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**GLOBAL WARMING POTENTIAL OF WILLOW BIOCHAR
AS A CARBON SINK IN FINLAND**

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TIIVISTELMÄ

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Hiilinieluna toimivan pajubiohiilen ilmastoa lämmittävä vaikutus Suomessa

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Tämän diplomityön tarkoitus oli arvioida pajusta tehdyn biohiilen käyttöä hiilinieluna Suomessa, laskemalla sen ilmastoa lämmittävä vaikutus eli global warming potential (GWP). Tämä tehtiin ”kehdosta hautaan”-tyyppisen elinkaariarvioinnin avulla, käyttäen GaBi Professional-ohjelmaa. Tulokseksi saatiin -1,1 kg CO₂-ekv/kg kuivaa biohiiltä, mikä osoittaa että pajubiohiili on selvästi hiilinegatiivinen ja siksi mahdollista käyttää hiilinieluna Suomessa. Tämä hiilen sitominen johtuu enimmäkseen biohiilen laittamisesta maaperään maanparannusaineeksi. Biohiilen tuotanto voi myös vähentää päästöjä epäsuorasti. Esimerkiksi pyrolyysin sivutuotteet, synteetikaasu ja bioöljy, voidaan käyttää fossiilisten polttoaineiden korvaamiseen. Tässä työssä niistä saatu ylimääräinen energia käytettiin sähkön tuotantoon ja korvaamaan verkkosähköä. Monia epäsuoria hyötyjä on mahdollista saada myös kun biohiiltä laitetaan maaperään, mutta niihin liittyvää tutkimusta ei ole vielä saatu loppuun, joten niitä tarkasteltiin ainoastaan herkkyystarkastelulla. Sen perusteella nämä epäsuorat maaperävaikutukset voivat lisätä biohiilen ilmastohyötyjä huomattavastikin, esimerkiksi lisääntyneen maaperän orgaanisen hiilen muodossa. Toisaalta myös biohiilen tuotannon päästölähteet tunnistettiin, ja kaikkein tärkeimmiksi havaittiin pajuhakkeen kuivaus sekä lannoitteiden tuotanto ja käyttö. Yksi tapa kehittää tuotantosysteemiä olisikin käyttää pyrolyysin sivutuotteiden energiaa pajuhakkeen kuivaukseen. On myöskin tärkeää huomioida maankäytön muutoksesta tulevat päästöt, kun viljellään energiakasveja. Pajun tapauksessa niitä voidaan vähentää kasvattamalla sitä vähätuottoisilla maa-alueilla, kuten entisillä turvesoilla.

ABSTRACT

Lappeenranta-Lahti University of Technology LUT
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Global warming potential of willow biochar as a carbon sink in Finland

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Examiners: Assistant Professor, D.Sc. Ville Uusitalo
Junior Researcher, M.Sc. Anna Claudelin

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The purpose of this Master's thesis was to assess the feasibility of using biochar made from willow as a carbon sink in Finland, by calculating its global warming potential. This was done with a cradle-to-grave life cycle assessment, using the GaBi Professional software. The result was $-1,1 \text{ kg CO}_2\text{eq/kg}$ dry biochar, showing that willow biochar is clearly carbon negative, and is therefore a potential carbon sink in Finland. Most of this carbon sequestration was the result of adding biochar to soil as a soil improvement material. Biochar production can also reduce emissions indirectly. For example, the pyrolysis co-products, syngas and bio-oil, can be used to replace fossil fuels. In this work, the excess energy they provided was used to produce electricity, and to replace grid electricity with it. Many indirect benefits are also possible when biochar is added to soil, but the research behind these is not conclusive, so their role was examined only with a sensitivity analysis. It was found that these indirect soil effects have the potential to significantly improve the climate benefits of biochar, for example by increased soil organic carbon. On the other hand, the emission sources from willow biochar production were also identified, and the most important ones were the drying of willow chips and fertilizer production and use. One way to improve the production system is to use the energy from the pyrolysis co-products to dry the willow chips. It is also important to pay attention to emissions from land use change when cultivating energy crops. In the case of willow, they can be reduced by cultivating it in marginal lands, such as former peat production sites.

TABLE OF CONTENTS

| | |
|--|-----------|
| LIST OF SYMBOLS | 6 |
| 1 INTRODUCTION | 7 |
| 1.1 Background..... | 7 |
| 1.2 Previous studies | 8 |
| 1.3 Objectives and limitations | 9 |
| 2 CARBON SINKS | 11 |
| 2.1 Rocks and oceans..... | 11 |
| 2.2 Biomass..... | 12 |
| 2.3 Carbon Capture and Storage..... | 13 |
| 3 THE PROPERTIES AND BENEFITS OF BIOCHAR | 15 |
| 3.1 Definition of biochar | 15 |
| 3.2 Biochar in soil improvement | 15 |
| 3.3 Biochar as a carbon sink..... | 17 |
| 3.4 Willow in biochar production | 19 |
| 3.5 Willow cultivation in marginal lands | 20 |
| 3.6 Economic feasibility of biochar production..... | 20 |
| 4 TECHNOLOGIES FOR BIOCHAR PRODUCTION..... | 22 |
| 4.1 Fast pyrolysis | 22 |
| 4.2 Slow pyrolysis | 23 |
| 4.3 Other technologies..... | 23 |
| 4.4 Energy requirements of pyrolysis..... | 24 |
| 5 LIFE CYCLE ASSESSMENT METHODOLOGY..... | 26 |
| 5.1 Goal and scope definition | 26 |
| 5.2 Inventory analysis | 27 |
| 5.3 Impact assessment..... | 27 |

| | | |
|----------|---|-----------|
| 5.4 | Interpretation | 28 |
| 6 | PHASES OF WILLOW BIOCHAR PRODUCTION..... | 29 |
| 6.1 | Raw material production..... | 29 |
| 6.2 | Transportation..... | 31 |
| 6.3 | Drying..... | 31 |
| 6.4 | Thermochemical conversion | 32 |
| 6.5 | End uses of biochar | 32 |
| 6.6 | Site restoration | 33 |
| 7 | LIFE CYCLE ASSESSMENT OF WILLOW BIOCHAR..... | 34 |
| 7.1 | Goal and scope definition | 34 |
| 7.2 | Inventory analysis | 36 |
| 7.2.1 | General data | 37 |
| 7.2.2 | Tractor-based operations | 37 |
| 7.2.3 | Herbicides and fertilizers | 39 |
| 7.2.4 | Transportation | 41 |
| 7.2.5 | Drying | 42 |
| 7.2.6 | Slow pyrolysis..... | 44 |
| 7.2.7 | Carbon abatement | 46 |
| 7.2.8 | The GaBi LCA model | 48 |
| 7.3 | Impact assessment..... | 52 |
| 7.4 | Interpretation | 54 |
| 7.5 | Sensitivity analysis | 56 |
| 8 | SUMMARY AND CONCLUSIONS..... | 60 |
| | REFERENCES..... | 62 |

LIST OF SYMBOLS

| | | |
|-----|-----------------------|--------------------------------|
| m | mass | [kg] |
| q | thermal energy | [kWh] |
| U | moisture on dry basis | [kg water/kg dry wood], or [%] |
| X | moisture on wet basis | [kg water/kg wet wood], or [%] |

Subscripts

| | |
|-----------|--|
| C | carbon |
| C,100 | carbon sequestered in soil for 100 years |
| chips,10% | willow chips at 10 % moisture, wet basis |
| w | water |

Abbreviations

| | |
|--------------------|--|
| CCS | Carbon Capture and Storage |
| CO ₂ eq | Carbon Dioxide Equivalent |
| db | Dry weight Basis |
| FU | Functional Unit |
| GHG | Greenhouse Gas |
| GWP | Global Warming Potential |
| IPCC | Intergovernmental Panel for Climate Change |
| LHV | Lower Heating Value |
| NPK | Nitrogen Phosphorus Potassium |
| SOC | Soil Organic Carbon |
| wb | Wet weight Basis |

1 INTRODUCTION

The most recent climate report from the Intergovernmental Panel on Climate Change (IPCC 2018) urges to limit the average global warming to 1.5 °C compared to pre-industrial levels. The temperature rise is already estimated to be 1 °C on average, and at regional level it can be much higher, so the consequences are already seen locally. (IPCC 2018, 51.) The 1.5 °C limit can be achieved only with immediate and drastic emission reductions, but they face plenty of political, economic and other challenges. IPCC (2018) considers multiple pathways to achieving the limit, and most of them take into account the fact that there probably won't be enough emission reductions soon enough. These pathways can still reach the limit, if they use carbon sinks to remove carbon dioxide from the atmosphere. Carbon sinks are especially important in so called overshoot pathways, in which the 1.5 °C limit is momentarily breached but then returned to. There are plenty of options for carbon sinks, and the one considered in this work is to bury carbon in the ground in the form of biochar.

1.1 Background

Biochar is one of the oldest soil enhancement materials. It was used already by the ancient civilizations living in the Amazon region to increase fertility of soil. The effect can still be seen in the soil today as better fertility and higher organic carbon stock. This finding is partly why there has been increasing scientific interest in biochar in the last couple of decades. Research has been done to identify how it works in the soil, what are the best raw materials for it, and how different production methods affect the end result. In some cases, biochar has even been shown to surpass all other soil improvement methods, which is another reason for the increasing interest towards it. (Lehmann and Joseph 2009, 3-4.)

Many possible uses have been identified for biochar: soil improvement, climate change mitigation, energy production, and waste management. For example, converting organic waste products into biochar helps in waste management. Excess heat and side products from pyrolysis can be used in energy production. When biochar is added to soil, it acts as a carbon sink, helping in climate change mitigation. And at the same time, it improves the soil quality through various mechanisms, which are later explained. (Lehmann and Joseph 2009, 5.)

Although a piece of biochar can serve all these functions during its life cycle, this work focuses on the climate change mitigation aspect.

1.2 Previous studies

Climate impacts of biochar during its life cycle have been studied previously. Most studies focus on biochar made from forest or crop residues, or other waste materials. For example a study by Ibarrola et al. (2011) included 10 different urban biodegradable waste materials, while Roberts et al. (2009) studied agricultural residues and switchgrass. They both found out that in most cases biochar is carbon negative during its life cycle, when produced by slow pyrolysis and applied to soil. However, Roberts et al. (2009) also suggests that switchgrass grown as an energy crop might not offer any carbon abatement at all, depending on how indirect land use change is calculated. This highlights the importance of using sustainable biomass in biochar production, which doesn't cause too much direct or indirect climate impacts. Purposefully grown energy crops might not always meet this requirement, but for example many organic waste materials do.

There are already some life cycle assessments of willow biochar, most recently by Hamedani et al. (2019). The study was made in Belgium and concluded that one ton of willow biochar results in net reduction of 2,1 tons of CO₂ from atmosphere, without considering land use change. Similar studies have not yet been made in Finland, though. There was one large research project about willow in 2015-2016, done in co-operation with several institutions, including Carbons Finland Oy and Technical Research Center of Finland (VTT). The results were published in a report by Ympäristöministeriö (2017). One of the results was that it is profitable to grow willow for energy or biochar production in marginal lands, such as former peat production sites (Ympäristöministeriö 2017, 13). This way willow cultivation wouldn't compete with food production. Sufficient fertilization is still required, but willow can utilize many alternative nutrient sources, such as wastewater sludge. There are also other reasons for using willow in biochar production. It is also the fastest growing tree in Finland, so it would be the most efficient way to utilize the available land area (Ympäristöministeriö 2017, 6). Willow has also a very porous structure, which gives the biochar better properties (Ympäristöministeriö 2017, 36-37).

1.3 Objectives and limitations

The purpose of this work is to find out the potential of willow biochar in climate change mitigation in Finland. A life cycle assessment (LCA) is done to find out how much greenhouse gases (GHG) are released from producing the biochar, and how much GHGs can be avoided or removed from the atmosphere by it. This results in the net global warming potential (GWP) of willow biochar, which is expressed in CO₂-equivalents. Based on the previous studies, the initial expectation was that the GWP would be highly negative, and biochar would be a good carbon sink. It is important to reliably quantify this carbon sink effect for example if the carbon offsets produced by it are to be sold in carbon markets.

The LCA is also used to recognize the most important factors affecting the climate change mitigation potential. Other environmental impact categories than GWP are not included in this work, because the focus is on climate change. The LCA is done with the GaBi Professional software. The data for calculating the GWP results are collected from literature, scientific studies, and from the database of GaBi Professional. No experimental data is used, but the values are chosen so that they are representative of a willow biochar production process in Finland. There are several willow varieties, and this work focuses on those which are cultivated as energy crops. Economics of biochar production are not calculated, they are only briefly talked about in a general level.

The life cycle of willow biochar includes production of the willow biomass, transportation, drying of the biomass, biochar production by slow pyrolysis, and applying the biochar to soil. An important limitation in willow farming is the omitting of indirect and direct land use change. This is done partly because willow can be grown in marginal lands, which reduces the land use change impacts. The CO₂-reductions by biochar result mainly from burying it into the soil, but also indirect reductions are possible. These include replacing grid electricity with electricity produced from the pyrolysis co-products. A system boundary expansion is done to take this into account. Applying biochar to soil can also indirectly reduce GHG emissions from the soil, but this is still under research. A lot of uncertainty is related to these indirect soil effects, so they are only considered with a sensitivity analysis.

The work begins with a theoretical part, which introduces the concept of carbon sinks and how biochar is one of them. Biochar properties, benefits, and production methods are also explained. The LCA part begins with general descriptions of the LCA methodology and the willow biochar production process. Then the actual LCA and its results are reported. Finally, the work is summarized and conclusions are drawn.

2 CARBON SINKS

Carbon sink has been defined as any process or mechanism which removes carbon dioxide from the atmosphere and stores it away (IPCC 2018, 558). There are many naturally occurring carbon sinks, but also some artificial sinks are being developed. If carbon sinks could be utilized in large scale by humans, the implications for climate change mitigation would be great. They would offer another major solution for stopping climate change, on top of emission reductions. They would be especially useful for industries that cannot reduce their emissions easily or cost-effectively, such as cement manufacturing and air travel (Fuss et al. 2018). And if despite the best efforts the CO₂-level rises too high, carbon sinks could in theory be used to bring it back to safer levels (IPCC 2018, 342). So far there is no large scale utilization of carbon sinks, but stopping climate change could very well depend on developing them (IPCC 2018, 158).

