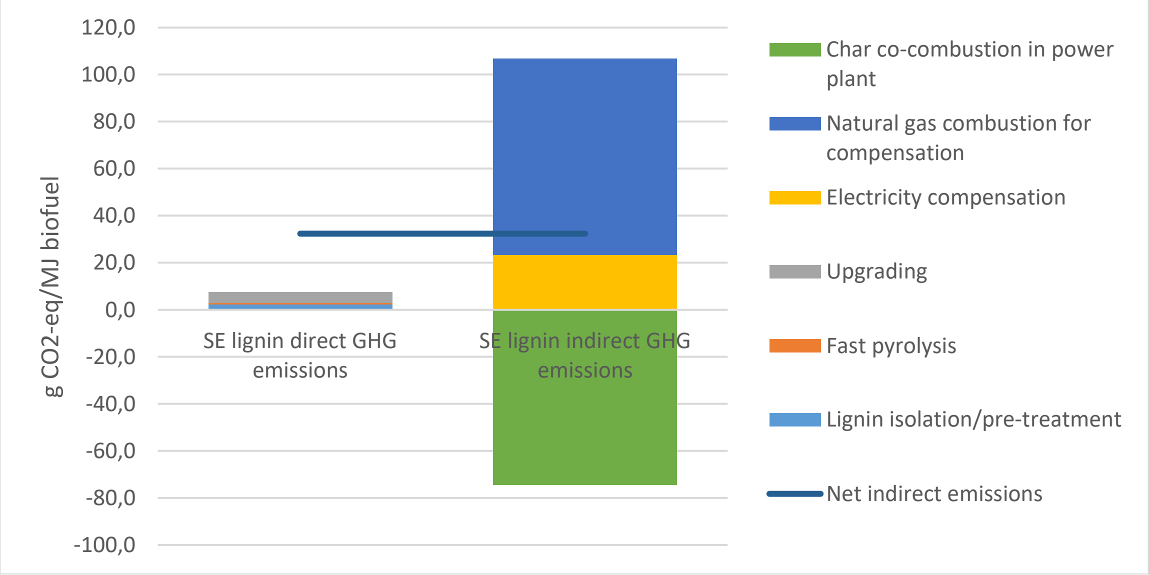
[80] (TheEngineeringToolbox, n.d.), value for bituminous coal C.

As for the Kraft lignin, it is assumed that the efficiency of the coal-fired boiler remains the same when char is co-combusted if <20% of coal is replaced. It is assumed that sufficient coal is consumed that all the char can be used. The same lorries are assumed as for the transportation of Kraft lignin in Finland. The energetic value of the excess char is 7756.38MJ/dt lignin, so 7756.38 MJ of coal is assumed to be replaced. This results in a mitigation of 813.3 kg CO2-eq /dt lignin or 74.4 g CO2-eq/MJ biofuel. The relevant values can be found in Table 45. The effect of the co-combustion of char on the overall GHG emissions of SE lignin conversion can be seen in Figure 22.

Table 45: The GHG emissions and input values of co-combustion of char in a coal-fired power plant.

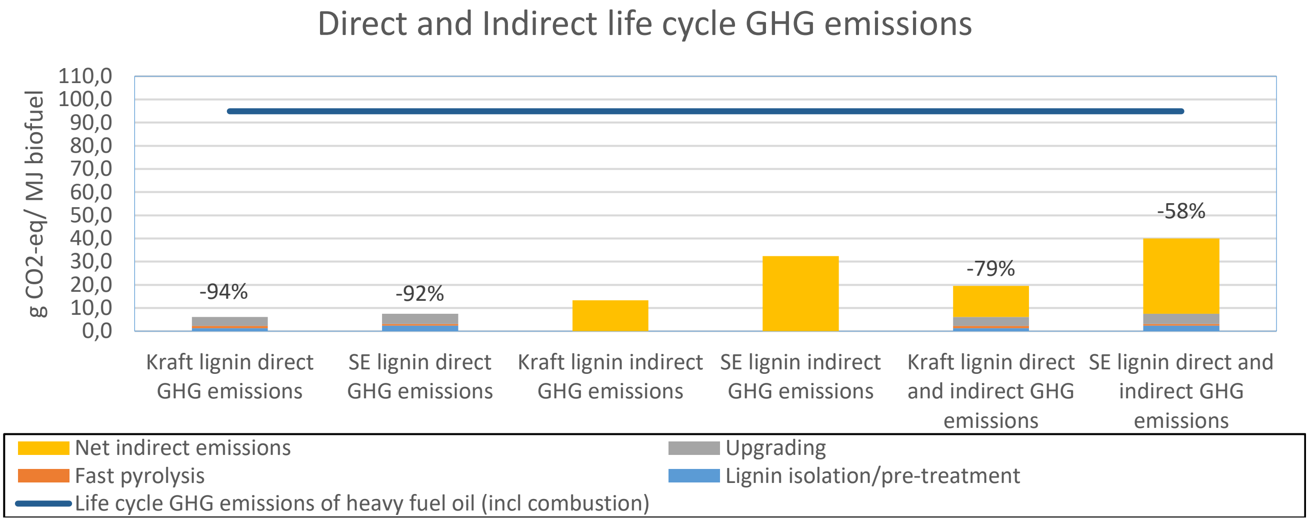
Co-combustion of biochar in coal fired power plant		
Excess char	7756,38	MJ/dt lignin
Assumed change in power plant efficiency	0%	
Emissions mitigated in power plant	**814,42**	**kg CO2-eq/dt lignin**
t char transported/dt	0,25	t/dt
Distance of transport	55	km
Transport	13,74	tkm/dt lignin
Emission from transport	1,17	kg CO2/dt lignin
Overall mitigated emissions from coal replacement by biochar	**813,25**	**kg CO2/dt lignin**
Overall mitigated emissions from coal replacement by biochar	**74,35**	**g CO2/dt lignin**

Figure 22: The effect of co-combusting the char in a coal-fired power plant.



From Figure 23 it can be seen that the GHG emission reduction with this configuration increases compared to the base case configuration. The Kraft lignin biofuel mitigates 79% of the GHG emissions, and the SE lignin biofuel mitigates 58% of the emissions. Kraft lignin conversion produces more char, therefore more char can be combusted in the coal-fired power plant and more GHG emissions mitigated.

Figure 23: The direct and Indirect emissions of Kraft and SE lignin conversion to marine biofuel, if char is used for co-combustion in a coal-fired power plant.



9 Discussion

9.1 GHG emissions

9.1.1 Direct GHG emissions

The direct GHG emissions of this study were 6.2 and 7.6 g CO2-eq/MJ biofuel for Kraft lignin and SE lignin conversion respectively. The direct emissions of SE lignin conversion are higher that of Kraft lignin conversion because the pre-treatment requires more energy than the LignoBoost process, and the SE lignin contains more oxygen and requires more upgrading.

The GHG emissions of the fast pyrolysis of forest residues calculated by Tews and Elliot (2014) were 26.7 g CO2-eq/MJ (only the pre-treatment and conversion stage). This included an additional 0.28 and 0.24 MJ hydrogen per MJ biofuel compared to biofuel from Kraft and SE conversion respectively (see the comparison of hydrogen input above). They assumed an internal hydrogen plant, that produced hydrogen from the pyrolysis off-gases, so it's difficult to compare the results.

Hsu (2009) calculated the life cycle GHG emissions from the fast pyrolysis of wood to produce gasoline and diesel. The results showed a GHG emission of 39 g CO2-eq/MJ fuel. This includes hydrotreating and hydrocracking, the hydrogen is produced from natural gas. A subdivision of the GHG emissions per MJ for each stage of the fuel production is not presented, but from a graph showing the GHG emissions per km it is clear that the upgrading is responsible for a large part of the emissions (51%). Also, the emissions from the stages before conversion were included (e.g. harvesting and logging). So, the emissions are much higher, but this is partly because emissions from the agricultural stage are included and more upgrading is done. Without these emissions, the results would be more similar to the results of this study.

It can be concluded that is difficult to compare the direct emissions of this research with the direct emissions calculated in other studies. The direct emissions of this result are lower than the emissions calculated by other studies, but this was expected because low severity hydrotreatment was assumed. More similar research should be conducted so the results can be compared and validated.

9.1.2 Indirect GHG emission

The indirect emissions of the Kraft lignin conversion route are 57.9 g CO2-eq/MJ biofuel, and for SE lignin conversion they are 63.7 g CO2-eq/MJ biofuel. This is for both conversion routes only due to electricity and natural gas combustion to compensate for the reduced energy production in the Kraft mill or lignocellulosic biorefinery because of the extracted lignin. The indirect are a little higher for the SE lignin conversion, because the boiler efficiency in a lignocellulosic biorefinery is higher than that of a recovery boiler, so more heat most be compensated for. Also, more char is produced from Kraft lignin, to replace natural gas. This even offsets the higher emission factors for electricity and natural gas in Finland.

9.1.3 GHG emission reduction potential

The lignin supply market shows that there are many large sources of lignin throughout the world, especially from the paper/pulp industry. There are not many lignocellulosic biorefinery yet, but this number is expected to increase significantly in the future, though it is very uncertain at what rate. This will be dependent on the fuel prices and biofuel incentives. As calculated in section 7.5, between 15.6 and 21.9 Mt of GHG emission could potentially be mitigated now, according to the results of this thesis. In ten years, this potential is expected to increase to roughly 22.4 to 29.0 Mt GHG emissions per year. This means that approximately between 1.6 and 2.3% of the overall shipping emissions could potentially be mitigated today and between 1.9 and 2.4% in ten years.

This is quite a large CO2 mitigation potential in absolute terms. If the lignocellulosic ethanol production increases as much as is aimed for through the targets set by several governments, the amount of lignin will increase even more than was projected in this study. Furthermore, if the technologies improve, the yields might improve and perhaps even more GHG mitigation could be possible. In relative terms, around 2 percent reduction is much less than is required in order to achieve the 2-degree targets. This means that biofuel production from lignin can be considered an important tool to reduce GHG emissions from the shipping industry, but it should not be the only tool since a larger GHG reduction is required.

9.1.4 Increasing the GHG mitigation potential

The Renewable Fuels Standard in the US requires a minimum GHG emission saving of 60% for any renewable fuel derived from cellulose, hemicellulose or lignin. The Renewable Energy Directive in Europe requires all biofuels that started production after the first of January 2017 to reduce 50% of emissions compared to fossil fuels. The emission reduction for Kraft lignin is 32%, and for SE lignin it is 25% compared to fossil fuel, calculated with the methods applied in this research. This is less than the required reduction, but it should be noted that a different method was used than required by the RFS and the RED. The emission reduction when using the required methods should be calculated, but it is possible that additional measures should be taken to increase the mitigation potential. Since the largest part of the emissions are from electricity use from the grid and natural gas combustion, changing the emissions from these two sources would have the largest effect on the results. This was also demonstrated by the sensitivity analysis.

Electricity and heat are two commodities that can be produced from many sources. There most important option to reduce the GHG emissions from electricity, is to use renewable electricity, e.g. from solar PV panels. This was assessed in section 8.1, and resulted in GHG emission savings of 72% for Kraft lignin conversion and 45% or SE lignin conversion.

