Carbon footprint of Lignin modified Asphalt mix

A tree to gate LCA Assessment (30 ECTS Master thesis)

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Executive Summary

Introduction

The preeminent activity affecting the amount and rate of climate change is greenhouse gas (GHG) emissions from combusting fossil fuels (IPCC, 2014). The transport sector within the infrastructure sector uses many fossil fuel based products, especially in the construction of asphalt roads which contain a high proportion of fossil-fuel derived products.The LCA of traditional asphalt sum up GHG emission of 550 kton CO_2 eq./ year; equivalent to 23% of overall GHG emissions of the infrastructure sector in the Netherlands (M. M. Bijleveld et al., 2015; Korevaar & Blok, 2018). Bitumen (fossil based derivative) in the asphalt mix accounts for 15% of total GHG emissions of the production of ZOAB (Zeer Open Asfalt Beton, i.e. porous asphalt) in the Netherlands (Rijkswaterstraat, 2018). Hence, the asphalt sector which is responsible for considerable amount of emission requires greener, waste and recycled materials to improve its sustainability. Biomass could be one of a possible solution in reducing the GHG emission of this vital sector. Lignin, one of the most abundant natural polymers (next to cellulose and hemicellulose),could be used as an alternative for bitumen, as it reflects the chemical structure of bitumen (van Vliet et al., 2016). Lignin can be supplied in large quantities as a by-product of paper and pulp mills and lignocellulosic biorefineries (Culbertson et al., 2016). To help explore the potential, this thesis aims to assess the GHG emission mitigation from lignin use in asphalt (ZOAB). This research uses Kraft lignin and steam explosion biorefinery lignin since Kraft is the dominant pulping method in the world, existing mills in Scandinavia are used for the input data (Benali et al., 2016; Gellerstedt, 2015) while for biorefinery, *Biobased delta* intends to develop a lignocellulosic biorefinery in the southwest of the Netherlands utilizing the steam explosion process which is used for the input data for the calculation of GHG emission (Vera et al., 2018). This research answer the following research questions:

> ***What would be the GHG emissions reduction (direct and indirect) if 50% of fossil-based bitumen is replaced with lignin (cradle-to- gate), and how much GHG emission could be reduced in infrastructure sector with implementation until year 2030 in the Netherlands?***

This study describes the replacement of 50% bitumen by lignin as theoretical research has been done on using lignin to replace the bitumen up to 50% in the asphalt mix (van Vliet et al., 2016), as roads are constructed in the Zeeland province and Wageningen University of the Netherlands using 50% bitumen and rest 50% lignin (Discussion fossil bitumen and Bio-bitumen, Personal communication, Bergen op zoom, 19 December, 2018). Also, this study will contribute to the knowledge of possible reduction in GHG emissions from the use of lignin in the asphalt mix (ZOAB), which could help the asphalt industry in commercialising the ZOAB with lignin and thereby reducing emissions from the Infrastructure sector in the Netherlands. This research was performed in cooperation with the AKC (Asfalt Kennis Centrum) and Biobased Delta.

Methods

A (cradle-to gate) consequential life cycle analysis (CLCA) is performed following ISO14040 guidelines, to assess the environmental impact of GHG emission (direct and indirect) of asphalt mixture (ZOAB) when fossil bitumen is replaced by lignin. A brief description of the system boundaries used in this research is presented in Figure 1. The techniques used for lignin isolation investigated are the 'Lignoboost' process (Kraft paper mill) and 'Steam explosion' technology (lignocellulosic biorefinery). The research analyses two possible scenarios for assessing the GHG emissions using LCA (cradle-to-gate). In the first scenario, a marginal amount of lignin is extracted from the Kraft pulp mill and SE biorefinery to replace fossil

bitumen and the remaining lignin is incinerated to provide heat and electricity. In the second scenario, lignin is completely isolated from the Pulp mill and refinery which requires additional natural gas or forest residues wood chips for the supply of heat and electricity in the respective refinery and pulp mill. In the calculation of GHG emission, lignin which is a biogenic product stores carbon and thus negative emissions are allocated to it (Levasseur et al., 2013). The only environmental impact considered in this research was global warming potential (GWP). The functional unit is **kg CO_2 eq./tonne of ZOAB.** Within the first scenario, baseline case uses mass allocation, where a marginal amount of lignin is extracted for the ZOAB mix and rest is used for internal heat and power, causing no indirect effects in the biorefinery and kraft pulp mill. Energy and economic allocation were also used to evaluate the impact on the results. In second scenario of complete lignin isolation, forest residues or natural gas were used for internal energy of the plants and different allocation mechanism such as mass, energy and economic.

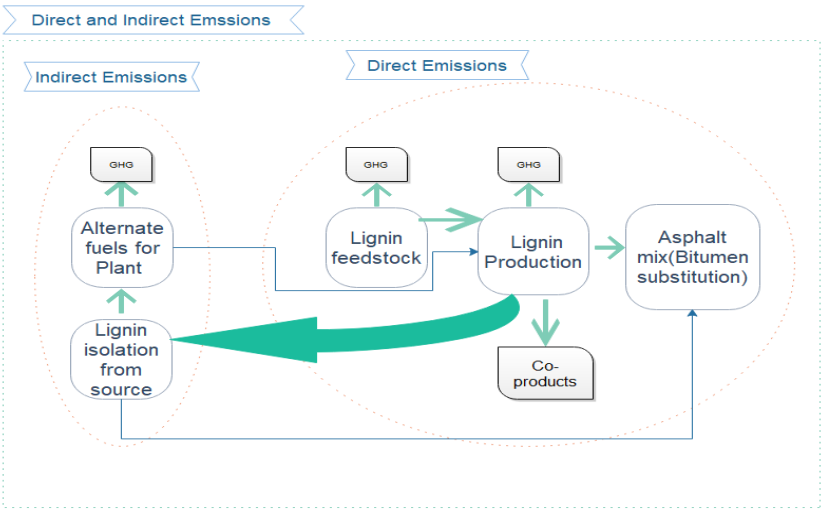

Figure 1 The system boundaries for the LCA

A SimaPro was created to assess the GHG emission of the scenarios with relevant CO_2-eq emission factors, and new results can be calculated if future developments or insights changes the variable.

Results

Figure 2 shows the baseline case, the optimal scenarios and sub-optimal scenarios when calculating the GHG emissions for both Kraft and biorefinery lignin ZOAB using different allocation mechanisms. The LCA assessment (cradle-to-gate) sums up GHG emission as 53.3 kg CO_2 eq./tonne of ZOAB (Kraft process) and 64.5 kg CO_2 eq./tonne of ZOAB (Biorefinery lignin) as compared to the 72.2 kg CO_2 eq./tonne of ZOAB (ZOAB regular) for baseline case. The reduction of ZOAB biorefinery lignin is low compared to ZOAB Kraft lignin as lignin isolation in the *Steam explosion* process requires more energy than the *Lignoboost* process along with feedstock used in refinery is from USA compared to Scandinavian feedstock used for Kraft mill. The biogenic carbon stored in the biorefinery lignin is more than Kraft lignin due to the carbon composition of the feedstock used in the process. As seen in Figure 2, the GHG emission value of 52.8 kg CO_2 eq./tonne of ZOAB is the optimal solution where forest residues wood chips are used as fuel in the mass allocation (Kraft lignin) while the sub-optimal solution is 65.2 kg CO_2 eq./tonne of ZOAB when natural gas is used as fuel in the energy allocation for ZOAB with lignin (biorefinery lignin). Most of the GHG reduction is due to lignin being a biogenic product and storing carbon.

Discussion and Conclusion

This research only assesses one environmental impact (Global warming potential) and only cradle-to-gate LCA assessment is performed. The baseline case results illustrate GHG emission reduction is

approximately 26% for Kraft lignin and 10% for SE biorefinery lignin per tonne of ZOAB compared to ZOAB regular. For the rest using different allocation in the given first and second scenarios the GHG emission reduction potential is between 18-27% Kraft lignin and 9-20% Biorefinery lignin ZOAB (compared to ZOAB regular) which reduces 2.7-4% and 1.35-3 % annual CO_2 emission in the infrastructure sector in the Netherlands. The emission saving is mostly due to carbon stored in the lignin. More robust calculation are needed for the refinery as it needs value from actual operational plant.

GHG reduction achieved with lignin from the biorefinery is limited, as energy requirement for the steam explosion process are high and as the feedstock (wood pellets) from the USA with high transport emissions compared to the feedstock for kraft lignin from Scandinavia.

From these results, it can be concluded that using lignin in ZOAB does mitigate the GHG emissions in the infrastructure sector and by 2030, 32.8 % CO_2 emission reduction is possible using Kraft Lignin ZOAB, while 14.1 % CO_2 emission reduction is possible using refinery lignin ZOAB in the Netherlands. The fate of biogenic carbon stored in the lignin during the use phase as well as end of life phase needs to be further assessed. Therefore, a cradle-to-grave LCA assessment needs to be performed to calculate the overall sustainability of using lignin in ZOAB.

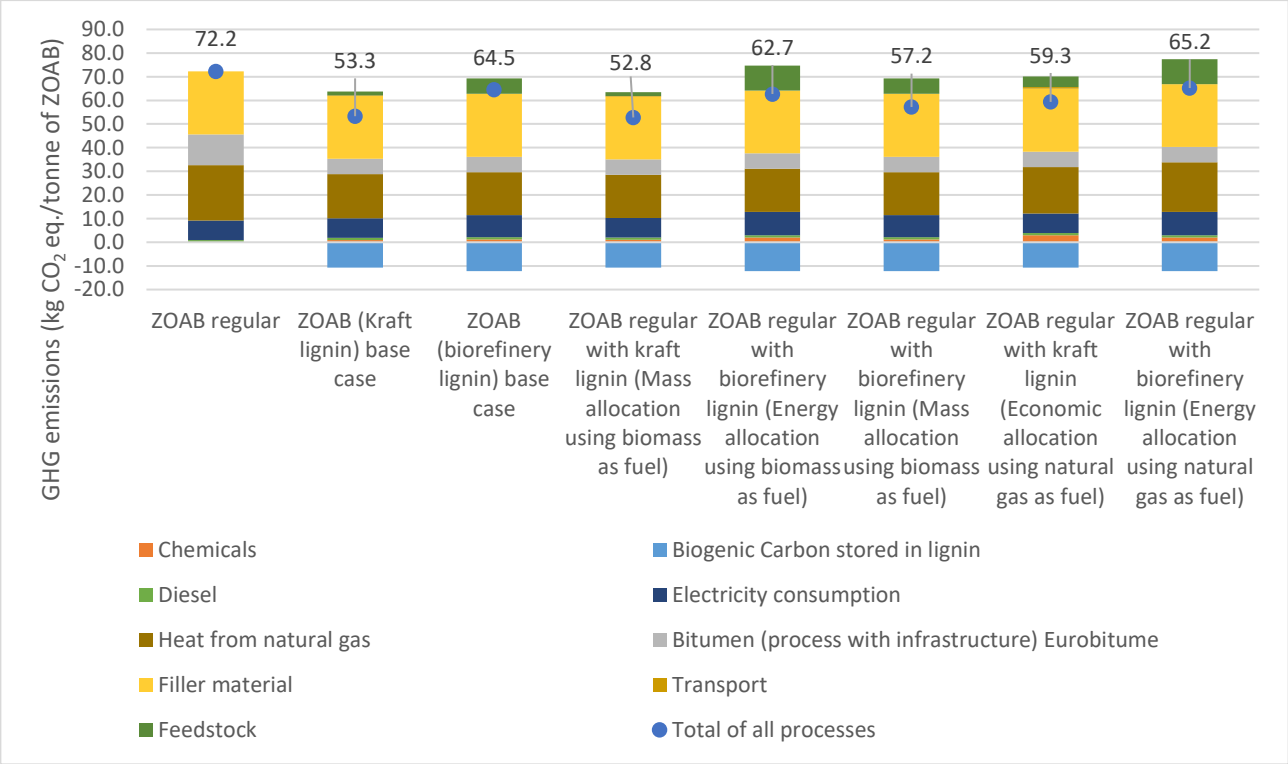

Figure 2 The comparison of ZOAB regular with ZOAB with lignin presented with the GHG emissions, and showing the most optimal and sub-optimal scenario considering lignin isolation in both Kraft mill and Biorefinery

Acronyms & Abbreviation

ALCA	Attributional life cycle analysis
Approx..	Approximate
CLCA	Consequential life cycle analysis
CO_2	Carbon dioxide
Dt	Dry tonne
EU	European Union
GHG	Greenhouse gas
GJ	Giga Joule
GWP	Global warming potential
H_2SO_4	Sulphuric acid
HHV	Higher heating value
IEA	International energy agency
IPCC	International panel on climate change
ISO	International standard organisation
Kton	Kiloton
LCA	Life cycle analysis
LCI	Life cycle Inventory
LNG	Liquified Natural gas
LHV	Lower heating value
Mton	Megaton
NaOH	Sodium Hydroxide
PLA	Polylactic acid
RES	Renewable energy supply
SE	Steam explosion
SLRP	Sequential Liquid-lignin recovery and purification
Wt%	Weight percentage
ZOAB	Zeer Open Asfalt Beton (Porous Asphalt)

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1.Introduction

The Paris climate agreement in 2015 has convened a long term goal to keep global temperature rise below 2°C above pre-industrial levels with aiming to maximize its increase with 1.5 ° C. This target seems is really hard with recent IPCC special report specifying global warming is going to reach 1.5 ° C between 2030 and 2052, if the global warming continues to increase at current rate(Masson-Delmotte et al., 2018). The Netherlands has transformed the Paris agreement as its primary objective to reduce the GHG emissions by 49% by 2030 and be fully carbon neutral by 2050 compared to 1990 levels(Rijksoverheid, 2018). For 2030, the target evaluates into 48.7 Mt CO_2 reduction which needs intensive structural changes in all sectors of Dutch Economy (electricity, industry, transport, agriculture and residential) along with a substantial increase in renewable energy supply. The Netherlands is already lagging behind with the RES share of 6.6 % in 2017(Centraal Bureau voor de statistiek, 2018) This is far away from the 2020 target as agreed within EU member states to be 14% share in final consumption (2009/28/EU). Since, wind power and photovoltaics are growing substantially, biomass is still the largest source of RES with a share of 61% in the EU and the Netherlands(Centraal Bureau voor de statistiek, 2018). Biomass is important for the sectors that are difficult to decarbonize or that have few alternatives to biomass including the materials such as chemicals and plastics, transportation, marine and aviation that use fossil energy carriers for production. The transition from the fossil based economy to a bio-based economy is therefore going to play a key role in meeting the above mentioned climate targets in the Netherlands.

The preeminent activity affecting the amount and rate of climate change is greenhouse gas (GHG) emissions from incinerating fossil fuels (IPCC, 2014). As Kenneth Deffeys said, “The fossil fuels are a onetime gift that lifted us up from subsistence agriculture and eventually should lead us to a future based on renewable resources”(Impending & Oil, 2001). The transport sector which uses mainly fossil-fuel based products, especially in the construction of asphalt roads which contain a high proportion of fossil-fuel derived products such as bitumen. The asphalt roads are responsible for various direct and indirect environmental impacts such as increment in the GHG emissions and air pollutants such as CO_2, NO_2 and fine particulate matter (Meijer et al., 2018). The global road infrastructure is over 21 million km , with an addition of around 3-4.7 million km of road infrastructure by 2050 which are surfaced with asphalt(Meijer et al., 2018). The Europe has approximately more than 5.2 million km of road infrastructure, in which the Netherlands has 0.1 million km hard surfaced road including 5000 km National trunk road(Egis, 2010; TNO, 2018). The global greenhouse gas emissions from the infrastructure construction and its operation is approximately around 70% including power plants, buildings and transport (SAHA, 2018), where the transport sector contributes to 17% of global GHG emissions (Olivier et al., 2017). Moreover, in the Netherlands the asphalt sector is responsible for 0.5 Mton of CO_2 emissions while the emissions of the road traffic from 1990-2017 (as seen in Figure 3) is 3 Mton of CO_2 emissions in comparison to other industries (CBS, 2018; Korevaar & Blok, 2018). The road sector makes a crucial contribution to the economic development and growth and brings important social benefits (Malkoc, 2015). Therefore, to reduce CO2 emissions from this vital sector, biobased material needs to be used in the road construction along with use of alternative sources of fuel for cars like hydrogen, electricity and LNG.

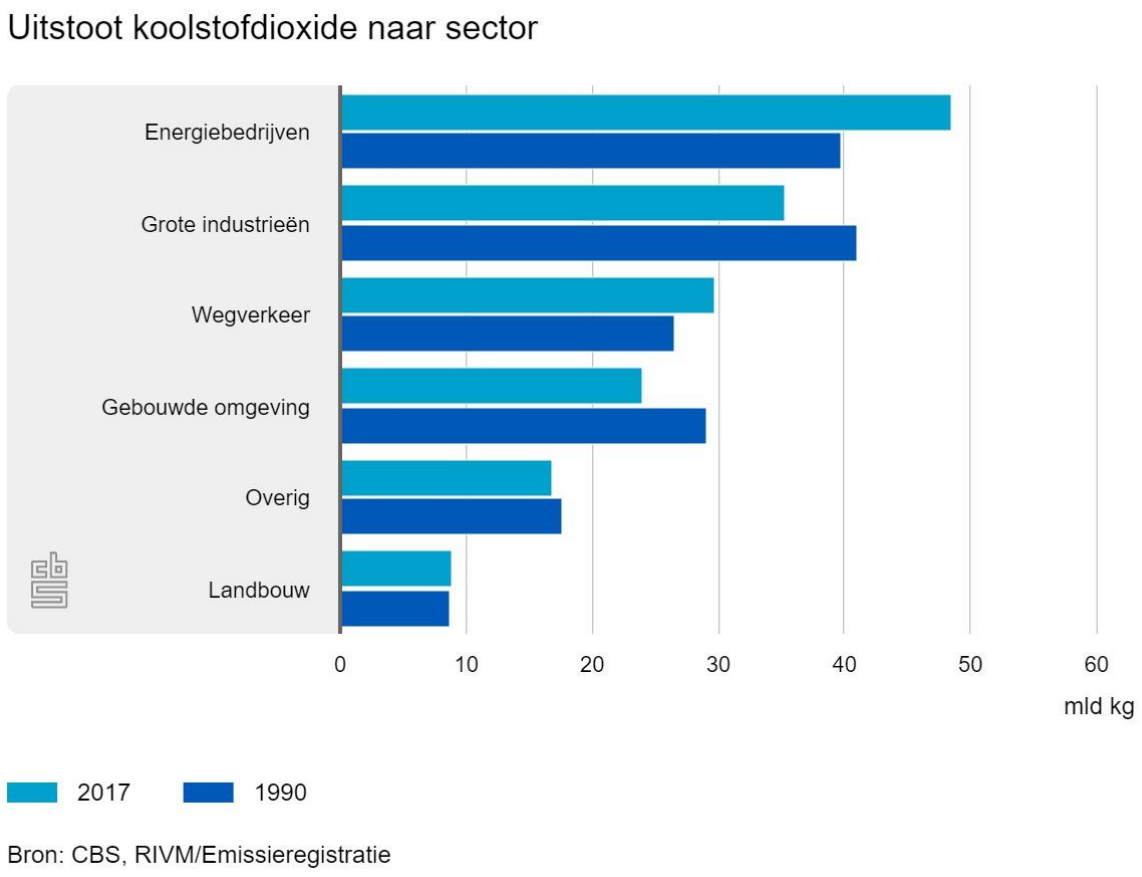

Figure 3 The carbon dioxide emissions per sector in the Netherlands (CBS, 2018)

Bitumen which is one of the fossil fuel component and is mostly used in the road infrastructure. Bitumen is obtained through petroleum distillation. Currently, bitumen supply chain is affected due to increase in the demand for the residues for new cokers[1] by refineries (Argus Media,2018). According to Shell bitumen pricing manager Keith Stone (Argus Media, 2018), use of residues in cokers is anticipated to increase up to 1.5 million b/d (barrels per day) compared to global bitumen consumption, which is 1.7 million b/d(100 mn ton/yr). This will affect the supply of bitumen and is expected to cause a price increase as shown in Figure 4 . Therefore, to promote sustainable practice and to create opportunities from price increase, the greener, waste and recycled materials need to be integrated into production of asphalt mixtures to improve the sustainability and cost efficiency of the asphalt pavement industry. This can be done by partial substitution of greener material into mixture of asphalt like reclaimed asphalt pavement (RAP), construction & demolition waste, lignin and bio binder from vegetable oil (Kowalski et al., 2016). Lignin could be a possible replacement for bitumen as it is most abundant natural polymers (next to cellulose and hemicellulose)which is present in plant material and due to its reflection of chemical structure of bitumen and therefore it could be used as an alternative for bitumen in applications like roofing or asphalt (van Vliet et al., 2016). Lignin is supplied in large quantities as a by-product of

[1] Coker in the refinery takes the lowest value bottom materials such as vacuum residue and cracks it to remove residue yielding the lighter fraction and solid carbon (pet coke). The Coker allows a refinery to eliminate most or all of the low value bottoms from crude oil to achieve higher yield of lighter products (McKinsey&Company, 2018).

paper and pulp mills and lignocellulosic biorefineries (Culbertson et al., 2016).

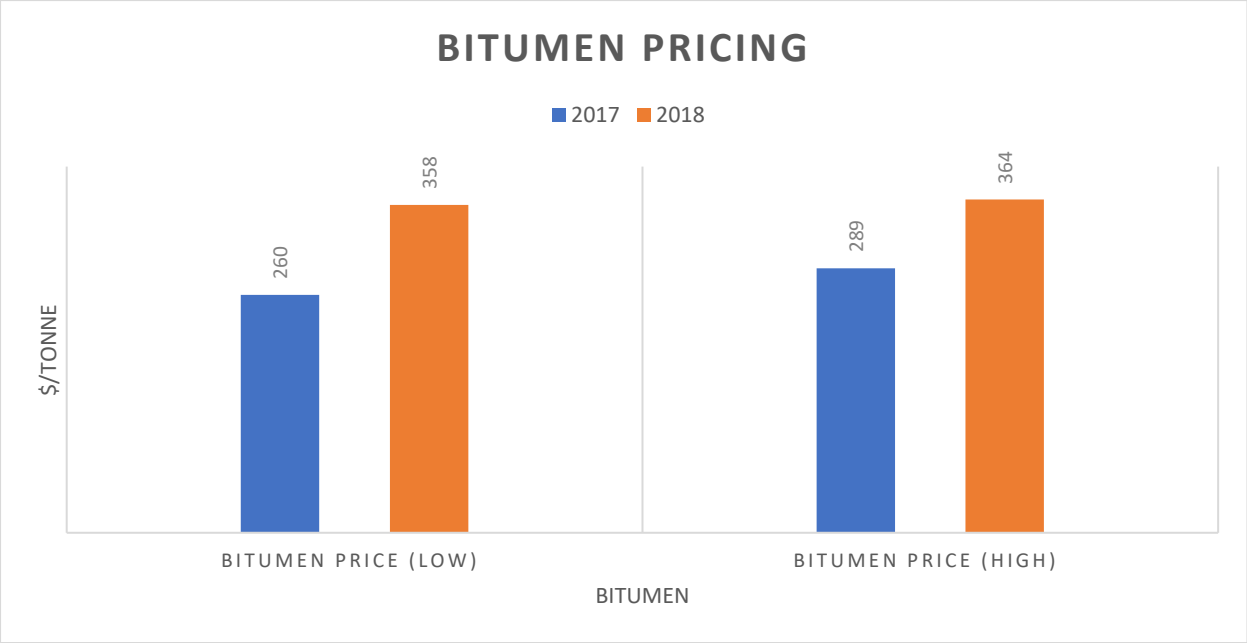

Figure 4 Bitumen pricing in the Netherlands in 2017 and 2018 (Argus Bitumen, 2017; Argus, 2018).

