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Master's thesis in Industrial Ecology

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Abstract

Global concerns about mitigation of greenhouse gas (GHG) emissions and enhancement of energy security has grown rapidly over the years. Therefore, it is important to investigate new renewable energy sources. Biomass is considered as one of them, it can be used for fuels and chemicals production. However, its application should be efficient and flexible, that is why biorefinery concept was proposed.

This study was aimed to determine the most sustainable way of bioethanol and bioplastic co-production based on literature review. To evaluate environmental performance of defined biorefinery system life cycle assessment (LCA) was used.

Results of LCA suggested, that production of HDPE in thermo-chemical biorefinery from poplar wood/forest residues has remarkably lower environmental impact than HDPE, obtained via fermentation from sugar beet. Reductions were also noted in such categories as global warming and fossil resource depletion, when thermo-chemically produced HDPE was compared to its fossil equivalent. However, switch from crude oil to biomass indicated an increase of impact in eutrophication and acidification. Comparison of poplar wood and forest residues as raw material for biorefinery showed, that forest residue is the best option, since its use minimized impact across all categories considered, and compared to fossil-based HDPE it has lower eutrophication potential. Therefore, it was concluded, that use of biomass should minimize contribution not just to global warming and fossil resource depletion, but to other impact categories as well, in order to avoid shift in pollution.

Another key finding of this thesis indicated the importance of accounting for biogenic carbon. In the program used for LCA biogenic carbon, which is emitted during the production of biobased HDPE and bioethanol, assumed to be neutral. Hence, it's contribution to GWP wasn't taken into account, what has led to unfair comparison between oil and biorefinery.

Sammendrag

Globale bekymringer for avbøtning av klimagassutslipp og forbedring av energisikkerhet har vokst raskt gjennom årene. Derfor er det viktig å undersøke nye fornybare energikilder. Biomasse regnes som en av dem, den kan brukes til produksjon av brensel og kjemikalier. Imidlertid bør anvendelsen av den være effektiv og fleksibel, det er grunnen til at bioraffinerikonsept ble foreslått.

Denne studien hadde som mål å bestemme den mest bærekraftige måten å bioetanol og bioplastisk samproduksjon på, basert på litteraturgjennomgang. For å evaluere miljømessige ytelser av definert bioraffineringsystem livssyklusvurdering (LCA) ble brukt.

Resultatene fra LCA antydte at produksjon av HDPE i termisk kjemisk bioraffineri fra poppelved / skogrester har bemerkelsesverdig lavere miljøpåvirkning enn HDPE, oppnådd via gjæring fra sukkerroer. Reduksjoner ble også notert i slike kategorier som global oppvarming og fossil ressursuttømming, da termokjemisk produsert HDPE ble sammenlignet med dens fossile ekvivalent. Bytt fra råolje til biomasse indikerte imidlertid en økning av påvirkningen i overgjødsling og forsuring. Sammenligning av poppelved og skogrester som råstoff for bioraffineri viste at skogrester er det beste alternativet, ettersom bruken har minimert innvirkning på tvers av alle kategorier som er vurdert, og sammenlignet med fossilbasert HDPE har den lavere overgjødslingspotensial. Derfor ble det konkludert med at bruk av biomasse skulle minimere bidraget ikke bare til global oppvarming og uttømming av fossile ressurser, men også til andre påvirkningskategorier for å unngå skift i forurensning.

Et annet sentralt funn av denne avhandlingen indikerte viktigheten av å gjøre rede for biogenisk karbon. I programmet som ble brukt til LCA, antok biogen karbon, som slippes ut under produksjon av biobasert HDPE og bioetanol, å være nøytral. Derfor ble det ikke tatt hensyn til bidraget til GWP, det som har ført til urettferdig sammenligning mellom olje og bioraffineri.

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1 Introduction

Cumulative anthropogenic greenhouse gas emissions exceed 2000 GtCO₂ since 1750, this led to the highest concentration of carbon dioxide, methane and nitrous oxide in the atmosphere. What in turns has resulted in global warming and led to such consequences as change of global water cycle, ocean acidification, surface ice melting, extreme weather and climate events. Moreover, the change in global average surface temperature affected many terrestrial, freshwater and marine species. Their geographic ranges, migration patterns and seasonal activities have shifted. (IPCC, 2014A) What in turns have disturbed the provision of ecosystem services and have negative effect on human systems. (Climate change consequences - Climate Action - European Commission, 2020)

Therefore, there is a clear scientific evidence, that adaptation and mitigation actions are required. According to IPCC report the drastic increase in GHG emissions is associated with use of fossil fuels. Consequently, new renewable energy sources are needed. Biomass was suggested as promising alternative to fossil fuels. It can be converted through different routes to heat, power as well as liquid fuels and chemicals. What is a big advantage, since the transport sector causes around 80% of all GHG emissions and it has been proven, that use of biofuel will lead to significant emissions reductions. (IPCC, 2011) For more efficient use of biomass the biorefinery concept was proposed. Biorefinery was defined as “*the sustainable processing of biomass into a spectrum of marketable products and energy*”. (IEA Bioenergy, 2009). This concept supposed to minimize environmental impact from production of fuels and chemicals, as well as create new opportunities for social and economic development. (Gnansounou & Pandey, 2017)

Many scientists have assessed economical and environmental visibility of biorefinery concept. In most of these studies biofuel and biochemicals, such as furfural were considered as final products. (Hernández, Romero-García, Dávila, Castro & Cardona, 2014), (Raman & Gnansounou, 2015), (Budzinski & Nitzsche, 2016)

However, nowadays one specific area of growing concern is the production of petroleum-based plastic. Currently it consumes 4-6% of the global oil production (Plastics Europe, 2017). What in turns negatively affects climate change and resource depletion. For mitigating the negative effect European commission suggested use of more sustainable materials for plastic production. (European Commission, 2020) Biomass is considered as one of these materials (Materials, 2020) Therefore, it is important to develop the biorefinery system, where fuel and plastic will be co-produced from biomass and assess its environmental impact. First research question accordingly is: *What are the most relevant biofuels and bioplastics and in which they should be produced?* It is answered by review of previously conducted studies as well as by comparison of results, obtained in LCA with findings of other researchers.

Few scientists have already assessed environmental sustainability of biobased polyethylene production. For example, S. Belboom and A. Léonard compared impact of polymers, produced via biochemical conversion of biomass, with their fossil equivalent. Yasunori Kikuchi, Yuko Oshita, Kazuya Mayumi and Masahiko Hirao analyzed environmental impact of polyethylene and polypropylene production from fossil resources and biomass through different pathways. (Belboom & Léonard, 2016), (Kikuchi, Oshita, Mayumi & Hirao, 2017) Nevertheless, there is lack of comprehensive studies on biorefinery system, where bioplastic and bioethanol would be co-produced. Therefore, the second research question is: *What is the environmental impact of specified biorefinery system?* It is addressed by performing a life cycle assessment of the biorefinery system.

This work consists of 6 chapters: introduction, literature review, methodology, results, discussion and conclusion. In the second chapter relevant information about biorefinery systems is given and previously conducted studies are reviewed. Third chapter provides information about method that was used for answering research question. In the fourth chapter results of the

life cycle assessment are presented and in the fifth key findings are discussed and compared with results from similar studies. In the sixth chapter the main findings are summarized.

2 Literature review

The literature review consist of 4 parts. In the first part the biorefinery concept is presented. Second part includes possible feedstocks and conversion methods in biorefineries. Then valuable products, that can be obtained from biomass are discussed and evaluated. In the fourth part relevant environmental assessment studies are analyzed and object of study is chosen.

2.1 Classification of biorefineries

As it was stated in the introduction biorefinery is *the sustainable processing of biomass into a spectrum of marketable products and energy*.

Biorefinery concept can be applied to different types of biomass (feedstocks). Furthermore, variety of conversion routes can be used for obtaining final products. Therefore, task 42 of IEA has developed classification system. Their classification was based on such criteria as platforms, product groups, feedstock groups and conversion processes. (de Jong et al., 2013) In the Table 1 bellow examples of each group are shown.

Table 1 Classification of biorefinery systems

Platforms	Final bio-based products	Group of feedstocks	Group of bio-processes
<ul style="list-style-type: none"> • C6 sugar • C5 sugar • Lignin • Syngas • Hydrogen • Pyrolysis liquid • Bio-oil • ... 	<ul style="list-style-type: none"> • Feed/food • Fuels • Heat • Electricity • Chemicals • Bio-materials 	<ul style="list-style-type: none"> • Energy crops • Forestry crops • Agricultural residues • Forestry residues • Algal biomass • Industrial residues 	<ul style="list-style-type: none"> • Enzymatic hydrolysis and fermentation • Gasification • Pyrolysis • Oil extraction • Protein extraction • Thermal cracking of oil • Trans-esterification of oil • Hydrogenation of oil • Fischer-Tropsh

C5/C6 sugars is one of the main biorefinery platforms, since sugars can be found in large number of feedstocks and can be easily extracted. Further they are mainly converted into ethanol through fermentation. (Gnansounou & Pandey, 2017)

Another important platform is synthesis gas. Interest to this product has increased significantly in the last couple of years, due to its low environmental impact and possible application of different types of feedstock and large amount of products, that can be obtained. (Dahmen, Henrich & Henrich, 2017)

Lignin is the most common compound in biorefineries, that is mainly used for electricity and heat generation. However, in the recent years it was found to be the most promising source of aromatic hydrocarbons. Many scientists are working now on conversion of lignin into valuable products, such as bio-oil, biogas and bio-char. (Cao et al., 2019)

Products that are the main interest in the market are energy, chemicals and biopolymers. Bioethanol, biodiesel and biomethane are products, which have been already produced and can be found on the market. A lot of biobased plastics, such as bio PET are also already in use. (Gnansounou & Pandey, 2017)

2.2 Main processes in biorefinery

Biorefining involves several multistep processes. First step is defined as feedstock selection, it also usually includes biomass pretreatment. The second important step is conversion of biomass into valuable products. (Ferreira et al., 2017) Some scientists also include use and end of life phases in in biorefinery process. (Julio et al., 2017) However, in this thesis main focus will be on the first two steps.