Several options exist to reduce the natural gas use. One option is to extract less lignin. It is argued by some researchers that 10-20% of the lignin can be extracted without influencing the energy balance of the paper/pulp mill (Gosselink, 2011). The global Kraft lignin production is currently 50-70 Mt, that means that 10-14 Mt can be removed without requiring additional heat and electricity inputs into the mill (assuming that 20% can be removed). This would significantly reduce the biofuel quantities that can be produced, but it would also significantly increase their CO2 mitigation potential. Another option is to combust forest residues instead of natural gas. Forest residues, like bark, are currently a waste product, but they could be burned to produce energy. This energy would be carbon neutral because of the carbon neutrality of biomass. A third option would be to invest in new, more modern equipment. For example, in a paper/pulp mill the energy consumption for evaporation of water for modern evaporators is only 390 MJ/t H2O, while currently often evaporators are used that require 450 MJ/t H2O (Manninen, 2010). The optimal configuration that yields the highest GHG reduction should be the subject of future research. This thesis and the excel model created for this thesis could provide the basis for future research on this topic.

Alternative uses of the char could also change the GHG mitigation potential. The assessment in section 8.2 shows that the net GHG emissions would be significantly reduced if the char is co-combusted in a nearby coal-fired power plant. The Kraft lignin conversion route would in that case mitigate 79% of the emissions, and the SE lignin would mitigate 58% of the emissions. These emissions reductions were calculated using the displacement method. If the energy allocation method was applied, which would also be appropriate since both outputs were used as fuels, different results will be obtained.

9.2 The most suitable conversion route

A MCA was conducted to assess the most suitable conversion route. Each of the assessed technologies has its up- and downsides and determining which one is most suitable for the conversion of lignin to biofuel requires extensive research. A LCA analysis would normally also be an important factor in this decision-making process. However, due to time constraints only one technology could be further researched and subjected to a LCA. Therefore, a simple Multi Criteria Analysis was performed to determine the technology that seems most suitable for the conversion of lignin to biofuel, without taking the GHG emissions into account. The MCA included 5 important parameters, but it is possible that other conversion technologies are also suitable, or maybe more suitable if the GHG emissions are included.

The type of lignin was also not included in the MCA, while it is possible that a lignin released with a high moisture content has a different optimal conversion technology than a dry lignin. For example, hydrothermal liquefaction required a wet lignin input, while pyrolysis required a dry input. Isolating the Kraft lignin from the black liquor for fast pyrolysis is quite carbon intensive. Perhaps hydrothermal liquefaction becomes a more suitable conversion technology. This could be assessed in future research by performing a LCA on the conversion of Kraft lignin to marine biofuel.

9.3 Data input quality

First of all, lignin is a very complex molecule, that differs between plant types (e.g. herbaceous or hardwood), but also within plant types and even within one plant; lignin grown in summer is different from lignin grown in winter. Therefore, similar types of fast pyrolysis experiments can yield different results. This leads to an uncertainty in the calculations based on these results. This uncertainty becomes clear when different values of Kraft lignin results in literature are compared, as is discussed below for the bio-oil yield. This inherent uncertainty could be reduced by conducting several identical experiments, with the required process conditions, on the same feedstock type from different places in a region (e.g. several eucalyptus SE lignin from South America), so that an average value for this feedstock can be obtained. These general values would provide a more solid basis for further calculations. In this section the main input quality issues are discussed.

Bio-oil yields

For lignin pyrolysis, higher temperatures are required than for biomass pyrolysis, and lower yields are obtained. Typical yields for lignocellulosic feedstock are 65-70% liquid bio-oil (Moirangthem, 2016), while oil yields of lignin pyrolysis are usually around 30-50% (Choi & Meier, 2013; de Wild et al., 2014; Nowakowski et al., 2010). De Wild et al. (2014) researched lignin pyrolysis at a temperature of 500°C (~42% oil yield), Nowakowski et al. (2010) had the highest oil yield in the temperature range between 450 and 510°C, though Choi & Meier (2013) obtained higher oil yields at 560°C than at 500°C for pyrolysis of Kraft lignin (38.09 and 29.95% resp.). This illustrates the uncertainty of the yields. The yields used for this study were 32 wt.% and 38.6 wt.% of dry oil for Kraft lignin and SE lignin respectively. These value fall within the range, but different yields have been obtained by the various studies, and the yield could also be a few percent points higher or lower.

Fast pyrolysis in- and outputs

Due to lack of information on the fast pyrolysis of the lignin from each isolation method, sometimes data from the fast pyrolysis of lignin from different isolation methods or different feedstock had to be used. If this was also not available, data from the fast pyrolysis of general biomass was used. The electricity and heat requirements for the pre-treatment, fast pyrolysis and upgrading were based on whole biomass conversion. Since lignin makes up only a part of biomass, and biomass has got a different composition from lignin, this can lead to inaccurate results. The composition of lignin isolated through different processes (Kraft, organosolv etc.) is also distinct, and also dependent on the type of feedstock. Therefore, to calculate the actual GHG emissions from fast pyrolysis of softwood Kraft lignin and hardwood SE lignin, more research is needed on the fast pyrolysis of products specifically.

Composition of SE lignin bio-oil

The elemental composition of bio-oil derived from SE lignin fast pyrolysis was not found in the literature. Since the composition of the oils derived from other types of lignin were very different from the SE lignin composition and the bio-oil is generally similar to the lignin, the elemental composition of the SE bio-oil was calculated from the elemental composition of the lignin. The same relevant changes in elemental composition as for the Kraft lignin was assumed. This was assumed to be the best option, but the elemental of an actual SE lignin bio-oil should be measured to validate this assumption.

SimaPro

Most of the emission factors of the different products were obtained from the EcoInvent database. These emissions generally contain all the life cycle emissions of the product. Sometimes the emission factor of the correct situation is not available in the database and the emission factor of a similar product was assumed, but the actual emissions could be quite different. The natural gas life cycle emission factor for Brazil was not available, so the emissions for liquid natural gas for the global market were used. The catalyst emissions of a Zeolite catalyst were used, because the emission factor of a Ru/C catalyst was not available. The hydrogen emission factor for the conversion route in Brazil and Finland was both based on the market in Europe.

General data quality issues

In general, the input data is derived from only one or two sources due to lack of relevant studies that discuss the in- and outputs. The heating values often had to be calculated with the equation from (Channiwala & Parikh, 2002), based on the elemental composition of the product and the LHV of the char from Kraft lignin was calculated from the energy balance. Since the LHV of the different product affects the results, more robust values should be obtained.

9.4 Kraft lignin isolation

The GHG emissions from the chemicals that are required for the LignoBoost process are a very uncertain factor in the results. For this research, the 0.1 t/t lignin of NaOH and 0.19 t/t lignin of H2SO4 were assumed, because these were the values used by Manninen (2010) and also fall within the range given by Benali et al (2016). However, very large ranges were given; between 0,065-0,13 t/dt lignin of NaOH and 0,19 t/dt lignin of H2SO4 according to Manninen (2010) and between 0.05 and 0.08 t/dt lignin for NaOH and between 0.09 and 0.25 t/dt lignin for H2SO4 according to Benali et al. (2016). To assess the effect of the ranges on the results, the results were obtained for the minimum and maximum values. The results can be found in Figure 24, number 2 (minimum) and 3 (maximum). For these values the emission factors from the EcoInvent database were used.

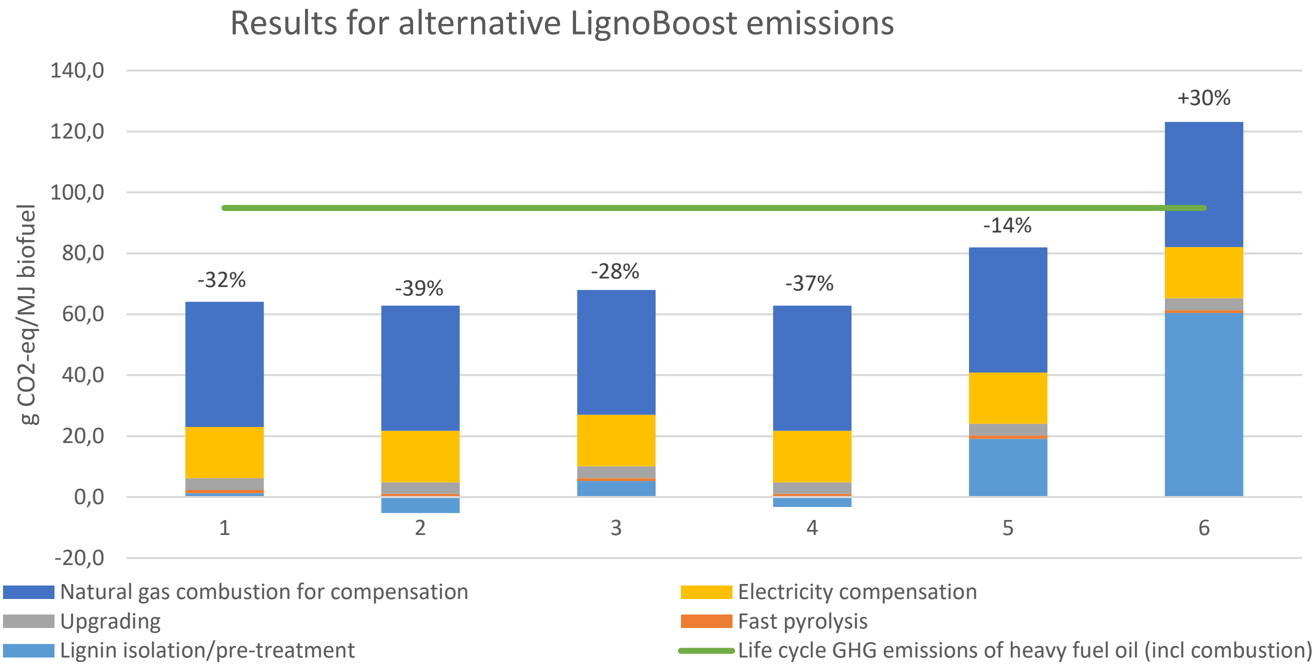
The CO2-eq emissions of the chemical use of the LignoBoost process as presented by Manninen (2010) and Benali et al. (2016) was much higher than the results calculated here. Manninen (2010) calculated a net increase of 7 kg per tonne of paper for the chemicals, which translates to 97.2 kg per tonne of lignin. From that they had already subtracted the 220 kg of CO2 that was consumed per tonne of lignin, so the actual GHG emissions from the NaOH and H2SO4 was 317.2 kg. Benali et al. (2016) calculated 52140 kg CO2-eq for 100 dt lignin, so 521.4 Kg CO2-eq/dt lignin. This also already includes approximately 220 kg of consumed CO2, so the actual emission of the chemicals NaOH and H2SO4 were calculated to be 741.2 kg CO2-eq/dt lignin. These values are much higher than the values calculated in this research, the difference is clearly shown in Figure 24, numbers 5 (Manninen) and 6 (Benali). Other emission factors were found in a report by the ISCC, which were obtained from Biograce (ISCC, 2011). The results of using these emission factors are also presented in Figure 24, number 4. The same chemical quantities were used as for this report.