1.1 Scientific background

Bitumen which can be specified as a black viscous mixture of hydrocarbons obtained naturally or as a residue from petroleum distillation. It is mostly used in the construction of roads as the glue or the binder mixed with aggregate particles to make asphalt concrete(Barth, 1962; Eurobitume, 2012). The use of fossil bitumen causes emission of CO_2 in the atmosphere which was sequestered for a long time leading to an increment of the CO_2 in the atmosphere (IEABioenergy,2018). The sulphur content of the lignin from various process is very little as compared to the fossil bitumen(van Vliet et al., 2016).

Lignin which is generally regarded as waste product of the pulp mills and biorefineries, is biodegradable (IPCC, 2006). Lignin which is generally used as a lower grade fuel to supplement heat and power for the operation of plant such as in the case of the Kraft process which produces pulp, black liquor and lignin in the Paper/pulp mill which is the dominant producer of pulp in world (Dias et al., 2007; Poopak & Agamuthu, 2011). Lignin (biogenic product) is an abundant organic renewable polymer which account for 15-40% of content in the plant surface, apart from cellulose and hemicellulose (Novaes et al., 2010). The use of biogenic product such as lignin have several advantage over the fossil products. The greenhouse gas emissions from the biogenic material are emissions directly resulting from combustion or decomposition of biologically-based materials other than fossil fuels (Levasseur et al., 2013). The use of lignin in the asphalt mix may be considered carbon neutral, because the CO_2 that is emitted by the use of natural gas and electricity in the asphalt production and mixing emitted CO_2 is recently taken by the biomass and does not cause no net increase in the atmosphere (all things considered the feedstock is re-grown to balance the carbon stock)(IEA Bioenergy, 2018). The biogenic carbon[2] (as shown in Figure 5) which is not emitted during

[2] It is described as quantifying the process of plants capturing CO_2 in the process of photosynthesis, and how it is lost in respiration and stored in biomass (both living and dead), thus finally biologically sequestered into long-term biological stores in the soil (Harris et al., 2018). This biogenic terrestrial carbon cycle has significant potential for GHG emission reduction, thus creating negative carbon emission as the carbon is being captured in the tree (Harris et al., 2018)

waste treatment is considered stored carbon which is allocated negative CO_2 eq. allocation (Levasseur et al., 2013). Shen et al (2010) take the case studies of the LCA (cradle-to-gate) of starch plastics and PLA from corn, which is allocated negative carbon emission. Similarly, the lignin can be allocated negative carbon emission as it is a biogenic product.

The quality of the asphalt mix depends on the binder properties. The complex structure of the lignin makes it environmentally, technically and economically difficult to use as a high quality fuel (Strassberger et al., 2014) similarly it could be said about the use of lignin as asphalt binder. Ragauskas et al (2014) conveys that the lignin has not been converted into a viable, commercially relevant feedstock, apart from being used in the few markets and other uses. Research is been done on the potential of using the lignin to produce chemical products, such as aromatic chemicals, additives, resins and coating materials (T. M. Bijleveld, 2016b; Faruk et al., 2016). Since, the chemical structure of lignin reflects to bitumen, it could be possible to partly replace bitumen with lignin, which could potentially reduce the fossil bitumen consumption as well as bind carbon for decades (van Vliet et al., 2016). Henceforth, lignin can be considered an alternative to fossil bitumen in the asphalt mix (Farooz et al., 2018; Kowalski et al., 2016). Furthermore, lignin is available all over the world, it can lead to a large potential of the production of lignin modified asphalt binder. However, currently lignin is used for the heat and electricity production. The price and quantity of lignin and bitumen are shown in Figure 6.

Lignin can be blended in different ratios with fossil bitumen. Lignin can be used as binder for the construction of roads with asphalt or reclaimed asphalt pavement. The various types of lignin extracted from different processes are mixed with bitumen in different penetration grades as shown in Table 1 (van Vliet et al., 2016). The asphalt pavements are measured by the penetration grade, which specifies the viscosity, consistency, or fluidity of the asphalt. It is measured by the permitting a standard needle, loaded to a weight of 100 grams, to penetrate into a sample of asphalt at the temperature of 25° C (Illiam, 1961). According to Illiam (1961), the penetration is continued for five seconds to measure the depth of the penetration in the units of one-tenth millimetres and the value is called the penetration number and it ranges from 10 to 300. The largest is the penetration, the softer the asphalt become. The penetration 70/100 is most commonly used penetration grade when substituting bitumen with lignin (Discussion fossil bitumen and Bio-bitumen, Personal communication, Bergen op zoom, 19 December, 2018). The lignin type in the penetration grade shown in Table 1 depends upon the isolation process and if the lignin has sulphur content or its free from it. The further details on the lignin and bitumen is explained in the Appendix 1 and 2.

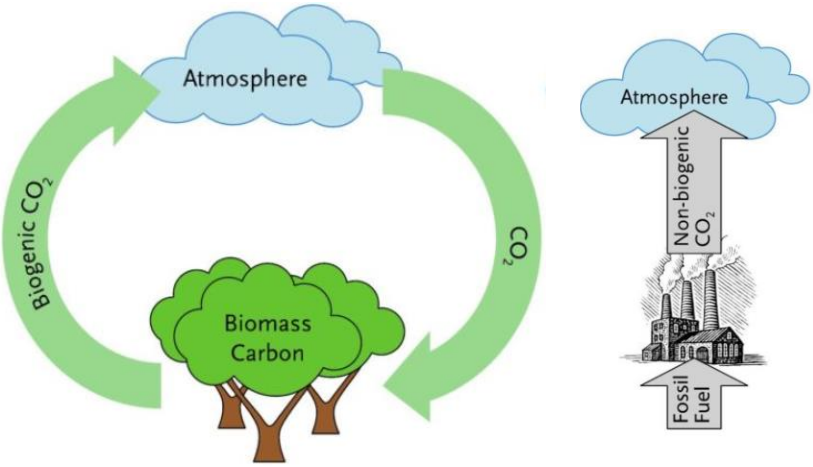

Figure 5 Biogenic carbon Source: (IEABioenergy, 2018)

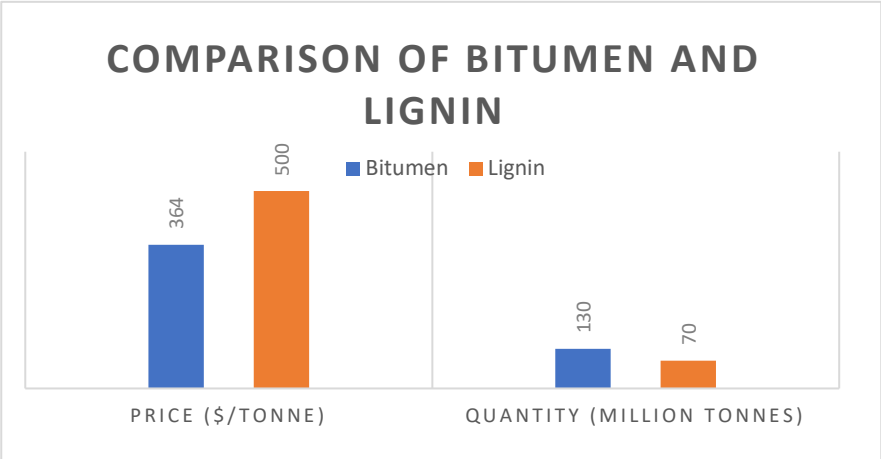

Figure 6 Comparison of bitumen and lignin(Argus, 2018; Gellerstedt, 2015)

Table 1 Blending with different types of lignin (van Vliet et al., 2016)

Type of lignin	Organosolv		Klason	Kraft	SHS
Amount of lignin in the blend (% m/m)	10 %	25 %	25 %	25 %	25 %
10/20	X				
70/100	X	X	X	X	X
160/220	X	X			

1.2 Research gap

The studies on the lignin valorisation are used for the materials and biochemicals. There are numerous studies on the availability of lignin such as using different techniques like Lignoboost, Lignoforce, SLRP, but a more descriptive overview of the different lignin streams and methods to isolate the lignin could not be found. This descriptive overview could be useful for industries aiming to valorise the lignin as there is a research done on the lignin valorisation to use it for the marine biofuels. T. M. Bijleveld (2016a)

did a study on production of marine biofuels from lignin to reduce GHG emissions of shipping sector which includes the future market potential of lignin as well as a GHG assessment of the suitable conversion routes in Brazil and Scandinavia. Studies are done on the calculation of LCA of the traditional asphalt production(Korevaar & Blok, 2018), also some studies are done on the LCA of using the polymer modified bitumen in asphalt mix(Kowalski et al., 2016). Studies also exist on the GHG assessment on whole lignocellulosic biomass conversion to more valuable and technical products, like aromatics, gasoline, ethanol or jet fuels (Fang et al.,2005; Hsu, 2012; Iribarren et al., 2012; Vera et al., 2018; Tews et al., 2014). Furthermore, there is research on the LCA on the extraction of lignin and using it for various applications like biofuels, catechols, polymer applications, bitumen modifiers, fossil based phenols and adipic acid (Bernier et al., 2013; Corona et al., 2018; Lettner et al., 2018; Montazeri & Eckelman, 2016; Tomani et al., 2011; van Vliet et al., 2016). Overall, the numerous studies exist on the technical or economic aspects of lignin conversion to oil or chemicals, however there is still no combination study on the LCA assessment of use of lignin in asphalt mix (Gosselink, 2011; Noureldin et al., 2014; Pandey & Kim, 2011; Riaz et al., 2016; van Vliet et al., 2016). This viewpoint is intriguing to be further researched and this tentative study tries to look upon the aspect of lignin use in the asphalt mix.

The lignin which is also the by-product of wood pulping and a major constituent of black liquor burnt in recovery boilers (Bernier et al., 2013). Lignin is also obtained from waste product of bio ethanol and pulp & paper industry and its mainly burnt as low grade boiler fuel (Strassberger et al., 2014). Some theoretical research has been done on using lignin to replace the bitumen up to 50% in the asphalt mix (van Vliet et al., 2016), as well as few roads are constructed in the Zeeland province and Wageningen University of the Netherlands using the lignin modified asphalt mix of blend of 50% bitumen and 50% of lignin (Discussion fossil bitumen and Bio-bitumen, Personal communication, Bergen op zoom, 19 December, 2018). However, there is no studies on the potential GHG emissions mitigation from the use of lignin. This study takes the first step towards the calculation of carbon footprint of use of lignin in the asphalt mix and potential GHG mitigation.

1.3 Problem definition

This thesis aims to quantify the potential GHG emission benefits caused by the replacement of fossil bitumen with lignin in the asphalt mix binder. Lignin could be a potential solution to reduce the GHG emission as well as bind carbon for decades in the asphalt.

In Europe, production of 1 ton of bitumen on average emits approximately 175 kg CO_2 eq. in 2015, bitumen production and use accounted for 1.7% of GHG emissions in the Netherlands (Korevaar & Blok, 2018). The annual GHG emission of Netherlands is approximately 195 million metric tonnes CO_2 eq. (Coenen et al., 2018; Korevaar & Blok, 2018), in which infrastructure sector is approximately 2.85[3] Mton CO_2 eq./yr (M. M. Bijleveld et al., 2015). In Netherlands, the whole chain of asphalt from the extraction to the end use gives us an approximate emission of 550 Kton CO_2 eq./yr. GHG emission(shown in Figure 7) which is equivalent to 23% of overall emission of the Infrastructure sector (Coenen et al., 2018; Korevaar & Blok, 2018; Kristel, 2016). In 2016, the infrastructure sector used approx. 8300 kton (36%) of asphalt in the Netherlands (Korevaar & Blok, 2018). Bitumen is responsible for 15% of overall GHG emission of the LCA of ZOAB (Rijkswaterstraat, 2018).

[3] This amount of emission was distributed between the material use as 67%, transport sector equivalent to 17% and activities at construction site as 16%(Korevaar & Blok, 2018)

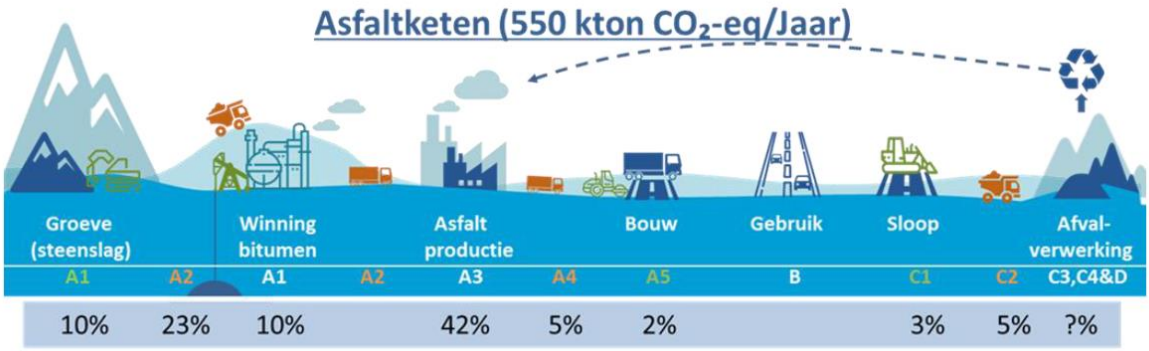

Figure 7 Overview and analysis of the asphalt chain (Korevaar & Blok, 2018)

This thesis aims to determine the potential of lignin as a substitute for fossil bitumen to mitigate GHG emissions (cradle-to-gate) in the asphalt production within the infrastructure sector in the Netherlands, in case for current and 10 years in future. Furthermore, this research looks into the bitumen substitution in lignin by 50% and the emissions resulting from the isolation of lignin upstream. Scandinavia and USA were considered for the feedstock supply because the data was available from those regions and the Netherlands import biomass from those regions. The current research gap along with the fossil bitumen substitution and further reduction in the GHG emissions in the asphalt sector leads to the following sub questions:

1. What is the GHG emission reduction (direct and Indirect) when lignin replaces fossil bitumen in 1 ton of ZOAB (porous asphalt) in the construction of national roads in Netherlands (Cradle-to-road)?
2. What are the GHG emission values when different fuel sources are used within different allocation mechanism to substitute the internal energy demand of the Pulp mill and biorefinery?
3. How much lignin based asphalt could be deployed in the Netherlands in the infrastructure sector in 2030?

   All these sub-questions lead to the main research question:

   What would be the GHG emissions reduction (direct and indirect) if 50% of fossil-based bitumen is replaced with lignin (cradle-to- gate), and how much GHG emission could be reduced in the infrastructure sector with implementation until year 2030 in the Netherlands?

1.4 Scope

The research is going to focus on the use of lignin replaced by bitumen by 50% in asphalt mix (ZOAB). The 50% substitution is taken into scope of this study as previous theoretical study outlined the replacement of bitumen partly by 50% of lignin (van Vliet et al., 2016) as well as roads are constructed in the Netherlands using blend of 50% of bitumen and 50% of lignin by mass (Discussion fossil bitumen and Bio-bitumen, Personal communication, Bergen op zoom, 19 December, 2018). Also, the geographical scope of this study will be limited to the Netherlands, but it could be expanded to Europe or global level depending on the availability of data. This research is going to focus on the cradle-to-factory-gate life cycle assessment (LCA) to assess only one environmental impact of GHG emission (i.e. carbon footprint) of different feedstock supply chain, logistics, isolation of lignin and use in the asphalt mix. The use phase and end-of-life (waste management) are excluded from the analysis.

Lignin Supply market: The Scandinavian and USA lignin market is assessed in this research where the discussion will be on the quantity of supply of lignin (in tonnes/year). The streams of the lignin identified to be used for this research are from Scandinavian Pulp mills and future lignocellulosic biorefinery in the Netherlands using feedstock from USA. Furthermore, other lignin supply streams assessed can be found in the appendix 3.

Lignin extraction process: This paper only assesses the lignoboost technology in Kraft process in the paper mills because it is the dominant pulping method in the world and most of the lignin in the world comes through this process(Benali et al., 2016; Gellerstedt, 2015), and the lignin assessed for this study is from the existing Kraft pulp mills in Scandinavia. For the case of biorefinery, it has two platforms: sugar and thermochemical to convert biomass into energy and fuels. This research will focus on the sugar platform where breakdown of biomass is done into aqueous sugars using chemical and biological means leaving the residue lignin (Vera et al., 2018). The steam explosion technology is assessed for the extraction of lignin and the following data for the GHG assessment is taken from the future lignocellulosic biorefinery in south west of the Netherlands to be built by Biobased delta (Vera et al., 2018).

1.5 Thesis Outline

This section provides with the whole structure of the thesis.

- Chapter 1: Introduces the problem, states the problem definition and discusses the research gap along with the scope of the research.
- Chapter 2: Theoretical section
- Chapter 3: Provides information on the important processes that were used in this research for the lignin isolation.
- Chapter 4: Gives information on the methodologies used for answering the research questions.
- Chapter 5 to 7: Detailed overview of the results. They can be further elaborated into different sections to get a good overview of the structure.
    - Chapter 5: Gives an explanation on the inputs used in this research.
    - Chapter 6: Gives the results of the LCA and the sensitivity analysis. In this chapter the GHG emission of the substitution of the bitumen from two types of lignin are determined.
- Chapter 7: Discussion on the results and their limitations. Also give recommendation for the future research.
- Chapter 8: Gives the conclusion of the result.
- Appendix 1: Lignin
- Appendix 2: Bitumen
- Appendix 3: Lignin supply market
- Appendix 4: Describe the other lignin isolation techniques

2.Theoretical background

This section gives the details of the important concepts used in this research and gives an detailed explanation of the concepts.

2.1 Life cycle analysis

A life cycle analysis is performed to calculate the GHG emissions over the lifetime of the product. According to ISO (2006), the Life cycle analysis outlines the environmental aspects and potential environmental impacts i.e. use of resources and the environmental consequences of releases all through a product's life cycle from raw material acquisition through production, use, end-of-life treatment, recycling and until final disposal (i.e. cradle-to-grave). The results from the LCA can be used to assist for different purposes such as identifying the opportunities on to improve the environmental performance, notify decision-makers, determining relevant indicators of environmental performance, or for marketing purposes(ISO, 2006).

This research uses ISO 14040 guidelines to perform the LCA and is further elaborated into four steps as shown in Figure 8 (ISO, 2006). These four steps are specified as goal and scope definition which includes the product to study and purpose of the LCA. Inventory analysis signify the construction of the model as well as calculation part for the emission and resources used in the life cycle. The impact assessment deals with the indicating impacts on the environment(Baumann & Tillman, 2004). Each of these steps are further discussed below.

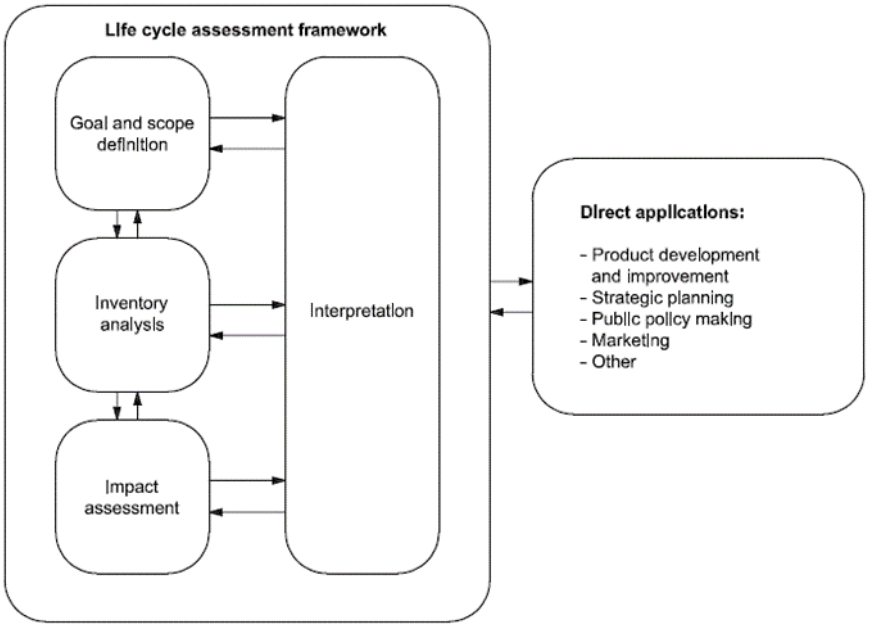

Figure 8 The different steps of an LCA as defined by ISO 14040 (ISO, 2006)

2.1.1 Goal and scope definition

The ISO standard 14041 (International Organization for Standardization, 1998) utilizes the following definition of 'goal': "shall unambiguously state the intended application, the reason for carrying out the study and the intended audience". The goal and scope definition should clearly be defined and be consistent with the intended application of defining the goal of the LCA, the production system, the

functional unit, the system boundaries, the allocation procedures, LCIA methodology and the impact categories(The International Standards Organisation, 2006).

LCA's can be divided into two parts attributional LCA's (ALCA) and consequential LCA's (CLCA). ALCA provides knowledge on the imprints of the processes used to produce, consume and dispose of a given product, but does not provides information on the indirect effects arising from the changes in the output of a product(Murphy, 2008). However, according to Murphy (2008), CLCA studies the consequence of change in the level of a output, consumption and disposal of a product including effects both inside and outside the life cycle of the product. In other words, CLCA is not limited to the cradle-to-grave boundaries of a product for the potential environmental consequences due to change in a process. This can be further elaborated as besides the direct emission from the life cycle of the product, the changes in the emission due to life cycle of the other products (indirect) are included (Benali et al., 2016). Therefore, reliable assumption needs to be made for the forecasting, modelling and quantifying impacts to avoid large uncertainties. LCA usually consist of the several environmental impacts (GHG emissions, eutrophication, acidification, human health, resource depletion) to give a detailed overview of the environmental impact over the life cycle of a product. This research only considers only one impact i.e. the GHG emissions, while others are excluded.

Furthermore, in addition to the LCA approach which usually consist of multiple environmental issues, single issue LCA approaches have been developed lately, which includes carbon foot printing and water foot printing. The approaches used here mostly focus on life cycle perspective using one impact category. In acknowledgment to global need for transparency in the GHG emissions of products, several carbon foot printing standards have been developed or are still under development which are GHG Protocol and the draft ISO 14067.(Goedkoop et al., 2016)

The allocation method influences the result and should be selected with proper reasoning. The allocation is the partitioning the input or output flows of a process or a product system between two or more product system(ISO, 2006). The allocated inputs and outputs of a unit process sum shall be equal to the sum of inputs and outputs of the unit process before allocation(The International Standards Organisation, 2006). The energy allocation method for the useful output is based upon their energy values. This method is most suitable for fuels as they are mostly used for their energy content. This method is mostly preferred by the European commission because it is easy to apply, predictable over time, and the results are usually easy to compare with other substitution methods (*Renewable energy Directives*, 2009). Other allocation method is the mass allocation which is used in the biorefinery based on the biochemical composition of different feedstock cellulose, hemicellulose and lignin(Vera et al., 2018). This method allocates the impact based on the mass to each output. Also, Economic allocation which is based upon the economic value, normalizes all the products to a common basis regardless of the purpose of their use(M. Wang et al., 2011). Moreover, the allocation method can be categorized also as system expansion method or the displacement method. This allocation provides detailed information on the actual emissions producing several products from the pathway. For this method, the emissions that are displaced by the use of lignin are subtracted from the overall emissions of the asphalt production.