2.2.1 Feedstock production

In biorefinery perspective biomass is defined as renewable biogenic organic material formed by natural or anthropogenic processes, that can be converted to fuels and chemicals. Biomass can be classified by source of raw material or as first, second and third generation feedstock. For instance, Samhita Mahapatra and Ramesh Pathy Manian in their research identified three major sources or raw materials for biofuels and biochemicals production: sucrose containing feedstocks (sugarcane), starchy materials (corn, wheat etc) and lignocellulosic biomass (forest residues, grasses etc). Sonil Nanda et al. defined first, second and third generation biomass. They considered food crops, such as corn, wheat and sugarcane as first generation feedstock; energy crops and wastes, which are mostly lignocellulosic materials – second generation feedstock; marine biomasses (microalgae and macroalgae) – third generation feedstock. (Mahapatra & Manian, 2017) (Nanda, 2018)

Even though, food crops are considered to be promising raw materials for biorefineries, many scientists assume, that there are lots of drawbacks associated with use of this type of feedstock. First of all, amount of sucrose and sugar containing biomass that is available is not sufficient to completely replace fossils fuels. In addition, their use in biorefinery systems will compete with food and animal feed production.

In contrast, second and third generation feedstock can be supplied on a large scale, don't cause food and fuel competition and contributes to environmental sustainability.

(Limayem & Ricke, 2012), (Alzageem et al., 2018)

However, due to more complex composition second generation biomass requires additional pretreatment to recover fermentable sugars for further conversion to fuels and chemicals. Lignocellulosic materials consist of 3 components: cellulose, hemicellulose and lignin. Percentage of these components varies depending on the source of lignocellulose. In the Table 2 bellow 4 types of the most promising lignocellulosic feedstock are presented. (Limayem & Ricke, 2012)

Table 2 Types of lignocellulosic feedstock

Type of feedstock	Description	References
Agricultural residues	Agricultural wastes are the residues obtained from production and processing of agricultural products such as crops, fruits, vegetables, meat, poultry, and dairy products. This type of biomass is easily available, has short harvest rotation period and does not lead to deforestation.	(Pattanaik, Pattnaik, Saxena & Naik, 2019)
Perennial grasses	Perennial grasses, such as switchgrass, miscanthus giganteus are lignocellulosic, low-cost feedstock, able to grow in variable environments including marginal lands. Around 50-70% of the crop can be used for ethanol production.	(Zabed, Sahu, Boyce & Faruq, 2016)
Woody biomass and forest residues	There are two types of wood: softwood (pine) and hardwood (poplar). Woody biomass has flexible harvesting time and low ash content, but it's use can lead to deforestation. This problem can be avoid is forestry residues are used: sawdust, wood chips, pruning residues, slashes, branches from dead trees, forest thinning.	(Zabed, Sahu, Boyce & Faruq, 2016)
Industrial residues and MSW	This type of biomass includes: integrated cupboard, paper, food residues, garden waste, metal, glass, plastics and textile. MSW has a great potential as a biorefinery feedstock and developing fast now.	(Zabed, Sahu, Boyce & Faruq, 2016)

In Table 3 biomass composition of various lignocellulosic feedstocks is shown.

Table 3 Lignocellulosic biomass composition

Raw material	Hemicelluloses	Cellulose	Lignin	Others (i.e., ash)	Reference
Agricultural residues	25–50	37–50	5–15	12–16	(Zabed, Sahu, Boyce & Faruq, 2016)
Hardwood	25–40	45–47	20–25	0.8	
Softwood	25–29	40–45	30–60	0.5	
Grasses	35–50	25–40	–	–	
Newspaper (Industrial waste)	25–40	40–55	18–30	–	

The biomass composition determines conversion efficiency and ethanol yield. Holocellulose (cellulose and hemicellulose) is a substrate for ethanol, therefore it's content will affect the amount of ethanol, that can be obtained. (Zabed, Sahu, Boyce & Faruq, 2016)

Algae is considered as third generation biomass and the most promising feedstock for fuel production. According to Pratima Bajpai it has number of advantages over other raw materials: 1) it is able to grow throughout the year 2) it has higher tolerance to high CO₂ concentration 3) lower water consumption during the cultivation stage 4) cultivation doesn't require pesticides, herbicides and fertilizers can be obtained from wastewater 5) has higher growth potential 6) able to grow under harsh conditions 7) no terrestrial land competition. Nevertheless, there are some drawbacks associated with use of algae as feedstock: 1) high cultivation costs 2) high energy consumption during the harvesting 3) difficult to concentrate the biomass. Therefore, third generation biorefineries are not as developed as the second and first generations. (Bajpai, 2019)

2.2.2 Conversion routes

First step in conversion of biomass into valuable products is pretreatment. Pretreatment is an important stage, where physical and chemical structure of biomass is modified in order to increase efficiency of conversion technology. Pretreatment technologies can be classified into four categories: physical, chemical, physicochemical and biological. (Mussatto & Dragone, 2016)

Physical pretreatment includes operations designed to modify physical properties of biomass without the addition of chemical reagents or microorganisms.

Chemical pretreatment is operations designed to change physical and chemical properties of biomass in the presence of a chemical.

Biological pretreatment is an alternative method, where properties of biomass are changed by use of microorganisms. (Treiche et al., 2020)

In Figure 1 bellow examples of pretreatment processes are given.

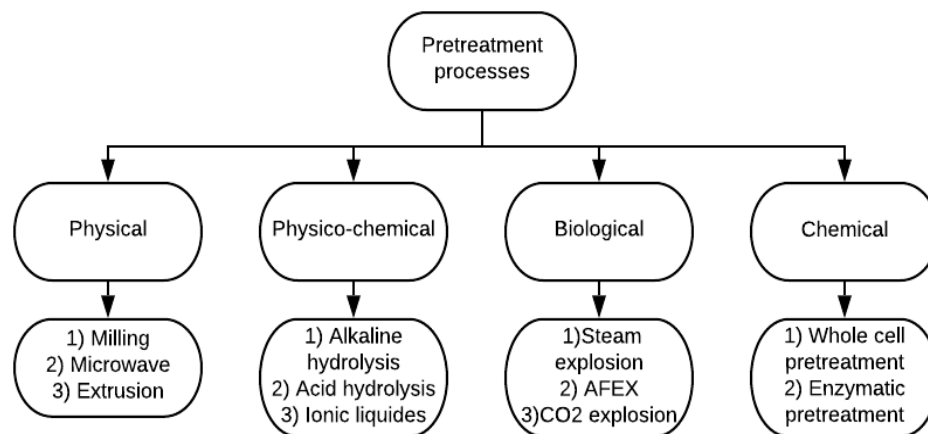


Figure 1 Classification of pretreatment methods

Pretreated biomass is then converted into valuable products. For today three main conversion pathways are recognized: thermo-chemical, bio-chemical and hydrothermal. Thermo-chemical route includes such methods as gasification, pyrolysis and liquefaction. Bio-chemical conversion can be performed by anaerobic digestion and fermentation. Hydrothermal pathway today is presented by supercritical water gasification. (Nanda et al., 2014)

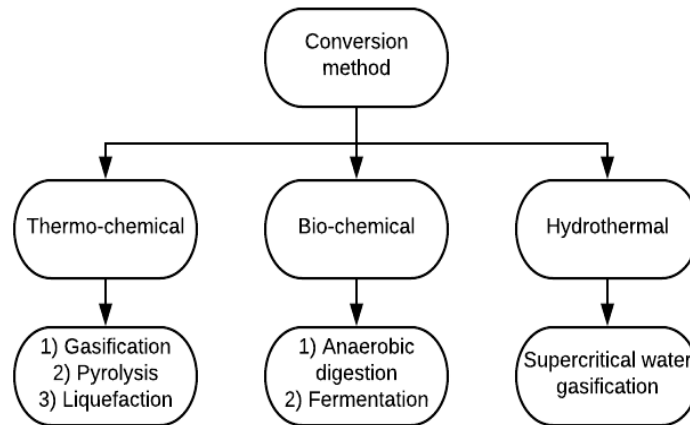


Figure 2 Biomass conversion pathways

Difference between these pathways is the base of the conversion processes. For thermo-chemical conversion it is pyrolysis, for bio-chemical – use of microorganisms and for hydrothermal – use of supercritical water. (Nanda et al., 2014)