Carbon can be stored in rocks, oceans, biomass, soil, and atmosphere. It is stored, released, and stored again, in a natural process called the carbon cycle. The sinks can vary a lot in sizes and in the time scales they operate. Research has been done to improve these naturally occurring sinks to make them store more carbon and faster, and to develop completely new ways to store carbon. (Riebeek 2011.)

2.1 Rocks and oceans

By far the largest carbon store are the rocks and sediments containing carbon, like limestone and shale. They are mostly made of calcium carbonate, and contain approximately 65 500 billion tons of carbon. They are formed over millions of years from the remains of different kinds of marine organisms. The carbon in rocks is stable for a long time, but even it is eventually released because of the movement of earth's tectonic plates and volcanic activity. (Riebeek 2011.) Although the formation of calcium carbonate and the rocks containing it is a complicated chemical process, it can be sped up by a simple process called enhanced weathering. In it, ground up rock is spread over land, where it can be naturally weathered by the rain. The research about this method is still inconclusive, but for example Fuss et al. (2018) suggests it could be a very significant carbon sink, with the potential to remove 2-4 Gt/y of carbon dioxide from atmosphere. This is for example more than biochar's estimated

potential, 0,3-2 Gt/y. As with all carbon sinks, enhanced weathering could be costly to implement and it could have some side effects. These include increased water pH and release of heavy metals from the rocks being weathered. (IPCC 2018, 345.)

Oceans store also huge amounts of carbon dissolved in the water, an estimated 37 000 billion tons. This carbon is used by organisms in their photosynthesis, but there are also chemical reactions leading to a stable form of carbon called bicarbonate. Normally the carbon uptake and release from the oceans are in equilibrium, but as the CO₂-levels in the atmosphere have risen, the carbon uptake rate has also increased. It is still much lower than the emission rate from burning fossil fuels, but given enough time, the oceans could take up most of the carbon released by humans. There is great potential in the oceans for storing carbon, so a lot of research has been done to understand their role in the carbon cycle and in climate change. (Riebeek 2011.) To enhance the carbon uptake, one method could be to counter the ocean acidity by alkalization. CO₂ causes acidity, but acidity also slows down CO₂ uptake. Another suggestion is to fertilize the oceans to increase the number of organisms capable of photosynthesis. Again, there is a lot of uncertainty about the effectiveness of these methods and their drawbacks. They could easily cause severe side effects to the marine ecosystems. (IPCC 2018, 345-346.)

2.2 Biomass

Plant biomass and soil are estimated to contain 550 and 2 300 gigatons of carbon, respectively. In the atmosphere there is about 800 Gt, of which 120 Gt is taken up every year for photosynthesis, mostly by plants and phytoplankton (Lehmann and Joseph 2009, 322). And every year about the same amount is released back from the metabolism of plants and animals, and when organic matter decomposes. In total, the net amount of carbon stored in biomass and soil changes very little. (Riebeek 2011.)

Plants can be still used to sequester carbon in many ways, often very cost-effectively and simply. These methods work by increasing permanently the amount of biomass and soil carbon stock, in areas where they don't exist or have been reduced. These include agroforestry, reforestation, afforestation, restoration of degraded land, and conservation agriculture. These offer many benefits at local scale, including better agricultural yield and

increased biodiversity. All these techniques have already been used for some time, and can be done at low cost or sometimes even for profit. (IPCC 2018, 343, 345.)

These methods can be very effective also in global scale, but sometimes problems may occur. Forestation might not offer any benefits in higher latitudes, because forests change the albedo and reflect less light, which can result even in local warming effect. Huge forested areas also increase requirements for forest management. Biomass and soil will eventually saturate with carbon, even forests will stop increasing their carbon stocks within a few centuries. A better option might be to use the available land for growing energy crops. They provide ways to remove carbon more efficiently and more permanently, such as bioenergy with carbon capture and storage (BECCS), and biochar. (IPCC 2018, 343-345.)

2.3 Carbon Capture and Storage

Carbon capture and storage (CCS) includes capturing carbon dioxide, transporting it, and storing it away underground, like in an old oil or gas well. CO₂ is typically captured from the CO₂-rich exhaust gas of a power plant, and many technologies are available for this. CCS has been in use already for some time and it is used by many industrial processes where CO₂ is either produced or consumed in large quantities, such as the beverage industry. The technology for CCS is therefore already well established. (Global CCS institute 2019.)

CCS could help in climate change mitigation if used with emission intensive processes, such as fossil fuel power plants or cement production. However, it might offer even more benefits if used together with bioenergy. This process is known as bioenergy with carbon capture and storage (BECCS). In this method, plants sequester CO₂ through photosynthesis, and the biomass is burned for energy. CCS captures the CO₂ from the flue gases, taking it out of the carbon cycle. CCS can prevent fossil fuels from increasing the CO₂-levels, but BECCS actually reduces them while providing energy at the same time. CCS technology is included to some extent in most climate scenarios by IPCC (2018). However, BECCS requires huge areas of land for growing the biomass to have a significant impact. On average, the climate change mitigation pathways of IPCC require 25-46 % of the agricultural land for energy crops, by the year 2100. Availability of land is clearly a big limiting factor for biomass-based

carbon sinks. Taking up so much land could also have some serious side-effects, including reduced food security and biodiversity. (IPCC 2018, 342-343, 346.)

Direct air carbon capture and storage (DACCS) is not restricted by the availability of land. DACCS could potentially remove large amounts of carbon dioxide from atmosphere, but capturing it directly from air is much more challenging than from flue gases. It requires more energy and is still very expensive. There have been only a few small-scale experiments, so there is a lot of room for improving the technology and its cost-efficiency. However, technology and costs are not the main obstacles for deploying and scaling up CCS. Currently there is not much funding for it, due to lack of political and public support. Without them, any technology cannot significantly contribute to climate change mitigation. (IPCC 2018, 158, 343, 346.)

3 THE PROPERTIES AND BENEFITS OF BIOCHAR

This work focuses mostly on the ways by which biochar could help in climate change mitigation. However, this black substance has also many other benefits and uses, such as in soil improvement and water treatment. The versatility of it comes from its physical and chemical properties, which in turn depend on the feedstock and production parameters. In some cases, these can be fine-tuned to best match the intended use of the biochar. For example, one of the best feedstocks in terms of climate change mitigation is willow. Willow not only makes high quality biochar, but it can also be cultivated in a sustainable way.

3.1 Definition of biochar

The European Biochar Certificate defines biochar as heterogeneous substance with high carbon and mineral content. It is made by heating biomass to 350°C - 1000°C in low oxygen conditions, in a process called pyrolysis. Charcoal is made in a similar way to biochar, and the difference between them is subtle. They are mostly distinguished by their intended use, but also to some extent by their quality and production method. While charcoal is typically burned and thus releases its carbon quickly back to the atmosphere, biochar is used in ways that keeps the carbon stable for longer periods. This means usually soil improvement, but there are also other end uses for it. Additionally, biochar is produced from sustainable biomass, with modern and clean pyrolysis technology. It can be made from almost any biomass, commonly agricultural or forest residues, including wood chips, straw and manure. The type of feedstock used affects its properties, like its carbon content. (EBC 2012, 6; Lehmann and Joseph 2009, 1-2.)

3.2 Biochar in soil improvement

Biochar is traditionally seen as a soil amendment substance, although its definition doesn't require that anymore. Biochar, or charcoal, has been long known to improve agricultural yields, and lately several explanations have been found for this. Perhaps most importantly, biochar can retain a lot of water, which is then available for plants in dry periods. This is possible because of its many pores of different sizes, as seen in figure 1. (Lehmann and

Joseph 2009, 3, 22-25; Singh and Kumar 2017, 466-467.) Willow wood is highly porous, which makes it a very good feedstock for biochar (Ympäristöministeriö 2017, 35-37).

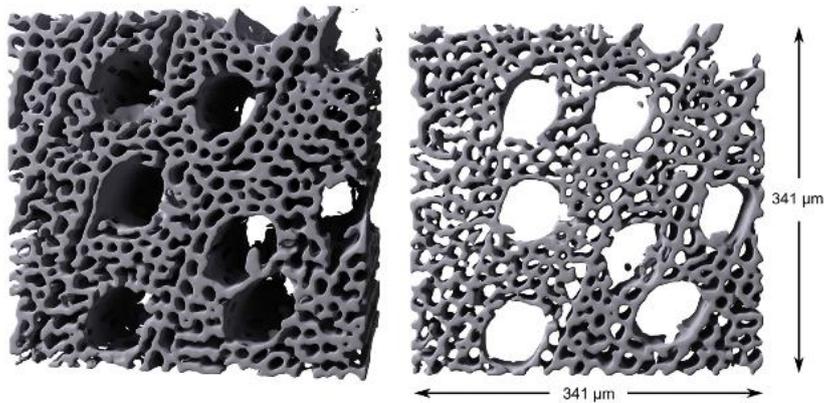


Figure 1. A 3D-image of willow biochar, showing its porous structure (Rasa et al. 2018).

Biochar also helps in fertilizing the soil, because it can hold nutrients and release them slowly over time. It can be a direct fertilizer, if it's made from a nutrient-rich feedstock, or if it's enriched with nutrients afterwards. However, even more important are its indirect effects on nutrient availability. Because of its big surface area and chemical properties, biochar retains nutrients and prevents them from leaching away from the soil. This improves the efficiency of fertilizers, which is seen as increased yield and reduced fertilizer requirement. (Lehmann and Joseph 2009, 22, 67, 71, 73; Singh and Kumar 2017, 466-468.)

There are also other ways by which biochar can improve plant productivity. It affects the soil properties beneficially, improving its density, porosity, and surface area. Together with better nutrient and water-holding capacity, this provides a good growing medium for plants, but also for the whole soil microbiome, which is important for soil fertility. Many of these improvements in soil quality can be directly explained by the increased soil organic matter content. (Lehmann and Joseph 2009, 22, 73, 85; Singh and Kumar 2017, 467-470.)

Another very important factor is the soil pH. Biochar increases soil pH, which can increase the yield significantly if the soil is acidic. However, in some studies biochar has caused negative effects, reducing the yield. This was thought to be caused by the pH, which increased too much. The effect of biochar depends also on how much of it is applied, what are the soil properties, and how it is made. There can be a lot of variation between different

soils and biochars, so understanding their properties is very important for achieving the desired results on plants. The highest yield increases have been reported when biochar has been applied to poor quality, acidic soil. (Lehmann and Joseph 2009, 68, 73-74, 212; Singh and Kumar 2017, 468.)

3.3 Biochar as a carbon sink

Plants are sequestering CO₂ all the time by photosynthesis, but it is soon released back when they are decomposed. It is also released if the biomass is burned for energy or when forest is burned for example to create farmland. However, the carbon can be made much more stable, if the biomass is turned into biochar. It is much slower to decompose, because it is made mostly of aromatic carbon rings. (Lehmann and Joseph 2009, 8, 190-191.) When added to soil, most of it stays sequestered for hundreds or even thousands of years, which is why it is considered to be a long-term carbon sink (Lehmann and Joseph 2009, 322; Singh and Kumar 2017, 469).

Not all carbon in biomass is turned into biochar in pyrolysis, though. Depending on the feedstock, about 50 % of the carbon goes into biochar in slow pyrolysis, the rest goes into pyrolysis gas and oil (Lehmann et al. 2006). A fraction of the carbon in biochar will also rapidly decay, within a few years of soil addition. This labile fraction has been assumed to be around 15-25 %, but it is difficult to determine precisely (Lehmann and Joseph 2009, 118, 328; Hammond et al. 2011). Also the stable carbon will eventually be decayed by natural forces, like erosion and the activity of bacteria and animals (Lehmann and Joseph 2009, 169-178). Most sources estimate it to last at least several hundreds of years, but char residues from old forest fires have been found to be over 10 000 years old (Lehmann and Joseph 2009, 184-186). The decay rate of biochar is very slow, and also very difficult to determine with certainty. It is known to depend on the feedstock, pyrolysis parameters, and soil properties (Lehmann and Joseph 2009, 113). For example, biochar made in higher temperature has more density and less volatile matter, making it more stable in the soil (Lehmann and Joseph 2009, 28-29, 188-189).

Biochar can reduce emissions also by other, indirect mechanisms. In many cases it has been proven to reduce GHG emissions from soil, including nitrous oxide (N₂O), methane (CH₄),

and carbon dioxide (CO₂). The reason for this is not entirely clear, but it has probably something to do with the changes in the physical properties of soil and the activity of soil microbes. The emissions depend heavily on the type of soil and biochar, and in some cases biochar has even increased them. (Spokas and Reicosky 2009.) Biochar could also increase the soil organic carbon (SOC) by increasing plant productivity and decreasing the decomposition of organic matter (Hammond et al. 2011). However, the research on many of these effects is still inconclusive, and only focuses on the short-term effects.

There are also other indirect effects. The use of irrigation and fertilizers can be reduced, because of increased nutrient and water retention capacity of soil, and because the overall productivity of soil increases. Reducing the need for nitrogen fertilizer is especially good, because its production and use causes a lot of emissions, especially N₂O. A biomass which would otherwise decompose anaerobically causing CH₄ and N₂O emissions can be turned into biochar, preventing those emissions. Also the co-products from pyrolysis can provide indirect emission reductions. They can provide energy, which can be used as a substitute for fossil fuels. (Lehmann and Joseph 2009, 321-324.)

There are some studies about the global carbon sequestration potential by biochar. A literature review by Fuss et al. (2018) found that the estimates range between 0,6 and 11,9 GtCO₂/a by 2050, but they conclude that the most realistic estimate is 0,3-2 GtCO₂/a. This number is mostly limited by the availability and price of biomass (Fuss et al. 2018). For the highest carbon sequestration, biomass must be grown purposefully for biochar production. To sequester 0,3 GtCO₂/a, it is estimated 40-260 million hectares of land is needed (IPCC 2018, 345). This could lead to massive land use change and competition with food production. It would also compete with other technologies for land, such as BECCS. The need for land can be avoided to some extent by using waste products for biochar production, such as forestry and agricultural residues and urban wastes. Lehmann and Joseph (2009, 323) found that these wastes alone could sequester 0,59 GtCO₂/a globally. There are not yet estimates on the biochar potential in Finland.