2.1.2Life Cycle Inventory Analysis (LCI)

In this process data is compiled and required calculations are done to quantify the relevant inputs and outputs of a product throughout its life cycle. The data to be included in the inventory should have

qualitative and quantitative data for each unit process that is included within the system boundary(The International Standards Organisation, 2006).

2.1.3Life Cycle Impact Assessment (LCIA)

This section of LCA aims to evaluate the magnitude and significance of the potential environmental impacts of a product(ISO, 2006). The results of the LCI will be used to calculate the overall GHG emissions(The International Standards Organisation, 2006). The GHG emissions is determined by the multiplication of the obtained emission by their emission factor with clearly stating all the assumptions used(IPCC, 2006; The International Standards Organisation, 2006). The GWP is one of the many categories that the LCA calculates apart from eutrophication, acidification, human health, resource depletion to give an overview of the environmental impact. In the LCIA, substances can be sorted out according to their impact on the environment (Golsteijn, 2014).

In the past few years, there have been growing concern about lack of consideration for temporal aspects of green- house gas (GHG) emissions in life cycle assessment (LCA) and carbon footprint analysis (Levasseur et al., 2013). Global warming potential which are developed by IPCC are expressed in the cumulative radiative forcing over a given time horizon (Forster et al., 2007; IPCC, 2006). The current LCA methodology are not accounted to provide any value to the temporary carbon storage, as the amount of carbon that is sequestered would be subtracted from the emission occurring at the end of storage period to deliver a net zero emission (Levasseur et al., 2012). The IPCC (2006) guidelines for national GHG inventories considers that carbon which is in biomass is released when harvested, following a stock change approach for which net emissions are estimated by calculating the net changes in carbon stocks of a biomass carbon pool over time. This approach contradicts the flow approach, where emissions are estimated by directly considering the GHG flows to and from the atmosphere (IPCC, 2006). Under the IPCC guidelines, to avoid double counting if the biogenic carbon is released later in the life cycle, for e.g. combustion of bioenergy, the related CO_2 emissions are not accounted for (Levasseur et al., 2013). This assumption about biomass carbon neutrality which is widely used is progressively criticized (Searchinger et al., 2009). The biomass combustion causes more GHG emissions per unit of energy compared to the use of fossil fuels, thus creating a carbon debt which is paid down when biomass starts to grows up and sequesters carbon from the atmosphere (Levasseur et al., 2013). However, by the time the biomass grows up, the additional amount of carbon emitted by the replacement of fossil fuels with bioenergy creates an impact on climate, especially for wood, because forests often take decades to mature (Levasseur et al., 2013). In LCA, impact assessment often excludes biogenic CO_2 emissions, because it assumes that the same amount of CO_2 was previously sequestered by biomass, giving a net zero emission (Frischknecht et al., 2007; Guinée, 2002).

Characterization factors are used to convert the GHG emissions into CO_2-eq emissions. The substances are multiplied by characterisation factor which reflects their relative contribution to the environmental impact (Golsteijn, 2014). To derive the mass value in the CO_2-eq., the GHG emission is multiplied by its characterisation factor (in kg CO_2-eq/kg GHG)(T. M. Bijleveld, 2016b). The characterisation factors were determined by IPCC and they account for the radiative efficiency and the lifetime in the atmosphere of GHGs (Stocker et al., 2013). The time frame used was Global Warming Potential (GWP) over a 100-year time frame. The characterisation values are presented in the Table 2.

Table 2: The Global warming Potential over a 100-year timeframe of the three main greenhouse gases (IPCC, 2014)

GHG	GWP
CO_2	1
CH_4	28
N_2O	265

2.1.4 Interpretation

This phase is used to interpret the results of the Goal and Scope, LCI and LCIA. This apprehension will lead to the conclusion, however within this the limitation of the LCA will be explained and recommendation will be provided (The International Standards Organisation, 2006).

2.2 Monte Carlo analysis

A Monte Carlo analysis is a statistical technique for analysing uncertain scenarios and providing probabilistic analysis of different situations (Raychaudhuri, 2008). The impact of the uncertainty of the key influential parameters can be assessed with the Monte Carlo analysis. It can be used to perform sensitivity analysis on the changes in the input variables for the desired outputs. A sensitivity analysis can determine uncertainties and stochastic nature among the decision variables who have largest influence on the results(Belvárdi et al., 2012). The Monte Carlo analysis is performed in the @Risk program which also includes sensitivity analysis. For the analysis, the key parameters should be identified, which can be the impact of the allocation mechanism in this case study.

3 Tree (Lignin) to road

In the previous chapter, the theories that are relevant in this thesis were discussed. This chapter focus on promising lignin sources and the processes that are most suitable for lignin isolation in a form suitable for substituting fossil bitumen in the asphalt mix.

3.1 Lignin sources and extraction techniques

The two sources considered for isolating lignin in this thesis are: Paper/pulp mills and lignocellulosic biorefineries. Both of them have different isolation techniques, and within each source also different techniques exist. The various technologies for the extraction of lignin from biomass depends on the process. The structure of the lignin differs between plant sources within the types of lignin (Strassberger et al., 2014; van Vliet et al., 2016). Further information on lignin can be found in Appendix 1.

The pulp/paper mills have the dissolution of lignin from wood in technical processes such as Kraft and sulfite pulping which results in the formation of cellulosic fibres used for packaging, printing papers and tissues(Gellerstedt, 2015). The biorefinery focus on the sugar platform where breakdown of biomass is done into aqueous sugars using chemical and biological means leaving the residue lignin(Vera et al., 2018). The fermentable sugars can be further processed to ethanol, aromatic hydrocarbons or liquid alkanes by fermentation, dehydration and aqueous-phase processing, respectively (Xiu et al., 2011).

3.1.1 Paper/pulp mills

At mills, different technologies are used to produce pulp, black liquor and lignin. The pulping process that is used affects the characteristics of lignin. The different pulping techniques are listed here, and their explanation cab be found in appendix 4.

1. Kraft process
2. Sulphite process
3. Alkaline process
4. Solvent process

The Kraft process is most relevant for this thesis as it is the largest producer of the lignin in the world, and also the isolation techniques that are used to isolate lignin from the waste stream of the Kraft process (black liquor)(Benali et al., 2016; Gellerstedt, 2015). The techniques used to isolate lignin are catalogued below and briefly explained in the appendix 4. The isolation technique which is the focal point of the Kraft process to extract lignin is Lignoboost process (briefly explained in the section 3.2).

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

3.1.2 Lignocellulosic biorefineries

In the lignocellulosic biorefineries, several methods exist to process lignocellulosic biomass into 5- and 6-carbon sugars and lignin. Through further downstream processing, the sugars can be converted into biobased products including fuels (ethanol) and biobased materials such as polylactic acid (PLA)(Vera et al., 2018). The most common methods in the lignocellulosic biorefineries, to isolate lignin from biomass are: steam explosion, dilute acid pre-treatment and alkaline hydrolysis pre-treatment (Kumar et al., 2009).

1. Steam explosion
2. Dilute acid pre-treatment
3. Alkaline hydrolysis pre-treatment

These three methods are principally relevant. However, this study focus only on the steam explosion (briefly explained in section 3.3) technique as the Biobased delta from which the data is used for the calculation of the results is going to use the same technique in their biorefinery in the Netherlands. The others are briefly explained in appendix 4.

3.2 Kraft pulp/paper mill and lignoboost

The Kraft process is the primary process for pulping in the world consisting of both chemical and mechanical steps. The Kraft process uses sodium hydroxide (NaOH) and sodium sulphide (Na_2S) as shown in Figure 9 (Benali et al., 2016; Tran & Vakkilainen, 2016). Kraft Lignin usually contain less than 1 or 2% of sulphur irrespective of the high sulphur environment involved in the Kraft process. The mass of the Kraft lignin can assist in its own isolation from the black liquor in the pulp/paper mill (Laurichesse & Avérous, 2014). The Kraft process includes heating and pre-impregnation of wood chips with uniform distribution of cooking liquor (Mehdipoor, 2011). The wood chips are then treated at constant temperatures of 160-170 ˚C under alkaline conditions and pressure in the presence of sulphide or bisulphide (Mehdipoor, 2011). This chemical treatment usually dissolves lignin and cellulose fibres together. It is usually processed in digester system, batch or continuous where batch is mostly used (van Vliet et al., 2016). The

content of the batch digester is transferred to the blow tank and then to pulp washers, where it processes through washing and bleaching. Then, it is pressed and dried into market grade pulp to be used(van Vliet et al., 2016; Wood Products Industry 10.2-1, 1995). The Kraft process yields about 10 tons of weak black liquor or about 1.5 tons of black liquor dry solid for the production of a ton of pulp (Tran & Vakkilainen, 2016). The black liquor which usually contain lignin is burnt in the boiler to produce steam and then it is used in turbo generators to produce electricity and natural gas is used for the generation of heat for operating the plant(Laurichesse & Avérous, 2014; Tomani et al., 2011). When the lignin is isolated completely for the use in the asphalt mix, the other sources of energy are required to fulfil the energy demands of the Paper mill to operate as lignin is used for the internal energy demand. The lignoboost process is used to extract lignin from the black liquor using the CO_2 to reduce the pH of black liquor which is taken from the evaporators of recovery section (Axegård et al., 2011; T. M. Bijleveld, 2016b; Fatehi & Chen, 2016). The lignin precipitated slurry is mixed with acidic filtrate and washed (T. M. Bijleveld, 2016a; Fatehi & Chen, 2016). Thus, generating small uncross linked lignin precipitates which is crushed and dried to obtain low ash content pure lignin powder(Tomani et al., 2011). Figure 10 shows a block diagram of the lignoboost process. The sodium hydroxide as shown in Figure 9 is used for neutralizing the recycled stream from the lignin isolation process to the evaporators, while sulphuric acid as shown in Figure 10 is used for washing the lignin cake(Benali et al., 2016; T. M. Bijleveld, 2016a; Fatehi & Chen, 2016).

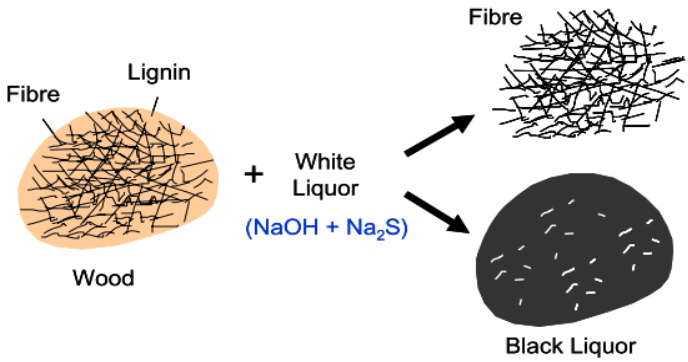

Figure 9 Kraft pulping process (Benali et al., 2016; Tran & Vakkilainen, 2016)

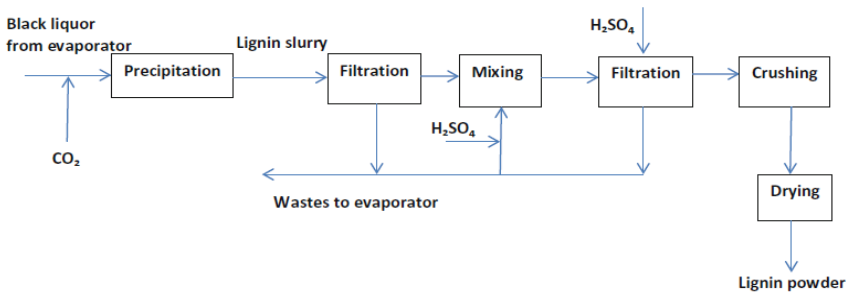

Figure 10 Block diagram of Lignoboost isolation processes(Fatehi & Chen, 2016)

3.3 Lignocellulosic biorefinery- Steam explosion

In the biorefinery, the steam explosion method will be used for the treatment of lignocellulosic biorefinery (Kumar et al., 2009). With this method, the biomass is infused with steam at 200°C or more under high pressure(Kumar et al., 2009). This process will liberate the fibres of biomass into three different parts: cellulose, hemicellulose and lignin as shown in Figure 11 (Vera et al., 2018). The enzymatic hydrolysis is used to process hemicellulose and cellulose into 5- and 6- carbon sugars(Vera et al., 2018). The xylose can be isolated from lignin and cellulose by the split-up process. The xylose is contained in the liquid filtered part which is further neutralized with NH4OH. The xylose is fermented into ethanol when diammonium phosphate (DAP) and corn steep liquor (CSL) is added to the neutralized liquid(Vera et al., 2018). The lignin can be extracted through reaction of fibrous material with aqueous or alkali solvent (NA2CO3) (Lange et al., 2015). The lignin from softwood is more modified and less reactive than from hardwood lignin (Shevchenko et al., 1999). The lignin produced is incinerated in the combine heat and power plant to produce steam and electricity for operating the biorefinery(Vera et al., 2018). The lignin isolated through this process should have dry and fine particles for the use in the asphalt mix. The complete lignin isolation constitute a scenario, where the other sources of energy such as natural gas or biomass needs to be taken into account to supplement the internal heat and energy demand of the refinery.

The steam explosion process is used for the isolation of lignin as lignin produced after steam explosion has low molecular weight and higher solubility than Kraft lignin in organic solvents(Lange et al., 2015). The lignin is almost sulphur free and the other advantage is the recovery of the high pressure stream and to use it for the processes downstream as an energy source (T. M. Bijleveld, 2016b; Bruijnincx et al., 2016; Gerbrandt et al., 2016; Shevchenko et al., 1999).

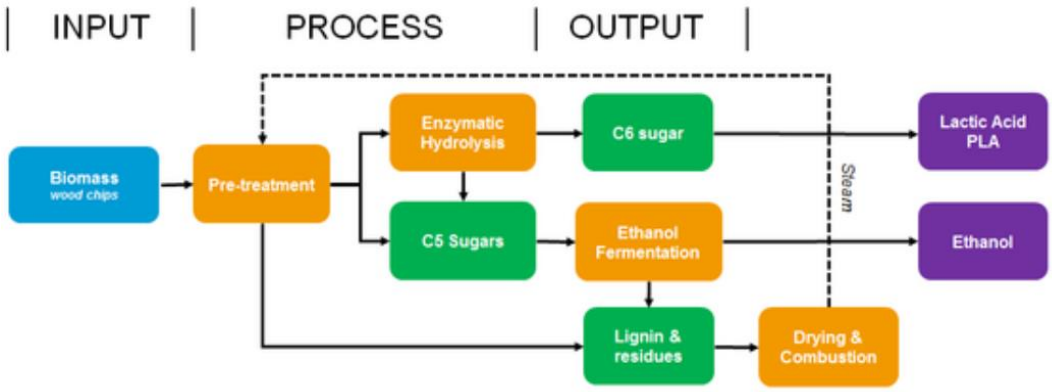

Figure 11 Biorefinery process (Port of Rotterdam, 2016)

4. Methods

In section 4.1, the method to obtain information regarding the lignin supply market. In section 4.2 description about the direct and indirect emission from the substitution of lignin (baseline case) is acquired by the LCA. Section 4.3 describes alternative to the lignin extracted from the Pulp mill and biorefinery for the heat and electricity generation assessed with LCA whereas section 4.4 gives detailed overview on the data collection methods.

4.1 The lignin market

The lignin supply market is assessed on the basis of the literature research. The quantity, location, feedstock type and separation process for the various lignin streams is assessed to get an overall view of the lignin supply chain. Based on this assessment the ideal lignin stream can be found to be used for the replacement of the fossil bitumen in the asphalt mix. This is mostly determined on the basis of the sulphur content, quantity and location of the lignin. This study focus on the Europe for the geographical scope of the Kraft process as most paper mills are located in the Scandinavian region and for the biorefinery, USA as the most of import of the biomass in the Netherlands comes from the brazil and the USA(T. M. Bijleveld, 2016a; Vera et al., 2018).

To assess the asphalt mixtures with the lignin, the ZOAB (porous asphalt) is assessed. This is mostly viable option for the assessment of the GHG emissions of lignin use in asphalt mix (Discussion fossil bitumen and Bio-bitumen, Personal communication, Bergen op zoom, 19th December, 2018).

4.2 Life cycle GHG assessment

This section focus on the LCA methodology to assess detailed direct and indirect GHG emission of asphalt mixture when fossil bitumen is replaced by lignin for two possible scenarios. First scenario provides details about when marginal amount of lignin is extracted from the Kraft pulp mill and biorefinery to be used as substitution of fossil bitumen and the remaining lignin is incinerated as fuel to provide energy in the respective plants of mill and refinery. The second scenario includes isolating all the lignin from the biorefinery and Kraft mill in replacing the bitumen and thus using either natural gas or biomass for the supply of heat and electricity in the respective refinery and pulp mill. The section 2.1 discusses about the theoretical background of LCA.

The following sections explains the methodology regarding the goal and scope definition of the LCA. They describe the LCA either CLCA or ALCA used to achieve the goal, the system boundaries, the functional unit and the allocation method. The following section is related to the LCI and methods used for the inventory analysis of each life cycle stage.

4.2.1 Goal

The goal of this LCA is to assess the direct and indirect GHG emissions associated with the use of lignin from the Kraft pulp mill and biorefinery in the replacement of fossil bitumen up to 50% in the asphalt road mixture (ZOAB). This research glance upon the change in the use of lignin from lower grade fuel to replace the fossil bitumen, so a consequential LCA was performed. This incorporates the effect of supplanting the lignin with an alternate fuel to create the heat and electricity that used to be produced from the lignin, so a consequential LCA was performed to calculate the GWP.

The research looks at the prospect of only the GHG emissions in the LCA. Since, this gives us the first-hand information on the emission of the use of lignin in the asphalt mix and whether if the emission

caused by the alternate fuel use in the Kraft pulp mill and biorefinery is less than or equivalent to the emission reduction caused by the replacement of the fossil bitumen by lignin.

4.2.2 System boundaries

The system boundaries that apply to this research in brief are shown in Figure 12. These boundaries gives an overview of the direct and indirect emission when lignin is isolated and used in the asphalt mix. The system is applicable to both the possibility of Kraft lignin and steam explosion biorefinery lignin. For more detailed overview of the system boundaries, Figure 13 and 14 showing the flow chart of Kraft process and SE biorefinery. The co-products are also included in the LCA. The lignin pre-treatment regards the processes that are required to obtain a lignin requisite for the Asphalt mix, which includes isolation from black liquor and also drying and grinding of a lignin sludge(T. M. Bijleveld, 2016a; Vera et al., 2018).

The considerable impact of removing the lignin from the source were included, but the other GHG emissions of the source also allocated to the main output which is not lignin. These emission fall outside the scope of system boundaries.

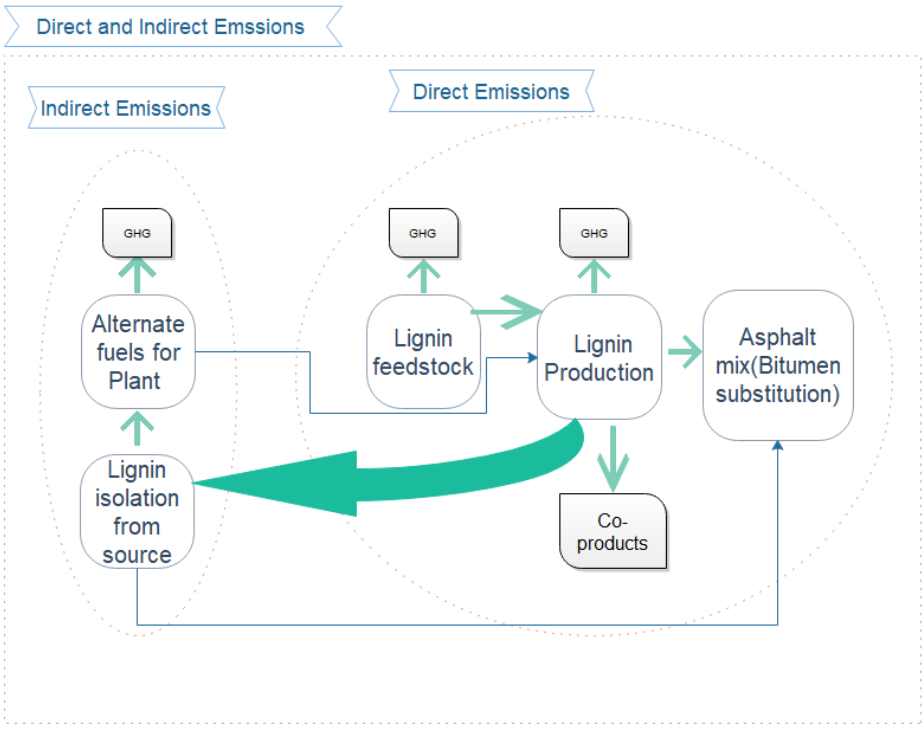

Figure 12 The system boundaries of the LCA that was performed in this research. The inner left system boundaries comprises the process that have indirect impact on the GHG emissions due to the isolation of lignin. The inner-right system boundaries involves all the process of LCA producing direct GHG emissions

4.2.3 Functional Unit

The functional unit that is used in this study to express the GWP associated with the replacement of the fossil bitumen with lignin in the ZOAB (porous asphalt) in the Netherlands is kg CO_2 eq./tonne of ZOAB. This describes the amount of the GHGs per ton of the final product which is easily comparable with other asphalt mixes. The functional unit is not described as CO_2 eq. emissions/ km of expressway quality road constructed as it would be impossible to assess the quantity of asphalt used in a km of road and compare with the other types of roads. The intermediate results were calculated in CO_2 eq. emissions/t lignin, then converted to required functional unit kg CO_2 eq./tonne of ZOAB.

4.2.4 Allocation Method

The valuable outputs are allocated on the basis of the mass, energy and price as the bitumen in the asphalt mix is replaced by the lignin. The greenhouse gases are allocated to the outputs which are used in the asphalt mix. In the case of complete isolation of lignin, to supplement the internal energy demand of the Paper mills and Biorefinery, the different fuel sources are used within these respective allocation mechanism.

4.2.5 Life Cycle Inventory

The life cycle inventory analysis is preformed after the goal and scope definition on both suitable use of lignin in the ZOAB layer. The data was collected through the scientific literature and interviews with experts in the field. There was a lot of variation in the values of in- and outputs of the process due to the use of different articles, due to which most suitable or average value was used. Mass and energy balances of the complete system was created, to ensure balance in the incoming and outgoing of the mass and energy.

The flow chart for the two cases Kraft lignin process and Biorefinery lignin which are shown in the respective Figure 13 and 14 with the system boundaries applied to the research. The routes of the lignin extraction from tree to the use in the road is the main technological criteria that is used in this research. Firstly, the exact technology to be used has to be defined, which includes all the sub-processes as well as energy and material flows. The baseline case used in this research came from the different scientific articles which assumes different scenarios. The route was subdivided into the following stages for convenience:

1) Lignin Isolation
   Constitute the in- and outputs related to the lignin isolation from the Kraft mill and steam explosion biorefinery.
2) Indirect effects
   If the extraction of lignin from Kraft mill or lignocellulosic biorefinery caused a change in their energy balance, there is indirect effect pertaining to this which is explained in this section.
3) Pre-treatment
   Constitute the in- and output of the necessary grinding, drying and feed handling of the lignin before it is suitable for the use in the asphalt mix.
4) Asphalt mix
   This step assess the substitution of the lignin in the asphalt mix by replacing the fossil bitumen which is prepared for road construction.
   Each of these stages with the inclusive process was discussed in detail in this section.