Anaerobic digestion is aimed to obtain biogas and fertilizers from organic material. It is a biochemical process in which organic compounds are metabolized into a gaseous mixture, using microorganisms in anaerobic condition. The obtained mixture of gases mainly consists of methane and carbon dioxide. (Handbook of Biofuels Production, 2016)

Biochemical conversion of biomass is based on the use of enzymes or microbial catalysts to hydrolyse carbohydrates into simple sugars. (Cadham, Van Dyk, Linoj Kumar & Saddler, 2016) Fermentation is one of the most important biochemical processes. It is carried out in the absence of oxygen and involves different microorganisms for production variety of alcohols, acids and gases. Fermentation can be applied to many types of feedstock, but pretreatment and acid or enzymatic hydrolysis is an essential step for the efficient conversion, especially for lignocellulosic biomass. As it was stated before each final product requires specific microbial catalyst. For example, for obtaining biobutanol *Clostridium* spp. is used, for bioethanol - *Saccharomyces cerevisiae*, *Candida albicans*, *Pichia stipitis*, and *Kluyveromyces* are mostly applied. (Gupta Goutam & Mondal, Monoj, 2019)

Supercritical water gasification is a promising concept for converting wet biomass with high water content to syngas. It is carried out in a gasifier in which the conditions of the critical point of water (374 °C and 22.1 MPa pressure) are used as a favorable atmosphere for biomass conversion. After the gasification process mix of H₂, CH₄, CO₂ and CO gases is obtained. This mixture can be separated and CO (syngas) or H₂ can be further used. (Bhaskar et al., 2011)

Liquefaction is one of the promising thermo-chemical conversion methods. It converts biomass into bio-oil by using catalytic reaction in pressure (5–10 MPa) and temperature (250–325 °C). Scientists recognize direct and indirect liquefaction. First for obtaining bio-oil and condensable organic vapours involves rapid pyrolysis. Second for production of bio-oil is using either an alkali, acidic or glycerine medium. It refers more to chemical upgrade than to thermo-chemical processing.

Pyrolysis is defined as thermal decomposition of biomass in the absence of oxygen. Lately it has received special attention, since such valuable products as charcoal, bio-oil and fuel gas can be obtained through it. Pyrolysis can be slow, fast and flash. Slow pyrolysis is a well-known technology, that is used in traditional charcoal klin. It operates in the temperature range of 550–950 K. Fast pyrolysis is carried out in the carefully controlled temperature in the 700–775 K range, in the inert atmospheric conditions. Usually the final products of fast pyrolysis are: 60–

75 wt.% of liquid bio-oil, 15–25 wt.% of solid char, and 10–20 wt.% of noncondensable gases, depending on the feedstock used. Flash pyrolysis has the operating temperature in the range of 777–1027 °C. It is used for production petroleum equivalent biomass crude oil. (Panwar, Kothari & Tyagi, 2012)

Gasification converts biomass into useful gases, such as syngas (mixture of CO and H₂). This conversion method operates at temperatures of 600–1000 °C and requires pretreatment of biomass. Gasification is carried out in the presence of a controlled amount of oxygen, steam or air to prevent combustion process. (Jeswani, Falano & Azapagic, 2015)

Most relevant gasification processes are fluidized-bed and fixed bed. In the fluidized-bed gasification biomass particles are turned into a fluid state through suspension in a gasifying agent. In fixed bed - the gas passes through the raw material while the gasifier zones are in “fixed” position. (Canabarro et al., 2013)

After passing the gasifier syngas should be cleaned up. During this step any impurities, such as sulphur and unreacted carbon, using carbon beds or amine are removed. For further conversion to fuels and chemicals purified syngas undergoes water-gas shift reaction to balance the H₂/CO ratio. (Jeswani, Falano & Azapagic, 2015) Afterwards it can be converted into power and electricity generation or into transportation fuels and chemicals. For upgrading syngas to fuels and chemicals different kinds of catalysts can be applied. For instance, ZnO and CuO are used for the production of methanol; cobalt, iron, and ruthenium catalysts used to produce alkanes and hydrocarbons waxes. For ethanol production mixed alcohol synthesis on Sulfided Molybdenum-Based Catalysts is usually conducted. Syngas fermentation pathway for biofuels and biochemicals production is now receiving interest. (Mishra & Mohanty, 2018) Since, it has been proven, that fermentation of syngas has significant advantages over the catalytic conversion due to ability of microorganisms to (i) work under moderate temperatures and pressures; (ii) be more tolerant than chemical catalysts to poisoning by sulfur, tars, and chlorine; (iii) accept a wider range of gas compositions; and (iv) achieve higher conversions and yields. (Benalcázar et al., 2017) In syngas fermentation pathway *Clostridium bacterium* is used for obtaining bioethanol from syngas. (Mishra & Mohanty, 2018)

The thermochemical conversion in turns also offers advantages over the biochemical route. Since, according to the Eduardo Almeida Benalcázar et al. it has (i) higher carbon yields, (ii) simpler process configuration, (iii) more flexibility on feedstock and (iv) wider scale-up possibilities. (Benalcázar et al., 2017)

2.3 Platform chemicals

For biorefinery concept it is important to identify platform chemicals. According to Sudhakar Takkellapati platform chemicals is a chemical, that can be a substrate for the production of various other higher value-added products. (Takkellapati, Li & Gonzalez, 2018) In 2004 Department of Energy made a list of 12 potential chemicals, that can be obtained from biomass. (Werpy et al., 2004). Later in 2010 two other chemicals were added in this list and now it includes: ethanol, furfural, hydroxymethylfurfural, 2,5-furandicarboxylic acid, glycerol, isoprene, succinic acid, 3-hydroxypropionic acid/aldehyde, levulinic acid, lactic acid, sorbitol, and xylitol. (Bozell and Petersen, 2010)

Takkellapati et al., in their work described all of the platform chemicals:

Furfural is an essential chemical for plastics, pharmaceutical and agrochemical industries, adhesives, and flavor enhancers. In biorefinery it can be produced from various types of feedstock. First sugars, presented in biomass are hydrolyzed to obtain monosaccharides, which are then converted into furfural by acid-catalyzed dehydration.

Hydroxymethylfurfural (HMF) is an important building block, its derivatives are used for synthesis of polymers, biofuels, polyurethanes, which are further used in coatings, elastomers, and adhesives. The most efficient way of producing HMF is through acid-catalyzed dehydration of fructose.

2,5-Furandicarboxylic acid (FDCA) is a potential substitute for petrochemical-based adipic acid and terephthalic acid. It also can be applied in polyesters, polyamides, and plasticizers production. FDCA can be synthesized by the oxidation of HMF or by starting from fructose in a two-step dehydration followed by oxidation, without HMF as intermediate.

Glycerol as feedstock has received significant attention in the past years, due to wide range of its application. Glycerol derivatives are used in production of polymers, coatings, adhesives, and lubricants. Nowadays 90% of glycerol is produced during the biodiesel manufacturing process.

Succinic acid is a key starting material for synthesis of fumaric acid, maleic acid, 1,4-butanediol, tetrahydrofuran, and γ -butyrolactone. In biorefinery succinic acid can be obtained via fermentation of sugars.

Demand for lactic acid is expected to grow in the next decade, since it is an important building block and its derivatives are used in the packaging market and textiles. Currently, lactic acid is commercially produced via fermentation of variety of sugars (glucose, sucrose, or lactose).

Levulinic acid is an essential chemical, it is used at pharmaceutical and cosmetic industries, as well as for production of plasticizers and fragrances. In high yields this acid can be obtained through acid-catalyzed hydrolysis of C₆ sugars. Due to availability of technologies, recently number of companies started commercial production of levulinic acid from lignocellulosic biomass. For instance, GF Biochemical for levulinic acid production uses their proprietary technology.

3-Hydroxypropionic acid (3-HP) and 3-hydroxypropionaldehyde (3-HPA) are not currently not produced on commercial scale directly from biomass. Despite of its toxicity 3-HPA and 3-HP are widely used for production of higher value-added chemicals, which are further used at water treatment, paper manufacture, mining, oil recovery, absorbents and synthesis of various polymers. For today. These platform chemicals are obtained from glycerol via fermentation or glucose at neutral pH by *E. Coli*.