3.4 Willow in biochar production

The genus of willow (*Salix*) includes hundreds of different varieties. Some are trees and some only shrubs. Willow is often the first plant to start growing on a newly exposed land. The best variety for biochar production is one that is well adapted for the cold climate of Finland, has high yield, and resistance to pests and other problems. Different varieties can be cultivated in the same area to make the crop more resistant to problems. (Tahvanainen 1995, 10-12.)

Almost any biomass can be used for biochar production, but willow has many advantages. It's the fastest growing tree in Finland, meaning it takes up more carbon and produces more biomass in smaller land area than other tree species (Ympäristöministeriö 2017, 6). It grows in a wide variety of soils, including some marginal lands. It can be harvested often, every 3 to 5 years. Its cultivation is simple, it's easy to plant and doesn't require replanting after each harvest, because it sprouts new shoots from the stem. Its physical properties are also very beneficial for soil improvement, due to the porous nature of the wood (see chapter 3.2). However, willow needs plenty of nutrients and water to grow well and to be profitable to farm. As with any energy crop, it also has the potential to cause indirect land use change, if it's cultivated in fields normally used for food production. (Tahvanainen 1995, 29-33, 53.)

Willow plantations remove nitrogen efficiently from water, but also filtrate other nutrients and pollutants, such as heavy metals. Therefore it can be cultivated near water bodies to form a buffer zone, to prevent nutrients from leaching from agriculture and causing eutrophication. Plantations have also been utilized in wastewater treatment, by spreading nutrient-rich wastewater over a willow field. The benefit is two-fold in both cases: willow gets nutrients and water to grow, and water gets cleaned. This also reduces the need for artificial fertilizers. Willow can also use fertilizers that are not recommended for food production, such as municipal wastewater sludge and some side products from industry. However, if the water or soil contains too much heavy metals, the willow cannot be used in biochar production. (Tahvanainen 1995, 18-20; Bhardwaj 2015, 121.)

3.5 Willow cultivation in marginal lands

Marginal lands include former peatlands, abandoned or low yield farmland, and other lands where traditional agriculture or forestry are not feasible (Hytönen 1995; Ympäristöministeriö 2017, 7). Especially cut-away peatlands have been of interest in Finland, because every year vast areas are released from peat production. Some research has been done about growing willow in these peatlands, for example Hytönen (1995) and Ympäristöministeriö (2017).

Willow cultivation in marginal lands could be beneficial in many ways. Most importantly it would prevent indirect land use change, because it wouldn't compete with food production. It would also provide a source of income for the landowner from a land that is not otherwise very productive. Willow plantation improves the soil by increasing ground biomass in the form of roots and fallen leaves. Increased plant coverage also reduces erosion and can prevent nutrients and organic matter from leaching from soil to water. (Hytönen 1995; Ympäristöministeriö 2017, 7, 18-20.)

Problems with cultivating willow on marginal lands are mostly to do with the lack of nutrients, but otherwise willow is not too discerning about where it grows (Caslin et al. 2015, 7). For example, peatland is almost absent of two important nutrients, phosphorus and potassium. These need to be added in high quantities in the establishment phase to make the conditions suitable for agriculture. On top of this, peat is slightly acidic which needs to be corrected by adding lime or ash. This need for fertilization could lead to more nutrients leaching to water, which must be taken into account. Precision fertilization and safety zones are some solutions for this, and the peat production sites have also existing systems for water treatment. (Hytönen 1995; Ympäristöministeriö 2017, 19.)

3.6 Economic feasibility of biochar production

Many studies have calculated the costs of biochar production in detail, but that is not in the scope of this work. Based on other studies, it is not yet economically feasible to produce biochar just for large scale soil application (Fuss et al. 2018). In the report by Ympäristöministeriö (2017, 4) the value of biochar was estimated to be 220 euros/m³. This

makes it feasible only for small scale gardening, water treatment, and other applications where the price is not a problem.

The costs of carbon offsets by different methods have been reviewed by Fuss et al. (2018). They give a rough estimate for offsetting CO₂-emissions by biochar soil application, which is 90-120 US\$/tCO₂. For reference, afforestation and reforestation would cost 5-50 US\$/tCO₂ and CCS-based methods 100-300 US\$/tCO₂ by their estimation. Biochar is not the most expensive method, but there is a lot of room to make it more cost-efficient. Several ways have been suggested for this. First, it could be used in more applications during its life cycle, such as in water treatment or as a filter media. Only then it would be added to soil, so its benefits would be multiplied. Biochar could also become more attractive if there were financial support schemes for it. For example, higher carbon tax and higher cost of carbon offsets would encourage biochar production. When the production increases, the cost would also go down because of economy of scale and improvements in production technology. (Fuss et al. 2018.)

4 TECHNOLOGIES FOR BIOCHAR PRODUCTION

Biochar is produced by pyrolysis, which is also called thermochemical conversion. Primitive pyrolysis processes have been used for thousands of years to produce charcoal for fuel. Also tar and other chemical products were made from wood by pyrolysis, before crude oil became available. The technology has changed a lot since then. Pyrolysis technologies were developed especially in the 1970s for bio-oil production, but later also the importance of biochar was realized. (Brownsort 2009, 3; Panwar 2019.)

In pyrolysis, organic matter is heated in absence of oxygen, leading to chemical decomposition (Brownsort 2009, 2). Several different processes fall under this definition, but they can also be called by other names than pyrolysis, depending on the source. The processes can be divided broadly into fast and slow pyrolysis. They differ by the process parameters, which in turn affect the amount and quality of the pyrolysis products. The main parameters are peak temperature, heating rate, residence time, and feedstock. These affect the properties of the biochar, such as surface area, pH, and amount of carbon in the char. (Basu 2018, 165, 185; Lehmann and Joseph 2009, 132, 342.)

The main products are char, gas, and liquids. The gas contains several combustible gases, such as carbon monoxide, hydrogen, and different hydrocarbons, and non-flammable gases such as carbon dioxide and nitrogen. Together these are known as synthesis gas, or syngas. The gaseous phase contains also many condensable vapors, which can be condensed into bio-oil. It consists of water, tars, and organic liquids. It can be burned to produce energy, or it can be processed further into different chemical products. The pyrolysis process can be optimized according to the purpose, for example for biochar production or energy production. (Brownsort 2009, 2, 9-10.)

4.1 Fast pyrolysis

Fast pyrolysis is used when bio-oil is the main product. In this process the feedstock is very quickly heated to about 400-650 °C. The residence time is very short, only a few seconds. The feedstock particle size must be very small to make the rapid heating possible. Quick removal of the vapor from the reactor is also important, so it doesn't have time to react into

other products. About 70 % of the dry feedstock mass is turned into bio-oil, but only 15 % into char. This is less char compared to slow pyrolysis, but the char has higher carbon content and less volatile matter, making it more stable in the ground. (Basu 2018, 163-164, 166; Lehmann and Joseph 2009, 132, 342.)

There are several types of pyrolysis reactors and many ways to classify them. They can be batch operated or continuous processes. The modern commercial reactors are usually continuously operated. Suitable reactors for fast pyrolysis include fluidized bed reactor, ablative reactor, and vacuum reactor. (Basu 2018, 176.)

4.2 Slow pyrolysis

Slow pyrolysis produces about equal amounts of char, gas, and liquid. It is used for biochar production, and the char yield can be as high as 35 % of the dry weight of the feedstock. The feedstock is slowly heated to 400 °C or more, and stays in the reactor from 30 minutes to several hours. This gives enough time for the secondary cracking reactions to occur, which converts the vapor into char and non-condensable gases. Slow pyrolysis is sometimes also called carbonization, as it produces carbon rich char. In some cases the liquid or gas are not collected at all, but combusted for energy. (Basu 2018, 157, 163; Lehmann and Joseph 2009, 342.)

Slow pyrolysis reactors were traditionally batch operated, but in commercial production continuous processes are used. The reactor is typically a horizontal tube-like kiln, and the biomass slowly passes through it. Reactor types for slow pyrolysis include drum kiln, screw pyrolyzer, and a rotary kiln. (Panwar 2019; Brownsort 2009, 4.)

4.3 Other technologies

There are other processes which can produce biochar by heating biomass, but are usually not included under the term “pyrolysis”. They differ based on the end goal and process parameters. For example, torrefaction is like slow pyrolysis, but occurs in a lower temperature of about 200-300 °C. The end product of torrefaction contains more volatile

matter compared to carbonization, because its goal is to maximize the mass and energy content of the char. (Basu 2018, 93-96.)

Gasification and flash pyrolysis are processes, which operate in higher temperatures than conventional pyrolysis, and the process is much faster. They are designed to produce syngas or bio-oil, but can produce also significant amounts of biochar. There is also a process called hydrothermal carbonization, which is used to produce carbon-rich materials from very wet feedstocks. It occurs in water, under high pressure and temperature. This way carbon can be recovered from feedstocks that would otherwise require a lot of drying before they could be used in conventional pyrolysis. (Brownsort 2009, 4.)

4.4 Energy requirements of pyrolysis

Thermal energy is needed during the pyrolysis process for several things. First, energy is needed to heat the biomass and the heat transfer medium to the reaction temperature. Some of this heat goes for drying out last of the water in the biomass. As the temperature increases, chemical reactions start to happen. This causes gases and vapors to be formed and released, and char is also formed. If even more heat is provided and the temperature is raised high enough, secondary cracking reactions start happening, turning the vapor into char and non-condensable gases. Some of these chemical reactions are endothermic and some exothermic. The exothermic reactions provide some heat, but not enough for heating the biomass and to compensate for all endothermic reactions and heat losses. (Basu 2018, 168-169, 175.)

There are many methods and designs for providing the heat needed in pyrolysis. Usually this is done by combusting part of the biomass or the pyrolysis products. This can happen inside the reactor, by providing a small amount of oxygen to the process. In commercial systems however, the combustion happens in a separate burner and the heat is transferred through a medium such as hot flue gas, as seen in figure 2. A fossil fuel such as natural gas can be used in the burner, but often the pyrolysis gases and vapors are used instead. (Basu 2018, 174-175; Panwar 2019.)

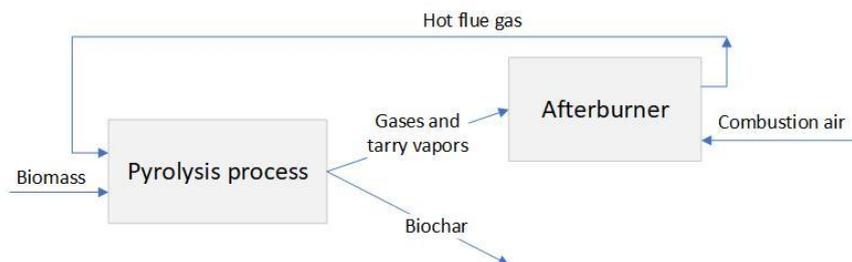


Figure 2. A simplified pyrolysis process where hot flue gas provides the heat for the process. Adapted from Panwar (2019).

There are many studies about the thermal energy need of pyrolysis, but it can vary a lot depending on the feedstock and process. Crombie and Mašek (2014) studied how a slow pyrolysis could be made self-sustainable. A review by them found out that the energy requirements are typically between 6-15 % of the higher heating value of the feedstock. If the process parameters are chosen properly, the produced syngas alone can contain this much energy, and provide all heat for the process. Rest of the pyrolysis products and the energy contained in them can be then used for other purposes. (Crombie and Mašek 2014.)

If the bio-oil or syngas are recovered and collected, they can be used for energy production in almost the same way as any traditional fuel: in a gas turbine, boiler, or a combustion engine. Some modifications might be necessary though, due to different fuel properties and emissions compared to fossil fuels. (Whitty et al. 2008; Wissmiller 2009, 20-25.) The pyrolysis plant can also directly provide heat for any process where it is needed, using for example waste products from another process as a feedstock. The excess heat can be also recovered for example by a steam boiler for electricity generation. (Pyrocal 2019.)

Energy produced from the pyrolysis products is considered carbon neutral, because it comes from renewable biomass. The plants sequester the carbon when they grow and release it when they decompose or are combusted. This doesn't result in net increase of carbon dioxide in the atmosphere. This is why pyrolysis energy can be used to replace fossil fuels and thus avoid a net increase in greenhouse gas emissions. (Brownsort 2009, 9-10.)

5 LIFE CYCLE ASSESSMENT METHODOLOGY

Life cycle assessment (LCA) is the method used in this work to quantify the carbon sink effect of willow biochar. The methodology for LCA is explained in the international standards ISO 14040:2006 and ISO 14044:2006, which are also used in Finland as national standards. LCA is a tool for assessing the environmental impacts of a product system. Its results can be used for example in decision-making, marketing, and to make the products more environmentally friendly. It includes four phases, which are explained in general level in this chapter. They are Goal and scope definition, Inventory analysis, Impact assessment, and Interpretation. These phases are done iteratively, so the results of one phase can cause changes in others. (SFS-EN ISO 14040, v, 7.)

5.1 Goal and scope definition

The goal and scope definition phase provides a framework for the study. Goal and scope can change as the study progresses and new information is gained. The goal of an LCA explains why the study is done and for what application, and to whom the results are communicated. Also the scope includes several important items. First, the product system and its functions are defined. A functional unit is chosen, to quantify how well the product system fulfills its function. The functional unit is important because all the flows are expressed relative to it. It also makes it possible to compare different products which all have a similar function. (Bruckman et al. 2016, 49; SFS-EN ISO 14040, 11-12; SFS-EN ISO 14044, 7-8.)

Then the system boundary is defined. This means that it is decided which unit processes and flows are included in the study. This depends on the assumptions, limitations, data quality requirements and the cut-off criteria, which are also established in the scope. Assumptions affect the reliability of the study, so they should be explained clearly. To better understand the flows and unit processes, a process flow diagram can be included. (Bruckman et al. 2016, 49; SFS-EN ISO 14040, 11-12; SFS-EN ISO 14044, 7-9.)