This shows that using the minimum or the maximum quantities of the range has a substantial effect on the results, the difference in 11 percent points. The emission factors from the IPCC (2011) report results in slightly lower GHG emissions than the emission factors from the EcoInvent database. If the GHG emissions of the Manninen (2010) report were used, GHG emission would still be reduced, but only by 14%. But if the GHG emissions of the Benali (2016) report would be used, the GHG emission would increase by 30%. It is assumed that the values of this report are correct, but it the reason of the high GHG emissions in the other two reports should be researched. Furthermore, it shows that lowering the chemical input also has a significant effect on the results. It should be researched what influences the chemical input and if the lower limits would be sufficient.

If the LignoBoost GHG emissions turn out to be higher than calculated for this report, producing biofuels from Kraft lignin will not useful to mitigate GHG emissions. This would then also change the biofuel potential substantially, because only the lignin from lignocellulosic biorefineries will be converted to biofuels. This currently regards 50 Kt per year, and is expected to increase to approximately 3.01 Mt per year. With the LHV of the fuel as calculated for this research, that means that roughly 1.76 PJ of biofuel can be produced now, and 117.1 PJ in ten years. Since one MJ of biofuel mitigates 39.5 g CO2-eq, the overall CO2 that can be mitigated by using these biofuels in the shipping sector is 0.07 and 4.63 Mt CO2-eq/yr, now and in ten years respectively. Since the overall emissions of the shipping industry are 961 Mt CO2-eq (in 2012), this translates to roughly 0.007% of the overall shipping emissions now.

The shipping emissions are expected to have increased with 50-250% from 2012 to 2050. Assuming a conservative 25% increase of the 2012 value up to 2026 (ten years), this means that roughly 0.39% of the emissions can be mitigated by the biofuel ten years from now.

Figure 24: The results of the LCA for the different GHG emissions for the chemical use during the LignoBoost process. Below this figure, a short description of each of the setups is presented.



1. Kraft lignin overall GHG emissions – Emission factors and quantities of this research
2. Kraft lignin overall GHG emissions - Emission factor this research, but with minimal chemical input
3. Kraft lignin overall GHG emissions - Emission factor this research, but with maximal chemical input
4. Kraft lignin overall GHG emissions - Emission factor ISCC (2015), quantities this research
5. Kraft lignin overall GHG emissions – CO2-eq emissions for LignoBoost from Manninen (2010)
6. Kraft lignin overall GHG emissions - CO2-eq emissions for LignoBoost from Benali (2016)

9.5 Biofuel yields

Tews and Elliot (2014) obtained a yield of 96.8 wt.% of bio-oil for low severity stabilisation of bio-oil from fast pyrolysis of forest residue. Tews et al (2014) calculated a biofuel yield of 33.7 wt.% of bio-oil for severe hydrotreatment and hydrocracking of bio-oil from forest residues. The yields obtained for this study were 70.3 and 69.o wt.% of bio-oil for Kraft lignin and SE lignin respectively. This is a credible yield, because it is lower than the study that performed very little upgrading and higher than the study that included much more upgrading.

9.6 Biofuel quality

For this research, it was assumed that the biofuel should have a Heff/C ratio of 1.4 to be of sufficient quality to serve as a drop-in fuel. For the considered bio-oils, it was found that almost all the oxygen and other impurities had to be removed in the hydrotreater to obtain this ratio. More hydrogen was required to obtain a Heff/C ratio of 1.4 than was required to meet the sulphur limit. If a lower Heff/C ratio, and a higher oxygen content, would be allowed, less hydrogen would be required. Tests on blending of the biofuel and fossil fuel are required to assess the stability of the blend. Ultimately, tests in real engines are required to assess the performance of the fuel and determine the minimum requirements.

9.7 Upgrading

For the hydrotreatment of the bio-oils several assumptions were made in order to calculate the hydrogen requirements and the composition of the obtained stabilised biofuel. These assumptions were made to structure the processes occurring during this stage. In reality, the substitution of the heteroatoms with hydrogen atoms and the formation of the hydrocarbon gases are very unstructured processes. Furthermore, some of the produced gases, e.g. HCl and NH3, are quite soluble in water, so it could be possible that part of these gases remains in the biofuel. In order to get a better picture of what the hydrogen consumption would be and the amount of the gases that are released, experiments should be conducted.

9.7.1 Hydrogen input for upgrading

The hydrogen input for the low severity hydrotreatment that was calculated in this research was compared to values found in the literature. Figure 25 presents the compared values. The hydrogen input is presented in wt.% of the bio-oil and in mol per mol O removed, because Han et al. (2013) assumed that the hydrogen input is directly related to the oxygen content. It is also presented in MJ H/MJ biofuel, so that it could be compared to the H input in the study by Zaimes et al. (2015) and Tews et al. (2014).

Figure 25: The hydrogen input of this research compared to that of other studies.

Hydrogen input to stabilise the bio-oil.	This study (Kraft)[81]	This study (SE)	Jones (2009)	Reference in Jones (2009)	Elliot (2007)	Wright et al. (2010)	Zaimes (2015)	Tews et al. (2014)	Tews and Elliot (2014)
H input (g H/100 g dry bio-oil)	5,0	5,4	4,96	3,45	5,01	4-5	8,16	4.8	0.06
H input (Mol H/Mol O removed)	3,73	3,73	2,22	Not known	Not known	2,22	Not known	Not known	Not known
H input (MJ H/MJ biofuel)	0,17	0,21	Not known	Not known	Not known	Not known	0,38	0.45	0.023
H input (Mol H/Mol O impurity removed, excl. H losses)	3,16	3,25	N/A	N/A	N/A	N/A	N/A	N/A	N/A

It was found that the hydrogen input per 100g of bio-oil was comparable to values used in the literature. Elliott (2007) aimed to minimize the hydrogen input by minimizing saturation of the bonds and aiming for only deoxygenation, just like this study, but the H requirement per mol O is unknown. The study by Zaimes et al. (2015), regarding the upgrading of fast pyrolysis oil from perennial grasses to road transportation fuels, required significantly more hydrogen. The upgrading includes full deoxygenation and full saturation of carbon chains, which explains why more hydrogen is required. Tews et al. (2014) required similar hydrogen inputs per 100g bio-oil, but like Zaimes et al (2015) a higher hydrogen input per MJ biofuel was required. This means that less biofuel could be produced with the same amount of hydrogen, so the hydrogen input was higher than for the biofuel of this study. This can be explained, because the produced biofuels were mostly diesel and gasoline, and only a little heavy oil. Wright (2010) regards the upgrading of corn stover biomass to gasoline, naphtha and some diesel, including hydrotreating and cracking. Jones (2009) studied the fast pyrolysis of poplar wood chips and the upgrading of the bio-oil to stabilization, but much higher process conditions were used (17 MPa and 230ºC). Their hydrogen input was equal to the hydrogen input in study, but the amount of H per mol removed oxygen was significantly less. If the other impurities that were removed in the model of this thesis were included and no losses were assumed, the H requirement per mol impurity removed are lower, but still higher than that of Jones (2009) and Wright (2010). This study assumed no saturation of the bonds and little cracking, so that does not explain why more hydrogen is consumed. The studies by Wright (2010) and Jones (2009) were based on computer models. In this study, we assumed three hydrogen atoms were required to remove one oxygen atom in the form of water and to replace it. Perhaps the other studies assumed that some oxygen removal would sometimes require less hydrogen, this should be further studied. This also shows the need for experimental results to assess the real hydrogen requirements. The larger hydrogen input assumed by Tews et al. (2014) and Zaimes (2015) shows that the hydrogen input calculated for this study is not exceptionally high. Tews and Elliot (2014) assumed low severity hydrotreatment, to only stabilise the bio-oil. According to their model, they required only 0.06 g H/100g dry oil, which is much less than the other studies, including this study. The lower heating value of the biofuel was only 14.1, which is very low and might not be useful as a marine biofuel. It probably still has a high oxygen content and a low Heff/C ratio.

The hydrogen input of this study seems a little high compared to similar studies. However, other studies show higher hydrogen inputs, so it is uncertain what the best value is. Experiments should be performed to assess the hydrogen input, to decrease the uncertainty of the input values and of the overall result.

9.8 System boundaries

For this research, only the gate-to-gate emissions were considered. This study showed the change in overall GHG emission that would occur of lignin would be converted to marine biofuels. All the changes in emissions were allocated to the lignin, because this gives a clear overview of the changes in GHG emissions that occur if the

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[81] The values of this research include the losses in the PSA. The hydrogen consumption in mol/mol O removed without the taking the losses into account would be 3.36 and 3.39 for Kraft and SE conversion route respectively. In wt. % of bio-oil it would be 4.5 and 4.9% for Kraft and SE respectively.

lignin is used for marine biofuel production. The LCA did not include the emissions from transport and storage of the biofuel, nor the emissions from biomass cultivation, harvesting or ethanol production. Before the conversion route is commercially exploited, a well-to-wheel LCA should be performed in order to assess the overall sustainability of the biofuel. In the well-to-wheel LCA, a different allocation method is probably more suitable (e.g. energy allocation between ethanol and lignin since both are used as fuel) and part of the emissions from the mill or refinery will be allocated to the lignin. This could yield very different results per MJ of biofuel, but the total change in emissions will remain the same.

9.9 Practical limitations

There are many challenges to commercialization of fast pyrolysis biofuels from lignin, e.g. scaling-up, quality of product, and cost reduction. Some of the main practical limitation are discussed here.

9.9.1 Technical issues

Fast pyrolysis of lignin has so far proven to be difficult, because the lignin tends to melt and agglomerate in the pyrolysis reactor, causing clogging (S. Zhou et al., 2015). A collaboration of researchers tried to pyrolyze several samples of soda lignin and weak acid hydrolysis lignin in 2010. None of the researchers were able to pyrolyze the soda lignin. Most of the weak acid hydrolysis lignin was pyrolyzed, but this contained around 50% of carbohydrates, which is thought to be the reason why it worked (Nowakowski et al., 2010). Even if batch pyrolysis works, the clogging makes it impossible to continuously feed the reactor, which is, according to some scientists, currently the largest technical barrier to pyrolyzing lignin for fuels and chemicals (Zhou et al., 2015). Research is currently being done to find solutions to this problem, without substantial increase in environmental or economic impacts. S. Zhou et al. (2015) have been able to successfully pyrolyze lignin by adding calcium hydroxide, Ca(OH)2. This reduced the phenolic hydroxyl, carboxylic acid and aldehyde groups in the lignin that caused the agglomeration and formed hydroxyl calcium phenoxides, phenolic alcohols, and phenolic carboxylate salts (S. Zhou et al., 2015). Calcium hydroxide is very promising as a cheap and safe pre-treatment that is readily available. Only small amounts of Ca(OH)2 are required and it is easily recovered by burning the char and leaching the ash with water. The heat could be used as process heat. The char could also be used as a bio based fertilizer (S. Zhou et al., 2015). The clogging was also found to be a problem during upgrading. The bio-oil clogs the hydrotreatment reactor and the catalyst, decreasing the catalyst activity. Different, more robust catalysts could possibly be a solution, as well as two hydrotreatment steps (Jones and Snowden-Swan, 2013). More research is required to solve these problems and find a solution that be commercialised. This research assumed no clogging of the lignin.