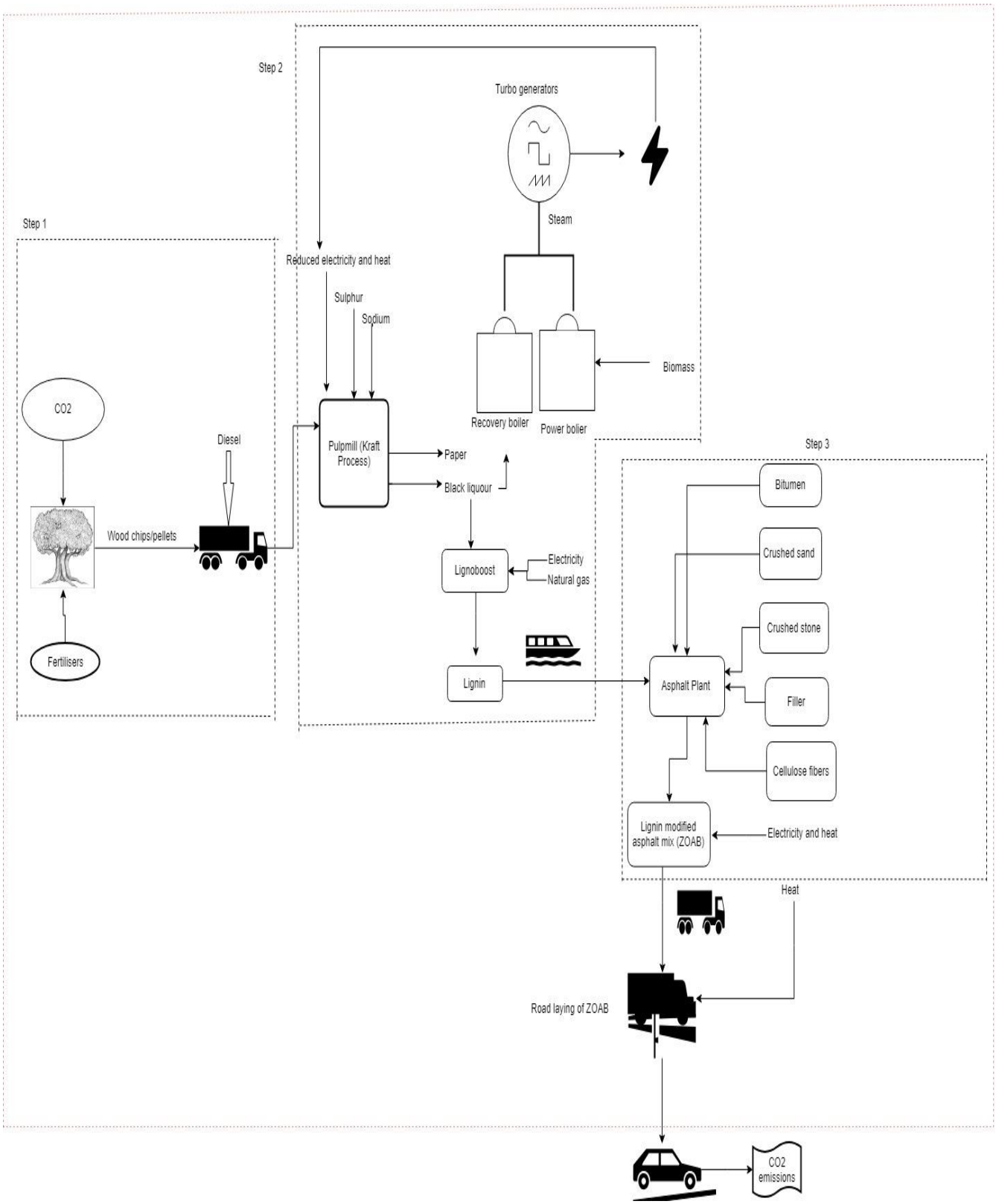

Figure 13 A flow chart of the material and energy flows for the lignin isolation from Kraft mill and substituting fossil bitumen in asphalt mix with the system boundaries

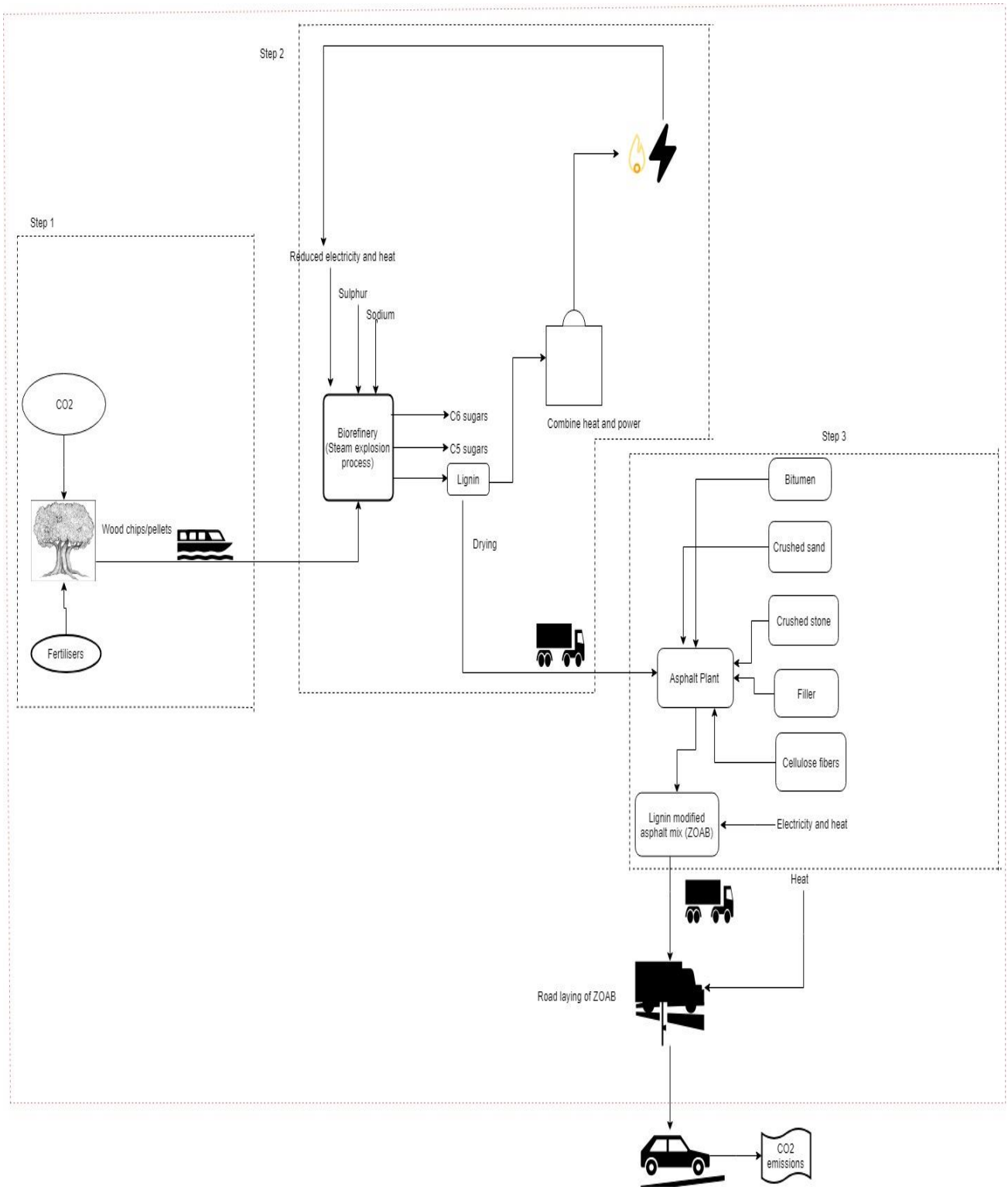

Figure 14 A flow chart of material and energy flows of lignin isolation from SE biorefinery and substituting fossil bitumen in asphalt mix with the system boundaries.

Lignin isolation

Kraft lignin isolation

The removal of lignin from the black liquor stream with the lignoboost process estimating half of the lignin is removed is assumed, construing to 300kg of lignin per tonne of pulp production(T. M. Bijleveld, 2016a). The extraction of lignin up to this amount do not have any impact on the properties of black liquor to be used for heat production, except there is a slightly lower LHV value. This means that the black liquor which is incinerated in the recovery boilers to produce steam and electricity, with less lignin now energy produced is low(T. M. Bijleveld, 2016a; Manninen, 2010). The other technologies that could be used for the lignin isolation is Lignoforce and SLRP, but those are still not commercially viable(Benali et al., 2016). The lignoboost process which uses CO_2 to isolate lignin is used in this study. Since, the lignin is a biogenic product, and it is composed of the Carbon, oxygen and other chemical substances. There is a fixed carbon sequestered in the lignin which is taken as negative emission in the calculation of ZOAB (porous asphalt) modified with lignin.

Steam explosion lignin isolation

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

Indirect impact

Kraft lignin

It is necessary to understand that the lignin isolation from black liquor does not affects the Kraft paper/pulp mill significantly, as black liquor is incinerated for internal energy demand. However, due to isolation of lignin there is a lower LHV value, meaning black liquor can be still burned for operating the recovery boilers but less energy is produced (Manninen, 2010). Since, there is reduction in electricity production, it is substituted by electricity from national grid, in this case Scandinavia as most of the Paper/pulp mill in Europe is in Scandinavia and the heat production is maintained the same as without lignin isolation. The additional energy that is required by the evaporators for the steam production from the black liquor is assumed to be obtained from the combustion of natural gas. Other possible choice is forest residues like bark or wood chips. Natural gas is considered most viable because of its availability and economical price in the Netherlands and Scandinavia (T. M. Bijleveld, 2016a; Eurostat, 2018; Karatzos et al., 2014).When lignin is completely isolated, additional natural gas can be used for the heat and power; or additional biomass could be used for the generating the same amount of energy required for the mill. Due to these scenarios, there is indirect impact on the sodium which is recovered from the electrostatic precipitator and bleaching plant (make up sodium) is enough to compensate for the sodium hydroxide required for neutralizing the recycled stream which is already included in the LCA inventory (T. M. Bijleveld, 2016a). The transport distance for the lignin to the Netherlands from the Scandinavian region is assumed to be around 2800 km and inland shipping route is used for the transportation (Benali et al., 2016; T. M. Bijleveld, 2016a; Manninen, 2010).

Steam explosion biorefinery

The lignin is generally used to supplement the heat and power in the lignocellulosic biorefinery. When the lignin is isolated, and used to mix in the asphalt, the biorefinery will have to substitute removed lignin just as in Kraft process for the CHP plant. The internal energy demand can be compensated by natural gas as it is easiest and cheapest option (Karatzos et al., 2014). Other possibility includes the used of additional biomass or extracting the marginal amount of lignin for use in asphalt and rest for energy in refinery (T. M. Bijleveld, 2016a; Vera et al., 2018).

Pre-treatment process

Kraft lignin pre-treatment

The transport of the lignin after the grinding and drying of the lignin which was already included in the Lignoboost process to the Netherlands from the Scandinavia region. This lignin transported to the Asphalt plant where it is mixed with the asphalt mix before laid off.

Steam explosion lignin pre-treatment

The moist steam explosion sludge is first pre-treated to avoid yield losses and reduce heat requirement. The pretreatment includes of mechanical grinding and drying, to get the dry and fine lignin particle for the use in the asphalt mix.

Asphalt Mix

This section provides detail on the component used in the ZOAB layer (porous asphalt) as shown in Figure 13 and 14 (Rijkswaterstraat, 2018; Vos-Effting et al., 2017). The components mainly includes fossil bitumen, crushed sand, crushed stone, cellulose fibers and filler. This study takes into account the substitution of the fossil bitumen (50%) by lignin which is supplied by the Kraft mill and biorefinery (Discussion fossil bitumen and Bio-bitumen, Personal communication, Bergen op zoom, 19th December, 2018; van Vliet et al., 2016). The asphalt mix is assessed to calculate the possible GHG emissions mitigation when lignin is used.

4.2.6 Life cycle Inventory Assessment

In this section, of the Life cycle Impact assessment expressed in GWP are calculated on the basis of all the relevant in- and outputs in the LCI in the required functional unit kg CO_2 eq./tonne of ZOAB. This leads to the overall GHG that were associated with this research. Thus the results are calculated first on the basis of allocation. Furthermore, within those allocation different source of energy such as natural gas, additional biomass is used for supplementing the heat and power required when we extract all the lignin from paper mills and biorefinery.

The baseline case within first scenario in this research for the Kraft process and biorefinery uses mass allocation in which the lignin is marginally extracted and rest is used for the internal heat and power generation, along with electricity from the grid and additional natural gas to maintain the heat production. Figure 13 which is subdivided into three parts showing the flow chart of Kraft process using the Lignoboost process for lignin isolation. Figure 14 which is also subdivided into three parts shows the flow chart of the biorefinery which uses steam explosion process for the lignin isolation. The first part or step introduces the feedstock of the pulp/paper mill and biorefinery. The second part explains the main process involved in the lignin production such as Kraft process (lignoboost) for paper/pulp mill and steam explosion process for biorefinery. All the allocations are done in this section, and in the situation of complete lignin isolation (second scenario) the use of additional energy sources is included in the calculation of GHG emissions. The third part focus on the asphalt production where the lignin from the previous step transported to asphalt plant is used in substituting the fossil bitumen in the ZOAB (porous asphalt) and mixed with other components such as crushed sand, crushed stone, filler material and cellulose fibres in production of ZOAB layer. Since, the baseline case uses mass allocation, the other cases are calculated by using the Economic allocation and Energy allocation when the lignin is marginally extracted and the rest is used for internal energy demand. However, in the case of when the lignin is totally extracted as output, there is requirement of additional fuel sources to supplement heat and power generation for operating the mill and refinery. These fuels sources are biomass or natural gas which are

used within the given allocation (mass, economic or energy) to create other cases to calculate the GHG emissions of the ZOAB. This way the research studies the different allocation along with different fuel sources.

The results calculated in this research are rounded up to approximated values as there is a large uncertainty in the input values due to the theoretical input values of the refinery as well as the chemicals used in Kraft process have a large range in their input values.

4.2.7 Uncertainty and Sensitivity Analysis

For the LCA, the uncertainty and sensitivity analysis of the results were done through Monte Carlo simulation which use @Risk 7.5 program in the Excel. The uncertainty analysis is done on the result of the GHG emission of biorefinery lignin ZOAB when we use different feedstock, for example Wood pellets from USA and Wood chips from Baltic region. However, the baseline case uses wood pellets from USA as feedstock (Vera et al., 2018). Therefore uncertainty analysis is done at @Risk program with 50000 iterations to see the ranges of the GHG emission with the change in the feedstock.

The sensitivity analysis is also performed using the @Risk program with 50000 iterations to calculate the probability of final answer as different allocation mechanism are used in the calculation along with different fuel sources for the internal energy demand, to provide strong base for the stochastic calculation(Belvárdi et al., 2012). The sensitivity analysis is done on the GHG emission of the Kraft lignin ZOAB to calculate the impact of the chemicals such as NaOH and H_2SO_4 which has large range in their input values.

4.3 Data Collection methods

4.3.1 Literature research

The information gathered through the literature research was used in this research. The sources used to obtain data were from the company with which NDA was involved AKC (Asfalt kennis centrum) and Biobased Delta. Also, the scientific and non-scientific articles were also involved in sourcing the data. The CO_2-eq emission factors of the energy substituents such as biomass were found from the EcoInvent 3 database. The natural gas emission factor was obtained from the IPCC (2006) guidelines, where the default values were used. The natural gas heating value used here is 35 MJ/m3 and efficiency factor of 56.6 kg/GJ (Coenen et al., 2018; IPCC, 2006). The emission value for the feedstock (wood pellets) to be used in the biorefinery is obtained from the data provided by Vera et al (2018) which is a previous research for the Biobased delta, approx. 0.250 kg CO_2 eq./ kg of wood pellets. For the Kraft mill, the emission value of feedstock (wood chips) is taken from Scandinavia which is from EcoInvent 3 database. The emission values of chemicals and electricity from the grid used in the calculation are taken from the EcoInvent 3 database. The calculations are done in the SimaPro, which uses EcoInvent database .The Lignin values for the Kraft mill and biorefinery were obtained from the research by T. M. Bijleveld (2016b) and Vera et al (2018) for the assessment of ZOAB expressed in GWP (Global warming potential).

4.3.2 SimaPro

The some inputs were obtained from the EcoInvent 3 database and then used with other inputs from the other scientific resources and interviews. These data were used in the model calculation in SimaPro v8.5.2.

5. Input Data

The assumptions are obtained from the different scientific articles and the interviews conducted with the companies involved in this project. This section gives an overview of the input data that leads to the calculation of the results.

The flowcharts shown in Figure 13 and 14 are subdivided into three parts which can be categorised as feedstock cultivation, lignin production and asphalt production. The input values are obtained from these parts of the flowchart and are modelled in SimaPro v8.5.2 and the life cycle assessment expressed in GWP is calculated and shown in the result section.

Feedstock cultivation (Step 1)

This section gives details on the feedstock cultivation and transport to the Pulp/ Paper mill and biorefinery, which includes the harvesting of the softwood like spruce and pine for the Pulp mill and stemwood for the refinery (see also Figures 13 and 14). (Valmet Media, 2016; Vera et al., 2018). Softwood (spruce and pine) is processed into wood chips in Scandinavia and transported to a nearby Pulp/ Paper mill to be further processed. Stemwood is harvested in the USA and processed into wood pellets and transported by shipping to the biorefinery in the south-west of the Netherlands for further conversation into sugars and lignin. Wood pellets are used due to their high heating value, higher bulk density, better handling, transport, storage and grindability characteristics. GHG emissions of the feedstock cultivation and supply for wood chips in Scandinavia is taken from the EcoInvent 3 database and for the wood pellets from USA which is based on the data provided by Vera et al (2018) as a previous study for the Biobased delta. The carbon content in the softwood used as feedstock for the Kraft process is 63-66 wt% where 66 wt% is used in the calculation of the carbon stored in lignin (Tomani, 2013). The carbon content in the stemwood used as a feedstock for the refinery is 58 wt% (Pakdel et al., 1992).

Lignin Production (Step 2)

This section provides information on the flow chart of pulp/paper mill and biorefinery for the lignin production as seen in Figure 13 and 14, where different allocation mechanism and different fuel sources are used and GHG emissions are assessed on the basis of it. If the complete lignin isolation occurs, then the internal heat and power demand is substituted by the use of the alternative fuel sources like Natural gas or biomass. The changes here impacts the results of the GHG emissions(kg CO_2 eq./tonne of ZOAB) of the ZOAB layer with use of respective lignin sources.

Asphalt production (Step 3)

This section describes the asphalt production as shown in Figure 13 and 14 when the lignin isolated from the previous step is transported to the asphalt production plant and then it is mixed with the other components such as bitumen, crushed stone and sand, cellulose fibres, fillers which are required for the ZOAB(porous asphalt) regular layer. The LCI data for the bitumen and other filler material (Sand, stone, fibres, filler medium) are used in the SimaPro modelling to calculate GHG assessment (E. Keizer, TNO, Personal communication, 30 January, 2019; Eurobitume, 2012). In this study, the lignin is used to substitute 50% of bitumen as previously studied (van Vliet et al., 2016), and also some road are constructed in the Zeeland-province as well as in the Wageningen University using the same composition of lignin and bitumen (Discussion fossil bitumen and Bio-bitumen, Personal communication, Bergen op zoom, 19th December, 2018 ; Rijkswaterstraat, 2018 ; Vos-Effting et al., 2017 ; WUR, 2015). The input required for the calculation of the GHG assessment of 1 ton of the ZOAB regular and ZOAB with the lignin is shown in the Table 3. The use of lignin has advantage in comparison to the fossil bitumen such as

reduction in the asphalt mix temperature by 25-40 °C and natural gas use by 2 m3 which could reduce the impact of GHG emission along with reduction in the fossil bitumen use (Buijs, J. Personal communication, 24 January, 2019).

Table 3 Input for 1 ton of ZOAB mix (porous Asphalt) and 1 ton of ZOAB with lignin (Buijs,J., NTP Infra Hattem, Personal communication, 8 January, 2019; Rijkswaterstraat, 2018; Vos-Effting et al., 2017)

Material	Raw material (kg)	Utilities	Raw material (kg)	Utilities
Anti dripping agent	2		2	
Lignin	0		26	
Bitumen 70/100	52		26	
Crushed sand	43		43	
Crushed stone	852		852	
filler medium type wigro 60k	51		51	
Diesel		0.117 litre		0.117 litre
Electricity		13.249 kWh		13.249 kWh
Natural gas		9 m3		7 m3
Temerature required for asphalt mix		170-180 °C		130 °C

5.1 Kraft Lignin input

This section gives an overview of the in- and outputs used in the life cycle assessment for calculating the GHG emissions of Kraft lignin, based on lignoboost process. The flow chart of the Kraft process (Figure 13) subdivided into three parts explained briefly above. The 1st part gives an overview of the feedstock from Scandinavia (softwood pulp from spruce and pine) (Valmet Media, 2016), emission value is from EcoInvent 3 database in SimaPro. The 2nd part mentions the lignin production(T. M. Bijleveld, 2016b), some amount of lignin isolated substitutes the internal energy demand of the plant and remaining is exported by inland shipping (EcoInvent database) to the Netherlands for mixing in the asphalt. Additional amount of electricity from grid and natural gas for heating is required (Manninen, 2010). The Kraft process produces 90-95% solid content black liquor, assuming the black liquor is extracted from the evaporators at 40% lignin of which 50% is removed(T. M. Bijleveld, 2016b; Manninen, 2010). The lignin transported to the asphalt plant can be seen in part 3, where it is mixed with bitumen and other components to form the ZOAB (porous asphalt).

For the baseline case, the electricity consumption for the lignoboost process for isolation of lignin is 55.556 KWh/tonne of isolated lignin(Manninen, 2010), which is obtained from the national grid (Scandinavia). The incineration of black liquor containing lignin is used to produce steam for the electricity production from turbine for internal requirement of plant(T. M. Bijleveld, 2016a). The CO_2 consumption value of 0.20 tonne/tonne of lignin is used from the ranges (as seen in Table 4) (Benali et al., 2016), assumed to be obtained from the lime kiln and it could be accounted as negative emissions(Manninen, 2010). The heat required for drying the lignin which has 7% moisture (0.324 GJ/t lignin) is also obtained from the lime kiln (Manninen, 2010). The energy consumption of evaporators is 450 MJ/t H2O of energy, as there is increase in the amount of water consumption by 2 m3/tonne of lignin due to washing of the lignin leading to an additional energy requirement of 900 MJ/tonne lignin(Manninen, 2010) provided by natural gas. The chemicals used in this research amounts to 0.20 t/t of lignin for H_2SO_4 and 0.13 t/t of lignin for NaOH and their emission value is taken from EcoInvent database (Benali et al., 2016; Manninen, 2010).The input values as shown below in section 5.1.1 and 5.1.2 are according to various allocation are programmed in LCA model in SimaPro and then GHG emissions are calculated.

Table 4 Inputs for the Lignoboost process (Kraft lignin) to be assessed for GHG emission (Benali et al., 2016)

Operating parameters and cost	Lignoboost™ process
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 cost ($/t of lignin)	100-150

5.1.1 Mass and energy flow of Kraft lignin

This section objectifies the mass and energy flows of the Kraft lignin (lignoboost isolation), showing all the relevant in- and outputs for the GHG assessment. The allocation is mainly used in the part 2 depicting the lignin production as shown in Figure 13, where the pulp production as well as lignin extraction occurs using Lignoboost process. The mass allocation describes the baseline case, while the energy allocation provides alternative case. The in-and output flows for both of allocation can be seen in Table 5 and Table 6.