Sorbitol is one of the most well-known and sought for platform chemicals. It is directly used in food, beverages, drugs, cosmetics, and applied as a key material for production of other value-added chemicals. On market scale sorbitol is obtained via transition metal-catalyzed hydrogenation of D-glucose, but it can also be produced in 2 steps: 1) enzymatic hydrolysis of cellulosic materials 2) hydrogenation. (Takkellapati, Li & Gonzalez, 2018)

Xylitol is widely used sugar substitute. It is an ingredient in such products as chewing gum and toothpaste. (Xylitol: Uses, effects, and possible benefits, 2020) Xylitol is commercially produced via the catalytic reduction of pure D-xylose (Takkellapati, Li & Gonzalez, 2018), but recently hemicellulose conversion method has been described by Dietrich et al. Xylitol is obtained via use of heteropoly acid or biomass-derived organic acid and Ru on carbon as catalyst for one-pot hydrolysis–hydrogenation (Dietrich et al., 2017)

Isoprene is a material, that is essential for polymer production, which are further used in footwear, mechanical instruments, medical appliances, sporting goods, and rubber tires. Currently this platform chemical is obtained from fossil resources, but its production from biomass via fermentation is under development. (Takkellapati, Li & Gonzalez, 2018)

Ethanol is considered as one of the most attractive feedstocks for producing renewable chemicals and materials. First of all, due to availability of different technologies for its production from biomass. As it was stated in previous chapter it is possible to obtain ethanol through biomass fermentation, as well gasification and mixed alcohol synthesis or via syngas fermentation. Further it can be used as transportation fuel, unfortunately now its application is limited, and ethanol has to be blended with gasoline for its use in vehicles. However, this issue can be solved in future by manufacturing vehicles, that can work on more concentrated solutions. Besides, use as fuel ethanol is an important building block for obtaining other valuable chemicals. Through acid-catalyzed dehydration ethylene and diethyl ether can be obtained. Acetone is another ethanol derivative, which is produced via dehydrogenation and further aldolization or ketonization. Propene is also a gas, that can be produced from ethanol, by use of catalysts. Robert A. Dagle et al. in their work also described production of such valuable products as 1,3-

butadiene, ethyl acetate, 1-butanol, acetic acid, ethylene oxide, hydrogen, ethylene glycol, acrylic acid, isobutene and others from ethanol. Besides, ethanol availability in large quantities, wide range of applications and developed conversion methods, reasonable price is another factor, that makes ethanol desirable product. (Dagle et al., 2020)

2.4 Environmental assessment studies on biorefinery systems

2.4.1 Methodological tools for environmental assessment

For identification of environmental impacts, that are generated in biorefinery process environmental assessment, as methodological tool is used. For today three main methods are applied for estimating environmental impacts of biorefinery. According to Valentina Aristizábal-Marulanda and Carlos A. Cardona Alzate these methods are physical-chemical analysis, impact categories and life cycle assessment. Physical-chemical analysis include calculation of biochemical oxygen demand (BOD) and chemical oxygen demand (COD). These data are used further used by some scientists to determine the organic burden in the wastewater streams of bio-based processes and biorefineries. Impact categories method include several tools. For example, Waste Reduction Algorithm (WAR), where potential environmental impact is quantified. WAR is mostly applied for comparison of biorefinery process configurations. Another tool is Gauging Reaction Effectiveness for the Environmental Sustainability of Chemistries with a Multi-Objective Process Evaluator (GREENSCOPE), which quantifies sustainability of the processes and able to generate the life cycle inventory data. (Aristizábal-Marulanda & Cardona Alzate, 2018) Life cycle assessment (LCA) is defined as a tool for evaluation of the inputs, outputs, and the potential environmental impacts of a product system throughout its life cycle, which can help to understand the environmental impacts of product from the acquisition of raw materials to final disposal. (2006a) The assessment can be performed in three ways: cradle-to-grave analysis, cradle-to-gate analysis and cradle-to-cradle analysis. In cradle to grave, full LCA is performed from manufacturing to the disposal stage. In cradle-to-gate assessment use and disposal stages are excluded from the system. Cradle-to-cradle is a variation of cradle-to-grave assessment, where the disposal stage is a recycling process. Life cycle assessment is a systematic approach, which consists of four stages: goal and scope definition, inventory analysis, impact assessment and interpretation of the results. (Muralikrishna & Manickam, 2017) This method is highly used worldwide and number of software and databases have been developed for it. For example, GaBi, EcoManager, LCA, LCAD, LIMS, LMS Eco-Inv, Tool, Bio-Grace, SimaPro, TEMIS, and Umcon. Life cycle assessment is very suitable for assessing environmental sustainability of biorefinery systems, due to its ability of dealing with complex and multi-disciplinary processes. (Aristizábal-Marulanda & Cardona Alzate, 2018) Therefore, in the literature review LCA studies are presented.

2.4.2 Previously conducted LCA of biorefinery systems

Lei Wang, Jade Littlewood and Richard J. Murphy in their work assessed environmental sustainability of bioethanol production through biochemical conversion in the UK. They considered wheat straw as a feedstock and functional unit was defined as 'to drive 1 km in a Flexible-fuel vehicle (FFV)'. Therefore cradle-to-grave assessment was conducted. In this research bioethanol (E100) was compared with conventional petrol. In addition 4 biomass pretreatment methods: steam explosion with and without acid catalyst, dilute acid, liquid hot water, wet oxidation were considered to identify the most efficient and environmental friendly bioethanol production method. The production system included: wheat straw cultivation, bioethanol production and end use in vehicles stages. During the second stage besides bioethanol, electricity is produced. To deal with co-production authors suggested use of allocation method, called system expansion. Credits, associated with avoided emissions from generation of an equivalent amount of the average UK National Grid electricity, were given.

Results of the study showed, that use of bioethanol from wheat straw in vehicles can save up to 45% GHG emissions and decrease fossil fuel by 75%. However, in such impact categories as eutrophication and acidification petrol was considered as preferable option. Scientists assumed that acidification potential is higher for bioethanol due to the combustion emissions in the CHP process and eutrophication is higher, as a consequence of fertilizers use during the wheat cultivation. The contribution analysis showed, that enzyme production is the biggest contributor to the most impact categories as well as feedstock cultivation. Another conclusion that was made by Lei Wang, Jade Littlewood and Richard J. Murphy was that definition of system boundaries significantly affect the results. When the effect of wheat straw removal is considered, impact associated with ethanol production increase accordingly. (Wang, Littlewood & Murphy, 2013)

Another scientist - V. Piemonte also estimated environmental performance of biorefinery, where bioethanol and electricity are co-produced. The aim of research was to compare environmental impact of first and second generation biorefinery. He considered wood residues and corn as raw materials for bioethanol and electricity co-production through fermentation. The scope of the study was defined as 'cradle-to-gate' with 1 kg of fuel as functional unit. Results showed, that, when economic allocation is applied, biorefinery, where wood residues are used as raw material has lower impact in resource depletion than corn based and fossil-based refineries. However, it has higher values in such end-point categories as human health and ecosystem quality, where acidification and eutrophication belong. (Piemonte, 2011)

Christin Liptow, Anne-Marie Tillman & Matty Janssen in their research assessed environmental performance of 2 ethylene production routes from woody biomass: fermentation and gasification. The functional unit of this study was 50000 t of ethylene. The system boundaries were defined as from cradle-to-gate. In gasification route the following stages were considered: feedstock acquisition and transportation, gasification and methanol synthesis, methanol-to-olefins process. During the last several products are obtained, such as a propylene and C4 compounds. Therefore, environmental burdens were allocated between them on economical basis. System of ethylene production via fermentation included: forestry activities, ethanol production via fermentation and dehydration of ethanol. Authors assessed such impact categories as: global warming, eutrophication, acidification and photochemical ozone creation. For global warming they didn't include biogenic CO₂, assuming that it is part of neutral carbon cycle. However, for deeper understanding of industrial process these emissions were presented in inventory.

Results indicated, that ethylene produced via gasification is preferable option. It also has lower values compared to its fossil equivalent in such impact categories as global warming and photochemical ozone creation. Nonetheless, both bio-chemical and thermo-chemical ethylene has higher impacts in acidification and eutrophication, what is according to scientists a consequence of NO_x emissions during gasification and emissions from enzyme use during the fermentation.

Researchers also made a conclusion, that fossil-based ethylene emits more fossil CO₂, compared to bio-based. However, biogenic CO₂ emissions are significantly higher for ethylene from biomass than for fossil-based ethylene. Biogenic CO₂ emissions from fermentation of biomass are two times bigger than emissions from thermo-chemical conversion (Liptow, Tillman & Janssen, 2015)

Bernabé Alonso-Fariñasa, Alejandro Gallego-Schmidb, Pedro Haroa and Adisa Azapagicb assessed environmental performance of thermo-chemical bio-ethylene production in comparison with bio-chemical and fossil-based. Functional unit was defined as 1 ton of ethylene. Scope of the study was cradle-to-gate and included 2 main stages: biomass supply and production of bio-ethylene and its co-products. Poplar wood was considered as feedstock for thermo-chemical conversion, when for bio-chemical sugar beet was chosen. In addition, three different ethylene production pathways were compared: 1) direct ethanol dehydration, with methanol, propanol and sulphur cake as co-products 2) indirect ethanol dehydration, with

sulfur cake as co-product 3) dimethyl ether to olefins, with liquefied petroleum gas (LPG), propylene and sulphur cake as co-products. For better visibility of the results system expansion, economic and energy allocation were applied.

Biogenic carbon was not considered, because use and end of life phases were not included. Therefore, according to the scientists, it is not known how long the carbon would be stored before its release to the atmosphere.

When three production routes were compared and system expansion is applied, indirect ethanol dehydration appeared to be the best option for 8 out of 11 impacts considered, such as abiotic depletion potential of elements (ADP), human toxicity potential (HTP), freshwater aquatic ecotoxicity potential (FAETP), marine aquatic ecotoxicity potential (MAETP), terrestrial ecotoxicity potential (TETP), photochemical oxidants creation potential (POCP), acidification potential (AP) and eutrophication potential (EP). For global warming potential (GWP), abiotic depletion potential of fossil fuel resources (ADP_f) and ozone depletion potential (ODP) the third production pathway is preferred option. When economic or energy allocation is applied, case 3 is still the best option for same three categories.