Scope also explains the method for dealing with multiple co-products from one process. Allocation is one such method, and in it the environmental impacts of the process are allocated between the products based on some characteristic, like weight. However,

allocation should be avoided if possible. Instead, the unit process should be divided into smaller processes, or the system boundary should be expanded to include the co-products. In scope, it is also decided which environmental impacts are focused on in the impact assessment phase and which impact categories, category indicators and characterization models are used. (Bruckman et al. 2016, 49; SFS-EN ISO 14040, 11-14; SFS-EN ISO 14044, 7-11, 14.)

5.2 Inventory analysis

In life cycle inventory analysis (LCI) data is collected from each unit process and the inputs and outputs of each process are quantified. Primary data can be collected from several sources, including by field measurements, literature, and databases. Data quality and quantity are determined by the goal and scope of the study. To ensure consistency of data, there should be clear documentation of the collection process and the factors which influence the inputs and outputs. Also a process flow diagram can be included here to show the unit processes and their interrelationships. (Bruckman et al. 2016, 49-50; SFS-EN ISO 14044, 11.)

After enough data is collected, some calculations with it are done. The data needs to be validated to ensure its quality and that the necessary flows have been accounted for. This can be done for example with mass and energy balances. For consistency, the flows shall be calculated in relation to some reference flow. An appropriate reference flow is selected separately for each unit process. In the end, all flows should be expressed relative to the functional unit. Data allocation or system boundary expansion are also done at this point. (SFS-EN ISO 14044, 13-14.)

5.3 Impact assessment

In impact assessment (LCIA) phase the potential environmental impacts of the product system are determined from the inventory data. First, the impact categories, category indicators, and characterization models are selected. Examples of impact categories are Global Warming Potential (GWP), Acidification Potential and Eutrophication Potential.

Only those categories are selected which are relevant to the product system and goal and scope. For each category there are indicators, for example GWP could be indicated by kilograms of carbon dioxide equivalent (kgCO₂eq). Next step is assigning the flows from LCI to the impact categories, known as classification. Then comes characterization, where the category indicator results are calculated. In this step, the characterization models are used for converting the flows into units of the category indicator. (SFS-EN ISO 14044, 16-20.)

There are also some optional elements in LCIA. Normalization can be done to better understand what the relative impact of each category indicator result is. Impact categories can be grouped together based on different characteristics, in a process called grouping. Weighting is another optional element, where the impact categories are given some weight factor. Lastly, additional data quality analyses are possible in this phase. (SFS-EN ISO 14044, 20-22.)

5.4 Interpretation

In the Interpretation phase results from Inventory analysis and Impact assessment are collected together, interpreted, and used to make conclusions and recommendations. The results of the study are reported clearly and consistently with goal and scope. This phase is also done iteratively with other phases. (Bruckman et al. 2016, 51; SFS-EN ISO 14044, 23-24)

At first the significant issues are identified from the Inventory analysis and Impact assessment results. This includes obtaining and structuring of data from those life cycle stages. Significant issues can include life cycle phases, input and output flows, and environmental impact categories. Then the results are evaluated, using sensitivity, completeness and consistency checks. Evaluation gives better understanding of the reliability of the results and makes sure that they are consistent with the goal and scope. After these, the conclusions, limitations and recommendations can be given. (Bruckman et al. 2016, 51; SFS-EN ISO 14044, 23-27, 36.)

6 PHASES OF WILLOW BIOCHAR PRODUCTION

In this chapter, the production process of willow biochar is explained in general level, from cultivating willow to its different end uses. Each life cycle phase is outlined, and the most important inputs and outputs are recognized. This chapter provides supporting information for the LCA, especially for Goal and scope definition and Inventory analysis.

6.1 Raw material production

The raw material for the biochar is in this case willow biomass, more precisely willow wood chips. Willow can be cultivated in any land suitable for agriculture, even in some marginal lands. It's not too picky about the soil type, but requires more water than conventional crops. It is the most productive in high quality soils where there are plenty of water and nutrients available. (Caslin et al. 2015, 7-8; Tahvanainen 1995, 23-25, 33-34.)

Before planting, the soil must be prepared by ploughing and harrowing. These are standard tractor operations, needed for example for weed control. The planting is done with a machine, which puts the un-rooted willow cuttings in the ground. These cuttings are about 20 cm long pieces of the willow stem, and they sprout new stems when put into soil. In the first year the roots are not yet well established, so irrigation might be needed. For the same reason willow cannot compete well with weeds in the first year and weed control is required. Mechanical weed control is preferred, but often herbicides are used, because they are more efficient to use. After the first year, neither irrigation nor weed control is usually needed. There is also the option to cut down the young willows (cutback) to induce the sprouting of more stems. This can improve yield and help in weed control, but is not always needed. (Tahvanainen 1995, 23-32, 38-39; Caslin et al. 2015, 7-24.)

Weed control begins with ploughing before planting. Herbicide is sprayed after planting, but before the cuttings have sprouted, because otherwise it will kill the willows. Herbicides can also be applied after the cutback if needed, before re-growth has begun. (Caslin et al. 2015, 25-27.)

Productivity of willow depends a lot on the availability of water, but also the amount of nutrients has a big effect on its yield. Organic and inorganic fertilizers are used in energy willow plantations to ensure a good yield. The amount of fertilizers depends on the specific soil and also how much nutrients are removed from the field with the biomass. The first application of fertilizers should be done one year after planting. However, fertilization becomes problematic after the willows have grown tall, because the plantation cannot be accessed with a tractor. According to Tahvanainen (1995, 37), fertilizers can be spread with a tractor in the first and possibly second year after growth has begun. It might be also possible after that, if there is a path for the tractor between the willows, although this is not always the case. The literature indicates that it is more common to do only one application of fertilizers after each harvest, when the field is still easily accessible with a tractor (Caslin et al. 2015, 33; Tahvanainen 1995, 37; Ympäristöministeriö 2017, 18). This application must cover the whole fertilizer need of the 3 to 5-year harvest cycle. In this case, it might better to use organic fertilizers, such as wastewater sludge. They contain slowly released nutrients, as opposed to inorganic fertilizers, which usually release the nutrients quickly. (Tahvanainen 1995, 33-37)

Yield means the increase in aboveground dry biomass, per hectare per year. This doesn't include leaves. In the first year the yield is usually less than 1 t/ha/a, so the year can be thought to be part of the establishment phase. In subsequent years the yield increases. In good soils with enough nutrients and water it could be over 10 t/ha/a, but in practice it is usually less. 8 - 10 t/ha/a is realistic in Finland, with proper soil management. (Tahvanainen 1995, 52-53; Ympäristöministeriö 2017, 4.) Yield can be increased with irrigation, and wastewater can be used for this. Usually irrigation is not used, though, because willow gets all the water it needs naturally, if the plantation site is chosen properly (Tahvanainen 1995, 33-34).

After 3 to 5-years of growth the plantation is harvested. The best season for this is winter, when the leaves have fallen and the ground is frozen. Several machines are available for this. They can be tractor-operated machines which produce chips or harvest the stems as whole. Whole rod harvesting is more expensive, but it makes drying easier. Whole rods also need to be transported to a separate chipping facility. Forage harvesters can be modified for harvesting willow, but not for whole rod harvesting. A tractor with a trailer is usually driving

alongside the harvester to carry the chips. Then then the chips are transported to a drying facility. (Caslin et al. 2015, 49-51; Tahvanainen 1995, 46-47, 52-53.)

6.2 Transportation

The next step is to haul the feedstock from the field to a drying facility, and after that to pyrolysis. Sometimes logistics includes also steps such as intermediate storage or external chipping facility. The last step is to transport the biochar to a field, where it will be applied to soil. Short transport distances can be covered with a tractor trailer, but in longer distances a truck is more economical. When transporting biochar, care should be taken to avoid losses of the fine biochar dust. However, this can never be completely avoided. (Bruckman et al. 2016, 54; Major 2010, 7, 13.)

6.3 Drying

Drying is an important pre-processing step for pyrolysis, because pyrolysis requires very low moisture. Fast pyrolysis and gasification are especially sensitive to it, but in slow pyrolysis moisture is less important because of longer residence time and slower heating. The moisture content of feedstock affects its weight and thus the transportation emissions, and also how much energy is needed to dry and pyrolyze it. When dry feedstock is used in pyrolysis, less energy is needed and emissions are easier to control. An optimal moisture for pyrolysis is generally around 10 % of the wet weight, or even less. This is very low moisture, compared for example to wood chips used in traditional power plants. (Lehmann and Joseph 2009, 151; Brownsort 2009, 6, 14.)

The moisture of willow depends on its species and age, younger trees having higher water content. If a willow is freshly cut in the winter and its age is 3-5 years, it can be expected to have a moisture in the 47 - 57 % range (Alakangas et al. 2016, 205; Tahvanainen 1995, 57). Wood chips must be dried right after harvest, because wet chips will start decomposing rapidly. If they are to be stored for long periods, moisture must be under 20 %. If stems are harvested whole, they can be dried passively in piles, so no external heat or forced air-flow

are needed. About 30 % moisture can be reached this way, which is dry enough for short term storage. (Caslin et al. 2015, 60-62.)

Wood chips require active drying, unlike whole stems. This is done by blowing hot or cold air at them. Warm air dries the chips very fast compared to cold air, but requires energy to heat the air up. In large scale operations costs are reduced by using waste heat from industry, such as flue gases or steam. Air can also be heated with solar energy or boilers. Many different drying systems are available, and for example ventilated grain floors work very well for wood chips (Caslin et al. 2015, 60-62). In this system, heated air is blown through holes on the floor under the chips. Depending on the dryer configuration, reaching the desired moisture level can take several day. (Forest Research 2011, 3-4, 6.)

6.4 Thermochemical conversion

After chipping and drying, the feedstock is ready for pyrolysis. Slow pyrolysis is the preferred method for producing biochar, as it yields the most solid matter. The process is explained in more detail in chapter 4.2.

The inputs for pyrolysis are wood chips and electricity. When the process is started, an external fuel such as natural gas might be needed. After start-up, part of the pyrolysis products can be used to provide the required heat. Usually at least the syngas is combusted, but also the bio-oil can be used for process heat. Any extra heat can be used for electricity production or any other application where heat is needed. Combustion of pyrolysis products can be considered to be carbon neutral, in the same way as burning any renewable biomass is carbon neutral. Therefore there are no net GHG emissions, and the only outputs relevant to this work are biochar and the excess heat. (Brownsort 2009, 9-10.)

6.5 End uses of biochar

Biochar can be applied to the ground using existing agricultural equipment. Suitable tractor-operated machines include different kinds of spreaders and broadcast seeders. These spread the biochar on top of the soil, and afterwards it must be incorporated into the soil by a plough.

Otherwise it could be lost by erosion due to wind or water. Another method is to apply it directly into soil by banding, which is normally used for seed or fertilizer application. To reduce costs, biochar can be mixed with lime, other fertilizers, or even liquid manure and applied together with those. This reduces the number of field operations and can also reduce losses. (Major 2010, 7, 12-15.)

There is no generally accepted application rate, because it depends so much on the soil, biochar, and crop. Application rates up to 50 tons per hectare have been reported, but more often a rate of 5 t/ha has been used in experiments. Biochar lasts long in the soil, so it doesn't need to be added often. (Major 2010, 8-10; Lehmann and Joseph 2009, 209-211, 350.)

This work focuses on biochar as a soil additive, but it has plenty of other applications, too. It can adsorb many harmful substances such as heavy metals and pesticides, making it useful in water treatment and remediation of contaminated soils. Biochar is sometimes added to animal feed, because it is proven to improve digestion and the health of animals. It is also used as an additive in composting and sludge treatment. In all these cases biochar can still act as a carbon sink, because it doesn't release the carbon unless it is combusted. Even if it has been used in some other application, it can still be added to soil. However, if it has absorbed heavy metals or other toxic substances, it shouldn't be put into agricultural soil. (Schmidt and Wilson 2014.)

6.6 Site restoration

The last phase of biochar production is decommissioning the willow plantation. This is done in the summer after the last harvest. The trees are killed by applying an herbicide. The dead stumps can be pulled up from the ground and burned, but it might be more beneficial to incorporate them into soil for example by a mulcher or a heavy rotovator. This way the root biomass improves the soil quality and it is also cheaper than pulling up the stumps. (Caslin et al. 2015, 64; Tahvanainen 1995, 50.)

7 LIFE CYCLE ASSESSMENT OF WILLOW BIOCHAR

In this chapter the LCA study and its results are reported. The process follows the standards ISO 14040:2006 and ISO 14044:2006, including all the phases which were outlined in chapter 5. To model the life cycle of the biochar, an LCA software called GaBi Professional (version 9.1) was used. The database used was GaBi Professional Database 2018, including several extensions.

7.1 Goal and scope definition

This study is done to estimate the potential of willow biochar produced in Finland to mitigate climate change, when applied to ground as a soil amendment. This is done by calculating the Global Warming Potential, in other words the net GHG emissions in CO₂-equivalents during the life cycle. This is also a master's thesis, to demonstrate knowledge of the field of environmental engineering. The thesis is published online, where it is available for anyone interested in biochar and climate change, including students, decision makers, and companies.

The scope of this study is cradle-to-grave, covering the whole life cycle of willow biochar from willow farming to applying the biochar to soil. Functions of the system include the production of biochar, and also the reduction of carbon dioxide emissions by sequestering carbon to the ground and by producing clean electricity. The functional unit is chosen to be one kilogram of dry biochar. The system boundary is shown in figure 3. A general description of the processes inside the boundary was given in chapter 6.