Table 5 Mass flows of Kraft lignin(Benali et al., 2016; T. M. Bijleveld, 2016b; Manninen, 2010)

Mass flows Kraft Lignin	IN			OUT		
Process	Product	Tonne of product/dt (dry tonne) of lignin[4]	Source	Product	Tonne of product/dt lignin	Destination
Lignoboost Isolation (including drying and grinding)	Black liquor	5.0[5]	Pulp mill	Ground and dried lignin	1.1	Asphalt plant
	NaOH	0.065-0.13[6]	Market	Concentrated black liquor (incl. chemicals)	2.4[7]	Recovery Boilers
	H_2SO_4	0.20	Market	Moisture from black liquor	2.0[6]	Out
	CO_2	0.20	Lime kiln	flue gas from Natural gas combustion	1.95 E-02[8]	Out
	Natural gas	1.95E-02	Market			

[4] Dry lignin is the lignin after the drying pre-treatment step assuming a moisture content of 7%.
[5] Assuming black liquor is extracted from evaporators at 40% of lignin, where 50% is extracted.
[6] From (Manninen, 2010).
[7] The sum of input and then minus the moisture evaporated from the black liquor in the evaporator.
[8] It contains CO_2, H_2O and N_2

Table 6 Energy flows of Kraft lignin (Benali et al., 2016; T. M. Bijleveld, 2016b; Manninen, 2010)

Energy flows Kraft Lignin	IN			OUT		
Process	Product	MJ of product/dt of lignin	Source	Product	MJ of product/dt lignin	Destination
Lignoboost Isolation (including drying and grinding)	Black liquor	27333.3[9]	Pulp mill	Ground and dried lignin	24400	Asphalt plant
	Electricity	200[10]	Market	Concentrated black liquor (incl. chemicals)	2933.3[11]	Recovery Boilers
	Heat for drying	1080	Lime kiln	Kinetic energy and heat losses	2180[12]	Out
	Natural gas	900	Market			

5.1.2 Economic allocation

Other alternative allocation is economic allocation where price assumption of Kraft pulp sold is 662 €/t and Kraft lignin is sold at 592 €/t (Natural Resources Canada, 2019).

5.1.3 Alternative fuels for heat and power generation

The baseline case uses some amount of lignin for internal energy demand along with the electricity from grid and small amount of natural gas for drying and rest of lignin is exported for mixing in asphalt. If complete isolation of lignin occurs, alternative fuel sources can be used within different allocation mechanism for the energy demand to operate the plant. These sources can either be biomass or natural gas. The amount required to be substituted for heat and power from these energy sources is 2180 MJ/dt (dry tonne) of lignin. Thus, different scenarios are formed which are modelled in SimaPro to calculate the GHG emissions.

5.2 Biorefinery lignin input

This section gives an overview of the in- and outputs used in the life cycle assessment for calculating the GHG emissions of biorefinery lignin on the basis of steam explosion process. The Figure 14 provides a clear description of the flows involved in the process from the feedstock supply of wood pellets (USA to the Netherlands), to the lignin production process in the biorefinery, and thus the mixing of lignin in asphalt (ZOAB) layer. The refinery operates on the electricity from the national grid (the Netherlands) along with the steam assumed to be available from chemical industries next to the biorefinery (Van Kooij,

[9] Calculated from (Manninen, 2010). In this, the heat and electricity are produced by recovery boiler in Kraft paper/pulp mill (5412 MJ/t pulp), then it is divided by the recovery boiler efficiency (69%) and then it is divided by amount of lignin isolated from black liquor per tonne pulp (0.3 tonne).
[10] From the national grid of Scandinavia
[11] The amount calculated from the black liquor input energy minus the lignin energy output.
[12] Calculated from the addition of electricity and heat input from the natural gas and the lime kiln.

A., Biobased delta, Personal communication, 24 January, 2019). Some amount of lignin is incinerated in CHP plant to generate the heat and power (Vera et al., 2018). The boiler used in the refinery is assumed to less efficient for lignin (85%) compared with natural gas (95%) (T. M. Bijleveld, 2016a). The energy requirement for the lignocellulosic biorefinery plant in the Netherlands is 1200357 GJ of steam and 43 GWh of electricity in a year to reach the 434 Kton (C5+C6) sugar capacity (Van der kooij, A., Personal communication, January 10, 2019).

The input values used in the calculation are theoretical values from the future lignocellulosic biorefinery, as the refinery still not exist. The chemicals used in this study are enzymes and ammonia and the input values is taken from the research done by Vera et al (2018). The values are then programmed in the SimaPro model and then the GHG emissions are calculated. Section 5.2.1 gives an overview of the inputs and outputs according to different allocation mechanism.

5.2.1 Mass, economic and energy flows

This section overviews the mass, economic and energy flows of the Biorefinery lignin (steam explosion) mentioning all the in- and outputs used for the calculation of GHG assessment.

The allocation is done in the lignin production as shown in Figure 14, where the cellulose and hemicellulose production as well as lignin extraction occurs using steam explosion process. The mass allocation describes the baseline case, while the economic and energy allocation depicts alternative cases. The in-and outputs flows for all allocation mechanism can be seen in Table 7, Table 8 and Table 9.

Table 7 Mass flows within the steam explosion biorefinery (Vera et al., 2018)

Mass flow biorefinery lignin	**IN**			**OUT**		
Process	Product	Kg of product/kg wood pellets dry	Source	Product	Kg of product/kg wood pellets dry	Destination
Steam explosion process	Wood pellets from USA	1[13]	Market	Ground and dried lignin	0.268[14]	Asphalt plant
	Enzymes	0.0048	Market	Cellulose	0.481[13]	Enzymatic hydrolysis
	Ammonia	0.00649	Market	Hemicellulose	0.2158[13]	Enzymatic hydrolysis
	Water	0.464	Market	Ammonium Acetate group	0.0272[13]	Out
	Steam	1.02	Market	Ash	0.0025[13]	Out
				Water content	0.475	Out
				Unknown	0.0067	Out
				Flue gas	1.02	Out

[13] From (Biobased delta tool, 20 September, 2018)
[14] From (C5+C6+Lignin, Biobased Delta, 20 January, 2019)

Table 8 The economic flow of the biorefinery lignin (Vera et al., 2018)

Economic flow biorefinery lignin	IN			OUT		
Process	Product	€/kg wood pellets dry	Source	Product	€/kg wood pellets dry	Destination
Steam explosion process	Wood pellets from US	0.150[15]	Biorefinery RAFAELA	Ground and dried lignin	0.250[16]	Asphalt plant
	Enzymes	4.900[16]	NREL (literature)	Cellulose	0.360[16]	Enzymatic hydrolysis
	Ammonia	0.285[16]	NREL (literature)	Hemicellulose	0.230[16]	Enzymatic hydrolysis
	Water	0.0008	Market	Ammonium Acetate group	0.06[16]	Out

Table 9 The energy flow of the biorefinery lignin (Vera et al., 2018)

Energy flow biorefinery lignin	IN			OUT		
Process	Product	MJ/kg wood pellets dry	Source	Product	MJ/kg wood pellets dry	Destination
Steam explosion process	Wood pellets from US	18[16]	Biorefinery	Ground and dried lignin	24[16]	Asphalt plant
	Electricity	0.1048[16]	EcoInvent	Cellulose	15.68[16]	Enzymatic hydrolysis
	Natural gas	35[17]	IEA	Hemicellulose	15.72[15]	Enzymatic hydrolysis
	Steam	1.830[15]	IEA	Kinetic energy and heat losses	0.1048	Out

5.2.2 Alternative Fuel use for heat and power generation

The baseline case uses some amount of lignin for internal energy demand along with the electricity from grid and small amount of steam from neighbouring industries, rest of lignin is exported for mixing in asphalt(Van Kooij, A., Biobased delta, Personal communication, 24 January, 2019). If complete isolation of lignin occurs, alternative fuel sources can be used within different allocation mechanism to supplement the internal energy demand to operate the refinery. These sources can either be biomass, natural gas or additional amount of lignin when marginal amount of lignin is supplied to asphalt plant and the required values are clearly described in Table 10. Thus, different scenarios are formed which are modelled in SimaPro to calculate the GHG emissions.

[15] From (C5+C6+Lignin, Biobased Delta, 20 January, 2019)
[16] From (Chen et al., 2018)
[17] From (IEA, 2005)

Table 10 Comparison of scenarios where the lignin is completely extracted from the biorefinery and various fuel such as biomass, Natural gas and lignin is used to supplement the heat and power required for the refinery(Vera et al., 2018; Van Kooij, A., Biobased delta, Personal communication, 24 January, 2019)

	Biomass		Natural gas		Lignin	
Capacity	645	kton wood pellets/y, db	645	kton wood pellets/y, db	645	kton wood pellets/y, db
Capacity	434	kton (C5+C6)/y	434	kton (C5+C6)/y	434	kton (C5+C6)/y
Steam required	655,933	ton/y	655,933	ton/y	655,933	ton/y
HHV steam	1830	kJ/kg	1830	kJ/kg	1830	kJ/kg
Energy content steam	1,200,357,929.32	MJ/y	1,200,357,929	MJ/y	1,200,357,929	MJ/y
Yield	67.28 %	Capacity of sugar/capacity of wood pellets	67.28%	Capacity of sugar/capacity of wood pellets	67.28%	Capacity of sugar/capacity of wood pellets
Electricity required	43000.00	MWh/y	43000.00	MWh/y	43000.00	MWh/y
HHV wood	18	MJ/kg	-		-	
Wood for steam production	78	Kton/y	-		-	
HHV natural gas	-		35	MJ/m3	-	
Natural gas for steam production	-		40,348,166	m3/y	-	
HHV lignin	-		-		24	MJ/kg
Lignin produced	-		-		156	Kton/y
Lignin for steam production	-		-		59	Kton/y
Remaining lignin	-		-		97	Kton/y

6.Results

6.1 Life cycle inventory of ZOAB regular (porous asphalt)

The LCI for the GHG assessment of the ZOAB regular (porous asphalt) including the fossil bitumen is shown below in Figure 15. The value shown here refers to the production phase of the ZOAB as the scope of the research is limited to only cradle-to- factory-gate. The results shown here includes bitumen, filler material (Sand, stone, fibres, filler medium), electricity from national grid, diesel is used for machinery use in the asphalt production and natural gas for the heating the asphalt mix. The GHG emission is equivalent to 72.2 kg CO_2 eq./tonne of ZOAB.

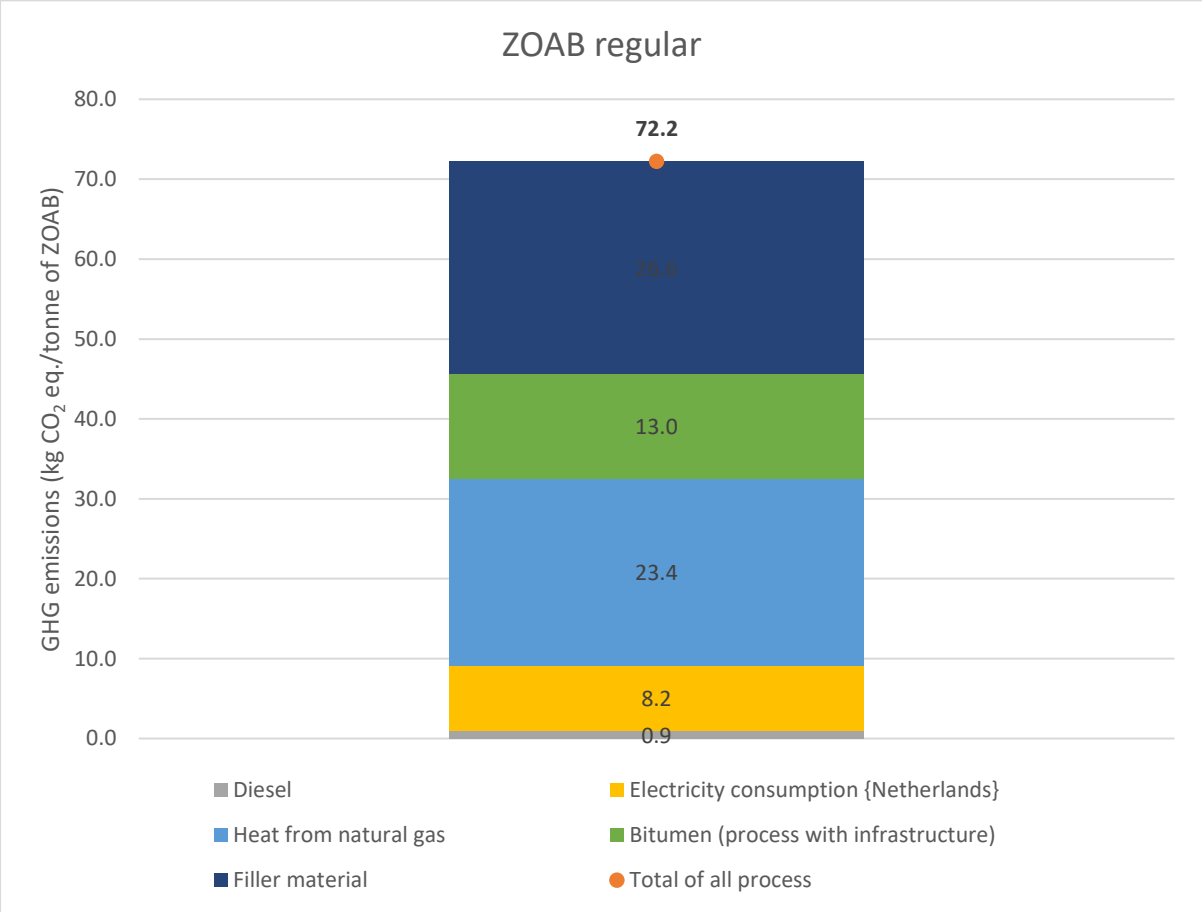

Figure 15 GHG emission (cradle-to-gate) from the assessment of the ZOAB regular (porous asphalt) in the Netherlands

6.2 Life cycle inventory of ZOAB with Kraft Lignin

The LCI of the ZOAB regular with the substitution of bitumen (50%) by lignin from Kraft mill for baseline case is shown in Figure 16 including carbon stored in lignin as it is a biogenic product. The results in comparison to the traditional ZOAB due to use of lignin reduces about 26% of the GHG emission (53.1 kg CO_2 eq./tonne of ZOAB) mostly due to carbon stored in lignin. The graph of the result includes various processes such as feedstock (Wood chips from Scandinavia) electricity consumption (both from Finland and the Netherlands), Chemicals (Sulfuric acid and sodium hydroxide), bitumen and other filler materials,

Heat from natural gas and Lime kiln, and transport from Scandinavia to the Netherlands through inland shipping route.

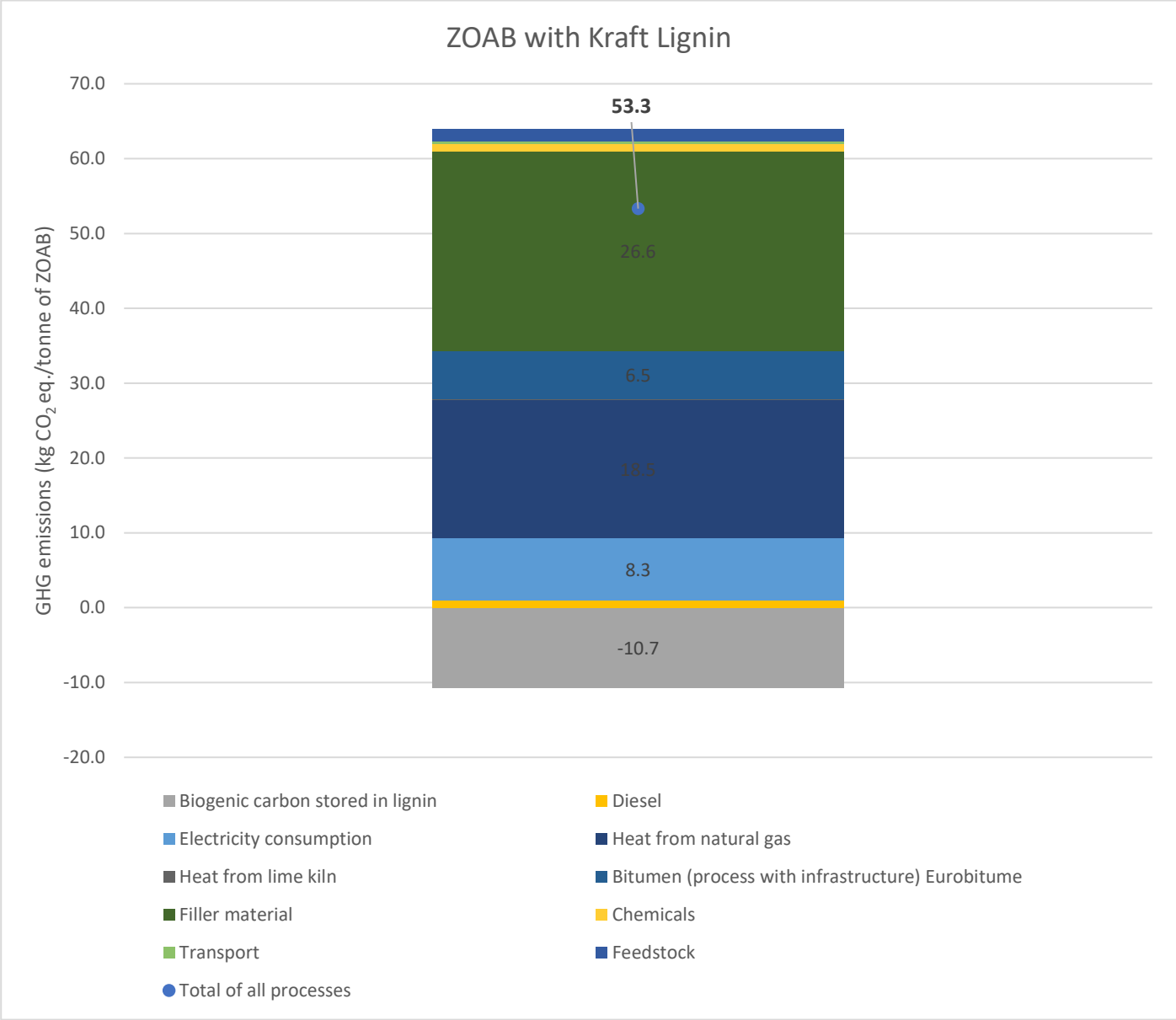

Figure 16 GHG emission assessment of the ZOAB with Kraft lignin

6.3 Life cycle inventory of ZOAB with biorefinery lignin

The LCI of the ZOAB regular with the substitution of bitumen (50%) by lignin from steam explosion process in biorefinery for baseline case as shown in Figure 17, including the carbon stored in lignin as it is a biogenic product(Levasseur et al., 2013). The results in comparison with the ZOAB regular have a 10% reduction in the GHG emission (64.5 kg CO_2 eq./tonne of ZOAB). The reduction is really low compared to ZOAB with Kraft lignin since the lignin isolation in the steam explosion process requires more energy than the Lignoboost process. Furthermore, the feedstock is wood pellets from USA and transported to the Netherlands by oceanic ship route as well as steam used in the process is produced from different fuel sources such as coal and natural gas (EcoInvent database for steam from Europe), which increase the

energy consumption. Other components include electricity from the grid (Netherlands), natural gas for heating and Chemicals (Ammonia and Enzymes).

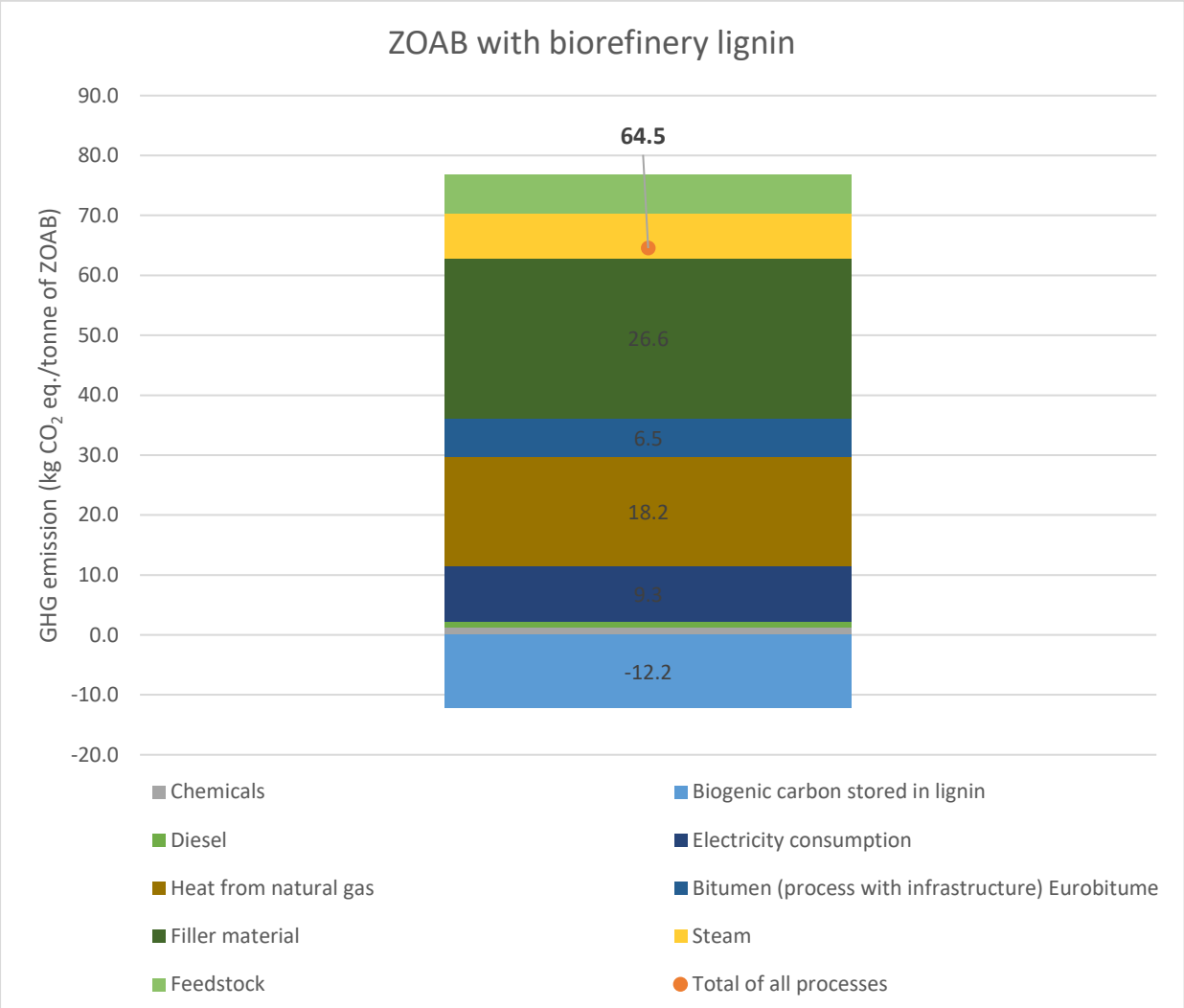

Figure 17 GHG assessment of ZOAB with biorefinery lignin

6.4 Comparison of the ZOAB regular with ZOAB with Kraft and biorefinery lignin

The comparison between the ZOAB regular with the ZOAB with the Kraft lignin and biorefinery lignin is shown in Figure 18. The difference is quite noticeable due to replacement of fossil bitumen as well as due to carbon stored in lignin. The difference in the carbon stored in lignin for both Kraft process and refinery emission is due to composition of carbon in the feedstock used for the respective processes.