Comparison of thermo-chemical pathway with bio-chemical showed, that the last is a better option just for 3 impact categories: HTP, FAETP and TETP. For the remaining impact categories at least one of thermo-chemical options was better than bio-chemical. This is a consequence of heat demand in the biological reactor, supplied mainly by fossil-fuel resources. Another reason is larger input of pesticides and fertilizers for sugar beet cultivation than for poplar wood.

The fossil-based ethylene has lower impact in all categories, except global warming potential and abiotic depletion potential of fossil fuel resources. For ADP_{fossil} impact is reduced by 84%–196% and for GWP by 66%–105%, depending on the production pathway. However, for the remaining categories values of thermo-chemically produced ethylene are higher, because of use of metal catalysts, pesticides, fertilizers.

Scientists made the same conclusion, as Christin Liptow et al., that use of bio-based ethylene can reduce dependence on fossil fuels and contribute to climate change mitigation, but might increase other environmental impacts. (Alonso-Fariñas, Gallego-Schmid, Haro & Azapagic, 2018)

Paraskevi Karka, Stavros Papadokonstantakis and Antonis Kokossis conducted a life cycle assessment of broad set of biomass-to-product process chains. They compared environmental impact of various bio-ethylene production pathways, using wood chips as feedstock. They also provided a comparative analysis for fossil based equivalent. One kilogram of valuable chemical was chosen as functional unit and scope was defined as cradle-to-gate. Global warming potential, water depletion and energy consumption were the only three categories for which results were presented.

For ethylene thermo-chemical pathway with syngas fermentation and further dehydration of ethanol has the lowest global warming potential, but significantly higher values for the remaining two categories. (Karka, Papadokonstantakis & Kokossis, 2017)

Eduardo Almeida Benalcázar et al., and Robert M. Handler et al. also analyzed environmental impact from production of chemicals through syngas fermentation. In both of these researches different types of feedstocks were compared and economical assessment was conducted. (Handler, Shonnard, Griffing, Lai & Palou-Rivera, 2015), (Benalcázar, Deynoot, Noorman, Osseweijer & Posada, 2017)

In life cycle assessment study, performed by Robert M. Handler et al., switch grass, corn stover and forest residues were compared as raw material for ethanol production. The LanzaTech fermentation process was used to obtain ethanol, so first biomass was gasified and then syngas was fermented. Scientists supposed that, thermochemical conversion can be applied to almost any kind of biomass and there are no significant differences in emissions associated with processing of particular type of feedstock. Therefore, Robert M. Handler et al., in their study included GHG credits and emissions associated with feedstock choice. They made a conclusion,

that forest residues as a feedstock have the lowest GHG emissions, that occur during the procurement and should be the best option. (Handler, Shonnard, Griffing, Lai & Palou-Rivera, 2015)

Temitope Falano, Harish K. Jeswani and Adisa Azapagic assessed environmental performance of biorefinery system, where ethanol, acetic acid, lactic acid and electricity are co-produced. In this study production of ethanol through fermentation from four types of second-generation feedstocks were compared: wheat straw, forest residues, poplar, and miscanthus. Results were also compared with ethanol, obtained from first generation biomass and ethanol produced from fossil resources in conventional refineries. The system was defined as cradle-to-gate and included: feedstock cultivation, harvesting and transportation; production of ethanol and co-products. For analysis 1 liter of ethanol was used as functional unit. To deal with multi-output first system expansion was used, and credits were given to the system for acids and electricity production; then economic allocation was applied.

Life cycle assessment showed, that when system expansion method is applied, such categories as global warming, human toxicity, ozone layer depletion potential, abiotic depletion potential, marine aquatic ecotoxicity potential and photochemical oxidant creation potential are negative for all 4 types of feedstocks, due to co-products credits. Poplar wood showed bigger emissions savings for 8 out of 11 impact categories and was chosen as the best option for this allocation method. In contrast, when economic allocation (85% of impact was allocated to ethanol, based on its quantity and market price) was applied, forest residues became the best option across most impacts. Poplar wood had slightly higher values and was considered as the second best.

Biobased ethanol was also compared with ethanol from fossil resources. Compared to ethanol from poplar, miscanthus, and forest residue, fossil-based ethanol is worse in most of the impact categories. However, it is better than ethanol from wheat straw in 6 out of 11 impact categories: acidification, eutrophication, freshwater, terrestrial and human toxicity, and land use. Authors came to conclusion, that most noticeable saving from second generation ethanol can be achieved in such categories as fossil resource depletion and GWP.

Scientists also came to the conclusion, that land use change effect significantly affects the results, if forest land is converted to grassland, the impact increases from -139 g CO₂ eq./L to 6800. Nevertheless, if grassland is converted to poplar forest, the GWP is reduced to -736 g CO₂ eq. because of the carbon sequestration by the forest. (Falano, Jeswani & Azapagic, 2014)

Same researchers assessed environmental performance of thermo-chemical biorefinery. They considered: wheat straw, forest residues, poplar, and miscanthus as raw materials for obtaining bioethanol. Production process included 6 stages: feedstock cultivation and collection, feedstock handling and drying, gasification, syngas cleanup and conditioning, alcohol synthesis and alcohol separation. One liter of ethanol was considered as functional unit. Besides ethanol, propanol and butanol were obtained during alcohol synthesis and impacts were allocated between these 3 products. When system expansion was applied, forest residues appeared to be the best option for 8 out of 12 impact categories, including global warming, eutrophication potential, human toxicity, fossil and mineral resource scarcity. For 7 categories results were negative, due to co-products credits. Forest residues showed better results than other feedstock types, when economic allocation was used and 81% of impact was allocated to ethanol, 17% to propanol and the rest to butanol. Nevertheless, no negative values were obtained in economic allocation. For better visibility of results ethanol from second generation feedstock was also compared with sugar beet and wheat ethanol (first generation). Environmental impact of ethanol from poplar and forest residue was lower than of ethanol from wheat and sugarbeet across all the categories considered.

Environmental impact of bioethanol, produced in thermo-chemical biorefinery from poplar wood and forest residues appeared to be lower than bio-chemical ethanol for 7 impact categories: global warming potential, abiotic depletion potential of elements, human toxicity potential, photochemical ozone creation potential, terrestrial ecotoxicity potential, freshwater aquatic ecotoxicity potential and land use. Authors explained it, as a consequence of lower chemicals

usage in thermo-chemical process. Nonetheless, emissions from gasification process significant contribute to acidification, eutrophication, marine ecotoxicity and ozone depletion, therefore bio-chemical ethanol has lower values in these impact categories.

System expansion was applied for comparison thermo-chemical and fossil based ethanol. Same conclusion as in previous work was made: biobased ethanol contribute to significant reductions in such impact categories as global warming, fossil resource depletion, ozone depletion, photochemical ozone creation and marine ecotoxicity, but has higher impact in acidification and eutrophication. Therefore, it is important to consider wide range of impacts, when making a decision.

In this research as well as in previous scientists agreed, that land use change is a critical factor for energy crops and should be considered carefully to avoid drawbacks. (Jeswani, Falano & Azapagic, 2015)

2.4.3 Most promising biorefinery system from the current literature

Regarding the feedstock, review showed, that forest residues is the best feedstock option, since in 3 out of 4 life cycle assessment studies scientists chose it as the preferable raw material. Poplar wood also was noticed by scientist and considered as the second best option. (Jeswani, Falano & Azapagic, 2015), (Falano, Jeswani & Azapagic, 2014), (Handler, Shonnard, Griffing, Lai & Palou-Rivera, 2015) Therefore, these two types will be considered as raw materials for biorefinery system.

Based on literature ethanol is the most attractive biofuel, due to abundance of information about its production and low costs. In addition, what is more important for biorefinery ethanol is a suitable platform for production number of valuable chemicals. That is why it was chosen as the platform chemical in this study.

HDPE was chosen as a main product in the biorefinery system under study. Since, as it was already stated in introduction, sustainable production of plastic is area of growing concern. According to the IPCC report chemical industry is responsible for around 15% of all anthropogenic GHG emissions and it keeps growing. (IPCC, 2014a) Over the last 4 decades global plastic production has quadrupled. However, its contribution to climate change is still underestimated. Even though, researchers showed that substitution of fossil-based plastic by bio-based can possibly contribute to 30% reduction of GHG emissions. (Zheng & Suh, 2019)

Polyethylene is one of the most sought for plastics on the market, it has the highest global volume production. (The world of plastics, in numbers, 2020) High density polyethylene is used in many industries, for example for construction of landfill liners, power and telecom cable conduits, sewage and drainage pipe, and automotive fuel tanks. Production of HDPE requires crude oil and consumes large amount of fossil energy. (Nguyen, Hsuan & Spatari, 2016) Total energy needed for processing of 1 ton of HDPE is 2.8 EJ, which is according to the IEA responsible for 240 million metric tons of atmospheric CO₂ emissions per year. Therefore, sustainable processing of HDPE is extremely important.