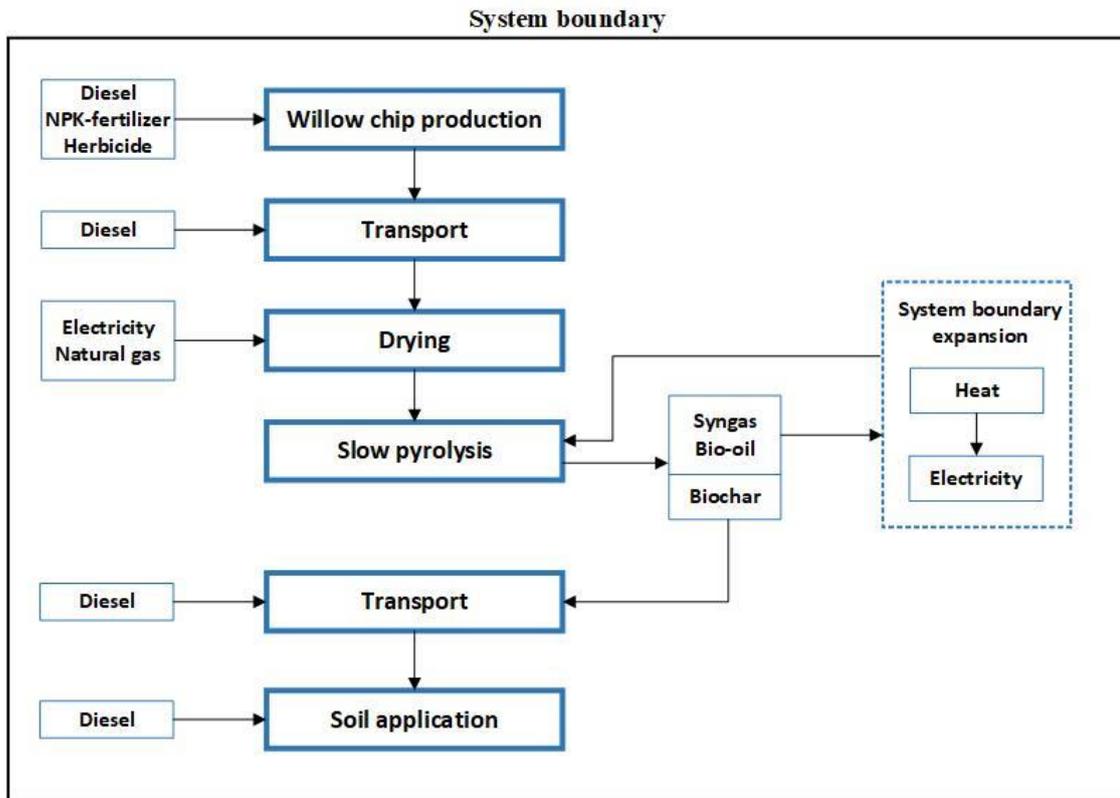


Figure 3. System boundary for the production and use of biochar.

To take into account all the emissions from the willow cultivation, the whole 25-year lifespan of a willow plantation is considered. Total emissions during this time are calculated, and they are divided by the total yield of willow in the same time period to get the average emissions. Cultivation of willow includes ploughing, harrowing, planting, herbicide application, fertilization, harvesting and chipping, and clearing of the plantation. Some of these operations are carried out only once, while some are done multiple times during the 25-year lifespan. The cultivation period doesn't include production of the willow cuttings, nor a cutback. Irrigation and pest control are rarely needed if at all, so their impact is assumed small and they are also left out. Indirect or direct land use change due to willow cultivation aren't considered in this work. It is assumed they are not significant, if willow is grown in marginal lands.

It is further assumed that the willow chips are produced directly by the harvester, so no separate chipping equipment is needed. The chips are then transported to the drying facility, which is located close to the pyrolysis facility. Screening or further size reduction of the chips should not be necessary in the case of slow pyrolysis, so these processes are not

included. The pyrolysis co-products syngas and bio-oil are not collected, but they are combusted to provide heat and electricity. This makes the pyrolysis process self-sustaining. It does require a fossil start-up fuel, but the amount is assumed negligible and is left out. This work doesn't also include emissions from constructing and manufacturing of the buildings and equipment used during the life cycle.

The pyrolysis co-products are an important energy source, both for maintaining the pyrolysis and for replacing fossil fuels, which can provide another way to reduce emissions. A system boundary expansion is done to take this into consideration. It is also the recommended way to account for multiple outputs from a unit process.

Biochar has also other indirect benefits, which come from the soil application. These indirect soil effects were already explained in chapter 3.2. However, most of these effects are not conclusively researched, and there is lot of uncertainty about quantifying them, especially in the long term. Therefore, they are not in the scope of this work, except that some of them will be considered in the sensitivity analysis.

The LCI data was obtained from the GaBi Professional Database 2018, and from literature and scientific studies, which are listed in the References. The GaBi model is documented in detail in chapter 7.2.8. This work focuses on climate change mitigation, so only one impact category is considered in the LCIA: *Climate change*. The impacts are determined with a characterization model called the *Baseline model of 100 years of the IPCC*. The results are expressed in kgCO₂eq per functional unit. The timeframe of this work is 100 years, because it is the typical timeframe of climate change studies. The stability of biochar in the soil is also calculated over 100 years, which is the case in most other studies also.

7.2 Inventory analysis

In inventory analysis, the inputs and outputs of each unit process are quantified. First some general data are determined such as the yield of the plantation. The unit processes are divided into tractor-based operations, fertilizer and herbicide production, transportation, drying, slow pyrolysis, and avoided emissions. It is also explained how this data is used in the GaBi LCA model.

7.2.1 General data

The yield is perhaps the most important factor and it is calculated first. Realistically, the plantation can produce 8 t/ha/a of dry matter on average (Ympäristöministeriö 2017, 4). In Finland, a typical harvest cycle is four years. (Tahvanainen 1995, 52-53.) During the whole life of the plantation it can be harvested six times before it must be renewed. This means the willows have 24 years to grow actively, and during that time the total production is 192 tons of dry matter per hectare. The average moisture content of freshly cut willow is about 52 % wet basis (Alakangas et al. 2016, 205; Tahvanainen 1995, 57). If this moisture is used, then the wet weight of the freshly harvested chips is 400 t/ha in 24 years. However, there are always some small losses of the feedstock during harvest, transportation, and other handling before it reaches the pyrolysis facility. These losses are assumed to be total of 5 % (Lehmann and Joseph 2009, 345). This leads to a net chip yield of 380 t/ha. It should be also mentioned that in reality the lifespan of the plantation is closer to 25 years, because the site preparation and decommissioning take about one additional year in total.

7.2.2 Tractor-based operations

Tractor-based operations are those which use an agricultural implement operated by a tractor, and all the ones needed in willow chip production are listed in table 1. Harvesting is included in these operations, because the emissions from a harvester are assumed to be similar to a tractor. In this work, only the diesel consumption of the field operation is considered, as well as emissions from manufacturing and combusting the diesel. Any emissions from the preparation of the machine, travel to and from the field, or manufacturing of tractors and other equipment are not included. Other inputs required in these field operations, such as fertilizers and herbicides, are addressed later.

Fuel consumption of a tractor can vary a lot, depending on the implement, soil type, tractor speed, tires, driver, and many other factors. For example, in ploughing the depth of the plough has a huge effect on fuel consumption. (Ahokas 2013.) To calculate the exact fuel consumption, all these factors would have to be known. This work doesn't go into such detail, but uses typical values found from literature. For example, Ahokas (2013) writes about the energy consumption of agricultural machines in Finland. Handler and Nadlinger

(2012, 10-12) on the other hand give a summary of two studies made in Germany and Austria. These two sources were used to estimate the typical fuel consumption of different field operations, in unit liters per hectare. If more than one value was found, usually their average was used. The results are shown in table 1. It includes also the number of times the operation is performed during the 25-year life of the plantation. Adding biochar to soil is not included in the table, but will be addressed later.

Table 1. Tractor-based field operations for willow cultivation and chip production (Ahokas 2013; Handler and Nadlinger 2012, 10-12).

| Field operation | Fuel consumption [l/ha] | Times in 25 years |
|---|--------------------------------|--------------------------|
| Ploughing | 22 | 1 |
| Harrowing | 6 | 1 |
| Planting | 10 | 1 |
| Fertilization | 2,5 | 6 |
| Herbicide application | 2 | 2 |
| Harvesting | 34 | 6 |
| Collecting chips with a tractor trailer | 4 | 6 |
| Site restoration | 22 | 1 |
| Total fuel consumption in 25 years | 307 | |

Ploughing, harrowing, and planting are only carried out once, when establishing the plantation. Fertilizer application is done one year after planting and then after each harvest except the last one, total of six times. It can be done for example with a tractor-mounted rotating spreader. Herbicides are applied once during the establishment, and a second time when the plantation is decommissioned to kill the tree stumps. Decommissioning and site restoration includes also breaking of the stumps for example by ploughing. This is assumed to consume the same amount of fuel as regular ploughing, 22 l/ha.

The fuel consumption of a willow harvester with chipping is not readily available. Willow can be harvested with a modified forage harvester, so a forage harvester is used to approximate the fuel consumption. Maize silage harvesting with a forage harvester uses 34

l/ha of diesel. This is more than a regular combine harvester (22 l/ha). (Handler and Nadlinger 2012, 12.) Maize silage harvesting includes cutting and shredding of the feedstock, so it can be assumed to be a good approximation for willow harvesting. The harvesting is carried out every four years, six times in total. To collect the chips, a tractor with a trailer drives alongside the harvester.

Adding biochar to soil is also a tractor-based operation, but not included in table 1. This operation requires a spreader, such as a solid manure spreader (Major 2010, 12-13). According to Handler and Nadlinger (2012, 12), the fuel consumption of manure spreading is 14 l/ha. The biochar is also incorporated in the soil by harrowing, which consumes 6 l/ha based on table 1. In total this makes 20 l/ha. The application rate is also needed, but determining a general value for it is not straightforward. It depends on the specific soil and biochar properties (Major 2010, 8-9). Based on Hammond et al. (2011) and Major (2010, 8-9), a value of 30 t/ha is chosen. Now the fuel consumption of biochar soil application can be expressed in liters per ton of biochar:

$$\frac{20 \frac{\text{l}}{\text{ha}}}{30 \frac{\text{t}}{\text{ha}}} = 0,67 \frac{\text{l}}{\text{t}}$$

This is a good enough approximation for the purposes of this study, but it does include some uncertainty. The fuel consumption can change a lot if different machinery is used, or if different application rate is chosen. It can be significantly lower especially if biochar application is integrated into the normal field operations. This wouldn't affect the overall results much, though.

7.2.3 Herbicides and fertilizers

Organic fertilizers, such as wastewater sludge, are not considered in this work. Instead, the plantation is fertilized with a chemical NPK fertilizer. It is easiest to apply when the willows haven't grown too tall for a tractor to drive on the field, in other words after planting and after each harvest except the last one (Caslin et al. 2015, 33). Therefore, it is assumed that fertilizer application happens only every four years, although in practice this could be also problematic. Because a lot of nutrients must be applied at one spreading, there is a risk of

them leaching out of the field before they are used by the plants. There are also regulations which limit fertilization. The frequency of the fertilization doesn't affect the overall results much, though.

NPK fertilizer consists of the most important nutrients for plants: nitrogen, phosphorus and potassium. The exact requirement of different nutrients is always case dependent and requires a soil analysis (Caslin et al. 2015, 31). In general, at least as much nutrients must be added as are removed with biomass. Nitrogen offtake by willow biomass is around 50-55 kg/ha/a, but even 60 kg/ha/a nitrogen fertilization is possible, according to Caslin et al. (2015, 31, 34). Tahvanainen (1995, 34, 36) suggests about 60 kg/ha/a when the yield is 8 t/ha/a, so that number is used in this work. This means that every four years, about 240 kg/ha of nitrogen should be added. However, there are some national regulations for nutrient application which might come in the way. For example, only 150 kg/ha of nitrogen can be applied to a field at one time (Valtioneuvoston asetus eräiden maa- ja puutarhataloudesta peräisin olevien päästöjen rajoittamisesta, 18 December 2014/1250). It might be possible to apply for a permit to use more nitrogen than that, but otherwise this could a limiting factor (Ympäristöministeriö 2017, 24).

The amounts of phosphorus and potassium are usually expressed relative to nitrogen, in the form of an NPK ratio. According to Tahvanainen (1995, 34, 36), willow needs an NPK ratio of 100-14-72, and this ratio has been proven successful in Finland. Also Caslin et al. (2015, 32) reports a very similar ratio. Using this proportion, 240 kg/ha of nitrogen corresponds to 33,6 kg/ha phosphorus and 172,8 kg/ha potassium. Sometimes the phosphorus and potassium are expressed as their oxides (P₂O₅ and K₂O), and this is also the case in GaBi. The conversion factors for the weights are obtained from the ratio of the molar masses, and they are 0,436 for phosphorus and 0,830 for potassium (Regulation of the European Parliament and of the Council 2003/2003/EC). Now the weights of the oxides are

$$\frac{33,6 \frac{\text{kgP}}{\text{ha}}}{0,436 \frac{\text{kgP}}{\text{kgP}_{2\text{O}_5}}} = 77,0 \frac{\text{kgP}_{2\text{O}_5}}{\text{ha}}$$

and

$$\frac{172,8 \frac{\text{kgK}}{\text{ha}}}{0,830 \frac{\text{kgK}}{\text{kgK}_2\text{O}}} = 208,2 \frac{\text{kgK}_2\text{O}}{\text{ha}}$$

To fulfill this nutrient requirement, a customized NPK fertilizer can be ordered with the right ratio of nutrients and specified strength. If the fertilizer strength is chosen to be 24-7,7-20,8 (% of N-P₂O₅-K₂O), then exactly 1000 kg/ha of the NPK fertilizer is needed. This is the amount that is spread in the plantation every four years. There are six harvest cycles, so total of 6000 kg/ha is used. It should be noted that as long as the nutrient ratio stays the same, the strength of the fertilizer doesn't matter too much, other than for the total weight. For example, if the strength is halved, the weight of fertilizer must be doubled.