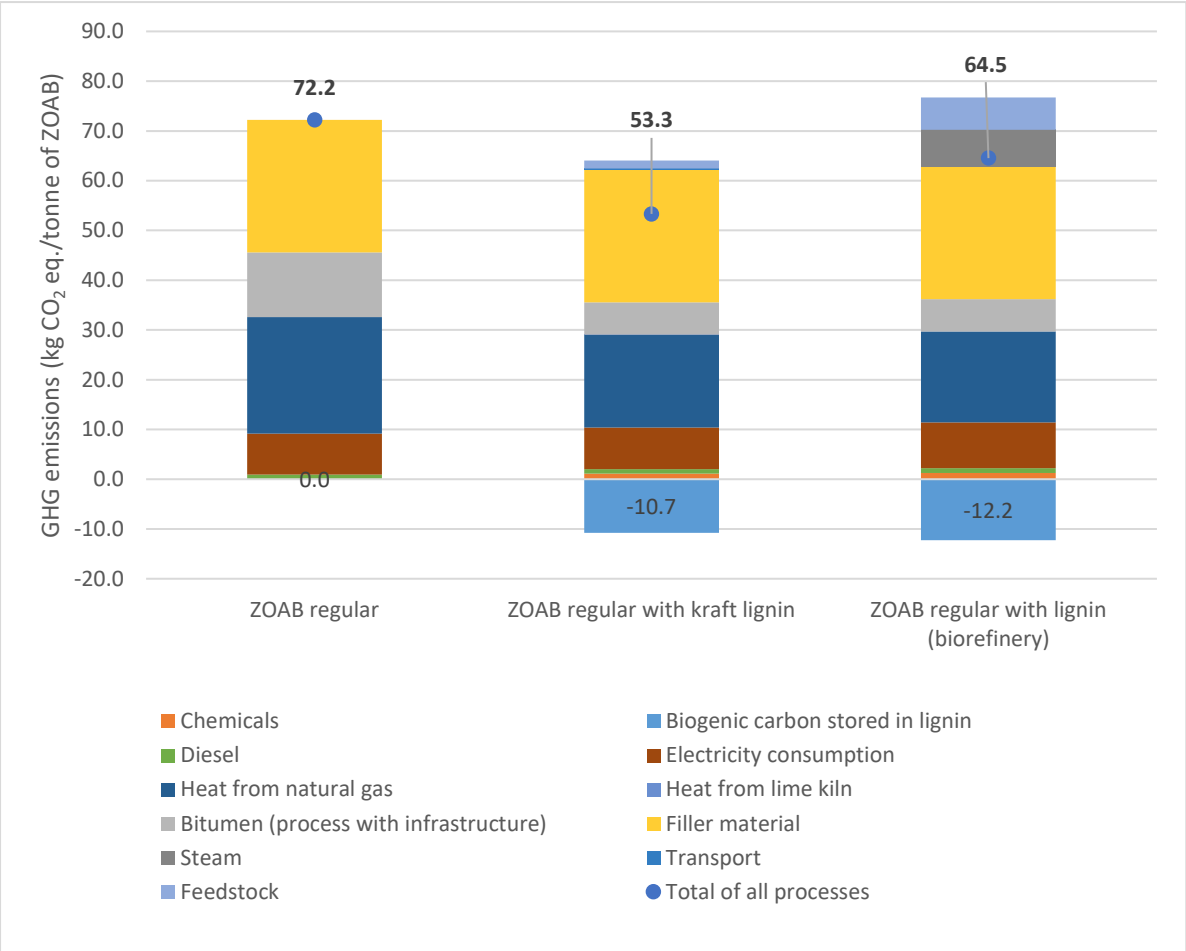

Figure 18 Comparison of GHG emissions of ZOAB regular and ZOAB with lignin in baseline scenario.

A quick glance at the emission values of the ZOAB regular compared with ZOAB with Kraft lignin (53.3 kg CO_2 eq./tonne of ZOAB) and steam explosion biorefinery (64.5 kg CO_2 eq./tonne of ZOAB) provides description of the potential GHG emission values. In the Netherlands as per section 1.3, asphalt production causes 550 kton CO_2 eq./year (cradle-to grave) emissions as shown in Figure 7 in the infrastructure sector and considering the scope (cradle-to-gate) 85% which is 467.5 kton CO_2 eq./year is annual GHG emission in the Netherlands for asphalt production. Bitumen is responsible for 15% of overall GHG emission of asphalt sector, thus 70.6 kton CO_2 eq./year is the annual GHG emission in the Netherlands.

The use of lignin can reduce around 26% of GHG emission for ZOAB (Kraft lignin) and 10% reduction in GHG emissions for ZOAB (steam explosion biorefinery lignin). Thus, annual saving is approximately about 18.2 kton CO_2 eq./year (3.9%) for kraft lignin ZOAB and 7.0 kton CO_2 eq./year (1.5%) for refinery lignin ZOAB in the infrastructure sector in the Netherlands. In 2030, with use of lignin, potential reduction of 32.82% (Kraft Lignin ZOAB) and 14.1% (refinery lignin ZOAB) from Infrastructure sector in the Netherlands assuming the GHG emission reduction starts from 2020 when ZOAB with lignin is commercialized.

6.2 Comparison of ZOAB with different allocation and fuels for energy generation

The second scenario where the complete lignin isolation is done, alternative energy carriers are used for the internal energy demand. Here, the ZOAB regular is compared with ZOAB with Kraft and biorefinery lignin using different allocation mechanism.

Economic Allocation

In comparison to the mass allocation (baseline case), the economic allocation global warming potential values are higher which can be clearly seen in the Figure 19 below as the values are 59.6 and 69.5 kg CO_2 eq./tonne of ZOAB for the Kraft lignin and steam explosion biorefinery lignin, which use can potentially reduce GHG emission by 17.5% (Kraft) and 4% (refinery) respectively.

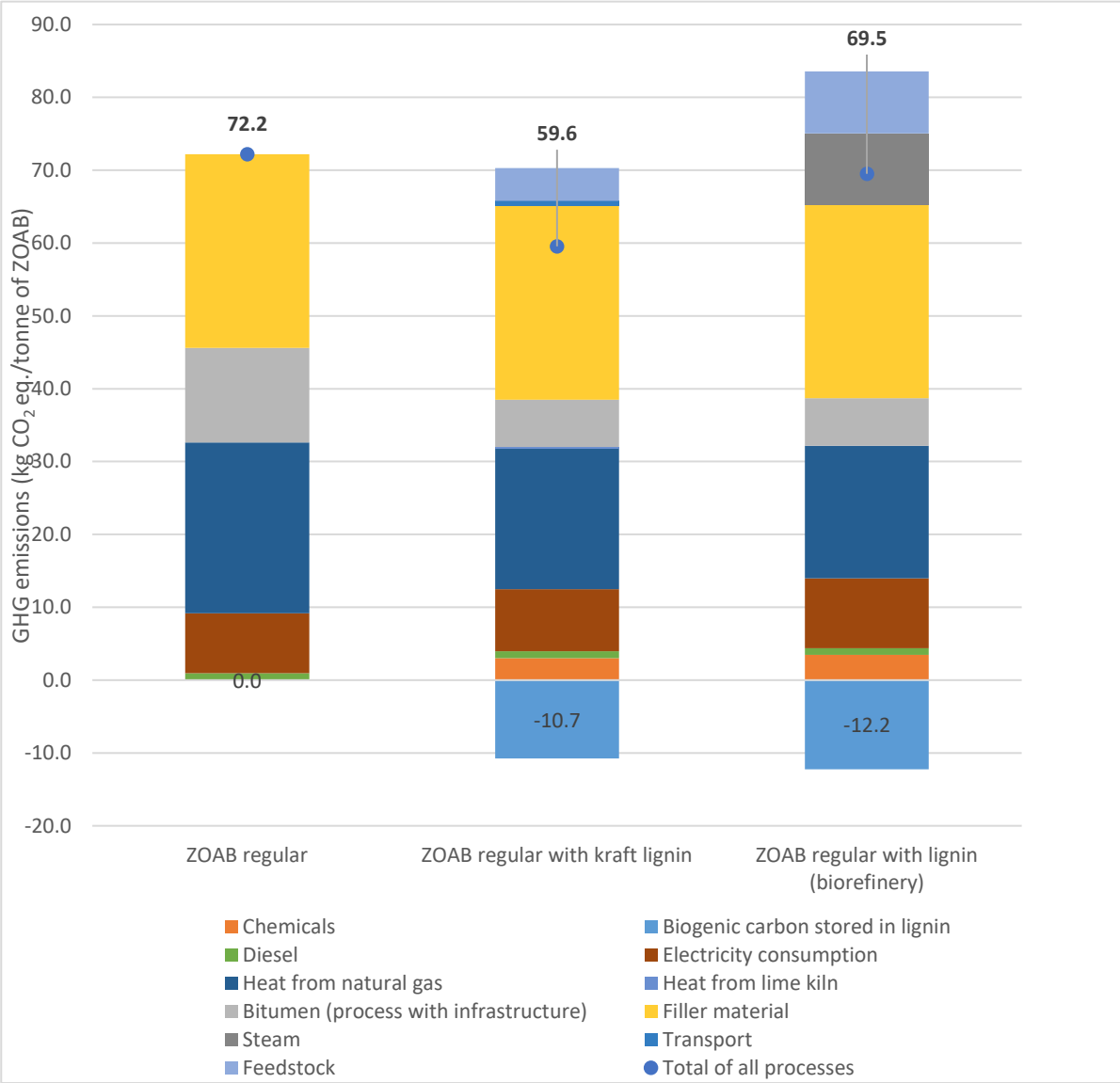

Figure 19 Comparison of GHG emissions of ZOAB regular and ZOAB with lignin in Economic allocation scenario.

Energy allocation

Energy allocation compared to the baseline case and economic allocation case shows the respective differences in the emission values as seen in the Figure 20, which are 59.4 and 74.6 kg CO_2 eq./tonne of ZOAB for the Kraft lignin and steam explosion biorefinery is quite higher than the other allocation. The potential reduction of GHG emissions are 17.5% for Kraft lignin, however for the refinery lignin the emission value is higher than the ZOAB regular which is a worst case scenario to be used in the calculation.

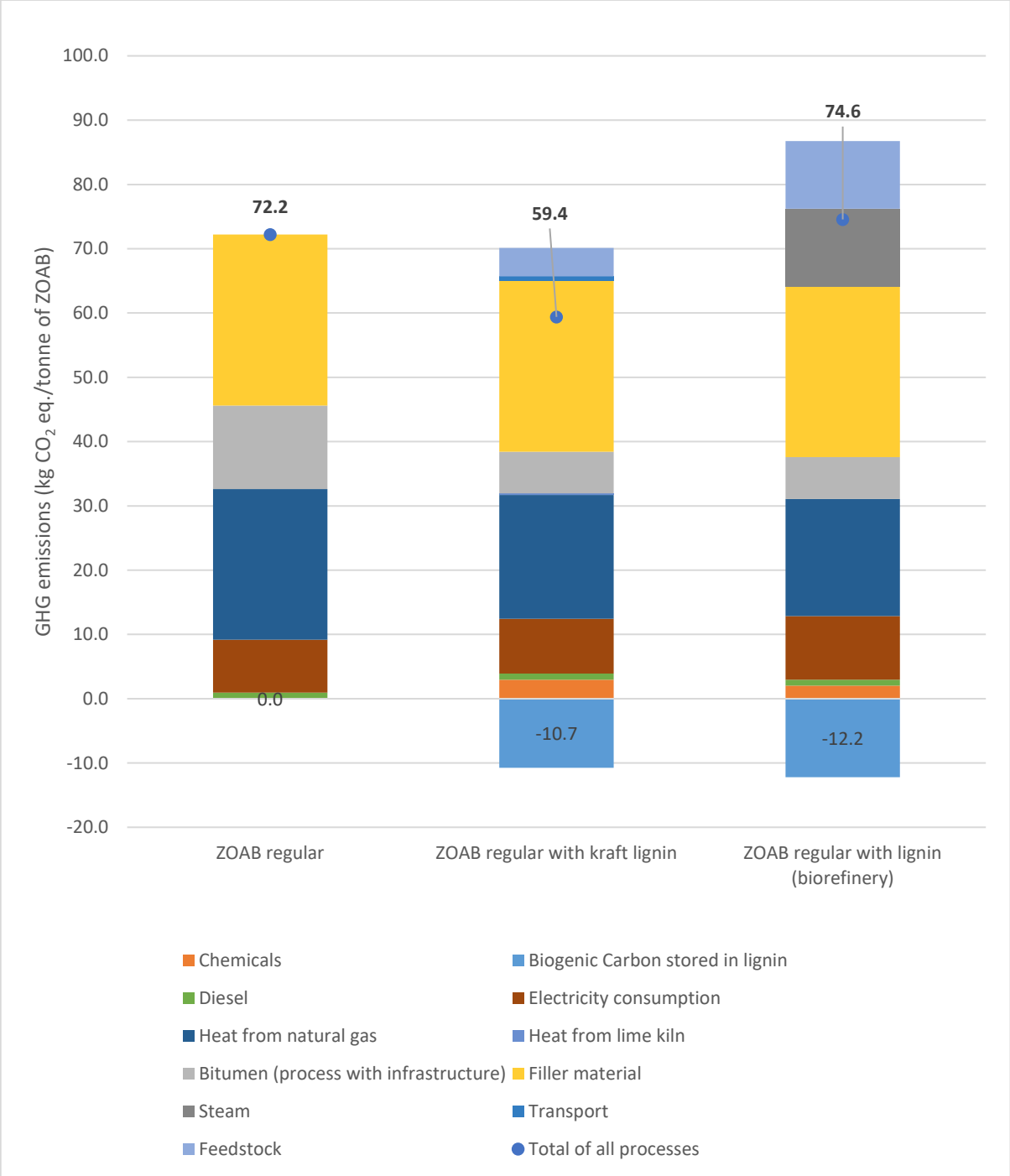

Figure 20 The GHG emissions of ZOAB regular and ZOAB with lignin in Energy allocation scenario

Comparison of different allocation

Comparison of GHG emissions from the ZOAB with lignin (both Kraft and SE biorefinery), in the baseline case which uses the mass allocation in compared to economic and energy allocation (as shown in Figure 21). Also, the comparison of the ZOAB regular with biorefinery lignin with feedstock from USA and Baltic region is seen in Figure 21.

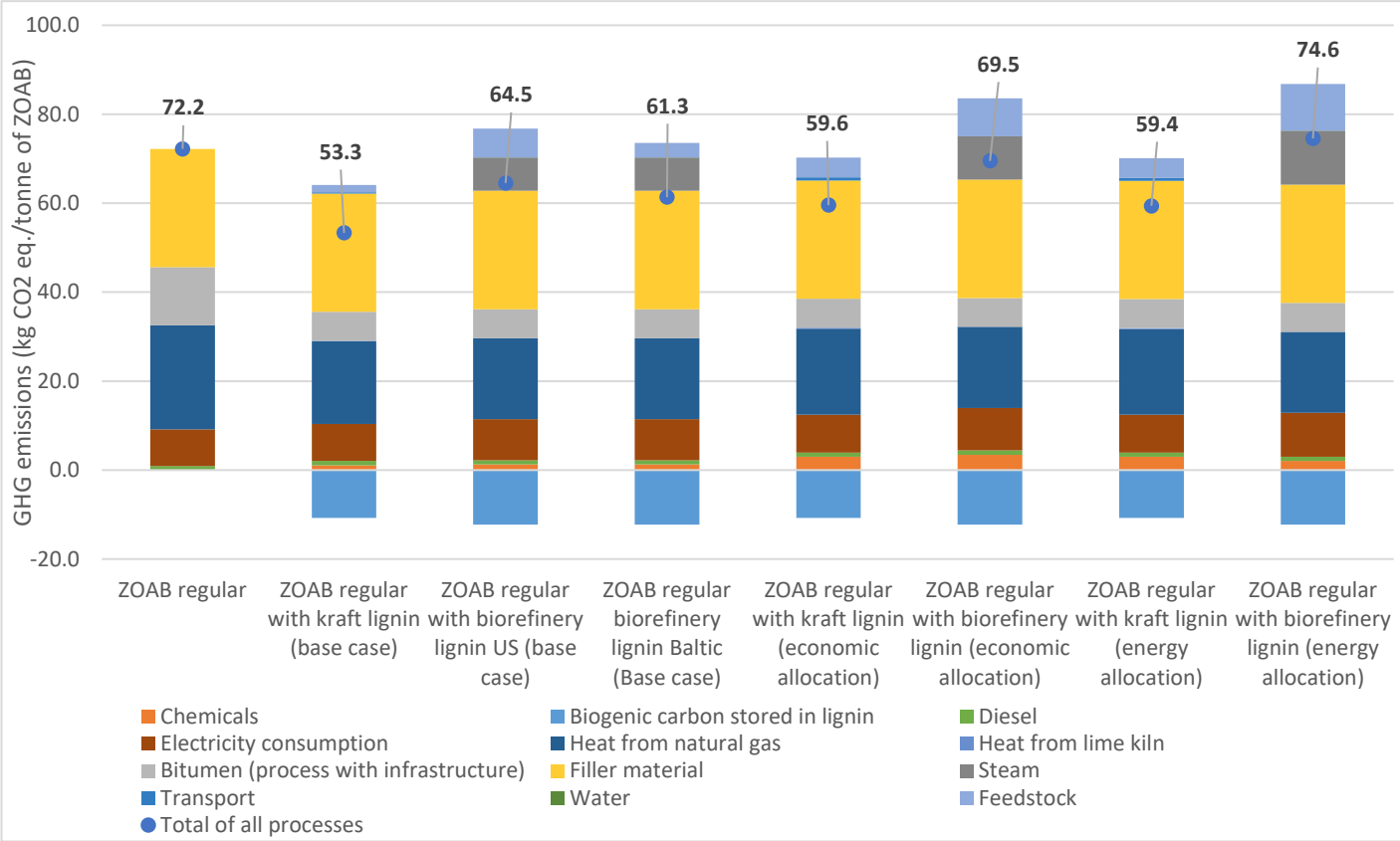

Figure 21 Comparison of GHG emissions of ZOAB regular and ZOAB baseline scenario along with economic and energy allocation.

Different allocation mechanism with different fuel sources

In the basic allocation (mass, economic and energy), the lignin is also used as fuel source for operating

Figure 20 Comparison of GHG emissions of ZOAB regular and ZOAB baseline scenario along with economic and energy allocation.

the plant for heat and power generation in addition to other sources. Thus, within these allocation, when lignin is completely isolated, to substitute the internal energy demand the additional fuel source for the heat and power generation to operate the mill and refinery such as biomass and natural gas. The amount of lignin used in the asphalt is marginalized when lignin is used as fuel for complete energy use.

Biomass as fuel

The results can be clearly seen in the Figure 22 below for the Kraft lignin and steam explosion biorefinery for the different allocation mechanism using biomass as fuel for substituting internal energy demand of the paper mill and refinery.

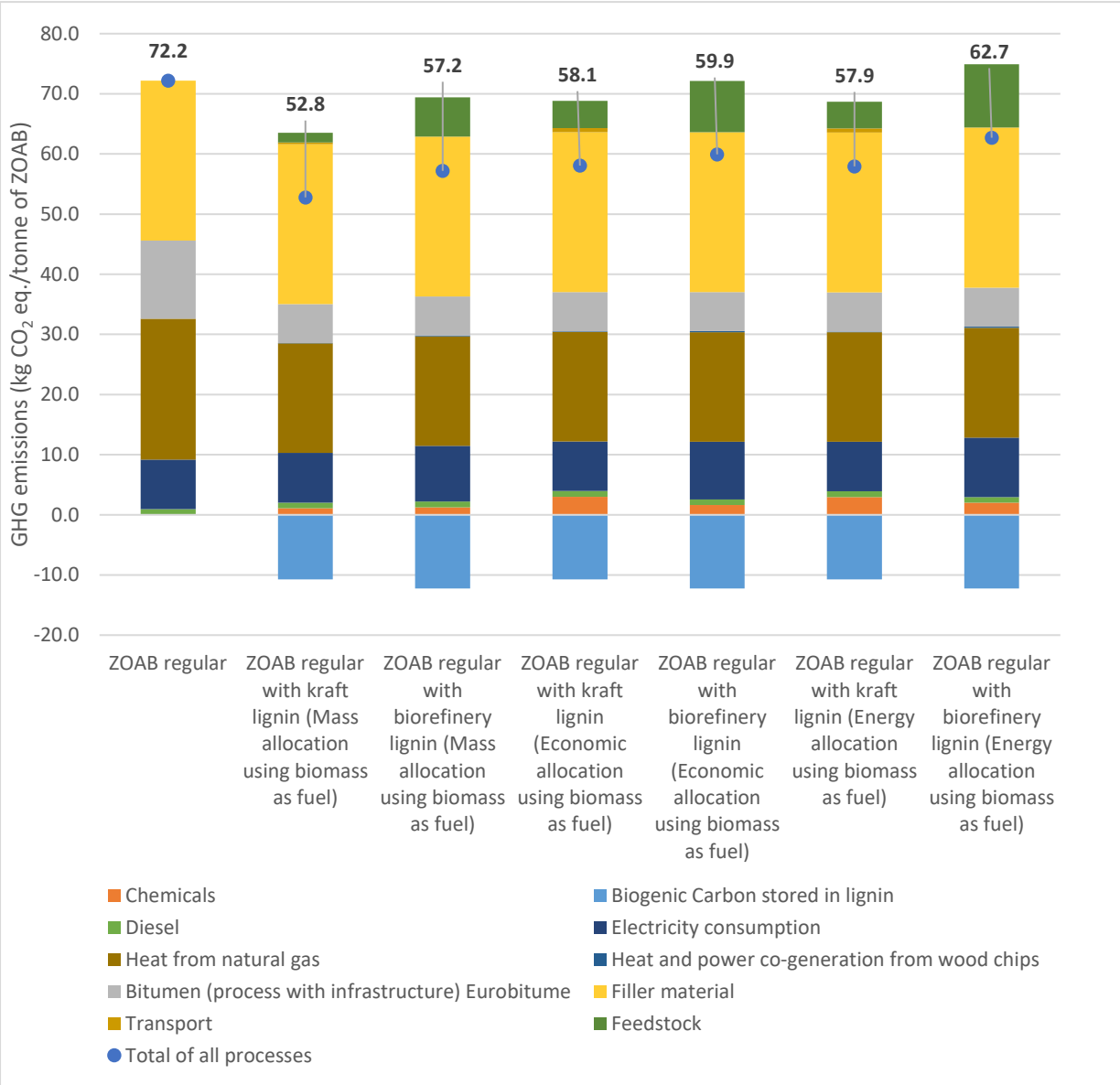

Figure 22 The comparison of ZOAB and ZOAB with lignin when biomass is used as fuel in various allocation mechanism

Natural gas as fuel

The results can be clearly seen in the Figure 23 below for the Kraft lignin and steam explosion biorefinery for the different allocation mechanism using natural gas as fuel for internal energy demand.