9.9.2 Biofuel concerns

There remain some technical concerns within the market with regard to biofuels. These concerns regard long term storage related to unstable fuel quality and micro biological growth, water content leading to acidity, degraded low-temperature flow properties. According to Ecofys (2012), this is due to unfamiliarity with biofuels, since these concerns are not recognised by current R&D projects, stakeholders and scientific articles. No pyrolysis standards for transportation fuels exist yet. In the US, a pyrolysis liquid specification was developed for combustion in several types of stationary burners. A European standard is currently under development for fast pyrolysis oils (Fivga & Mayer, 2016). However, it will be difficult to set a standard for lignin fast pyrolysis oils, because the bio-oils coming out of the reactor often has different characteristics. This is due to the inherent variability of the lignin.

9.9.3 Scaling up possibilities

The technical issues mentioned in section 9.10.1 limit the commercialisation and possibilities to scale up of lignin fast pyrolysis. But besides these technical issues, lignin has interesting possibilities to scale up. Even a small lignin withdrawal can be interesting when considering a pulp mill with an annual pulp production of 690000 tonnes (e.g. the Joutseno pulp mill in Finland) or even 3.5 Mt (The Três Lagoas pulp mill in Brazil that is planned to open in 2017). A withdrawal of 50% of lignin would already mean that roughly 172.000 or 875.000 t per year could be extracted respectively ((Tomani, 2013)). A biofuel production of 43.000 and 218.750 t could be produced from the two mill respectively, assuming the biofuel yield of 0.25 t/dt lignin as calculated in this study. A container ship of 7.000 to 8.000 TEU driving at slow steaming speed (20 knots, a common speed), consumes approximately 100 tonnes of fuel per day (Hofstra University, n.d.). So, from the biofuel produced from 50% of the lignin of a large paper/pulp mill, a medium sized cargo ship can drive 430 days, so more than one year. From extracting 50% of the lignin of a very large paper pulp mill, a medium sized containership can sail for 6 years straight. These can be considered useful quantities.

9.9.4 Costs of conversion route

The costs were not considered for the LCA in this research. An approximate cost indication was taken into account when choosing the most suitable conversion technology, but for the process configuration that was assumed for the LCA, the costs were not taken into account. The costs are important, because commercialization of a technology only occurs if it is cost-effective, a high GHG emission mitigation potential alone is not sufficient. Producing biofuels from lignin in a cost-effective manner has so far proven difficult, hence the saying: You can make anything from lignin, except money (Arnold, 2008). However, fast pyrolysis is considered a cheap technology and technological improvements may prove this saying wrong. Therefore, it is recommended to conduct a more in-depth research on the costs of the conversion route assessed in this research.

9.10 Functional unit

The GHGs per tonne per kilometre (tkm) would also have been an appropriate functional unit, as this takes the combustion characteristics of the fuel into account. However, these emissions differ per ship and engine and are therefore more difficult to compare with alternative fuels. Furthermore, to acquire these emissions, the fuel first needs to be tested in an engine. So, although the fuel can affect the functioning of the engine and thus the emissions from combustion, this has nog been taken into account for this research. However, it is recommended that future research will determine the emissions per tkm, to also include the emissions from combustion and to assess any losses in engine efficiency.

10 Conclusions

This study assessed the lignin supply market and the current global marine biofuel potential, both now and in ten years. Also, the most suitable conversion route to produce marine biofuel from lignin was assessed, followed by a CLCA to assess the direct and indirect GHG emissions from two case-studies in Brazil and Scandinavia. This chapter describes the conclusions that can be drawn from the study.

From the assessment of the lignin supply market and biofuel potential, it can be concluded that large amounts of lignin are available worldwide, and that this quantity is expected to grow in the future. Kraft lignin is the most abundantly available lignin currently and will still be the most abundant lignin in ten years. Currently only 6 lignocellulosic biorefineries exist, but this number is expected to grow in the future. The biofuel potential is currently approximately 12.55 – 17.55 Mt of biofuel per year and is expected to increase to 18.7 – 25.0 Mt of biofuel per year. This could currently replace roughly 5.2% of the total marine fuel consumption and is expected to increase to roughly 6.0% in ten years.

From the multi criteria analysis that was performed on the conversion technologies, considering the bio-crude yield, the bio-oil quality, the valuable by-products, app. costs and market status, it was concluded that fast pyrolysis is the most suitable conversion technology. For the Finnish case, Kraft lignin was considered the most suitable feedstock, isolated through the LignoBoost process. For the Brazilian case, lignin from a lignocellulosic biorefinery was found most suitable, it was isolated through steam explosion and pre-treated to dry, fine particles. For both conversion routes the lignin was converted to bio-oil through fast pyrolysis and subsequently upgraded to stable biofuel through low severity hydrotreatment.

The direct and indirect GHG emissions of Kraft lignin conversion are 6.2 and 57.9 g CO2-eq/MJ biofuel, respectively. For the SE lignin conversion, the direct and indirect GHG emissions amount 7.6 and 63.7 g CO2-eq/MJ biofuel, respectively. The overall GHG emission reduction of using biofuels in ships compared to fossil fuel is approximately 32% for Kraft lignin conversion and 25% for SE lignin conversion. A current overall GHG emission reduction potential of 15.6 and 21.9 Mt was calculated from the results of this thesis. In ten years, this potential is expected to increase to roughly between 22.4 and 29.0 Mt GHG emissions per year. This means that approximately between 1.6 and 2.3% of the overall shipping emissions could potentially be mitigated today and between 1.9 and 2.4% in ten years.

From these numbers, it can be concluded that producing marine biofuels does mitigate GHG emissions in the shipping industry, though the reduction is not very large. It was concluded that other configurations of the optimal conversion routes should be considered to increase the GHG emission mitigations. The results are very sensitive to the emission factors of natural gas and electricity, reducing these could achieve large GHG emission reductions. One configurations that assumed use of the excess biochar to replace fossil coals in coal-fired power plants and one configuration that assumed the use renewable electricity were assessed. Both configurations caused a large increase in GHG emission savings for the Kraft lignin conversion route. For the SE lignin conversion route the increase in emission savings was smaller. More alternative configurations should be studied to find the optimal configuration that yields the highest emission reduction. Natural gas and electricity are also the two products that cause the large indirect GHG emissions. Both conversion routes have a high uncertainty, which should be reduced by improving the quality of the input data to obtain more robust and reliable results.

Before fast pyrolysis of lignin can be commercially used to produce biofuels and decrease the GHG emissions of the shipping sector, there are some barriers to overcome. Fast pyrolysis of lignin has so far proven to be difficult, because the lignin tends to melt and agglomerate in the pyrolysis reactor, causing clogging. Furthermore, it should be assessed if the conversion route is cost-effective and can compete with fossil fuels. This should be researched in future studies.

It can be concluded that the use of biofuels from lignin could be effective in mitigating emissions, but even if the GHG emission savings are increased and the technical barriers are overcome, the quantity of biofuels is not sufficient to realise a large reduction in the GHG emissions of the shipping industry. Therefore, marine biofuels from lignin could be important to reduce the GHG emissions from the shipping industry, but additional measures should also be researched and implemented.

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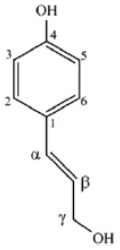
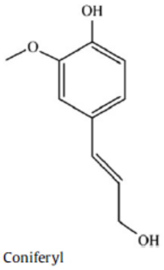
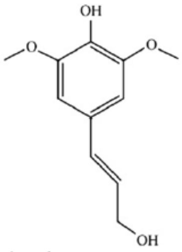
Appendices

Appendix 1: Lignin

This thesis assesses the lignin supply market, the lignin biofuel potential, the most suitable lignin conversion route to marine biofuel and the GHG emissions from lignin conversion to marine biofuel. This appendix explains what lignin is.

The cell wall material of plants consists of lignocellulosic biomass, that in turn consists of three main components: cellulose, hemicellulose and lignin. Lignin makes up 15-35% of the dry lignocellulose and it is the largest renewable source of aromatics on earth (Azadi et al., 2013). Lignin has several functions within a plant, like influencing the permeability and thermal stability of a cell wand, but its most important function is to add strength and rigidity (Haghdan et al., 2016). The amount and type of lignin differs per biomass type. Softwood contains the highest amount of lignin, followed by hardwood. Grasses contain the least amount of lignin (Azadi et al., 2013). The higher heating value of lignocellulosic biomass shows a linear relation with the lignin content (Azadi et al., 2013).
Chemically, lignin is made up of crosslinked aromatic phenolic compounds and three primary aromatic alcohols: p-coumaryl, coniferyl and sinapyl alcohols (Ruiz et al., 2013), containing zero, one, and two methoxyl groups, respectively. Just like the lignin content differs for each biomass types, the ratio of these primary monomers differs too, as presented in Figure 26. Generally more than two-thirds of the linkages in lignin are ether linkages, also these linkages vary across the different types of wood and plants (Azadi et al., 2013). The molecular structure of lignin, and therefore also its characteristics, depend on the origin of the lignin, the external properties during growth (such as climate and season) and the isolation and pre-treatment technologies that were used to isolate the lignin of the hemicellulose and cellulose (Bruijnincx et al., 2016).

Figure 26 (Azadi et al., 2013): The chemical structure of the three aromatic alcohols found in lignin, together with their occurrence in the lignin of the different types of biomass (softwood, hardwood and grasses). Also the lignin content of each biomass types is presented.

	Lignin (wt%)	Phenylpropane unit (%)		
Structure				
		Coumaryl	Coniferyl	Sinapyl
Softwood	27–33	–	90–95	5–10
Hardwood	18–25	–	50	50
Grasses	17–24	5	75	25

Appendix 2: General lignin isolation techniques

Several techniques exist to isolate the lignin, that each alter the molecular structure of the lignin. The isolated lignin is called "technical lignin", of which different types exist, depending on the isolation process (Bruinincx et al., 2016). Technical lignin has less cleavable bonds then natural lignin and is more difficult to process (Bruinincx et al., 2016). The isolation techniques in the paper/pulp mills differ from the techniques used in the lignocellulosic biorefinerys. The main isolation techniques from both sources are described in this appendix.

Paper/pulp mills

At paper/pulp mills, different pulping processes can be used to separate the cellulose, hemicellulose and lignin in the biomass. The pulping process that is used affects the characteristics of the lignin. The lignin is released with the waste stream from which it can be removed through different methods. This appendix describes the four main pulping processes that exist. The resulting lignins can be subdivided into sulphur containing lignin and sulphur free lignin (Laurichesse & Avérous, 2014). These lignins are shortly described below, and an overview of their properties is presented in Table 46. After these descriptions, the main lignin isolation techniques that exist to isolate the Kraft lignin from the black liquor produced in a Kraft paper/pulp plant were described in more detail, because this was relevant for this thesis.