Fertilizers cause also indirect emissions, when the nitrogen added to soil converts into nitrous oxide (N₂O). The amount depends on the soil type and climate, but usually it is estimated that 1 % of the nitrogen turns into N₂O. This is what IPCC recommends as a default estimate for nitrogen fertilizers. To convert N to N₂O, a factor of 44/28 is used. (IPCC 2019.) Previously it was determined that 240 kg of nitrogen is needed every four years, total of six times. Now the total N₂O emissions can be calculated during the whole plantation lifespan:

$$0,01 * 6 * 240 \frac{\text{kg}_N}{\text{ha}} * \frac{44}{28} = 22,63 \frac{\text{kg}_{\text{N}_2\text{O}}}{\text{ha}}.$$

To estimate the emissions from herbicide use, an herbicide called Trifluralin is chosen because it can be found from the GaBi Professional database. From a datasheet for Trifluralin it can be seen that the application rate depends on the soil type and crop. A typical application rate is 1,7 l/ha, and the concentration of the product is 480 g/l (ADAMA New Zealand 2018). Herbicide application is done two times, as previously explained. Based on this, the total amount of pure Trifluralin can be calculated:

$$2 * 1,7 \frac{\text{l}}{\text{ha}} * 0,480 \frac{\text{kg}}{\text{l}} = 1,63 \frac{\text{kg}}{\text{ha}}.$$

7.2.4 Transportation

Transportation is divided into two phases. First, the willow chips are taken from the cultivation site to the drying facility and pyrolysis plant. Then biochar is transported from the pyrolysis plant to a field. In both phases, the average transport distance is assumed to be the same. Statistics Finland (2017) makes a statistic of the average transport distances of

different goods by truck in Finland. The average distance for energy wood, firewood, and wood chips was 68 km in 2017. This number changes a little bit from year to year, but 68 km is used in this work because it is the most recent data available.

7.2.5 Drying

Drying is done with a ventilated floor dryer, which works by blowing hot air through the floor under the chips. Energy is needed to heat the air and to run the fans. Fossil fuels are a common heat source for drying, so natural gas is chosen for that purpose (Mujumdar 2015, 26, 1078). Electricity for the fans is taken from the grid.

$$q = 0,68 * m_w, \quad U \geq 0,30 \quad (1)$$

$$q = (2,036 - 4,524 * U) * m_w, \quad U < 0,30 \quad (2)$$

$$U = \frac{X}{1-X} \quad (3)$$

| | |
|-------|--|
| m_w | mass of water that is to be removed from the wood [kg] |
| q | heat requirement for removing water [kWh] |
| U | moisture on dry weight basis (db) [kg water/kg dry wood] |
| X | moisture on wet weight basis (wb) [kg water/kg wet wood] |

The heat energy required for removing water can be estimated by using the vaporization heat of water, which is 0,68 kWh/kg at 25 °C. However, some of the water is bound more tightly in the cell walls of the wood so more energy is required to release and vaporize it. According to Härkönen (2012), the water is in free form when the moisture on dry basis (U) is over 30 %. In this case, the heat energy needed for drying wood is the same as the vaporization heat for water (equation 1). But when the moisture is under 30 %, equation (2) can be used for a rough estimate. This equation is obtained by assuming the energy requirement increases linearly as the moisture U decreases, and when $U = 0$, the energy need is three times the vaporization heat of water (2,036 kWh/kg). Equation (3) can be used to convert wet basis moisture to dry basis. (Härkönen 2012, 10-13.)

Based on chapter 6.3, it is assumed the initial moisture of wood is 52 % (wb), which is the same as 108 % (db). It is then dried to 10 % (wb) (same as 11 % (db)), which is the typical moisture requirement for pyrolysis. If one kilogram of fresh wood chips at 108 % (db) moisture is considered, then 0,376 kg of water must be removed from it to reduce the moisture to 30 % (db). This can be put to equation (1) to get the heat energy, and the result is 0,256 kWh. Similarly, to further reduce the moisture from 30 % to 11 % (db), 0,091 kg of water must be removed. Now equation (2) must be used, where U is the average of 11 % and 30 %. The average is 20,5 %, which is the same as 0,205 kg water/kg dry wood. This results in 0,100 kWh of heat. When these results are summed up, a total of 0,356 kWh/kg_{chips,52%} is needed to evaporate the water. In total, 0,467 kg of water is removed, so the mass of the chips is reduced from 1 kg to 0,533 kg.

Dryers have always some heat losses, which can be very significant in some dryer types. Information about the overall thermal efficiency of different wood chip dryers is scarce. Based on literature, it is assumed the total thermal efficiency of the dryer is 60 % (Forest Research 2011, 3; Mujumdar 2015, 1082, 1084). This means that 40 % of the heat is lost with exhaust air and other losses. Considering this, the drying of 1 kg of fresh wood chips from 52 % to 10 % (wb) requires 0,593 kWh of primary energy. The effect of this assumption will be considered in the sensitivity analysis.

There is not much information available about the electricity consumption of hot air drying. The report by Forest Research (2011, 5-7) includes some studies. For example, in an experiment by Nordhagen (2010), 28 m³ of wood chips were dried from 52 % to 7 % (wb). This was done in a container, using excess heat from a hydropower plant. The fan moving the hot air consumed 270 kWh of electricity in about three days. If the bulk density of the chips is assumed to be 350 kg/m³ (Caslin et al. 2015, 116), then it can be calculated that the electricity consumption in this experiment was 0,028 kWh/kg of fresh wood chips.

The Forest Research report (2011) includes also another study about heated air drying, but the original study is not available anymore. Reportedly, it involves a tray grain dryer, with a capacity of 21 tons of wood chips. They are dried from 34 % to 7,5 % moisture (wb), using 60 °C air. The fan consumed 943 kWh of electricity and the weight of the chips was reduced to 15,3 tons. (Forest Research 2011, 6.) Based on this information, the electricity consumption

was 0,167 kWh/kg of water. Therefore it can be calculated that drying the wood chips from 52 % to 10 % would require 0,078 kWh/kg electricity. This is more than double of what Nordhagen (2010) suggests, indicating the electricity consumption can vary a lot between different drying systems. For this work, a value of 0,05 kWh/kg of fresh wood chips is chosen, because it is between the before mentioned results.

7.2.6 Slow pyrolysis

The pyrolysis process is optimized to produce biochar. It takes willow chips, heat and electricity as an input. All the heat and electricity are provided by combusting the volatile compounds released in the process, as explained in chapter 4.4. Any excess thermal energy is recovered and turned into electricity. This can be done for example with a steam boiler and a turbine (Pyrocal 2019). The excess electricity is then used to substitute for the average grid electricity of Finland. Carbon dioxide emissions from pyrolysis or combustion of pyrolysis products are not included, because the willow biomass can be thought as renewable and carbon neutral energy source (Brownsort 2009, 9-10). Startup fuel is also not considered, as the amount is assumed to be negligible. This work focuses on slow pyrolysis in general and does not address any specific pyrolysis technology.

The yields of biochar, syngas, and bio-oil can be realistically 35 %, 35 %, and 30 % of the feedstock dry weight, respectively (Hamedani et al. 2019; Lehmann and Joseph 2009, 132, 348). Moisture of the feedstock is 10 % (wb) when it arrives to the pyrolysis plant. Therefore the yields of biochar and syngas are both

$$(1 - 0,1) * 0,35 = 0,315 \frac{\text{kg}}{\text{kgchips},10\%}$$

If this is expressed in terms of the functional unit, 1 kg of dry biochar takes 3,17 kg of willow chips to produce. Bio-oil is produced by condensing all the condensable vapors, including water vapor. The 10 % moisture content of the feedstock must be added to the bio-oil. Some water is also formed in the process by chemical reactions, but it is already included in the 30 % yield. Now the total yield of bio-oil is

$$(1 - 0,1) * 0,30 + 0,1 = 0,37 \frac{\text{kg}_{\text{oil}}}{\text{kg}_{\text{chips},10\%}}$$

After pyrolysis the char is completely dry, but it starts to slowly absorb moisture from the air. According to Antal and Grønli (2003), the moisture will increase to 3-8 % (wb) within a few weeks. Based on this, it can be assumed the biochar moisture has reached an equilibrium of 5,5 % by the time it is transported away from the pyrolysis facility. This causes a small change to the biochar weight and carbon density, which will be taken into account in later life cycle phases.

Many studies address the pyrolysis heat requirement of different feedstocks, but no exact value for willow chips can be found. A literature review by Alhashimi and Aktas (2016) found that the thermal energy for pyrolyzing forestry residue chips is in the range 0,4-0,8 kWh/kg. Daugaard and Brown (2003) studied several feedstocks, of which pine is the closest to willow. They found pine requires 0,49 kWh/kg at 7 % moisture, which is inside the range given by Alhashimi and Aktas (2016). Based on this, the thermal energy requirement for pyrolyzing the willow chips is chosen to be 0,50 kWh/kg_{chips,10%}.

The electricity requirements of slow pyrolysis systems are not so easily available. Jonsson (2016, 40) compared three commercial slow pyrolysis systems and found that their electricity consumption was in the range of 0,015-0,055 kWh/kg_{feedstock}, depending on the plant size. Harsono et al. (2013) used data from palm oil empty fruit bunch pyrolysis and obtained a value of 0,11 kWh/kg_{feedstock}. Lehmann and Joseph (2009, 347) assume the consumption is 0,04 kWh/kg_{feedstock} for fast pyrolysis. Electricity consumption seems to depend heavily on the specific equipment, size of the plant, and the included pre-processing steps of the feedstock. Based on the available literature, 0,05 kWh/kg_{chips,10%} seems like a reasonable estimate for the purposes of this work.

The pyrolysis system can be set up in many ways, depending on the purpose. In this work, it is assumed that the volatilized compounds are extracted from the reactor and combusted in a burner, as was shown in figure 2. Part of the heat released in the burner is used to provide thermal energy for the pyrolysis process in the form of hot flue gas. Rest of it is directed to a boiler to produce electricity. The total heat-to-electricity conversion efficiency is assumed

to be 35 %, which can be achieved when burning fossil fuels or biomass in a boiler (Breeze 2014, 324). Part of the electricity is then used by the process itself, and the rest is put to the grid.

The lower heating values of bio-oil and syngas are used to calculate the produced heat. Syngas LHV can vary a lot depending on the process parameters and feedstock, but a value of 11 MJ/kg_{gas} (3,06 kWh/kg_{gas}) is used in some studies (Crombie and Mašek 2014; Hamedani et al. 2019). Bio-oil LHV is typically in the range 3,6-5 kWh/kg_{oil}, depending on the water content (Alakangas et al. 2016, 184; Basu 2018, 160). The LHV of fast pyrolysis oil made from forest residues is about 4,2 kWh/kg_{oil}, when the water content is taken into account (Alakangas et al. 2016, 185). This value is used in this work. Now the total thermal energy produced is

$$3,06 \frac{\text{kWh}}{\text{kg}_{\text{gas}}} * 0,315 \frac{\text{kg}_{\text{gas}}}{\text{kg}_{\text{chips},10\%}} + 4,2 \frac{\text{kWh}}{\text{kg}_{\text{oil}}} * 0,37 \frac{\text{kg}_{\text{oil}}}{\text{kg}_{\text{chips},10\%}} = 2,50 \frac{\text{kWh}}{\text{kg}_{\text{chips},10\%}}$$

0,50 kWh/kg_{chips,10%} of heat is needed for the pyrolysis reaction. Total electricity production is therefore

$$0,35 * (2,50 - 0,50) \frac{\text{kWh}}{\text{kg}_{\text{chips},10\%}} = 0,70 \frac{\text{kWh}}{\text{kg}_{\text{chips},10\%}}$$

The pyrolysis process uses 0,05 kWh/kg_{chips,10%} electricity. Now the net electricity production can be calculated on functional unit basis:

$$\frac{(0,70 - 0,05) \frac{\text{kWh}}{\text{kg}_{\text{chips},10\%}}}{0,315 \frac{\text{kg}_{\text{dry char}}}{\text{kg}_{\text{chips},10\%}}} = 2,07 \frac{\text{kWh}}{\text{kg}_{\text{dry char}}}$$

7.2.7 Carbon abatement

Carbon dioxide is sequestered by storing the biochar in soil, and emissions are also avoided by replacing grid electricity with clean electricity from pyrolysis. To determine the amount of carbon stored in the soil, the carbon content of biochar is needed and also some idea of

the stability of the carbon. The carbon content can vary a lot, depending on the feedstock and pyrolysis parameters. According to Basu (2018, 184), it can range between 50-90 %. Antal and Grønli (2003) report the fixed carbon content of different wood biochars to be in the 70-80 % range, when pyrolysis temperature is 450 °C. For willow biochar, an experimental study by Rasa et al. put the fraction of elemental carbon at 74 % of dry biochar. Hamedani et al. (2019) used 75 %, and the same value is used in this work.

It is highly uncertain how long biochar stays stable in the soil or how fast it decays, and different methods for estimating this have been used (Lehmann and Joseph 2009, 184). In many studies it is assumed that the fraction of labile carbon in biochar is either 15, 20, or even 25 % (Hamedani et al. 2019; Hammond et al. 2011; Lehmann and Joseph 2009, 328; Roberts et al. 2009). After 100 years, the labile carbon has been released, and depending on the assumptions, part of the stable carbon has also decayed. For example, Hammond et al. (2011) assumed a 15 % labile fraction, while the non-labile carbon decays linearly over 500 years. With these assumptions, they calculated that only 68 % of the carbon would be left in the ground after 100 years. Some others assume this number is 80 % (Bruckman et al. 2016, 63; Hamedani et al. 2019; Roberts et al. 2009). Based on these studies, it is assumed that 75 % of the carbon is still in the soil after 100 years. The effect of this assumption is observed with a sensitivity analysis.