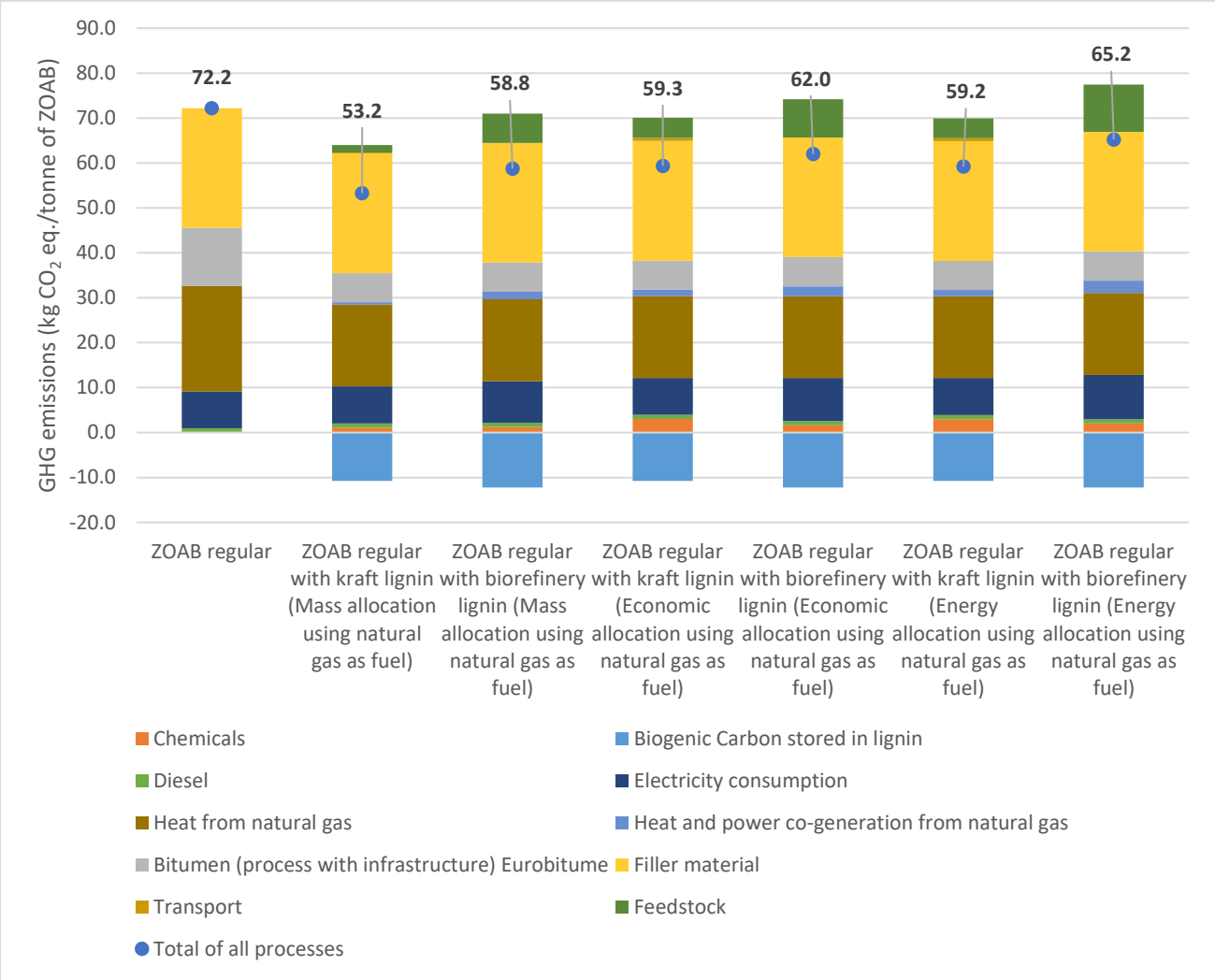

Figure 23 The comparison of ZOAB and ZOAB with lignin when natural gas is used as fuel in the different allocation mechanism

Optimal and Sub-optimal GHG emissions

The comparison of different allocation mechanism with different fuel sources yields variation of GHG emission values of ZOAB with lignin. From these variation three optimal and three sub-optimal case solution are compared as shown in Figure 24. Within these values the potential reduction of GHG emission by 27% (52.8 kg CO_2 eq./tonne of ZOAB) is the optimal solution where the biomass is used as fuel in the mass allocation (Kraft lignin) while the sub-optimal solution gives a potential reduction of 9% (65.2 kg CO_2 eq./tonne of ZOAB) when natural gas is used as fuel in the energy allocation for ZOAB with lignin (biorefinery lignin). Thus, annual saving is approximately about 4% for the optimal case ZOAB and 1.35% for sub-optimal case ZOAB in the infrastructure sector in the Netherlands. In 2030, potential reduction of 33.5% (optimal case ZOAB) and 12.7% (Sub-optimal case ZOAB) from Infrastructure sector in the Netherlands.

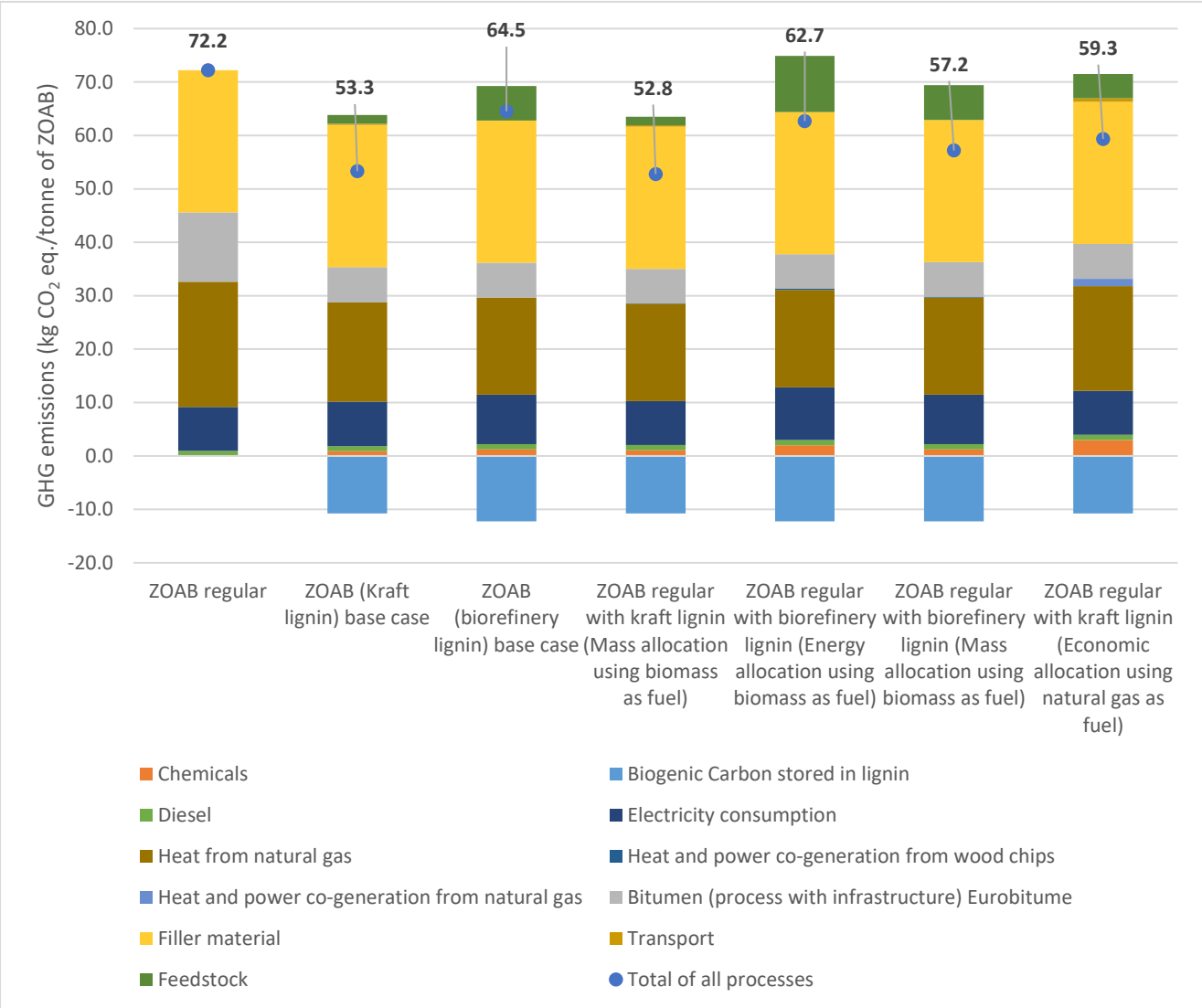

Figure 24 comparison of GHG emissions of the optimal and sub-optimal scenarios of ZOAB with lignin

Uncertainty and sensitivity analysis for the SE refinery lignin ZOAB

This section presents the uncertainty and sensitivity analysis of the results for the Biorefinery lignin use in the ZOAB with the change in the input variable of feedstock as well as for Kraft lignin ZOAB due to the large range in the chemicals used as a input. The criteria and uncertainty that was appointed to them is presented in appendix 5.

Uncertainty analysis

The mean calculated GHG emission of SE lignin conversion is 64.5 kg CO_2 eq./tonne of ZOAB (as seen in Figure 25), it uses the feedstock (wood pellets) from the USA for the GHG assessment. When compared to the feedstock from the Baltic region, the GHG assessment value is 61.3 kg CO_2 eq./tonne of ZOAB (Figure 21). Also, Table 19 in Appendix 5 gives an overview of different GHG vales using wood pellets as feedstock with different emission values. The uncertainty analysis shows that there is 90% certainty that the results fall between 56.5 and 72.4 kg CO_2 eq./tonne of ZOAB (as seen in Figure 25). Since, the GHG emissions of ZOAB regular is 72.2 kg CO_2 eq./tonne of ZOAB, it is possible that the emissions of refinery

lignin in ZOAB is higher than of ZOAB regular as seen in the economic allocation (Figure 20). There is approximately 94% chance that the GHG emission of SE refinery lignin are lower than ZOAB regular.

The result shows a large uncertainty and clearly most relevant input data is required of the feedstock value to be used in the calculation to obtain more reliable results. This is possible by finding the values of existing refinery, not the theoretical values, so an average can be calculated.

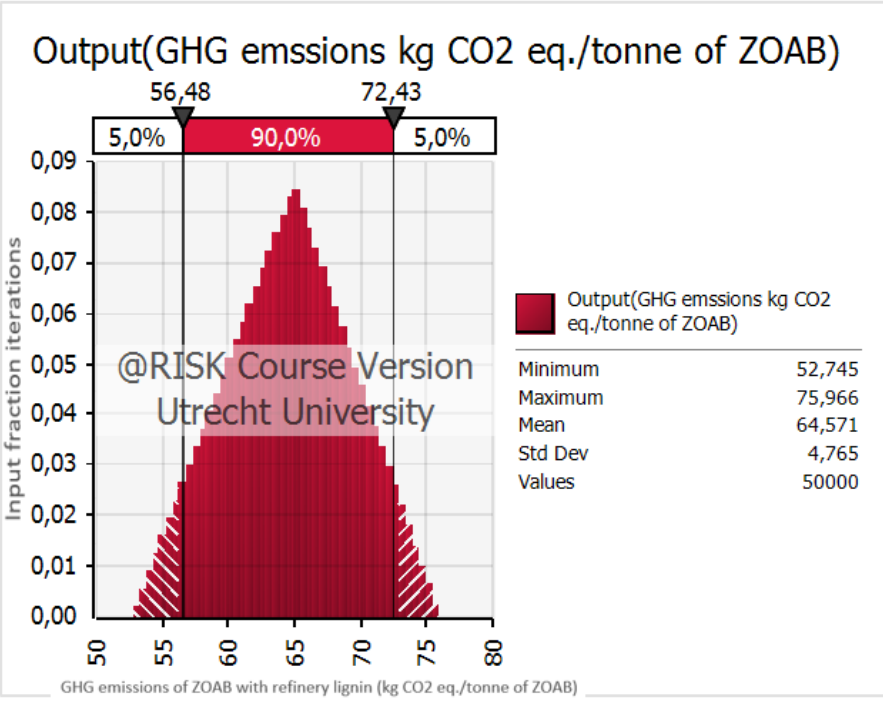

Figure 25 The uncertainty analysis of the SE refinery lignin ZOAB for baseline case. The x axis shows the value of the results of ZOAB in kg CO_2 eq./tonne of ZOAB and the y-axis shows the fraction of total iterations that resulted in these values.

Sensitivity analysis

A sensitivity analysis was performed on the input parameters of the Kraft lignin ZOAB which are chemicals such as NaOH (sodium hydroxide) and H_2SO_4 (sulphuric acid). The sensitivity analysis address the issue of the impacts of these parameters on the outcome result of GHG emission of Kraft lignin ZOAB. The emission factor values changes due to the range in the chemical input as seen in Table 20 in Appendix 5.

In the Kraft Lignin ZOAB, the results are more sensitive to the input of the sodium hydroxide (as seen in Figure 26) as the consumption of NaOH have a large range (Table 4) when used in the Lignoboost process. Sulphuric acid is sensitive to the output result of GHG emissions after the sodium hydroxide as also there is large range in the values to be used in the input for the calculation of the results. More research needs to be done to assess the average input values of the chemicals used.

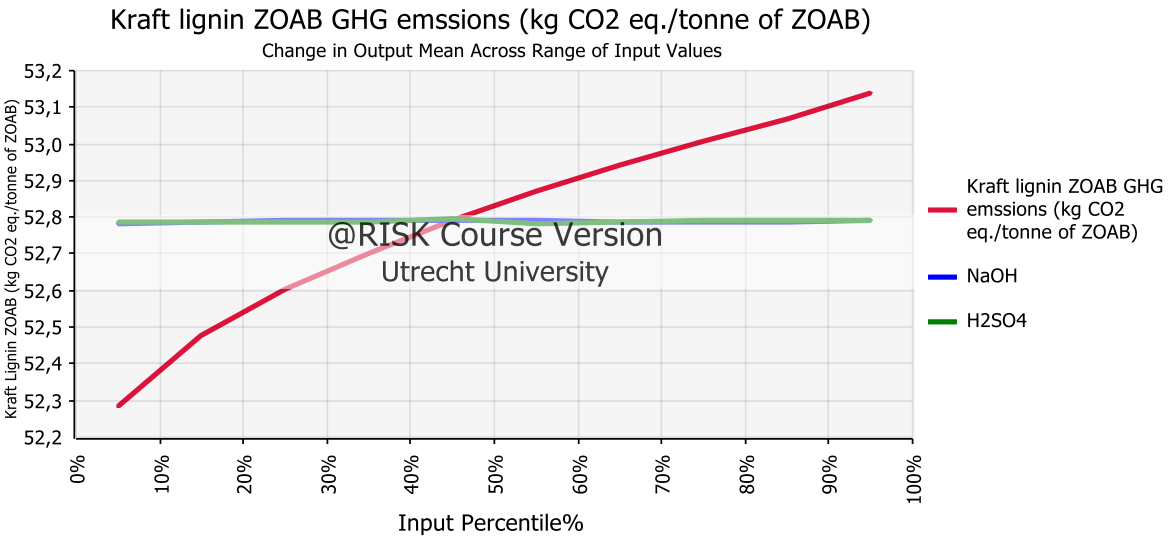

Figure 26 The chemical parameters (NaOH and H_2SO_4) which have influence on the GHG emissions from Kraft lignin ZOAB.

7.Discussion

7.1 GHG emissions

The LCA allocation method used for the calculation of the GHG assessment is displacement method instead of the system expansion method as lignin being the co- product in the Kraft process and refinery process is allocated the carbon emission. Thus, the emissions that are displaced by the use of lignin are subtracted from the overall emissions of the asphalt production. A downside of this method is it requires the use of the LCAs of the non-fuel products that are displaced and can create distorted results if a large part of the products is still non-fuel (M. Wang et al., 2011).

The GHG emissions for the baseline case for the ZOAB layer (porous asphalt) were 53.3 and 64.5 kg CO_2 eq./tonne of ZOAB for the Kraft lignin and steam explosion lignin use respectively. The values obtained from the baseline case for ZOAB with lignin are lower than the ZOAB regular (72.2 kg CO_2 eq./tonne of ZOAB) until the production phase. These values can potentially create a positive impact for the GHG emissions mitigation in the asphalt production which is not large in value as most of the saving is due to the carbon stored in lignin. The baseline case can reduce approximately 3.9% reduction in GHG emissions using Kraft lignin in ZOAB and approximately 1.5% reduction in GHG using SE refinery lignin in ZOAB in the infrastructure sector of the Netherlands annually. In 2016, the infrastructure sector in the Netherlands used approx. 8300 kton of asphalt (Korevaar & Blok, 2018), and considering the assumption of replacing 50% of bitumen in lignin, 1 tonne of ZOAB requires 26 Kg of lignin (Table 3). Therefore approx. 215.8 kton of lignin would be required in a year in the Netherlands for the available amount of asphalt in the top layer of road assuming 8300 kton is used in the ZOAB layer. Since, the assumption of 50% blending of lignin and bitumen is not commercially available except few cases of road that are constructed in Zeeland province of the Netherlands using the mix of 50-50 % of lignin and bitumen ZOAB (Discussion fossil bitumen and Bio-bitumen, Personal communication, Bergen op zoom, 19 December, 2018).

The different allocation mechanism and different fuel sources gives different values of GHG emissions for ZOAB with Kraft lignin and SE biorefinery lignin such as 52.8 kg CO_2 eq./tonne of ZOAB for mass allocation with use of biofuel which is the most optimal solution while the 65.2 kg CO_2 eq./tonne of ZOAB is the sub-optimal solution when the energy allocation is used for the refinery lignin when natural gas is used as fuel, which can reduce approximately 4 % and 1.35% reduction in GHG emission of Infrastructure sector of the Netherlands. The GHG reduction is between 18-27% for the Kraft lignin ZOAB and within 9-20% for the Biorefinery lignin ZOAB when compared with the ZOAB regular. Thus, the annual reduction in the Infrastructure sector ranges from 2.7-4 % for Kraft lignin ZOAB and 1.35-3 % for Biorefinery lignin ZOAB.

The GHG emission of the steam explosion lignin is higher than that of Kraft lignin because the lignin isolation requires more energy in the biorefinery than the lignoboost process. Also, the wood pellets for the biorefinery is supplied from the USA. If the feedstock for the biorefinery is supplied from the Baltic region, the GHG assessment value is 61.3 kg CO_2 eq./tonne of ZOAB in comparison to 64.5 kg CO_2 eq./tonne of ZOAB (for USA feedstock), which is more relevant as the feedstock for Kraft lignin comes from the Scandinavia region. However, the Netherlands imports most of the biomass from USA, hence the GHG assessment for biorefinery lignin is evaluated on the feedstock from USA. There is also a large uncertainty in the values of biorefinery lignin ZOAB as seen in Figure 25, since all of the input values used in the calculation are theoretical values. The calculation requires most relevant input values from the existing biorefinery to calculate the average value of GWP. The sensitivity analysis done on the chemical

input of the lignoboost process (Kraft mill) for lignin isolation to be further used in the ZOAB layer shows the impact of the values in the result of GHG emissions as seen in Figure 26.

There should be more research into this prospect, as this study focus only on the production phase (cradle-to-gate). The further studies could be done until the cradle-to-grave; where the focus could be until the use phase as well as including the recycling phase of the ZOAB with lignin.

7.2 GHG emission reduction potential

The lignin supply market gives us details on the large sources of the lignin throughout the world, especially from the pulp/paper industry which is the major source. The lignocellulosic biorefineries are not in large number as seen in appendix 3, but they are expected to increase in the future. This will be dependent on the demand for the 2nd generation sugars as well as lignin use in the chemicals, binders and other materials. If the lignin use in the asphalt production increase, the expected outcome could be a potential large GHG emissions mitigation. There is a possibility that the lignocellulosic biorefineries might increase more than as aimed by the target set by several governments, the amount of lignin in the market could increase. This value could be further increased if the substitution of bitumen by lignin increases more than 50% in the ZOAB, which still needs to be further looked into.

7.3 Kraft lignin isolation

The GHG emissions from the use of chemicals that are required for the Lignoboost process have a very uncertain factor in the results. In this research, the 0.13 t/t of lignin for NaOH and 0.20 t/t of lignin for H_2SO_4 values were assumed, because these values were used by Manninen (2010) and they fall within the ranges given by Benali et al (2016). However, there were uncertainties in the ranges given as seen in Table 4; between 0.065-0.13 t/dt lignin for NaOH and 0.20 t/dt of lignin for H_2SO_4 according to Manninen (2010) and between 0.05-0.08 t/dt of lignin for NaOH and between 0.09-0.25 t/dt of lignin for H_2SO_4 according to Benali et al (2016). The values could have a potential effect on the GHG emissions values of the Kraft lignin ZOAB. As seen in Figure 26, the NaOH and H_2SO_4 have an impact on the GHG emissions values of ZOAB.

7.4 Steam explosion biorefinery lignin isolation

The GHG emissions from the use of chemicals and other materials required for steam explosion process have a large uncertainty in the results due to fact that the values are from the biorefinery which is going to be constructed in the southwest of the Netherlands (Vera et al., 2018). Since, these values are theoretical values and not the practical ones. There could be a substantial effect on the results when the biorefinery starts operating and actual values could be imported and used in the calculation of the results or the data from the existing biorefinery is used. The feedstock used in the process also varies from USA to Latvia in Europe as seen in Figure 21, also there is a large uncertainty in the results of GHG emissions of ZOAB (as seen in Figure 25).

7.5 Data input quality

First and foremost, lignin is a very complex molecule, that differs within plant types (e.g. Miscanthus giganteus or softwood), but also within plant types and also within the same plant; the weather also affects the lignin. Therefore, similar types of ZOAB with lignin experiments can yield different results. This leads to a uncertainty in the calculation based on these results. These uncertainties could be reduced by several identical experiments done by using the same feedstock type from a different places in a region

(e.g. several stem wood SE lignin from US), therefore an average value could be found for this research. These values could provide a solid basis for further calculations.

SimaPro

Most of the emission factors of the different products were obtained from the EcoInvent database. The values from this database generally contain all the life cycle of the product. Since, these database could have not actual emission factors and there could be no similar product, sometimes the emission factor of a similar product is assumed. For example, the steam used in the refinery is assumed to be average steam in the Europe while for the Netherlands the average steam production was not available in the Eco Invent database. Since, it is average value of the Europe it could be produced from mix of coal and natural gas as in the eastern part of Europe the coal is used in the large quantities. While, in the Netherlands natural gas is used for production of steam. This can create a large difference in the emission of the steam used in the biorefinery process. In a similar way, the average value of the Europe for the natural gas is used for the combined heat and power generation as one for the Netherlands is not in the EcoInvent database.

General data quality issues

In general, the input data used in this research is from only one or two sources due to lack of relevant studies that discuss the in- and outputs . The heating values were sometimes calculated from the equation from Channiwala & Parikh (2002) based on the elemental composition of the product. The values for economic balance or energy balance was assumed or calculated from the mass balance. As these values are relevant for the calculation of the results, the input values should be obtained from the scientific articles or existing Pulp mill and Biorefinery to calculate the actual average value of GWP.

7.6 System boundaries

For this research, only cradle-to- factory-gate (until production phase) emissions were considered. This study showed the change in the overall GHG emissions that would occur when lignin from Kraft process or Steam explosion biorefinery is used in the ZOAB production. These changes in the emission were allocated to lignin, to give a clear overview of the changes in GHG emissions if the lignin is used for ZOAB production. The LCA did not include the existence of biogenic carbon stored in the lignin, the reduction possibility of Scope 3 emission[18] (indirect) of using the ZOAB with lignin, the quality of road after a particular timeframe, the end-of-life behavior of ZOAB, and also the recyclability of the ZOAB with lignin. The biogenic carbon stored in lignin needs to be reviewed clearly as it is a biogenic product and in contact with moisture and air, is it possible that microorganism will degrade the lignin in the asphalt. These needs to be further reviewed. Therefore, a cradle-to-grave LCA should be performed to analyse the overall sustainability of using lignin in ZOAB considering the aforementioned conditions.