From review of previously conducted LCA it is obvious, that thermo-chemical production of ethanol has lower environmental impact than bio-chemical. (Jeswani, Falano & Azapagic, 2015), (Liptow, Tillman & Janssen, 2015) Obtained syngas can be further converted into ethanol through fermentation or mixed alcohol synthesis. Even though syngas fermentation showed better results for global warming potential, mixed alcohol synthesis is considered to be more suitable for this study, due to abundance of information and further use of chemical conversion technologies for obtaining HDPE. (Karka, Papadokonstantakis & Kokossis, 2017) Therefore, based on literature biorefinery complex, in which high density polyethylene and ethanol is produced via thermo-chemical conversion of poplar wood/forest residues was considered as object of study. Production pathway is discussed in more detail in the next section.

3 Methodology

The life cycle assessment in this study is conducted according to the guidelines of the ISO 14040/44 standards (2006a, 2006b). According to the standards life cycle assessment consists of 4 phases: goal and scope definition, inventory analysis, impact assessment and interpretation of the results. The LCA framework is illustrated in Figure 3 below.

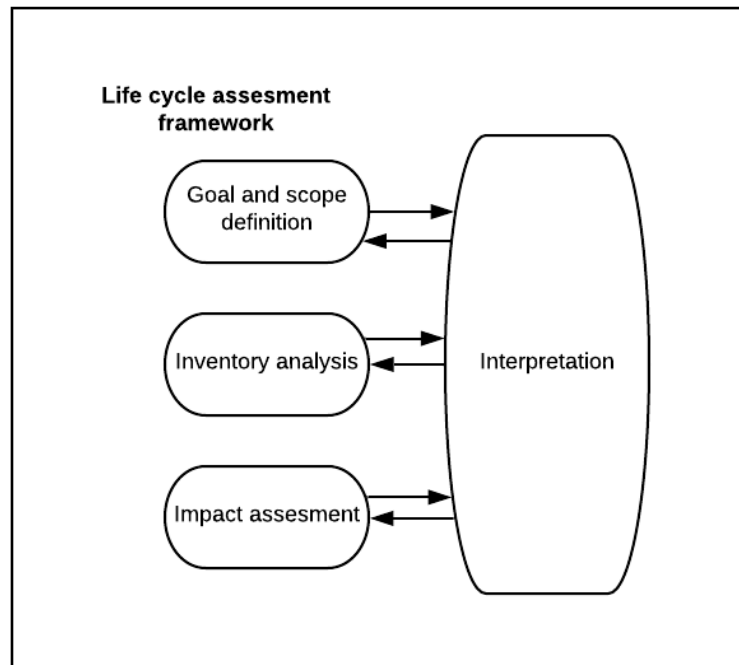


Figure 3 Life cycle assessment framework

During first phase reasons for carrying out the study as well as the system boundaries are defined. In this step functional unit, allocation, assumptions, data requirements and other system criteria are described. Second phase includes description of material and energy flows within the system and its interaction with the environment. Impact assessment is aimed to evaluate the significance of potential environmental impacts using the results of the life cycle inventory analysis. Last phase involves result presentation and review.

Life cycle assessment is essential for product development and improvement, strategic planning and policy decisions. (2006a, 2006b).

3.1 Goal and scope

The goal of study is to estimate life cycle environmental impacts of biorefinery system, in which high density polyethylene and ethanol are co-produced via thermo-chemical conversion of biomass. In addition, two types of lignocellulosic biomass will be compared: poplar wood and forest residues.

The scope of this study is 'cradle to gate', from cultivation of biomass (cradle) to the gate of the plant. As it is shown in the Figure 4 below two subsystems are considered: Subsystem 1 - biomass supply, which includes cultivation, harvesting and transportation; Subsystem 2 - production of bioethanol and HDPE, which includes three main process areas: biomass to ethanol, ethanol to ethylene and ethylene to HDPE. The use and disposal phase are excluded from the system boundaries. Transport of materials, such as agrochemicals used in Subsystem 1 and minerals/chemicals used in Subsystem 2 are included. Furthermore, impacts, that are

associated with construction and decommissioning of the production plant were found negligible and therefore are also excluded from the boundaries. (Alonso-Fariñas et al., 2018)

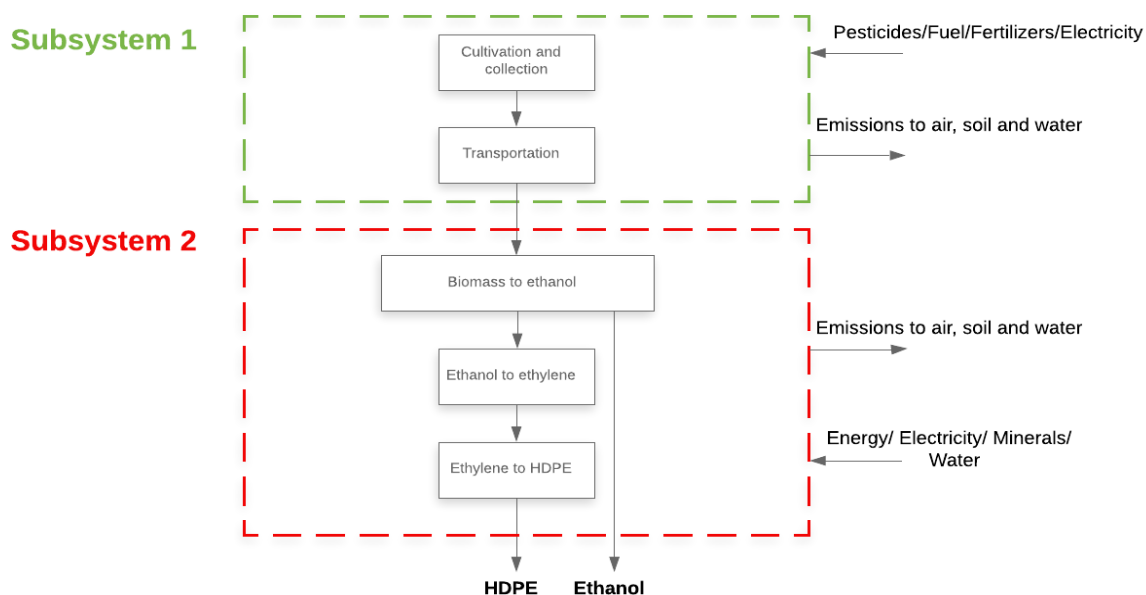


Figure 4 System boundaries considered for the production of HDPE and ethanol via the thermo-chemical route

Functional unit that of life cycle assessment was defined as 1 kg of HDPE and 1 kg of ethanol was considered as a co-product. Reasoning behind this choice was presented in the previous chapter.

HDPE was chosen as a main product, because it has higher market price and energy content. (Trading economics, 2020), (ICIS, 2020)

(Williams, 2017), (Statistics on the Plastic Resins Industry, 2020)

3.2 System description

The plant size is considered to be 2205 dry ton/day, with 8406 operating hours per year. (National Renewable Energy Laboratory, 2007) It is assumed to be located in the south of Norway near Oslo, as there are suitable climatic conditions and poplar wood have been already cultivated by Seim Trees and Plants AS. (Seim, 2020) The average distance between the plant and the field is assumed to be 14 km.

The production process consists of 2 subsystems and 7 major process steps, that are shown in the Figure 5 below: Subsystem 1 - biomass supply: cultivation and collection, transportation; Subsystem 2 – production of ethanol and HDPE, that includes 3 process stages and 5 process steps:

1. Biomass to ethanol, that consists of drying of biomass, gasification and alcohol synthesis. Further - subsystem 2.1
2. Ethanol to ethylene – dehydration of ethanol to obtain ethylene. Further - subsystem 2.2
3. Ethylene to HDPE – polymerization of ethylene to obtain polyethylene. Further - subsystem 2.3

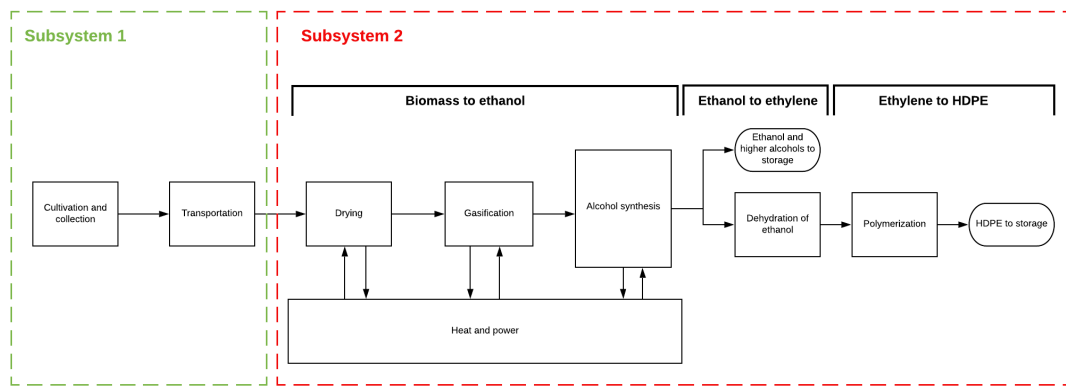


Figure 5 Production process

3.2.1 Biomass supply – Subsystem 1

Polar wood and forest residues were chosen as feedstock. As it was stated in section 2.4 of this paper forest residues and poplar wood were considered as the best raw material for biorefinery system by many scientists.