Before the amount of sequestered carbon can be calculated, the losses of biochar during transportation and soil application must be considered. These losses are assumed to be 5 %, although in some case studies the total losses have been reported to be as high as 30 %. This is mostly caused by wind losses in the application phase, and can be reduced with proper management practices, such as wetting the char or applying it together with a slurry of manure. (Major 2010, 7, 13; Hammond 2011.) Based on these values, the carbon sequestered in the soil for 100 years can be calculated on functional unit basis:

$$(1 - 0,05) * 0,75 \frac{\text{kg}_{\text{C},100}}{\text{kg}_{\text{C}}} * 0,75 \frac{\text{kg}_{\text{C}}}{\text{kg}_{\text{dry char}}} = 0,53 \frac{\text{kg}_{\text{C},100}}{\text{kg}_{\text{dry char}}} = 1,96 \frac{\text{kg}_{\text{CO}_2,100}}{\text{kg}_{\text{dry char}}}$$

C carbon

C,100 carbon after 100 years

In the GaBi model, the carbon sequestration is needed on wet biochar basis, because that is the reference flow in this case. The moisture content was assumed to be 5,5 %. When this is taken into account, the previous result changes a bit:

$$(1 - 0,055) \frac{\text{kg}_{\text{dry char}}}{\text{kg}_{\text{char},5,5\%}} * 1,96 \frac{\text{kg}_{\text{CO}_2,100}}{\text{kg}_{\text{dry char}}} = 1,85 \frac{\text{kg}_{\text{CO}_2,100}}{\text{kg}_{\text{char},5,5\%}}.$$

The GHG emission reduction by replaced grid electricity can be calculated when the amount of produced electricity and the average emission factor for grid electricity are known. The net electricity yield was already calculated to be 2,07 kWh/kg_{dry char}. The five-year average emission factor of electricity production in Finland is 0,158 kg CO_{2eq}/kWh (Motiva 2019). However, lot of uncertainty is caused by the fact that the average emission factor doesn't tell which electricity production method is replaced in reality. If for example renewable electricity is replaced by pyrolysis electricity, no emission reductions would be obtained. A more accurate method is not in the scope of this work, so the average emission reduction is:

$$0,158 \frac{\text{kg}_{\text{CO}_2\text{eq}}}{\text{kWh}} * 2,07 \frac{\text{kWh}}{\text{kg}_{\text{dry char}}} = 0,327 \frac{\text{kg}_{\text{CO}_2\text{eq}}}{\text{kg}_{\text{dry char}}}.$$

7.2.8 The GaBi LCA model

The data collected in the previous chapters was used to make an LCA model in GaBi professional software (version 9.1). The resulting model is shown figure 4. It shows the unit processes of the model and the names and quantities of the flows between them. The flows are shown relative to the functional unit, 1 kg of dry biochar.

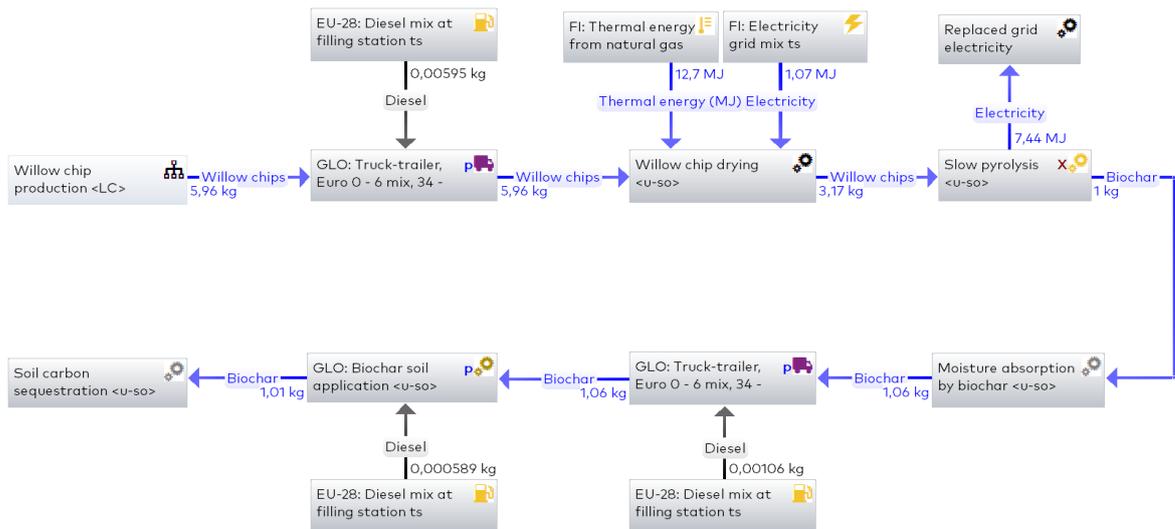


Figure 4. The life cycle model of willow biochar made with GaBi Professional.

The model starts with a process called *Willow chip production*, which is actually a plan including all the processes needed for willow cultivation. This plan is shown in figure 5.

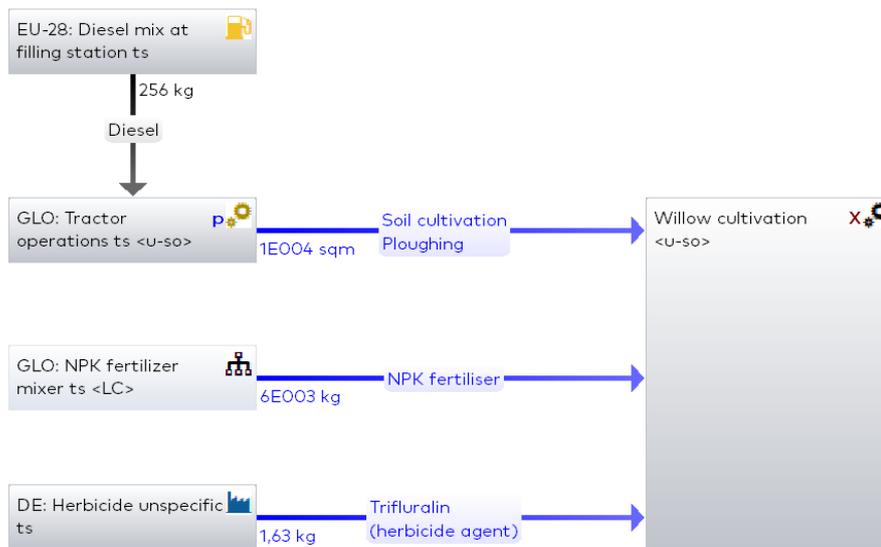


Figure 5. The GaBi plan for willow chip production.

In this plan, the flow quantities are expressed relative to one hectare of willow plantation. All the field operations done with a tractor are included in the unit process called *GLO: Tractor operations ts <u-so>*. This process is a copy of a process called *GLO: Soil cultivation: ploughing (medium, 83 kW) ts <u-so>*, which can be found from the GaBi database. A copy was made to be able to change the parameter values of the process and to

rename it. It takes diesel as an input, total of 307 l/ha, or 256 kg/ha. For output it gives an area of one hectare.

The fertilizer production was modelled with a plan from the GaBi database called *GLO: NPK fertilizer mixer ts <LC>*. This plan can be used when the strength of the N-P₂O₅-K₂O fertilizer is known in per cents. This was calculated in chapter 8.2.3. In the model, the NPK fertilizer is manufactured from ammonia, potassium chloride, and raw phosphate. It gives the mass of the NPK fertilizer as an output.

The herbicide unit process was also taken from the database, and it is called *DE: Herbicide unspecific ts*. It doesn't require any inputs, and outputs the amount of pure Trifluralin per hectare, which was previously calculated to be 1,63 kg/ha.

All these processes are connected to a unit process called *Willow cultivation*, which was created as a new process. Its inputs and outputs are presented in table 2. All flows except *Willow chips* are already in the GaBi database. The N₂O emissions from nitrogen fertilizer are modelled by including them in the outputs of this unit process as an elementary, non-tracked flow.

Table 2. Flows of the *Willow cultivation <u-so>* unit process.

| Inputs | Quantity |
|---|------------------------|
| NPK fertiliser [Agro chemicals] | Mass [kg] |
| Soil cultivation ploughing [Areas] | Area [m ²] |
| Trifluralin (herbicide agent) [Agro chemicals] | Mass [kg] |
| Outputs | |
| Willow chips [Renewable resources] | Mass [kg] |
| Nitrous oxide (laughing gas) [Inorganic emissions to air] | Mass [kg] |

The environmental impacts of diesel manufacturing are taken into account with the unit process *EU-28: Diesel mix at filling station ts*, available in the GaBi database. Diesel is needed for tractors in willow cultivation and biochar soil application, and also for transportation by trucks. Transportation is the next step after *Willow chip production <LC>*, and it is done with a truck-trailer. The unit process is *GLO: Truck-trailer, Euro 0-6 mix, 34-*

40 t gross weight/ 27t payload capacity, from the GaBi database. It takes into account trucks with different Euro emission classes, so it represents an average truck process. The default utilization factor of the truck is only 0,61, meaning the truck is not always full. This value is left as it is, to take into account that the truck probably returns back empty after delivering its cargo. This same unit process is used also when transporting the biochar to field.

A new unit process was created for drying, called *Willow chip drying <u-so>*. It takes as input willow chips, thermal energy, and electricity. Its output is willow chips, which weight is reduced by the amount of removed water. Thermal energy is provided by a unit process called *FI: Thermal energy from natural gas ts*, from the GaBi database. It represents the use of natural gas in a heat plant in Finland, with 100 % efficiency. The energy losses were included when calculating the heat requirement for drying, in chapter 7.2.5. Electricity comes from the national grid, which in GaBi is a process called *FI: Electricity grid mix ts*.

A new unit process was created also for pyrolysis, called *Slow pyrolysis <u-so>*. This is a simple process, which takes the willow chips as an input and gives biochar as an output. The output flow is fixed to 1 kg of dry biochar, so GaBi calculates all flows on functional unit basis. The pyrolysis process outputs also excess electricity, which is part of the system expansion. A unit process called *Replaced grid electricity <u-so>* was created to implement this. The electricity is an input for this process, but it also takes a non-tracked input called *Carbon dioxide [Inorganic emissions to air]*. This way GaBi knows to reduce from the results the amount of carbon dioxide that was avoided by replacing grid electricity.

To represent the moisture absorption by biochar, a process called *Moisture absorption by biochar <u-so>* was created. Its output is higher than the input by the amount of absorbed moisture. After this the biochar is transported to a field, where it is applied to soil. This is modeled with a unit process called *GLO: Biochar soil application <u-so>*. This phase involves tractor operations similarly to the willow cultivation, so the unit process is again a copy of the *GLO: Soil cultivation: ploughing (medium, 83 kW) ts <u-so>*. However, a flow called *Biochar [Renewable resources]* has been added to both its input and output. The default output, *Soil cultivation ploughing [Areas]*, is not needed so it is turned into a non-tracked flow. Area is still the reference flow of this unit process, so the flows of diesel and biochar are entered relative to hectares. This unit process models two things: the tractor

emissions of biochar soil application, and the losses of biochar during transportation and soil application. Because of the losses, the mass of the biochar in the output is 5 % smaller than in the input.

The actual carbon sequestration is implemented with the final unit process, called *Soil carbon sequestration <u-so>*. Its only purpose is to take two inputs, *Biochar [Renewable resources]* and *Carbon dioxide [Inorganic emissions to air]*. The carbon dioxide is a non-tracked flow. From this, GaBi can calculate the amount of carbon dioxide removed from the atmosphere by biochar soil application.

7.3 Impact assessment

The impact assessment focuses only on the *Climate change* impact category. To quantify the potential climate change impacts of biochar production, a characterization model called the *Baseline model of 100 years of the IPCC* is used. In this model, all the greenhouse gases are converted into CO₂-equivalents using the GWP100 factors. These factors tell how much the greenhouse gas absorbs energy, or how much potential warming it can cause over 100 years, relative to CO₂ (EPA 2017). The results are given on functional unit basis, in this case in kg CO₂eq/kg dry biochar. GaBi includes several impact assessment methods, and a method called *CML 2001 - Jan 2016* is chosen because it uses GWP100 factors published by the IPCC (Leiden University 2016). The results are shown in figure 6.

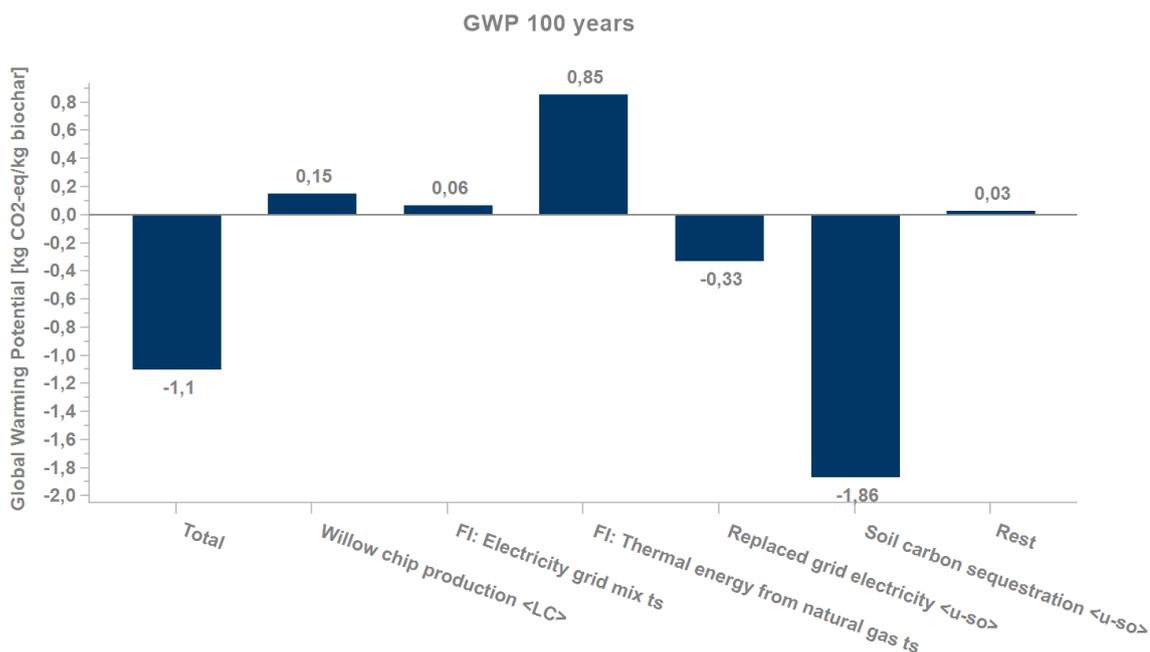


Figure 6. Global warming potentials of willow biochar production phases.

The results show that production of 1 kg of dry willow biochar can cause 1,1 kg net removal of CO₂eq from atmosphere. Figure 6 also shows the most significant unit processes contributing to this result. The processes called *Electricity grid mix* and *Thermal energy from natural gas* include the emissions from electricity and heat production for drying of willow chips. *Replaced grid electricity* and *Soil carbon sequestration* are the two carbon abatement processes, so their values are negative. *Rest* includes all the processes which have very negligible effect on the total result, such as the emissions from transportation and diesel manufacturing. Finally, *Willow chip production <LC>* includes emissions from the tractor operations, fertilizer and herbicide manufacturing, and N₂O production due to nitrogen fertilization. The GWPs of these unit processes are shown in more detail in figure 7. The N₂O emissions are included in *Willow cultivation <u-so>*, and this process doesn't have any other emissions. *GLO: Tractor operations ts <u-so>* accounts for all the field operations listed in table 1.