[18] The Scope 3 emissions are all indirect emissions which are not present in scope 2 that occur in the value chain of the organisation (GHG protocol, 2011)

8.Conclusions

This study assessed the GHG mitigation potential of using the lignin in the asphalt (substituting bitumen) in 1 tonne of ZOAB (porous asphalt) in the Netherlands and also the possible saving in GHG emission in the Infrastructure sector in the year 2030 in the Netherlands. This research used CLCA (displacement method allocation) to assess the direct and indirect GHG emissions from the two case studies of lignin isolation and substitution of bitumen in the ZOAB by lignin. These case studies were the lignin from the Lignoboost process in Kraft pulp/paper mill using the feedstock (wood chips) from Scandinavia and lignin from the steam explosion process in the biorefinery using the feedstock (wood pellets) from USA.

From the assessment of the lignin market and isolation techniques, it can be concluded that large amount of lignin is available in large quantities, and it is expected to grow further in future. Kraft lignin is the most abundant lignin in the world and biorefinery lignin is expected to rise in future. The lignin can be used to replace the bitumen in the asphalt production and the expected GHG emissions mitigation from the same is quite satisfactory. However, the large amount of saving is due to biogenic carbon stored in lignin.

The GHG emission for the baseline case of ZOAB with lignin with mass allocation and using some amount of lignin to be combusted for heat and power generation yielded 53.3 and 64.5 kg CO_2 eq./tonne of ZOAB for the Kraft process and steam explosion biorefinery. **The potential emission reduction of ZOAB with lignin compared to ZOAB regular is approximately 26% for Kraft lignin and 10% for biorefinery lignin.** Thus, the annual potential GHG mitigation in infrastructure sector in the Netherlands is about approximate 3.9% for Kraft lignin and about 1.5% for biorefinery lignin. In 2030, potential reduction of 32.82% CO_2 emission is possible (Kraft lignin), for refinery lignin 14.1% CO_2 emission reduction from infrastructure sector in the Netherlands assuming the GHG emission reduction starts from 2020 when ZOAB with lignin is commercialized. Within other possible cases, the potential reduction of GHG emission possible is 27% (52.8 kg CO_2 eq./tonne of ZOAB) which is the optimal solution where the biomass is used as fuel in the mass allocation (Kraft lignin), while the sub-optimal solution gives a potential reduction of 9% (65.2 kg CO_2 eq./tonne of ZOAB) when natural gas is used as fuel in the energy allocation for ZOAB with lignin (biorefinery lignin). These can reduce approximately 4 % and 1.35% annual GHG emission of Infrastructure sector of the Netherlands. By 2030, 33.5% and 12.7% reduction for the optimal and sub-optimal in infrastructure sector. These calculations are based upon the cradle-to-gate life cycle assessment for calculation of GWP (global warming potential). The lignin required for replacing bitumen in the asphalt layer (ZOAB) assuming approx. 8300 kton of asphalt is used in the Netherlands in a year is approx. 215.8 Kton which is small compared to availability of lignin in the world which sums up to 70 Mton.

From this numbers, it can be clearly concluded that using lignin in the asphalt production does mitigate GHG emissions in the asphalt industry. The results are sensitive to the allocation mechanism and different fuel sources which provides a clear overview of the expected results if there is a change in the system. The chemicals used in the Kraft process have large ranges as shown in Table 4, and their sensitivity to the GHG emissions of the ZOAB with lignin is observed in Figure 26. Thus, the average value needs to be found for the calculation as different articles have different value. More robust calculation is needed for the biorefinery lignin once the plant starts operating and the actual values could be used for calculation GHG emissions or if the values are taken from an existing refinery as shown in Figure 25 which shows a large uncertainty in the results of GWP of refinery lignin ZOAB (there is 90% certainty that the results fall between 56.5 and 72.4 kg CO_2 eq./tonne of ZOAB). Both process have a large uncertainty,

which should be reduced by improving the quality of the input data to obtain more robust and reliable results.

Furthermore, this research only studied the cradle-to-gate GHG emissions mitigation of ZOAB with the use of lignin. Therefore, a LCA assessment should be done on the cradle-to-grave to assess the overall sustainability of the lignin use in the asphalt industry in future studies. The current technology is suitable for replacing the bitumen in the ZOAB layer, thus other prospects of replacing the bitumen in the different layer of road needs to further assessed. This assessment should also look on the prospect of timeframe of carbon stored in the road, or the probability that the carbon is released again in the atmosphere after some years, scope 3 emissions and recyclability. If all of this happens, what could be possible impact on the LCA results.

Finally, it can be concluded that use of the lignin from Kraft and SE biorefinery in the asphalt production could be effective in mitigating emissions in the Infrastructure sector in the Netherlands by 2030. Since, this study takes cradle to gate assessment , the cradle-to-grave assessment still needs to be further reviewed to calculate the overall sustainability of using lignin in ZOAB with importance given to assessment of biogenic carbon stored in the lignin during the use phase as well as end of life phase.

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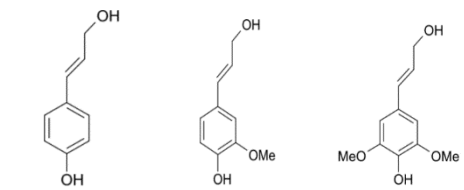
Appendices

Appendix 1: Lignin

This study focus on the lignin isolation techniques and the GHG emission reduction from the replacing of bitumen with lignin by 50% in the asphalt road.

The cell wall material of the plants consist of the lignocellulosic biomass, which in turn consist of three main components like cellulose, hemicellulose and lignin. Lignin is around 15-35% of dry cellulose (Benali et al., 2016). Lignin is a primary part of wood is an amorphous polymer consisting of irregular cross link structure arising from an enzyme-mediated dehydrogenative of three phenylpropanoid monomers such as p-coumaryl, coniferyl and synapyl alcohols as shown in figure 27 (D. Wang, 2008). Lignin functions within a plant include influencing the permeability and thermal stability of a cell wand, but more importantly it add strength and rigidity to the plant(Faruk et al., 2016). Lignin conjointly with cellulose is responsible for the woody cells walls of plants as well as cementing material between them(De Jong & Van Ommen, 2014). Lignin also a by-product of e.g. pulp and paper mill and with the advent of lignocellulosic biorefinery which also gives lignin as by product of the C6 and C5 sugar production, it is becoming more abundant. Most biomass consist of 20-30 wt% of lignin which is stored between the space of cells and has larger higher heating value (HHV) than carbohydrates (De Jong & Van Ommen, 2014). The molecular structure and characteristics of lignin depends on its origin, as well as external properties it is subjected during growth (such as climate and season) and the isolation and pre-treatment technologies that were used to isolate lignin of the hemicellulose and cellulose in lignocellulosic material as shown in table 11 (Cheng & Timilsina, 2011; Lettner et al., 2018; Ragauskas et al., 2014).



P-coumaryl Coniferyl Synapyl

Figure 26 (D.wang, 2008) Types of lignin

Table 11 Contents of cellulose, hemicellulose, and lignin in common lignocellulosic materials.

Source: Cheng, Jay J., "Status and barriers of advanced biofuel technology: a review."

Lignocellulosic Materials	Cellulose%	Hemicellulose%	Lignin%
Hardwoods stems	40–55	24–40	18–25
Softwood stems	45–50	25–35	25–35
Switch grass	45	31.4	12–20
Miscanthus	40	18	25
Coastal Bermuda grass	25	35.7	9–18
Corn stover	35–40	17–35	7–18
Wheat straw	30	50	15
Rice straw	36–47	19–25	10–24
Cotton seed hairs	80–95	5–20	0
Newspaper	40–55	25–40	18–30
White paper	85–99	0	0–15

Appendix 2: Bitumen

Bitumen can be specified as a black viscous mixture of hydrocarbons obtained naturally or as a residue from petroleum distillation. It is mostly used in the construction of roads as the glue or the binder mixed with aggregate particles to make asphalt concrete (Barth, 1962). It is also used in construction industry for its characteristic waterproofing and thermoplastic behaviour (Tauste et al., 2018). Bitumen is a colloidal system consisting of the micelles of high polarity and molecular weight, known as asphaltenes responsible for aggregate adhesion (Tauste et al., 2018). There are various types of bitumen available with different properties and specification, used according to the requirements of the Industry. The penetration grade bitumen which is manufactured at different viscosities is categorized as refinery bitumen(Arjun, 2009). The various grades of bitumen are shown in Table 12 (Interchem, 2011).

Table 12 Types of Paving Grade Bitumen Source: (Interchem, 2011)

OMV paving grade bitumen according EN 12591								
Type of binder			OMV Paving grade bitumen					
			20/30	30/45	35/50	50/70	70/100	160/220
Requirement / Characteristic	Test Method	Unit	Range of Values					
Penetration at 25°C	EN 1426	x 0,1 mm	20-30	30-45	35-50	50-70	70-100	160-220
Softening point	EN 1427	°C	55-63	52-60	50-58	46-54	43-51	35-43
Nass change at 163°C	EN 12607-1	%	≤ 0,5	≤ 0,5	≤ 0,5	≤ 0,5	≤ 0,8	≤ 1,0
Retained Penetration	EN 1426	%	≥ 55	≥ 53	≥ 53	≥ 50	≥ 46	≥ 37
Increase softening point	EN 1427	°C	≤ 8	≤ 8	≤ 8	≤ 9	≤ 9	≤ 11
Flash point	EN ISO 2592	°C	≥ 240	≥ 240	≥ 240	≥ 230	≥ 230	≥ 220
Fraass breaking point	EN 12592	°C	≤ -5	≤ -5	≤ -5	≤ -8	≤ -10	≤ -15
Solubility	EN 12592	% (m/m)	≥ 99	≥ 99	≥ 99	≥ 99	≥ 99	≥ 99
Dynamic viscosity at 60°C	EN 12596	Pa.s	≥ 440	≥ 260	≥ 225	≥ 145	≥ 90	≥ 30
Kinematic viscosity at 135°C	EN 12595	Mm^2/s	≥ 530	≥ 400	≥ 370	≥ 295	≥ 230	≥ 135

Appendix 3: Lignin Supply Market

Pulp/paper mills

By the time of 2010, the Pulp/paper industry produced around 50-70 Mt lignin (Laurichesse & Avérous, 2014; Strassberger et al., 2014). Most of this lignin 40-55 Mt was from the Kraft lignin, extracted from the black liquor waste stream in the Kraft pulping process (Bruijnincx et al., 2016; Johannes & Gosselink, 2011). The current amount of the Kraft pulp is 130 Mt with the amount of lignin from all the processes such as Organosolv, soda and sulphite pulping is 70 Mt (Argus, 2018; Gellerstedt, 2015; van Vliet et al., 2016). The majority of lignin (>95%) is used for the combustion of electricity and heat production, whereas a small part is used for the commercial applications (Laurichesse & Avérous, 2014; Peng et al., 2015).

The global estimate of the paper and paperboard amounts to approximately 400 Mt, which is exponentially increasing due to increase in the consumption in Asia (T. M. Bijleveld, 2016b). It is assumed that the global production is going to increase to 500 Mt in 2025 (Irena, 2018). Many paper and pulp mills exist in the world, this research shows the ones in Scandinavia, since only the lignin conversion routes in these regions are assessed. Table 13 shows the largest pulp/paper mills in the Scandinavian region with

details including feedstock, production process and electricity. Table 14 shows the newly planned paper/pulp mills and extensions of some current mills.

Table 13 The largest existing paper/pulp mills in Scandinavia (T. M. Bijleveld, 2016a)

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	

Table 14 The largest planned paper/pulp mills in Scandinavia (T. M. Bijleveld, 2016a)

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	

Lignocellulosic biorefinery

Biorefinery could be defined as a refinery that produces gaseous or liquid biofuels, chemicals or other products that are produced at traditional refineries, using agricultural or forestry biomass feedstock (first, second or third generation) (Bajpai, 2013). The ethanol production from second generation lignocellulosic biorefineries is commercialized now started, therefore not so many of them exist. As shown in Table 15, the ethanol production in the lignocellulosic biorefinery amounts to 394 million litres per year along with lignin production of 157 kton/yr. The production is still low as compared to the paper/pulp mills.

In the future, the market for the cellulosic ethanol is expected to rise partly driven by government imposed renewable fuel mandates especially in Europe (Holm-Nielsen & Ehimen, 2016). There is also a plan to build a biorefinery in the southwest of the Netherlands by Biobased delta (Vera et al., 2018). Table 16 shows the planned biorefineries to increase the production of lignin by 106 kton.

Table 15 The lignocellulosic biorefineries with ethanol and lignin production (T. M. Bijleveld, 2016b)

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**	

Table 16 The planned lignocellulosic biorefineries (T. M. Bijleveld, 2016b)

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**		

Appendix 4: Lignin isolation

There are numerous techniques to isolate the lignin, that can alter the molecular structure of the lignin and thus leading to "technical lignin", of which different types exist differing in the chemical structure as well as in their physicochemical properties (T. M. Bijleveld, 2016a; Bruijnincx et al., 2016). The isolation techniques differ in Pulp/paper mills than the one used in the lignocellulosic biorefinery (T. M. Bijleveld, 2016b).

Paper/Pulp mills

The Paper/pulp mills have different pulping process which also affects the characteristic of the lignin. The lignin is released with black liquor which can be isolated through different techniques (T. M. Bijleveld, 2016a). This appendix gives an overview on the four main pulping process that exist which can be further subdivided into the lignin containing sulphur and sulphur free (T. M. Bijleveld, 2016b; Laurichesse & Avérous, 2014). They are briefly explained below, an overview of their properties are shown in the Table 17. The main isolation technique used to remove lignin from the black liquor in a Paper/pulp mill which is Kraft process is described in more detail as it is more relevant for the thesis.

Sulphur Lignin:

1) Lignosulphates (from the sulphite cooking process)
   The sulphite cooking process uses an aqueous sulphur dioxide (SO2) and a base (calcium, sodium, magnesium or ammonium), to generate a black liquor consisting of sulphur (Bruijnincx et al., 2016). The properties of the Lignosulphates are hydrophilic in nature, high molar mass and polydispersity index with high ash content and carbohydrates (Bruijnincx et al., 2016; Laurichesse & Avérous, 2014). As per the Laurichesse & Avérous (2014) lignin is mostly used for industrial application such as binder, dispersing agent or cement additives.

2) Kraft Lignin (Kraft process)
   It is the dominant pulping process in the world comprising various steps, both mechanical and chemical using sodium hydroxide and sodium sulphate to separate biomass components (T. M. Bijleveld, 2016a; Bruijnincx et al., 2016). Kraft lignin usually have less sulphur content around 1 or 2%, irrespective of using high sulphur condition for the process (Laurichesse & Avérous, 2014). They are commercially available from the hard wood and soft wood like birk, pine and spruce (Bruijnincx et al., 2016).

Sulphur free lignin:

3) Soda lignin(from the alkaline pulping process)
   It differs from the Kraft lignin and Lignosulphates as no sulphur regents are used and the structure is close to that of natural lignin(T. M. Bijleveld, 2016b; Bruijnincx et al., 2016). Soda lignin contain small amount of the ash and carbohydrates and the extraction is based on the hydrolytic cleavage of the native lignin (Bruijnincx et al., 2016). If the pH is adjusted, lignin can be precipitated from black liquor (Laurichesse & Avérous, 2014).

4) Organosolv lignin (from the solvent pulping process)
   The structure is immensely dependent on the process conditions. They are of highest purity in the technical lignin, even if they are hydrophobic they can easily dissolve in organic solvents(T. M. Bijleveld, 2016b; Bruijnincx et al., 2016). If you adjust few of parameters, like acidity, temperature and concentration, the lignin can be isolated(Laurichesse & Avérous, 2014).

Table 17 The properties of technical lignin from pulp/paper mils (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

Several methods have been identified to isolate Kraft lignin from waste stream of paper/pulp mills(Benali et al., 2016).

1) Acid precipitation through sulphuric acid
   This process uses sulphuric acid for the precipitation of lignin from the black liquor by decreasing the pH to 3 and then its washed and filtered(T. M. Bijleveld, 2016a). The sulphur content of lignin is high due to use of sulphur (Kosa et al., 2011).

2) CO_2 precipitation (Lignoboost)
   It uses CO_2 to decrease the pH of the black liquor from 12-14 to around 9.5-10.5. The lignin is precipitated and is washed and filtered. CO_2 is converted into carbonate salts and it is epitomized by the Lignoboost process(T. M. Bijleveld, 2016b; Kosa et al., 2011). The process is an economical and efficient isolation process where the black liquor is extracted and acidified by using CO_2(Fatehi & Chen, 2016). The additional H_2S is generated when lignin is precipitated which is mixed with an acidic filtrate and followed by washing to form small, uncross linked lignin precipitate. Then, crushed and dried to form a lignin powder(Benali et al., 2016; Fatehi & Chen, 2016). NaOH and H_2SO_4 are required for the process like washing the lignin cake and neutralize the recycled stream from the lignin isolation process to the evaporators(Benali et al., 2016; T. M. Bijleveld, 2016b).

3) Lignoforce System
   This process focus on the improving the washing and filtration process of the Lignoboost process, the black liquor oxidation step to be integrated prior to the Lignin precipitation to eliminate the sulphur compounds and convert parts of the organic compounds into carboxylic acids(Benali et al., 2016). The first commercial plant was at West Fraser mill located at Hinton, Canada with a target about 10000 tonnes of dry lignin extraction(Maki et al., 2017).

4) Sequential liquid lignin recovery and purification (SLRP)
   The SLRP technology comprises the separation and purification of the Lignin contained in the black liquor which is first pressurized(Benali et al., 2016). The precipitation of lignin occurs by introduction of the liquid into adsorption column and treating with CO_2 and the pH is reduced to 9-10(T. M. Bijleveld, 2016a). The separation occurs which leads to the formation of dense lignin-rich phase and light lignin-depleted phase(Benali et al., 2016). As shown in Table 18, the difference between Lignoboost, Lignoforce and SLRP.

Table 18 The parameters of three different lignin production (Benali et al., 2016)

Operating parameters and costs	LignoBoost™ process [17, 18]	LignoForce system™ [19, 20]	SLRP™ [22, 23]
CO_2 consumption (t/t)	0.15–0.25	0.20–0.30	0.14–0.18
O_2 consumption (t/t)	0	0.15–0.25	0
Incremental NaOH (t/t)	0.05–0.08	0.08–0.16	0
Water (t/t)	2.00–2.50	4.0–5.00	1.20
H_2SO_4 (t/t)	0.09–0.25	0.10–0.20	0.09
Precipitation yield (%)	70.00	67.00	55.00
Precipitation reactor pressure (kPa)	101.33	101.33	345–1380
Precipitation reactor temperature (°C)	60–70	60–70	80–120
Lignin ash content (%, w/w)	0.02–1.00	0.10–0.70	≤1
Lignin sulphur content (%, w/w)	1.30–3.40	1.40–1.70	2.00–3.00
Chemical costs[a] ($/t of lignin)	100–150	129–227	Not available

[a]The costs are based on the following prices: CO_2 ($300/t); H_2SO_4 ($150/t); NaOH ($600/t); O_2 ($35/t)

5) Ultrafiltration

This method uses membranes and pressure driven, not requires much energy. It faces challenges like the flux decline, identification of the suitable membrane and black liquor composition variables (Benali et al., 2016).

6) Electrolysis

The electrochemical process, the separation is driven by the electric potential gradient. The process removes the Na+ ions from the black liquor through a membrane, thus lowering the pH and causing precipitation of the lignin(Benali et al., 2016).

7) Electrodialysis

The Electrodialysis process uses two selective permeable membranes which permit the migration of the OH-, HS-, HCO(3-) and SO4(2-) to the anode and Na+ to the cathode. This process can lead to the lower energy demands and lower operating cost compared to conventional electrolysis. However, there might fouling can occur and pre-treatment of black liquor might be necessary(Benali et al., 2016).

Lignocellulosic biorefineries

In this process, different methods are used to separate the lignin from the cellulose and hemicellulose. The most commonly method used are steam explosion, dilute acid pre-treatment, alkaline hydrolysis pre-treatment. These methods are briefly explained here.

1) Steam explosion method

This is most common method used for the pre-treatment in the lignocellulosic biorefineries where biomass is impregnated with steam at 200°C or higher with high pressure(Kumar et al., 2009). When there is rapid pressure drop, the fibres of the biomass are liberated into three components (Lange et al., 2015). The lignin can be procured through the extraction of fibres using alkali or aqueous solvent, or by the sugar fermentation to ethanol with the lignin left behind in the fermentation liquid (Bruijnincx et al., 2016). Lignin have a lower molecular weight and higher solubility in organic solvents than Kraft lignin, also it contain little carbohydrates and wood extractive impurities (Bruijnincx et al., 2016; Lange et al., 2015). The lignin from these process are completely or almost free from sulphur (Bruijnincx et al., 2016). This pre-treatment

process can recover high pressure steam and use it for other processes more downstream, and it does not require any chemicals (Gerbrandt et al., 2016).

2) Dilute acid pre-treatment
This process is used by the NREL and several pilot and commercial operations (Gerbrandt et al., 2016). Acid catalyst, mainly SO_2 or CO_2, is used for accelerating the process and decrease the degradation of the sugars compared to the steam explosion pre-treatment method(Kumar et al., 2009; Smaranda, 2010). The process involves the soaking of the biomass in the dilute acid, prior to steam explosion (Gerbrandt et al., 2016). During the sulphuric acid, small amounts of sulphur are incorporated into lignin(Shevchenko et al., 1999). The process requires a subsequent neutralisation step which makes it less energy efficient than steam explosion excluding pre-soaking (Gerbrandt et al., 2016).

3) Alkaline hydrolysis pre-treatment
This method uses bases and lower temperature and pressure compared to other methods. It is performed at the ambient conditions, but re-treatment times are in the order of hours or weeks (Gerbrandt et al., 2016). The alkali agents such as sodium, potassium, calcium, and ammonium hydroxides are used for pre-treatment, where sodium hydroxide is most commonly used. Whereas, calcium is also effective and cheapest option (Gerbrandt et al., 2016; Kumar et al., 2009)

Appendix 5: Uncertainty and Sensitivity analysis

The input variables that were considered were thought to be important throughout the LCA of the ZOAB with lignin. First of all the GHG emission factors are important and were obtained from EcoInvent database or from literature, but they are general values and the emission factor of the products in the actual case may be different. For example, the emission factor for the feedstock used for biorefinery is from wood pellets from USA. However, if the feedstock is taken from the Baltic region, the emission factor is different as seen in the Table 19 and the uncertainty in the results of GHG emission of biorefinery ZOAB is calculated.

Table 19 The emission factor of the feedstock required for the Biorefinery process and respective GHG emission of ZOAB with biorefinery lignin

Change	Input emission factors wood pellets (kg CO_2 eq./kg of wood pellets)	Output (GHG emissions kg CO_2 eq./tonne of ZOAB)	Remarks
20%	0.300	65.8	-
10%	0.275	65.2	-
0%	0.250	64.5	From USA(Vera et al., 2018)
-10%	0.225	63.9	-
-20%	0.200	63.2	-
-49.20%	0.127	61.3	From Latvia(Vera et al., 2018)

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 the chemical parameters as NaOH and H_2SO_4 used in the Kraft mill have a large range due to their input values as shown in Table 4 in section 5.1. The emission factor changes due to this large ranges and the sensitivity to these values on the results of the GHG emission of the Kraft lignin ZOAB is presented in Table 20.

Table 20 The emission factor of the chemicals required for the Kraft process and respective GHG emission of ZOAB with Kraft lignin

NaOH emission factor values (kg CO2 eq./kg of unit)	H_2SO_4 emission factor values	Kraft lignin ZOAB emission (kg CO2 eq./tonne of ZOAB)	Input (t/t)[19]
0.0136	0.00304	52.4	NaOH-0.05; H_2SO_4-0.009
0.0177	0.00845	52.7	NaOH-0.065; H_2SO_4-0.25
0.0354	0.00676	53.1	NaOH-0.13; H_2SO_4-0.20

[19] From (Benali et al., 2016; Manninen, 2010)