Sulphur lignins:

1) Lignosulfonates (from the sulphite cooking process)
2) Kraft lignin (from the Kraft cooking process)

The sulphite cooking process uses an aqueous sulphur dioxide (SO_2) and a base (calcium, sodium, magnesium or ammonium), which results in a technical lignin containing a substantial amount of sulphur. They are water soluble, have a high molar mass and a broad polydispersity index (Laurichesse & Avérous, 2014). Furthermore they have a high ash content and contain a significant amount of carbohydrates (Bruinincx et al., 2016). From the four types of technical lignins, these are most used for industrial applications, e.g. as binder, dispersing agent or cement additives (Laurichesse & Avérous, 2014).

The Kraft pulping process is the dominant pulping method in the world and comprises several steps, both chemical and mechanical. It uses sodium hydroxide and sodium sulphite to separate the different biomass components. Kraft lignins generally contain less than 1 or 2% sulphur, despite the high sulphur environment of the Kraft process. Kraft lignin can be isolated from the black liquor in a Kraft paper/pulp mill and have a low molar mass (Laurichesse & Avérous, 2014).

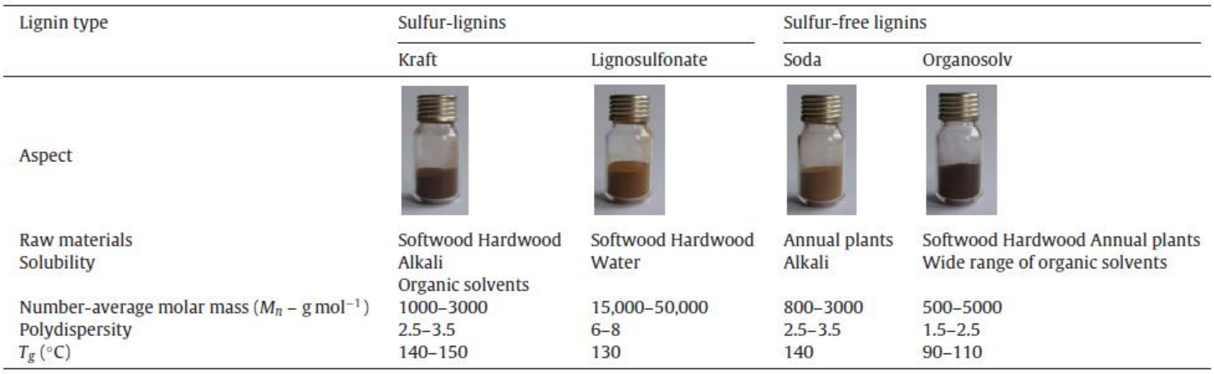
Sulphur-free lignins

3) Soda lignin (from the alkaline pulping process)
4) Organosolv lignin (from the solvent pulping process)

The structure of sulphur-free lignins is close to that of natural lignins. Soda cooking processes are mostly used on annual plants, like bagasse or straw. The Lignin extraction is based on the hydrolytic cleavage of the native lignin, resulting in a relatively unmodified soda lignin. The lignin can be precipitated from the black liquor by adjusting the pH (Laurichesse & Avérous, 2014).

OrganoSolv lignins are the purest of the technical lignins and have the highest quality. They are hydrophobic, but are easily dissolved in organic solvents. Different organic solvents can be used, e.g. ethanol/water mixture, acetic acid with a small fraction of mineral acid or a mixture of formic acid, acetic acid and water. Also these lignins can be isolated from the solvent by adjusting a few of the parameters, like acidity, temperature and concentration (Laurichesse & Avérous, 2014).

Table 46: The properties of the four main technical lignins from paper/pulp mills (obtained from (Laurichesse & Avérous, 2014).



Lignin type	Sulfur-lignins		Sulfur-free lignins	
	Kraft	Lignosulfonate	Soda	Organosolv
Aspect				
Raw materials	Softwood Hardwood	Softwood Hardwood	Annual plants	Softwood Hardwood Annual plants
Solubility	Alkali Organic solvents	Water	Alkali	Wide range of organic solvents
Number-average molar mass (M_n – g mol^{-1})	1000–3000	15,000–50,000	800–3000	500–5000
Polydispersity	2.5–3.5	6–8	2.5–3.5	1.5–2.5
T_g (°C)	140–150	130	140	90–110

Kraft lignin isolation from black liquor

Six methods have been identified to isolate the Kraft lignin from the waste stream of paper/pulp mills (Benali et al., 2011).

7. Acid precipitation through sulphuric acid
8. CO_2 precipitation (LignoBoost)
9. Sequential liquid lignin recovery and purification (SLRP)
10. Ultrafiltration
11. Electrolysis
12. Electrodialysis

1. During sulphuric acid precipitation, the Kraft lignin is precipitated from the black liquor by decreasing it pH by adding sulphuric acid. The black liquor is decreased to a pH of around 3 and the Kraft lignin is precipitated. It is obtained by washing and filtering. The use of sulphuric acid leads to an increased sulphur content of the lignin (Kosa et al., 2011).

2. The second method uses CO_2 to decrease the pH of the black liquor, but only to around 9.5 or 10.5 (from an original pH of 12-14). The lignin then precipitates and is washed and filtered. CO_2 is consumed during the process and converted to carbonate salts. This method is exemplified by the LignoBoost process

(Kosa et al., 2011). It is generally regarded as an economical and efficient isolation process (Fatehi & Chen, 2016). In this process, the black liquor is extracted from the evaporators and is acidified by using CO_2. At this lower pH, the lignin precipitates in a precipitation tank, and additionally H2S gas can be generated. The precipitated lignin slurry is subsequently mixed with an acidic filtrate, followed by a washing stage. This generates small, uncrosslinked lignin precipitates. It is then crushed and dried to form a lignin powder (Fatehi & Chen, 2016). Figure 27 shows a block schedule of the LignoBoost processes, while some important parameters are presented in Table 47. NaOH and H2SO4 are required for the process. H2SO4 is needed to wash the lignin cake, NaOH is needed to neutralize the recycled stream from the lignin isolation process to the evaporators.

Figure 27: A block schedule of the LignoBoost isolation processes (obtained from Fatehi & Chen, 2016)

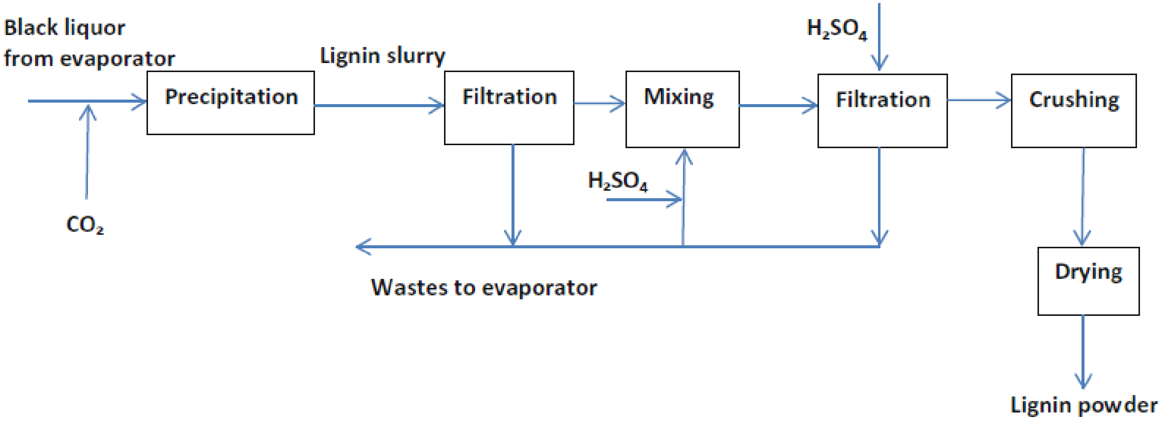
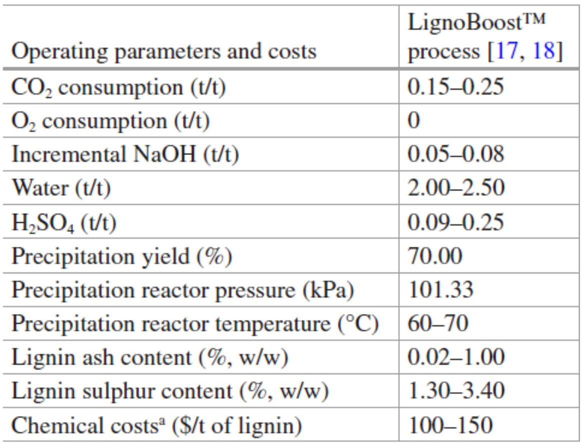


Table 47: Some important parameters of the lignoboost process, as presented by Benali et al. (2016).



Operating parameters and costs	LignoBoost™ process [17, 18]
CO_2 consumption (t/t)	0.15–0.25
O_2 consumption (t/t)	0
Incremental NaOH (t/t)	0.05–0.08
Water (t/t)	2.00–2.50
H_2SO_4 (t/t)	0.09–0.25
Precipitation yield (%)	70.00
Precipitation reactor pressure (kPa)	101.33
Precipitation reactor temperature (°C)	60–70
Lignin ash content (%, w/w)	0.02–1.00
Lignin sulphur content (%, w/w)	1.30–3.40
Chemical costs[a] ($/t of lignin)	100–150

3. During SLRP the black liquor is first pressurized. The lignin is then precipitated by introducing the liquid into an adsorption column and treating it with CO_2. The pH is reduced to 9 or 10 and lignin is precipitated. Separation then occurs, leading to the formation of 2 phases: a dense lignin-rich phase and light lignin-depleted phase (Benali et al., 2016).

4. Ultrafiltration makes use of membranes. It is pressure driven and does not require much energy. This method faces challenges such as flux decline, identification of suitable membrane and black liquor composition variations (Benali et al., 2016).

5. With electrochemical processes the separation is driven by an electric potential gradient. Electrolysis removes the Na+ ions from the black liquor through a membrane, thus lowering the pH and causing precipitation of the lignin.

6. Electrodialysis required two selectively permeable membranes that permit the migration of OH-, HS-, HCO(3-) and SO4(2-) to the anode and Na+ to the cathode. This can result in lower operating costs and energy demands than that of conventional electrolysis. However, also here fouling can occur and pre-treatment of the black liquor might be necessary (Benali et al., 2016).

1.2 Lignocellulosic biorefineries

At lignocellulosic biorefinerys, different methods are used to separate the lignins from the cellulose and hemicellulose, and there is no consensus yet on what is the best one. The most commonly used methods are steam explosion, dilute acid pre-treatment, alkaline hydrolysis pre-treatment. These three methods are described here.

5) Steam Explosion pre-treatment
This is the most commonly used method for pre-treatment in lignocellulosic biorefineries (Kumar et al., 2009). During the steam explosion pre-treatment, the biomass is impregnated with steam at 200°C or higher and under high pressure. At these high temperatures, water acts as an acid (Kumar et al., 2009). A rapid pressure drop liberates the fibres of the biomass and releases the three biomass components (Lange et al., 2015). The lignins can be obtained by extraction of the fibrous material with an aqueous or alkali solvent, or by fermenting the sugars to ethanol and leaving the lignin behind in the fermentation broth (Bruinincx et al., 2016). Lignins that are released after the steam explosion pre-treatment have a lower molecular weight and higher solubility in organic solvents than Kraft lignins (Lange et al., 2015). They contain only little carbohydrates and wood extractive impurities and resemble the native lignin more than any other technical lignins (Bruinincx et al., 2016), but steam explosion lignins from softwood will be more modified and less reactive than those from hardwood (Shevchenko et al., 1999). These lignins are completely or almost completely sulphur free (Bruinincx et al., 2016). Other advantages of this pre-treatment method are the possibility to recover the high pressure steam and use it as an energy source for other processes more downstream, and the fact that is does not require any chemicals (Gerbrandt et al., 2016).