Elemental composition of poplar wood (National Renewable Energy Laboratory, 2007) and forest residues (Nurek, 2019) is presented in Table 4 below.

Table 4 Elemental composition of feedstock

	Poplar wood	Forest residue
Component	%	
Carbon	50.88	50.84
Hydrogen	6.04	5.8
Nitrogen	0.17	0.66
Sulfur	0.09	0.2
Oxygen	41.9	41.5
Ash	0.92	1

Input data for poplar wood supply were taken from C.Reyes Valle and A.L.Villanueva Perales study on biomass gasification. For that reason, same assumptions were made 1) land use change is not considered, since poplar is already cultivated by Seim company in that region; 2) the emissions related to preparation and sowing of the land are distributed among all biomass harvested at the end of a rotation period; 3) the emissions associated with chipping are included in this stage.

According to the C.Reyes Valle and A.L.Villanueva Perales life of poplar is 16 years and consists of 3 cycles. The trees are cut to the ground after each cycle, and by the end of the third incseticide is used to remove the roots. After 3 months new cuttings are planted.

To conduct the life cycle assessment the following data was included: consumption of fertilizer, insecticide, herbicide, fungicide and diesel, as well as electricity and direct and indirect N₂O ground emissions. (Reyes Valle et al., 2015)

Second type of lignocellulosic biomass that was chosen for this study – forest residues from softwood, scots pine specifically, since according to the ministry of agriculture and food of Norway Norwegian spruce and Scots pine are the most common species. Furthermore, Norwegian government is interested in use of forest residues for bioenergy production, because

logging debris, like tops and branches, is generally left in the forest, unused. (Regjeringen.no, 2020) For this type of raw material diesel and transportation were assumed as the only input parameters, since in her study, Hanna Karlsson concluded, that there are no other inputs and outputs associated with forest residues supply. Just diesel is needed for collection, forwarding, loading, unloading and comminution. (Karlsson et al., 2014)

For both feedstocks return distance of 14 km is chosen. It is considered that the plant is located in the centre of a circle surrounded by the land 20 km away from Myson.

3.2.2 Production of ethanol and HDPE – Subsystem 2

The process design for ethanol production from woody biomass is based on report made by S. Philipps, where the thermochemical pathway is described in detail. (National Renewable Energy Laboratory, 2007) For obtaining ethylene from ethanol same process configurations as in C. Liptow research on polyethylene production from sugarcane were used. (Liptow & Tillman, 2012) HDPE production process was adopted from studies made by Treenate et al., and Tillman et al. (Treenate, Limphitakphong & Chavalparit, 2017), (Tillman et al., 1992)

3.2.3 Biomass to ethanol – Subsystem 2.1

1) Drying

The first process after biomass has been delivered to the plant via trucks according to Philipps (National Renewable Energy Laboratory, 2007) is feed handling and drying. Trucks are weighed and biomass is dumped into a storage pile. Afterwards wood chips go through magnetic separator to get rid of large particles. Next step is drying, it is accomplished by the direct contact of wood chips with hot flue gas. Used exhaust gas is sent to cyclone and filter and then emitted to the atmosphere. Biomass is dried from 50 % moisture content to 5 % and conveyed to the gasifier train. Moisture content for both types of feedstock is assumed to be 50% to meet the requirements of production plants, described at Philipps et al. (National Renewable Energy Laboratory, 2007)

2) Gasification

In the gasifier train syngas is obtained by indirect gasification. Heat for the process is supplied by circulating synthetic olivine between the gasifier vessel and the char combustor. For the design case the resulting gasifier temperature is 1,633°F (889°C) and the char combustor is 1,823°F (995°C). Fresh olivine mixed with MgO and is added in rate of 0.01% to account for losses. The gasifier operating parameters, conversion efficiencies and composition of syngas exiting the gasifier is presented in Table 5 bellow. (National Renewable Energy Laboratory, 2007)

Table 5 Gasifier Operating Parameters, Gas Compositions, and Efficiencies (National Renewable Energy Laboratory, 2007)

Gasifier outlet gas composition	mol% (wet)	mol% (dry)
H ₂	15	25.1
CO ₂	7.4	12.4
CO	25.1	41.9
H ₂ O	40.2	-
CH ₄	9	15.1
C ₂ H ₂	0.3	0.4
C ₂ H ₄	2.5	4.1
C ₂ H ₆	0.1	0.2
C ₆ H ₆	0.1	0.1
tar (C ₁₀ H ₈)	0.1	0.2
NH ₃	0.2	0.3
H ₂ S	0.04	0.07
H ₂ :CO molar ratio	0.6	
Gasifier efficiency	76.6% HHV basis	
	76.1% LHV basis	

Exiting the gasifier syngas is then sent to particulates removal. Two cyclones are used to separate syngas from ash and olivine. After cyclone separators syngas goes through clean up and conditioning. During this stage acid gases, such as CO₂ and H₂S are removed in amine scrubber and syngas is compressed.

3) Alcohol synthesis

Alcohol synthesis is considered as the main part of the plant. Here syngas, that is entering the reactor is compressed and heated to meet the synthesis conditions of 1,000 psia and 570°F (300°C). After that syngas is converted to the alcohol mixture across the fixed bed catalyst. To separate alcohols from unconverted syngas the mixture is cooled. After cooling the alcohols are sent to condensation and purification. Unconverted syngas is sent back to the gasification section. In Figure 6 bellow the reaction for mixed alcohol synthesis are presented.

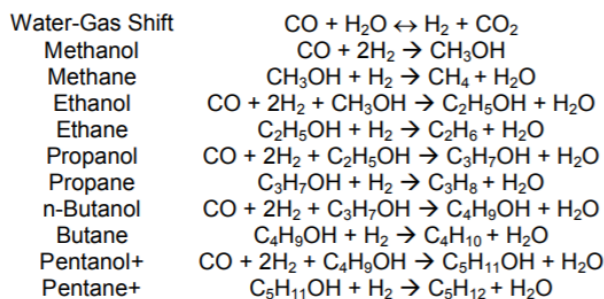


Figure 6 System of Reactions for Mixed Alcohol Synthesis

In this particular study a modified Fischer-Tropsch catalyst was used, specifically a molybdenum-disulfide-based (MoS₂) catalyst, due to its high alcohol selectivity. Performance results of mixed alcohol synthesis are presented in Table 6.

Table 6 Mixed Alcohol Reaction Performance Results

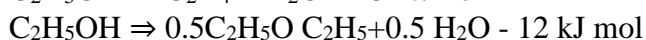
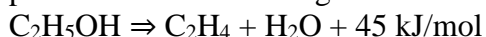
	Results Used in Process Design
Total CO Conversion (per-pass)	60%
Total Alcohol Selectivity (CO ₂ -free basis)	90%
Gas Hourly Space Velocity (hr ⁻¹)	4000
Catalyst Alcohol Productivity (g/kg catalyst/hr)	600

Alcohol separation is also part of this step. Mixture of alcohols is de-gassed, dried, and separated into three streams: methanol, ethanol, and mixed higher-molecular weight alcohols. Methanol is further used to increase the ethanol yield. Part of ethanol and higher alcohols are cooled and sent to the storage. The rest of ethanol is used for HDPE production.

According to the plant design, suggested at Philips et al. ethanol production plant does not purchase any power from the grid. It was designed to be energy self-sufficient. Power is obtained from steam cycle using steam turbine and from syngas using process expander. Steam cycle produces steam by recovering heat from the hot process streams throughout the plant. For power generation this steam is sent to extraction steam turbine/generator. Process expander is also used for power generation, it changes the psia of unconverted syngas from 965 to 35. (National Renewable Energy Laboratory, 2007)

3.2.4 Ethanol to ethylene- Subsystem 2.2

Ethylene is obtained through catalytic dehydration of ethanol. For highest ethylene yield temperature should be between 300°C and 500°C. Increase will lead to acetaldehyde as a reaction product, decrease results in production of diethyl ether. (Mohsenzadeh, Zamani & Taherzadeh, 2017) Inventory data and plant design for this process were taken from C. Liptow study on production of LDPE from sugarcane ethanol, which in turns was based on patent, that Braskem applied in their green ethylene technology: “Process for Production of ethylene from ethyl alcohol” (Liptow & Tillman, 2012) (Braskem, 2020) According to it, dehydration is conducted in a multilayer adiabatic reactor and an Al₂O₃–MgO/SiO₂ mixed catalyst is used. The required temperature is 450 °C and ethanol concentration – 95%. Reactions for dehydration process are the following:



After leaving the reactor the product mixture is washed with water in a column and then with an alkali in another column, after washing mixture is dried and separated into light and heavy fractions in distillation columns. Ethylene selectivity in this process is 97%. (Yakovleva, Banzaraktsaeva, Ovchinnikova, Chumachenko & Isupova, 2016)

3.2.5 Ethylene to HDPE - Subsystem 2.3

For obtaining high density polyethylene ethylene is polymerized in fluidized bed catalytic reactor at a temperature of 110 °C. After polymerization the melted plastic is pelletized and sent to the storage. (Treenate, Limphitakphong & Chavalparit, 2017), (Tillman et al., 1992)

According to Sara Belboom and Angélique Léonard the only inputs to this step are heat and electricity. The yield of the conversion is equal to 99%. (Belboom & Léonard, 2016)

3.3 Life cycle inventory

The data used for environmental assessment refers to production of 1 kg of HDPE.