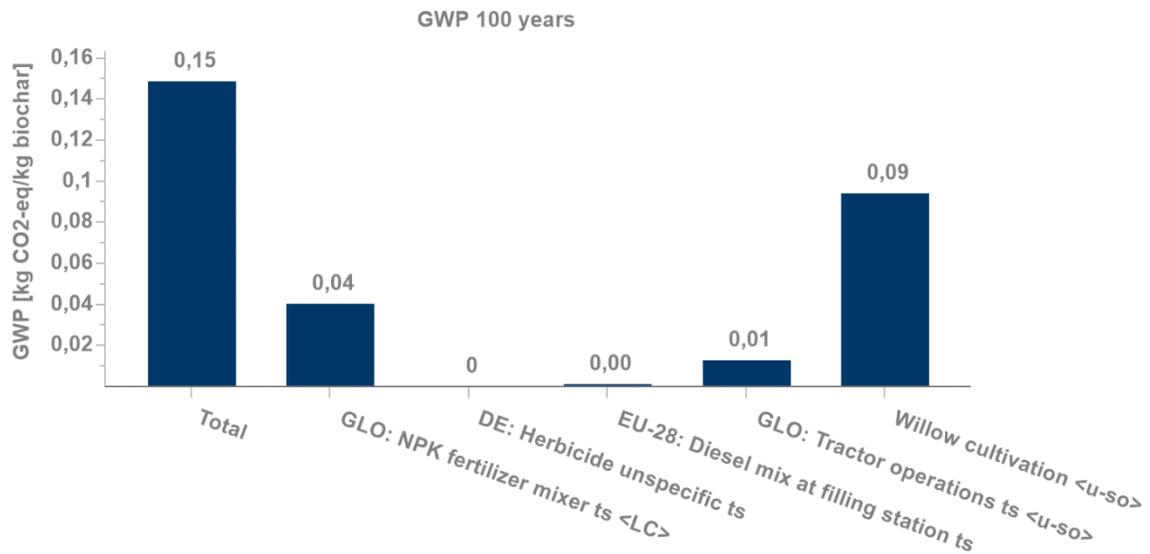


Figure 7. Global warming potentials of willow chip production processes.

7.4 Interpretation

The LCIA results show that the global warming potential of willow biochar is clearly negative. This supports the assumption that willow biochar could help in climate change mitigation, if it could be produced sustainably in a large scale. Two important processes are the cause of this carbon mitigation: biochar soil application, and electricity generation from the pyrolysis by-products. The process of applying biochar into soil causes most of the mitigation, removing 1,86 kg CO₂eq/kg dry char. This is enough to offset the emissions from the biochar production and much more. Therefore, biochar production should aim to maximize the amount of char ending up in the soil. This means maximizing the yield of char and the stable carbon contained in it, and minimizing any losses of char especially in the soil application phase.

Excess electricity generation can also contribute to the emission reduction, but only if the electricity is used to replace non-renewable electricity. In this work it was assumed to replace average grid electricity in Finland, resulting in emission reduction of 0,33 kg CO₂eq/kg dry char. This is a significant amount, although only a fraction of that of the biochar soil application. The system expansion shows that the co-products of biochar production can be an important factor in reducing emissions, if they are used to replace fossil fuels.

There are also other ways by which biochar could remove or reduce greenhouse gases, but weren't included in this assessment. These are the indirect effects, such as soil effects, which were presented in chapter 3.3. Hammond et al. (2011) and Ibarrola et al. (2011) took several of these effects into account in their LCA studies and found that in different slow pyrolysis biochar systems they contribute roughly 20-30 % of the carbon reduction. This effect was mostly caused by an increase in plant productivity which lead to increased soil organic carbon stocks. The amount is significant but highly uncertain, as mentioned. Because of this uncertainty the indirect soil effects were left out of this work, but if they become better understood in the future they should certainly be taken into account.

The LCIA results show that the most emission intensive unit process is drying. Producing the electricity and heat for drying causes total emissions of 0,91 kg CO₂eq/kg dry char. This is almost exclusively due to the intensive heat requirement, which is satisfied by burning natural gas. Fortunately, there are several ways to improve the drying process, which would also greatly benefit the overall LCA results. An obvious improvement would be to change the fuel for renewable biomass, such as wood chips or agricultural residues. Some dryers can even use (renewable) electricity for heating the air (Mujumdar 2015, 26). The heat requirement could be also reduced by using passive drying or cold air for at least part of the way. This would, however, increase the drying time significantly, and the willow stems might have to be harvested and stored whole. Another method is to use waste heat for drying, or in this case, the excess energy from the pyrolysis process. If this energy is used for electricity production and for replacing grid electricity, the GHG reduction would be only 0,33 kg CO₂eq/kg dry char. This is not enough to offset the emissions from drying. Therefore, the excess energy would be better used for drying the feedstock than producing electricity, as this could completely remove the need for natural gas. From the LCI data of pyrolysis and drying it can be seen that all their energy requirements could be met by using the energy contained in the syngas and bio-oil. Some energy might even be left over.

The next biggest emission source is willow chip production. This is mostly due to N₂O emissions from using nitrogen fertilizer, and production of the NPK fertilizer, as seen from figure 7. One significant way to reduce GHG emissions could be to recycle nutrients by using wastewater or wastewater sludge to fertilize the willows. This would be better also because organic fertilizers release their nutrients more slowly. In willow farming,

fertilization is often done in one big application after the harvest, but this is problematic because the nutrients might be released too soon and leach away from the field. There are also legal limitations for how much nutrients can be added at one time to a field, so it might be necessary to think of an alternative fertilization strategy which addresses these problems.

Tractor field operations and herbicide production have small GHG emissions compared to fertilizers, as seen from figure 7. Also the processes included in the *Rest* category in figure 6 have very insignificant impact on the results, only 0,03 kg CO₂eq/kg dry char. Of this, 0,02 kg CO₂eq comes from transporting the willow chips. The rest, including transportation of biochar, diesel production, and biochar soil application, contribute only 0,01 kg CO₂eq/kg dry char to the result. Therefore, these processes could be left out of this study without affecting the results.

An important limitation of this work is the omission of direct and indirect land use change, which are often caused by energy crops. In the worst case, land use change could make biochar into a carbon source instead of a sink (Roberts et al. 2009). Therefore its effects are important to consider and prevent if possible. One solution is to cultivate willow on marginal lands, as was assumed in this work. This would reduce the need to clear new agricultural land for example by cutting down forests. Many other sustainable practices also go well with biochar production. For example, reducing consumption of animal products would reduce the need for agricultural land, which could be then turned into energy crop production (IPCC 2018, 265). Alternatively, biochar could be produced from other sustainable feedstocks, such as waste products from households, agriculture, or forestry.

7.5 Sensitivity analysis

Sensitivity analysis looks at a few chosen variables and assumptions, which, based on the LCIA and LCI, might have a significant impact on the end result. Each variable is changed by a certain amount while others stay constant. The amount of change is chosen based on the ranges found from literature for each variable. The analysis is presented in table 3. It lists the chosen parameters as well as their original and changed values. The LCA result calculated with this new value is presented in the last column, and it includes in brackets the

change in per cents compared to the original result, -1,1 kg CO₂eq/kg dry char. If the parameter change leads to increased carbon dioxide removal, the change is positive (+).

Table 3. Description and results of the sensitivity analysis.

| Parameter | Change | Result [kgCO ₂ eq/kg _{dry char}] |
|-------------------------------|-------------------------------------|---|
| Willow yield | 8 → 10 t _{dry} /ha/a | -1,13 (+2,7 %) |
| Heat source for drying | Natural gas → Biomass | -1,90 (+72,7 %) |
| Dryer thermal efficiency | 60 → 85 % | -1,35 (+22,7 %) |
| Char yield from pyrolysis | 35 → 25 % | -0,87 (-20,5 %) |
| Electricity to grid | 2,07 → 0 kWh/kg _{dry char} | -0,77 (-30 %) |
| Stable carbon after 100 years | 75 → 70 % | -0,98 (-11,4 %) |
| | 75 → 80 % | -1,22 (+10,9 %) |
| Change in soil organic carbon | 0 → 6,3 tC/ha | -1,91 (+73,6 %) |
| | 0 → -3,6 tC/ha | -0,63 (-42,7) |

It can be seen that increasing the willow yield doesn't change the results much. This is likely because emissions from willow cultivation are relatively small, at least if there are no land use change effects. Increasing the yield might also mean increase in fertilizer use, which might negate the benefit. Still, higher efficiency would be desirable, because less land is needed, which improves cost efficiency and reduces possible land use change.

The greatest way to reduce emissions from biochar production would be to avoid using fossil fuels in drying, or in any life cycle stage for that matter. The effect of this can be seen when natural gas is changed to biomass as a heat source for drying. In GaBi, this was done by using *FI: Thermal energy from biomass (solid) ts*, instead of *FI: Thermal energy from natural gas ts*. This led to 73 % increase in the mitigated carbon dioxide. Probably a similar increase would be obtained if the thermal energy came from waste heat, or from the pyrolysis process, as was explained previously. Thermal efficiency of drying is another important parameter, when fossil fuel is used. Increasing it from 60 % to 85 % improves the result by 23 %, which is quite significant.

If the char yield of pyrolysis was decreased by 10 percentage points, 20,5 % less carbon would be removed. This could be the case if the pyrolysis parameters were not optimized for

char production, or if fast pyrolysis was used (Lehmann and Joseph 2009, 132). Therefore the char yield should be considered carefully, when designing the pyrolysis system. Less biochar means more syngas or bio-oil, but from the global warming standpoint, the amount of stable char is more important.

The effect of replacing grid electricity was assessed by completely removing it, for two reasons. First, the carbon mitigation effect happens only if fossil electricity is replaced, not if the electricity is renewable. Second, there are pyrolysis facilities which don't produce any electricity. They can use the pyrolysis co-products or excess heat for something else, or not even utilize them at all. In these cases, the net carbon removal would be 30 % reduced. This supports the notion that using the co-products of pyrolysis for replacing fossil fuels in some way could significantly increase the climate change mitigation effect of biochar production.

The amount of carbon which ends up sequestered in the soil depends on several factors, including the carbon content of biochar, stability of the carbon in soil, and biochar losses during soil application and transportation. Perhaps the most uncertain is the stability of carbon over hundreds of years in the soil. If the assumed percentage of stable carbon differed by 5 percentage points, the result would change by about 11 %. The result is clearly sensitive to assumptions made about the amount of stable carbon ending up in soil.

One of the most uncertain aspects of adding biochar to soil are the indirect soil effects, as mentioned a few times. Although they are generally proven to reduce the GHG emissions from soil, it is not so simple. Depending on the properties of the biochar and soil, the effect can sometimes be non-existent, or even negative. (Hammond et al. 2011; Spokas and Reicosky 2009.) To give an idea of these effects, the change in the soil organic carbon (SOC) is included in this analysis. This is the most important indirect soil effect, according to Hammond et al. (2011). In their study they assume that 30 t/ha of biochar is applied to a wheat field, and they consider what would happen if this increased the SOC by 6,3 t_C/ha, or decreased it by 3,6 t_C/ha. These values are used also in this analysis. It is found that increasing the SOC by 6,3 t_C/ha would increase the mitigated carbon dioxide by almost 74 %. Decreasing it by 3,6 t_C/ha would however decrease the net result by 43 %. This shows that the result can be very sensitive to the indirect soil effects. If willow biochar could be

proven to improve especially SOC, its potential to mitigate climate change would improve significantly.

8 SUMMARY AND CONCLUSIONS

The result of the LCA is that willow biochar can potentially mitigate 1,1 kg CO₂eq/kg dry biochar over 100-year timescale. This makes it clearly a carbon sink. The result was found to be sensitive to several assumptions and parameters, some of which include a high degree of uncertainty. The most uncertainty is related to the time of how long biochar stays stable in the soil, and the indirect soil effects. These are still lacking in research especially in the long term, and seem to vary a lot depending on the biochar raw material and soil type. This makes it difficult to quantify exactly how much carbon dioxide could be mitigated by any kind of biochar.

The result was also found to be sensitive to other assumptions, including what is the thermal energy source for drying, and how the pyrolysis co-products are utilized. It was assumed that natural gas was used for drying, which turned out to be the single biggest emission source during the entire life cycle. It is clear that the climate performance of biochar can be significantly improved by avoiding the use of fossil fuels in the most energy intensive life cycle phases, mainly drying and pyrolysis. The pyrolysis co-products are a carbon neutral energy source, so it would be a good idea to use them to provide the energy for these processes. This work considered using the excess energy from the pyrolysis co-products for electricity production and replacing grid electricity with it, which had a clear positive impact on the climate performance of biochar. On the other hand, willow cultivation or transportation don't affect the end result much.

Although this and other studies suggest that willow biochar could help in climate change mitigation, it's not so straightforward to scale up its production. A few issues were identified, which must be addressed before that. First, biochar's large scale production is not currently economically profitable. This could be changed if the carbon offsets could be sold in the carbon market, or if it was subsidized. Another problem that came up is that willow production could require huge land areas, which could lead to land use change. This has been identified as one of the biggest problems for all biomass-based carbon sinks. In this work it was assumed that willow is cultivated in marginal lands, such as former peat production sites. This is a potential way to reduce the impacts from land use change. Further studies are

required, though, to find out how much degraded land suitable for willow cultivation there is in Finland.

Perhaps the best way to think of willow, and biochar, is as a part of a larger effort for climate change mitigation. Willow is only one sustainable feedstock for biochar among many others, such as forest and agricultural residues. Biochar is also only one of many possible carbon sinks, although it does have great potential. Besides removing carbon from atmosphere, it can provide energy, jobs, soil improvement, and it can help in waste management and water treatment. However, to get the full benefits of biochar, there must be both public and private interest and acceptance towards it. To achieve this, the research and knowledge about it must be increased.

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