6) Dilute acid pre-treatment
This process has been adopted by the NREL and several pilot and commercial operation exist (Gerbrandt et al., 2016). Acid catalysts, mainly SO_2 or CO_2, can be used to accelerate the process and decrease the degradation of the sugars compared to the normal steam explosion pre-treatment method (Kumar et al., 2009; Smaranda & Tucu, 2010). The biomass is first soaked in a dilute acid, before steam explosion is applied (Gerbrandt et al., 2016). In the case of sulphuric acid, small amounts of sulphur can then be incorporated into the lignin (Shevchenko et al., 1999). This pre-treatment requires a subsequent neutralisation step, making it less energy efficient than steam explosion without acid pre-soaking (Gerbrandt et al., 2016).

7) Alkaline hydrolysis pre-treatment
This pre-treatment method makes use of bases and uses lower temperature and pressures than the other methods. It can be performed at ambient conditions, but the re-treatment times are in the order of hours or even weeks, instead of minutes or seconds. Sodium, potassium, calcium, and ammonium hydroxides are suitable alkaline pre-treatment agents, of which sodium hydroxide has been studied the most. However, calcium is also effective and it is the cheapest option.

Appendix 3: Conversion technologies and upgrading processes

Two main process pathways exist to convert lignin into biofuel: thermochemical and biochemical. Thermochemical processes use a combination of heat, pressure and catalysts to produce an energy dense liquid from the lignin. Biochemical processes uses biological organisms to convert the biomass first to sugars and then to a liquid fuel (Karatzos et al., 2014). Biochemical conversion of lignin is challenging because of its complexity and inherent heterogeneity (Lin et al., 2016; Zhao et al., 2016). Although recent research has been exploring the potential of biochemical processes to convert lignin to liquid biofuel and the results are promising (Zhao et al., 2016), it is assumed biochemical conversion will not yet play a role in the recent future. Therefore, this pathway is not further discussed in this thesis. Thermochemical conversion of lignin has long been researched, and several promising thermochemical conversion processes have been identified. Besides these conversion technologies, also desulphurisation and/or upgrading of the crude oils might be necessary to obtain oils of sufficient quality for the marine industry. A short description of the main upgrading processes is also presented here. Fast pyrolysis and hydrotreatment are already explained in section 3.2 and 3.3, but are also included here to give a complete overview.

Conversion technologies

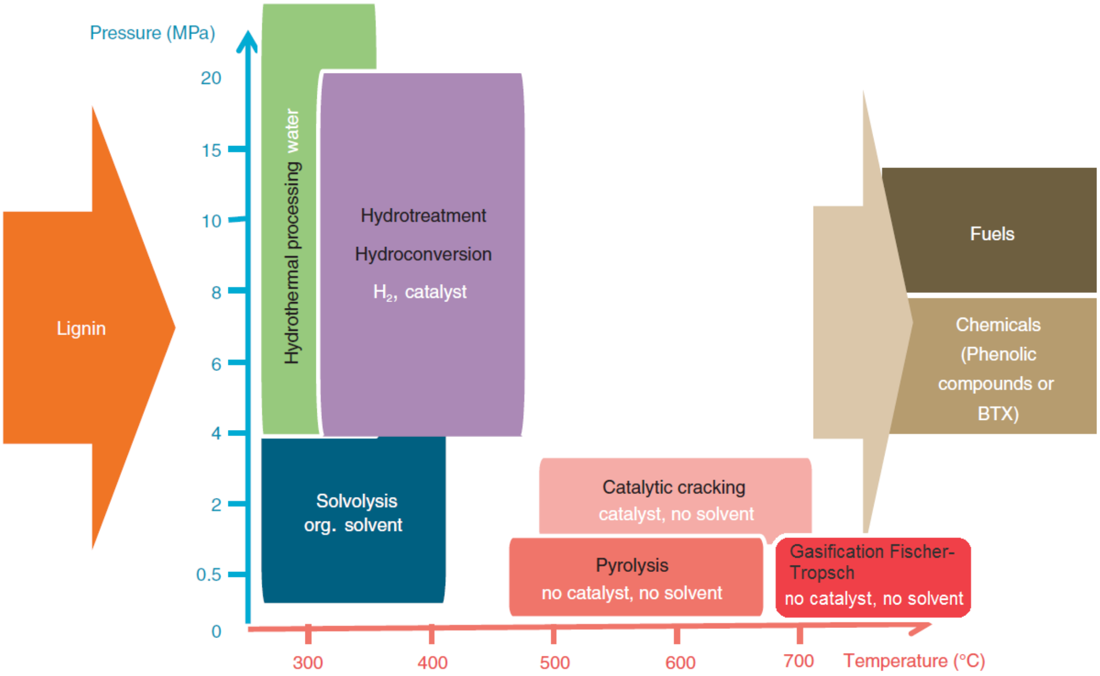
6. Pyrolysis
    - Fast pyrolysis
    - Fast pyrolysis with staged condensation
    - Slow pyrolysis
    - Catalytic pyrolysis
7. Hydrothermal liquefaction (HTL)

8. Solvolysis
9. Catalytic hydroconversion
10. Gasification with Fischer-Tropsch synthesis

Upgrading processes
11. Hydrotreatment
12. Hydrocracking
13. Catalytic cracking

A clear overview of the processes and the process conditions that are required for each of them is modified from Joffres et al. (2013) (Figure 28). Each of these technologies yields a different amount and different type and quality of oil. A general description of each of them is presented below.

Figure 28: The thermochemical processes that could be used to convert lignin into a liquid marine biofuel, and their process conditions (modified after Joffres et al., 2013).



Conversion technologies

2.1 Pyrolysis

The technology of pyrolysis has been developed for over 30 years (Zhou et al., 2016). It can be described as the thermal conversion of biomass occurring in the absence of oxygen, producing gas, pyrolysis oil and charcoal (Blin et al., 2007). The amount of each product is dependent on the pyrolysis method, the characteristics of the biomass, and the reaction parameters (Blin et al., 2007). Four types of pyrolysis were considered for this research: A) fast pyrolysis; B) fast pyrolysis with staged condensation; C) slow pyrolysis; and D) catalytic pyrolysis.

Fast pyrolysis reactor types

With fast pyrolysis, the lignin is very quickly converted to mostly vapours and aerosols, together with some charcoal and gas. A homogenous liquid is obtained after cooling and condensation. This liquid has around half the heating value of conventional oils (Bridgwater, 2012). To obtain high oil yields, a moderate pyrolysis temperature is required (around 500°C), with high heating rates (10^3 - 10^5 °C/s), short vapour residence times to minimise secondary reactions (< 2s) and fast quenching of the vapours to generate the bio-oil (Bridgwater, 2012; Lu et al., 2009). To obtain such a high heat transfer rate, the total interface surface of the biomass should be large, so the biomass should be ground to particles generally smaller than 3 mm. The biomass should be pre-dried to a water content of less than 10% to minimise the water content in the oil. Also the char should rapidly be removed to minimise vapour cracking (Bridgwater, 2012). The yield of bio-oil from fast pyrolysis could be as much as 75% on a dry-feed basis. The produced char and gases could be used for the processes, leaving ash and flue gas as the only wastes (Bridgwater, 2012). Typical yields for biomass feedstock are 65-70% liquid bio-oil (dry feed basis), 15-20% char (a black charcoal-like powder), and non-condensable gases (Moirangthem, 2016). For lignin pyrolysis lower oil yields have been reported; 40-60% oil, 30-40% char and 8-20% gas (de Wild et al., 2014; Joffres et al., 2013). All the lignin types are degraded in the same way, but the yields may vary (Pandey & Kim, 2011). Fast pyrolysis oils are used in boilers to generate heat and power, but direct use in marine engines is not possible without modifications to the engine. Raw pyrolysis oils have a high viscosity, high acidity and low thermal stability, causing issues on the operation of engines in the long term (Chong & Bridgwater, 2016). Therefore, some upgrading is required.

Lignin must enter the fast pyrolysis reactor as fine, dry particles. Therefore, it is often first pre-treated to avoid yield losses and reduce the heat requirements. The pre-treatment comprises of mechanical grinding and drying of the feedstock (Wright et al., 2010). Grinding is important to increase the surface area of the biomass and thus ensure its fast and homogeneous heating. This step is energy consuming and expensive (Wright et al., 2010). The particle size should be reduced to a maximum 5 mm, though usually a particle size of 2 or 3 mm is preferred (Ringer et al., 2014; Wright et al., 2010; Zaimes et al., 2015). Drying is important because the moisture takes up much of the process heat and reduces the pyrolysis performance and yield. The feedstock must be dried to a moisture content of less than 10% to ensure that the moisture content of the produced bio-oil remains below 30%, which is the moisture content at which phase separation start occurring (Wright et al., 2010). Less moisture in the feedstock means less moisture in the bio-oil and thus higher stability and higher heating value. However, since drying is an energy intensive process, the feedstock is generally not dried to a moisture content of 0%, but a moisture content of 7% or 8% is considered sufficient (Ringer et al., 2006; Tews et al., 2014; Wright et al., 2010; Zaimes et al., 2015).

Different types of reactors exist for fast pyrolysis, of which the most important are: 1. bubbling fluid beds 2. Circulating fluid beds and transported beds 3. Rotating cone 4. Ablative pyrolysis (Bridgwater, 2012; Choi & Meier, 2013). Currently only the fluidised beds (both bubbling and circulating) can be applied on a commercial scale (Zhou et al., 2016). However, the pyrolysis of lignin with the fluidized bed reactors proves difficult, since the lignin formed highly porous char that caused bed agglomeration and the melting of the lignin caused the screw feeders to plug (Nowakowski et al., 2010). Nowakowski et al. (2010) therefore recommended the use of a different reactor design for lignin. The most common designs (including the fluidised bed reactors) are shortly described below.

Bubbling fluid beds

This technology is well understood, easy with regard to construction and operation, is has good temperature control and efficient heat transfer. They give good and consistent performance with oil yields from pyrolysis of wood. The residence time of vapour is less than that of the char. The fresh char is pyrophoric (it spontaneously combusts in contact with air), so careful handling and storage is required. Biomass particles of 2-3 mm are required to achieve a sufficient heating rate (Bridgwater, 2012).

Circulating fluid beds and transported beds

Circulating fluid beds (CFB) can potentially handle large amounts of throughput, since this system is also used in large scale in the petroleum industry. It has many of the features that bubbling fluid beds have, but the residence time of the char is about the same as that of the vapours. The char is weaker due to the increased gas velocities, which can lead to a higher char content in the bio-oil, unless char removal steps are included. Heat is supplied by recirculating heated sand. The char is burned to heat the sand, so no access char is released (Bridgwater, 2012).

Rotating cone

A relatively recent reactor type that works like a transported bed reactor, but the transport is driven by centrifugal forces in a rotating cone, instead of gas. It is a complex system. The vapours are collected and processed the same way as in the other reactor types. Char and sands fall on fluid beds outside the cone, to be lifted to a second combustion bed where the char is combusted to heat the sand that is transported back into the cone. Less carrier gas is needed than for fluid bed and transported bed systems (Bridgwater, 2012).

Ablative pyrolysis

For ablative pyrolysis, the heat is transferred from the reactor walls to the biomass that is pressed against it. The pressure increases the heat transfer rate. There is a high relative motion between the particle and the reactor walls, that generally have a temperature below 600°C. Larger biomass particles can be used than with the other reactor types and there is no need for an inert gas, which leads to more efficient vapour collection. This reactor type requires smaller process equipment, but because it is mechanically driven it is more complex. Also scaling up is more difficult for this reactor, because it is dependent on the surface area (Bridgwater, 2012).

Fast pyrolysis with staged condensation

A recent development is the stepwise condensation of the fast pyrolysis vapours, which can enhance the quality of the bio-oil. During stage condensation, the pyrolysis vapours are passed through several condensers that are gradually decreasing in temperature. Each condenser consequently collects a liquid fraction that is both physically and chemically different from the liquids collected in the other condensers. The heavy components with the highest condensing point will condense in the first condenser and with decreasing temperature of the condensers also the intermediate and light components will precipitate.

This leads to a bio-oil that contains almost no water and therefore has a higher heating value than regular pyrolysis oils (Gooty et al., 2014). Gooty et al. (2014), researched the fractional condensation of fast pyrolysis vapours from kraft lignin that resulted in 23,5% oil yield, with an HHV of 30 MJ/kg and a water content of less than 1 wt.%.

Slow pyrolysis

Slow pyrolysis differs from fast pyrolysis in heating rate and residence time of the solid phase in the reactor. Slow pyrolysis generally yields more char and less oil than fast pyrolysis. However, pyrolysis oils still form a significant by-product from slow pyrolysis (Cordella et al., 2013). Technical limitations of slow pyrolysis make it an unsuitable candidate for good quality biofuel production. The primary product is cracked in the reactor due to the high residence times which can affect the bio-oil yield and quality. Furthermore, a large energy input is required due to the high residence times and the slow heating rates (Jahirul et al., 2012). Residence time may vary from minutes to hours (Dickerson & Soria, 2013)

Catalytic pyrolysis

Catalytic pyrolysis is pyrolysis preformed in the presence of a catalyst or hydrogen. It basically integrates the processes of fast pyrolysis and catalytic cracking into one step (for an explanation of catalytic cracking, see process number 9). A catalyst is used inside the reactor to increase deoxygenation reactions so that a less oxygenated bio-oil is produced (Karatzos et al., 2014). Preferably, fluid catalytic cracker (FCC) type reactors are used. The bio-oil yield is around 30-40% of starting biomass and is more viscous than the bio-oil from non-catalysed fast pyrolysis (Bridgwater, 2012). Different catalysts can be used, depending on the type of feedstock (G. Zhou et al., 2016). A few important catalysts and their effects on the oil are described here:

1. Zeolite catalyst: Different zeolite catalysts can be used, depending on the type of feedstock (G. Zhou et al., 2016). A few relevant zeolites for lignin conversion are explained here:
    - Zeolite H-USY can be used in combination with fast pyrolysis in a batch reactor to obtain an oil yield of almost 75%, containing more hydrocarbons. However, a large amount of catalyst was required (four times the amount of lignin) and a batch reactor is not ideal (Joffres et al., 2013).
    - Ni-ZSM-5 zeolites cause the production of a more deoxygenated and less acid fuel, thus more suitable to be used as fuel. The overall liquid yield remains unchanged (Joffres et al., 2013). If this catalyst is combined with the use of acetone as a solvent for the lignin, a higher level of deoxygenation can be reached and alkylated aromatic products (e.g. toluenes and xylenes) become predominant in the liquid. With this combination, the liquid yield is only 43 wt.% of the initial lignin. The gas yield is around 19 wt.% and the char yield around 38 wt.% (Joffres et al., 2013). However, Li et al. (2012) researched the catalytic fast pyrolysis with HZSM-5 zeolite on Kraft lignin and concluded that a large amount of the catalyst is required to deoxygenate the lignin-derived oxygenates. A catalyst-to-lignin ratio of 20 was required to obtain only aromatics and hardly any oxygenates (X. Li et al., 2012).
2. Non-sulfided NiMo/SiO2-Al2O3 and Cr2O3/Al2O3 catalysts: Increases the pyrolytic oil yield and modifies the composition. Methoxyphenols products were replaced by phenol, cresols and xylenols (Joffres et al., 2013).
3. Calcium formate: Has also been identified as an effective catalyst to reduce the oxygen content of the product (Joffres et al., 2013).

2.2 Hydrothermal liquefaction

Hydrothermal liquefaction (HTL) of biomass has extensively been researched (Karatzos et al., 2014). HTL can be done in sub- and supercritical conditions. For supercritical conditions the temperature and pressure need to be very high, above 380°C and 23 MPa, which is expensive and the main process occurring is gasification (Toor et al., 2011). Therefore subcritical conditions are generally preferred for the production of liquid biofuels (Joffres et al., 2013). Subcritical HTL generally occurs under moderately high temperatures, between 280°C and 370°C, and high pressure, between 10 and 25 MPa (Toor et al., 2011). In these conditions the water is still in a liquid phase, and works as both a reactant, solvent and a catalyst (Raikova et al., 2016; Toor et al., 2011). The biomass needs to be diluted to a concentration of 5 – 25% with water (Raikova et al., 2016). HTL of lignin has several advantages over other conversion methods. Firstly, a big benefit is that since water is used, the biomass does not need to be dried beforehand like with pyrolysis. Drying is an energy intensive process; thus, this can be very beneficial for the energy consumption of the conversion system. Secondly, the nitrogen oxides and sulphur oxides are dissolved in the water, so no further treatment is needed to remove them. Thirdly, in the conditions of HTL water can be used as a hydrogen source (Kang et al., 2013). However, the high temperatures and pressures required for HTL pose challenges for the industrial use of the process, since high investment costs are needed for materials that can withstand these conditions (Toor et al., 2011).

The main products of HTL are a bio crude with a relatively high heating value, char, water soluble substances and gas. The bio crude is generally low in oxygen since deoxygenation can occur through donation of hydrogen by the water The temperature, heating time and heating rate are the most important parameters of the liquid yield (Kang et al., 2013). Significant amounts of solid residues are produced during HTL of lignin. The liquid phase obtained from several tests of HTL of lignin was not an oil phase, but merely organics dissolved in the water phase (Toor et al., 2011). Mixtures of water-ethanol, water-phenol, water-acetone, and water-formic acid can also be used (as long as the mixtures are not over 50/50 (v/v), we still speak of hydrothermal liquefaction and not yet of solvolysis). A 50/50 mixture of water with ethanol has proven to be the most effective in increasing the solubility of lignin and preventing cross-linking reactions (Joffres et al., 2013). However, overall, hydrothermal liquefaction without the use of a catalyst is not considered very suitable to convert lignin to bio-oil (Joffres et al., 2013).

2.3 Solvolysis

Solutions of organic solvents like alcohols, formic acid and phenols and water can be used to increase the yield and the quality of the liquid and inhibit the char production, under relatively mild reaction conditions (Kang et al., 2013; Toor et al., 2011). They increase the solubility of lignin and its decomposition products and if they have a low supercritical point, the HTL reaction conditions can be substantially lowered. However, these solvents can be expensive and their use and recycling may cause environmental problems (Kang et al., 2013). Of these solvents, ethanol is often mentioned to be the most suitable, due to its reaction efficiency and economic and environmental characteristics (Lee et al., 2016). A mixture of ethanol and formic acid causes a high-quality liquid, mainly consisting of aliphatic hydrocarbons and phenols. The formic acid may also function as a hydrogen source (Joffres et al., 2013). Tetralin is often used because it is an organic solvent that can be both hydrogenated and dehydrogenated. Furthermore, because it is organic, it can be used to stabilise radicals and limit the formation of long condensed carbon chains. However, solvolysis alone is not found to be sufficient to transform lignin into liquid biofuels (Joffres et al., 2013).

2.4 Catalytic hydroconversion

Catalysts can serve to help the solvents by activating hydrogen and promoting hydrogenation or hydrogenolysis. Different catalysts exist, that can be subdivided into metallic, oxide or sulphide heterogeneous catalysts. Transition metal sulphide catalysts are generally preferred, since the sulphur that can be present in the lignin can form H2S in presence of hydrogen, which is poisonous for metal catalysts. Hydrocracking has also been researched, using bifunctional catalysts that induce both hydrogenation and hydrocracking. This combination is well known from the conversion from coal and this could be easily adapted to lignin (Joffres et al., 2013).

2.5 Gasification with Fischer-Tropsch synthesis

Figure 29: The stages of biomass to liquid conversion through gasification Fischer-Tropsch (source: (Noureldin et al., 2014)

Several steps are required to convert biomass into a clean Fischer-Tropsch fuel, as is shown in Figure 29. The first step involves converting the biomass to a syngas that is rich in hydrogen and carbon monoxide. This gasification happens on an oxygen-blown fluidised bed gasifier and requires high temperatures, around 700 - 800°C (Natarajan et al., 2014). Gasification is a complex process where many reactions occur, but the key reactions are presented below (obtained from Noureldin et al. (2014)):

Primary reactions

$$C + O_2 \rightarrow CO_2 \quad (1)$$

$$C + H_2O \rightleftharpoons CO + H_2 \quad (2)$$

Secondary reactions

$$C + 2H_2 \rightleftharpoons CH_4 \quad (3)$$

$$C + CO_2 \rightleftharpoons 2CO \quad (4)$$

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \quad (5)$$

Gasification allows for a wide variety of feedstock to be used, from which a consistent intermediate gas can be generated (Noureldin et al., 2014). However, since many reactions take place during the gasification, the gas needs to be cleaned before FT synthesis to remove any impurities, CO_2 or sulphur (Noureldin et al., 2014). After this the CO/H2 ratio is adjusted to the preferred ratio, by addition of hydrogen from steam methane reforming. The obtained syngas can catalytically be converted through Fischer-Tropsch synthesis into hydrocarbon liquids. The type of biofuel depends on the process characteristics (Ecofys, 2012). Fischer-Tropsch synthesis involves the following chemical reaction to occur:

$$CO + 2H_2 \rightarrow (CH_2) + H_2O$$

This process is very mature and many commercial reactors already exist. The process can be used to create hydrocarbons of different carbon structures. The FT fuels are considered ultra clean since they do not contain any sulphur or aromatics, and the emissions associated with their combustion are low, compared to fossil crude oil (Noureldin et al., 2014). Different catalysts can be used, but for the production of liquid fuels, cobalt-based catalysts are preferred (Noureldin et al., 2014). The FT primary liquid obtained after the FT reaction can be upgraded through hydrocracking and hydrotreatment if necessary (Natarajan et al., 2014). From the cooling of the FT reactors and from the off-gas, large amounts of heat and electricity can be used or sold to increase the overall efficiency of the process (Natarajan et al., 2014). As can be seen in Table 48, the synfuel yield for lignin is higher than for the other biomass components (Noureldin et al., 2014).

Table 48: Stoichiometric synfuel yield of various biomass constituents in kg synfuel/kg biomass (obtained from Noureldin et al. (2014)

Biomass	Model compound	Stoichiometric synfuel yield
Cellulose	$C_6H_{10}O_5$	0.35
Glucose	$C_6H_{12}O_6$	0.31
Hemicellulose	$C_5H_8O_4$	0.35
Lignin	$C_{10}H_{12}O_3$	0.53
Furfural	$C_5H_4O_2$	0.49
Starch	$C_6H_{10}O_5$	0.35
MSW	$C_6H_{10}O_4$	0.41

Disadvantages of this thermochemical conversion route are low feedstock utilisation, and the large amounts of wastewater and CO_2 that are generated during the gasification step (Noureldin et al., 2014).

Appendix 4: Upgrading processes

Bio-oils, especially those produced from pyrolysis, can contain impurities like sulphur, nitrogen, oxygen and chlorine. This can cause the bio-oils to be corrosive, viscous and highly oxygenated with a low H/C ratio, making them difficult to store, transport and refine. Therefore, they require upgrading to remove the impurities and stabilise the oil. This can be done through hydroprocessing (hydrocracking or hydrotreatment) or catalytic cracking (Brown et al., 2013).

3.1 Hydrotreatment

Hydrotreatment removes the chlorine, nitrogen, sulphur and oxygen impurities (as HCl, NH3, H2S and H2O respectively) under atmospheric or slightly increased pressure, with minimal cracking of the molecules (Jechura, 2016). This is a cheaper route than hydrotreatment with high pressures and it is already commercialised. However, a high amount of coking can occur and the resulting oils are still of relatively poor quality (Xiu & Shahbazi, 2012).

Catalysts are required for the hydrotreatment process, but which one is most suitable is hard to determine. In general, two types of catalysts exist, sulphide catalysts and transition metal catalysts. Of both types, different catalysts have been developed and tested, and both are found to have advantages and disadvantages. Sulphided catalysts are extensively studied and cheap, but they can cause sulphur leaching, induce severe coking and they are intolerant to water, which is a problem considering the general moisture content of lignin derived bio-oils. Transition metal catalysts are better reusable, show higher reactivity and require lower temperatures. However these catalysts are not usable in presence of sulphur, which means Kraft lignin ought to be desulphurised before upgrading, and they are expensive (Mu et al., 2013).

3.2 Hydrocracking

Hydrocracking removes oxygen from a bio-oil by cleaving the carbon-oxygen bonds with hydrogen in presence of a catalyst. It then produces CO_2 and H2O, thus removing the oxygen from the oil. Removing the oxygen leads to a more energy dense, non-corrosive oil from which the water can easily be separated. Unfortunately, the process requires the use of large amounts of hydrogen that is generally supplied under high pressure to increase the solubility of the H2 in bio-oil. In current technologies, pressures between 75 and 300 bars are applied and the temperatures range between 250 and 400°C (Dickerson & Soria, 2013). This increases the costs of producing bio-oil substantially and also negatively influences the sustainability of the conversion route. It is possible to produce the required hydrogen from the biomass itself, however using natural gas is a more economical option that is usually preferred (Karatzos et al., 2014).

The catalyst and the operating conditions both influence the final output. It is important to find the right balance between residence time, temperature, deoxygenation, gas and coke formation. Different catalysts result in different oil yields, require different temperatures and induce different amounts of char formation. Research is currently still performed on improving the catalyst longevity and effectiveness. Also the reduction of hydrogen consumption is studied by using a liquid with an easily donated, acidic proton that lowers the required hydrogen pressure, like formic acid (Dickerson & Soria, 2013).

3.3 Catalytic cracking with zeolites

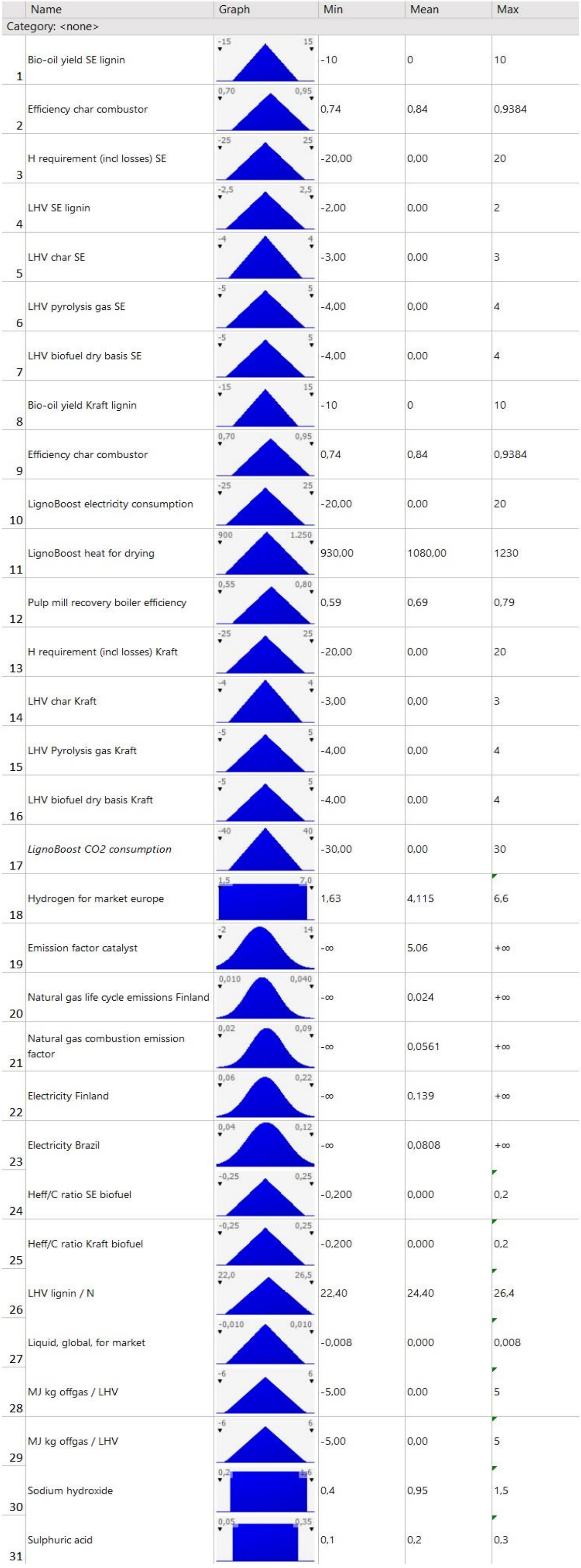
Zeolites are porous structures that induce cracking and dehydration of the bio-oils. They can produce aromatics under atmospheric pressures and without the use of hydrogen. This leads to an upgraded bio-oil, however still with a low LHV compared to deoxygenated fuels, due to a lower H/C ratio and higher O/C ratio. This is because no hydrogen is actually added to the oil. The temperatures that are generally used range between 350 and 600ºC. The zeolites remove the oxygen from the oil through the production of cokes and CO_2. Coke production is still a problem, since it causes coking of the catalysts (Dickerson & Soria, 2013). Due to this undesirable coke production and other polymerisation reactions, the oil yields are reduced to around 15 to 23 wt.% of the original bio-oil (Dickerson & Soria, 2013; Karatzos et al., 2014). Zeolite cracking works best on bio-oils with a H/C ratio of at least 1.2 (Dickerson & Soria, 2013).

Appendix 5: Uncertainty and Sensitivity analysis

Table 47 shows the parameters that were considered for the uncertainty and sensitivity analysis. It als shows the uncertainties that were chosen for each of them, with a short explanation.

The parameters that were considered were thought to be important throughout the LCA of lignin conversion to marine biofuel. First of all the GHG emission factors are important. They were obtained from EcoInvent or from literature, but these are general values and the emission factor of the products in the actual case may be different. For example, the hydrogen emission factor for the market in Europe was used for both cases. The actual value in Finland may be different, and this is especially the case for Brazil, which of course is not part of Europe. Other critical parameters for the LCA are the yields and heating values of the pyrolysis oils, fuel gas and chars that result from the fast pyrolysis process. These were also considered. The lignoBoost process is responsible for the largest part of the direct GHG emissions of the Kraft lignin conversion. Because its influence on the outcome is so large, it is important to assess the sensitivity of the overall result on these parameters, so the chemical, natural gas, CO2 en electricity consumption of this process are included.

Table 49: The uncertainty assumed for each of the relevant parameters. The probability distribution functions (PDF) were either normal (e.g. number 5), triangular (e.g. number 1) or uniform (number 12).



	Name	Graph	Min	Mean	Max
Category: <none>					
1	Bio-oil yield SE lignin	-15 15	-10	0	10
2	Efficiency char combustor	0,70 0,95	0,74	0,84	0,9384
3	H requirement (incl losses) SE	-25 25	-20,00	0,00	20
4	LHV SE lignin	-2,5 2,5	-2,00	0,00	2
5	LHV char SE	-4 4	-3,00	0,00	3
6	LHV pyrolysis gas SE	-5 5	-4,00	0,00	4
7	LHV biofuel dry basis SE	-5 5	-4,00	0,00	4
8	Bio-oil yield Kraft lignin	-15 15	-10	0	10
9	Efficiency char combustor	0,70 0,95	0,74	0,84	0,9384
10	LignoBoost electricity consumption	-25 25	-20,00	0,00	20
11	LignoBoost heat for drying	900 1.250	930,00	1080,00	1230
12	Pulp mill recovery boiler efficiency	0,55 0,80	0,59	0,69	0,79
13	H requirement (incl losses) Kraft	-25 25	-20,00	0,00	20
14	LHV char Kraft	-4 4	-3,00	0,00	3
15	LHV Pyrolysis gas Kraft	-5 5	-4,00	0,00	4
16	LHV biofuel dry basis Kraft	-5 5	-4,00	0,00	4
17	*LignoBoost CO2 consumption*	-40 40	-30,00	0,00	30
18	Hydrogen for market europe	1,5 7,0	1,63	4,115	6,6
19	Emission factor catalyst	-2 14	-∞	5,06	+∞
20	Natural gas life cycle emissions Finland	0,010 0,040	-∞	0,024	+∞
21	Natural gas combustion emission factor	0,02 0,09	-∞	0,0561	+∞
22	Electricity Finland	0,06 0,22	-∞	0,139	+∞
23	Electricity Brazil	0,04 0,12	-∞	0,0808	+∞
24	Heff/C ratio SE biofuel	-0,25 0,25	-0,200	0,000	0,2
25	Heff/C ratio Kraft biofuel	-0,25 0,25	-0,200	0,000	0,2
26	LHV lignin / N	22,0 26,5	22,40	24,40	26,4
27	Liquid, global, for market	-0,010 0,010	-0,008	0,000	0,008
28	MJ kg offgas / LHV	-6 6	-5,00	0,00	5
29	MJ kg offgas / LHV	-6 6	-5,00	0,00	5
30	Sodium hydroxide	0,2 1,6	0,4	0,95	1,5
31	Sulphuric acid	0,05 0,35	0,1	0,2	0,3