3.3.1 Biomass supply

Inventory data for poplar wood supply was adopted from Bernabé Alonso-Fariñas et al., which in terms was following the model described in Nemecek and Schnetzer. (Nemecek and Schnetzer, 2012) The data is summarized in Table 7 bellow. (Alonso-Fariñas et al., 2018)

Table 7 Life cycle inventory data for poplar wood production

Process poplar wood supply				
Input from environment				
Category	Name in EcoInvent database	kg/biomass kg	kg/kg HDPE	kg/kg ethanol
Fertilizers	NPK compound (NPK 15-15-15), at plant/RER Mass	6.10E-03	1.92E-01	4.60E-02
	Nitrogen fertiliser, as N {GLO} market for Cut-off, S	2.54E-03	8.02E-02	1.92E-02
Pesticides	Pesticide, unspecified {GLO} market for APOS, S	6.00E-06	1.89E-04	4.53E-05
	Glyphosate {GLO} market for Conseq, S	5.00E-05	1.58E-03	3.77E-04
	Pesticide, unspecified {GLO} market for APOS, S	4.00E-06	1.26E-04	3.02E-05
Diesel kg	Diesel {CH} market for APOS, S	8.43E-04	2.66E-02	6.36E-03
Electricity kwh	Electricity, medium voltage {NO} market for APOS, S	2.00E-05	6.31E-04	1.51E-04
Output to environment				
Emissions to air	Carbon dioxide	2.63E-03	8.30E-02	1.98E-02
	Carbon monoxide	9.58E-06	3.02E-04	7.23E-05
	Methane	1.40E-07	4.42E-06	1.06E-06
	NM VOC, non-methane volatile organic compounds, unspecified origin	4.36E-06	1.38E-04	3.29E-05
	Nitrous oxide	1.00E-07	3.16E-06	7.55E-07
	Nitrogen oxides	3.71E-05	1.17E-03	2.80E-04
	Particulates	3.77E-06	1.19E-04	2.84E-05
	Sulphur dioxide	8.50E-07	2.68E-05	6.41E-06
	Ammonia	1.68E-08	5.30E-07	1.27E-07
	Polycyclic aromatic hydrocarbons	2.80E-09	8.84E-08	2.11E-08
	Ammonia	4.70E-05	1.48E-03	3.55E-04
	Nitrous oxide	2.40E-05	7.58E-04	1.81E-04
	Nitrogen oxides	5.00E-06	1.58E-04	3.77E-05
Emissions to water	Nitrate	6.15E-04	1.94E-02	4.64E-03
	Phosphate	1.10E-05	3.47E-04	8.30E-05
	Cadmium	1.30E-08	4.10E-07	9.81E-08
	Copper	5.10E-08	1.61E-06	3.85E-07

	Zinc	3.06E-07	9.66E-06	2.31E-06
	Lead	2.00E-08	6.31E-07	1.51E-07
	Nickel	5.90E-08	1.86E-06	4.45E-07
	Chromium	1.95E-07	6.16E-06	1.47E-06
Emissions to soil	Cypermethrin	6.00E-06	1.89E-04	4.53E-05
	Gliphosated	5.00E-05	1.58E-03	3.77E-04
	Mancozeb	4.00E-06	1.26E-04	3.02E-05
Transport	Transport, freight, lorry >32 metric ton, euro4 {RoW} market for transport, freight, lorry >32 metric ton, EURO4 Cut-off, S	1.40E+01	4.42E+02	1.06E+02
	Biomass	1.00E+00	3.16E+01	7.55E+00

In Table 8 inventory data for forest residues supply is presented. (Karlsson et al., 2014)

Table 8 Life cycle inventory data for forest residues production

Process forest residues supply			
Input from environment			
Name in EcoInvent database	unit/biomass kg	unit/kg HDPE	kg/kg ethanol
Diesel {CH} market for APOS, S	2.10E-01	1.47E-01	3.52E-02
Transport, freight, lorry >32 metric ton, euro4 {RoW} market for transport, freight, lorry >32 metric ton, EURO4 Cut-off, S	1.40E+01	4.42E+02	1.06E+02

3.3.2 Biomass to ethanol

Inventory data for ethanol production was adopted from Phillips et al. (National Renewable Energy Laboratory, 2007) Inputs and outputs are given for each process: drying, gasification, alcohol synthesis. Material and energy inputs are assumed to be the same for both types of biomass, since elemental composition of forest residues and poplar wood doesn't have significant differences and H₂/CO ratio that affects the syngas yield is the same for both types of feedstock. (Conesa & Domene, 2013)

Table 9 Life cycle inventory data for drying process

Process Drying			
Input from the environment			
Name in EcoInvent database	kg/biomass kg	kg/kg HDPE	kg/kg ethanol
Biomass	1.00E+00	3.16E+01	7.55E+00
Output to environment			
Wastewater	6.94E-01	2.19E+01	5.24E+00
Nitrogen, atmospheric	1.45E+00	4.56E+01	1.09E+01
Oxygen	6.13E-02	1.93E+00	4.62E-01
Argon	2.47E-02	7.78E-01	1.86E-01
Biogenic Carbon Dioxide	4.86E-01	1.53E+01	3.67E+00
Sulfur dioxide	3.10E-03	9.79E-02	2.34E-02
Nitrogen dioxide	7.32E-04	2.31E-02	5.52E-03
Olivine Silicates, unspecified	3.81E-03	1.20E-01	2.87E-02

Table 10 Life cycle inventory for gasification process

Process Gasification			
Input from the environment			
Name in EcoInvent database	kg/biomass kg	kg/kg HDPE	kg/kg ethanol
Argon	2.29E-02	7.23E-01	1.73E-01
Sand {GLO} market for APOS, S	1.49E-03	4.70E-02	1.12E-02
Nitrogen	1.40E+00	4.40E+01	1.05E+01
Oxygen	4.26E-01	1.34E+01	3.21E+00
Water, completely softened, from decarbonised water, at user {GLO} market for Cut-off, S	3.64E-02	1.15E+00	2.74E-01
Dried biomass	5.26E-01	1.66E+01	3.97E+00
Output to the environment			
Biogenic Carbon Dioxide	1.43E-01	4.52E+00	1.08E+00
Sulfur	2.94E-04	9.28E-03	2.22E-03
Silicates, unspecified	9.60E-05	3.03E-03	7.24E-04
Syngas	7.71E-01	2.43E+01	5.81E+00

Table 11 Life cycle inventory for alcohol synthesis

Process Alcohol synthesis			
Input from the environment			
Name in EcoInvent database	kg/biomass kg	kg/kg HDPE	kg/kg ethanol
Syngas	7.71E-01	2.43E+01	5.81E+00
Water, completely softened, from decarbonised water, at user {GLO} market for Cut-off, S	9.30E-02	2.94E+00	7.02E-01
Output to the environment			
Other alcohols	2.37E-02	7.48E-01	1.79E-01
Ethanol	1.33E-01	4.18E+00	1.00E+00

3.3.3 Ethanol to ethylene

For ethylene production process inventory data from C. Liptow work was used. Inventory for this process is presented in Table 12. (Liptow & Tillman, 2012)

Table 12 Life cycle inventory for ethylene synthesis

Process Ethylene synthesis			
Input from the environment			
Name in EcoInvent database	kg/biomass kg	kg/kg HDPE	kg/kg ethanol
Ethanol	5.41E-02	1.71E+00	4.08E-01
Electricity, medium voltage {NO} market for Cut-off, S	5.72E-02	1.81E+00	4.32E-01
Natural gas, high pressure {NO} market for natural gas, high pressure Cut-off, S	1.78E-01	5.62E+00	1.34E+00
Output to the environment			
Methane	4.77E-05	1.51E-03	3.60E-04
Water	1.16E-02	3.67E-01	8.78E-02
Ethanol	1.20E-04	3.79E-03	9.05E-04
Biogenic Carbon Dioxide	1.04E-02	3.28E-01	7.83E-02
Ethylene	3.18E-02	1.00E+00	2.40E-01
Carbon monoxide	6.36E-06	2.01E-04	4.80E-05
Dinitrogen monoxide	3.82E-07	1.20E-05	2.88E-06
NMVOC	3.50E-07	1.10E-05	2.64E-06
NO _x	4.77E-05	1.51E-03	3.60E-04
NMVOC, non-methane volatile organic compounds, unspecified origin	3.18E-06	1.00E-04	2.40E-05

3.3.4 Ethylene to HDPE

To obtain inventory data for polymerization process several studies were used. (Treenate, Limphitakphong & Chavalparit, 2017), (Tillman et al., 1992)

Table 13 Life cycle inventory for polymerization process

Process Polymerization			
Input from the environment			
Name in EcoInvent database	kg/biomass kg	kg/kg HDPE	kg/kg ethanol
Electricity, medium voltage {NO} market for Cut-off, S	6.65E-02	2.10E+00	5.02E-01
Heat, from steam, in chemical industry {RER} market for heat, from steam, in chemical industry Cut-off, S	3.36E-03	1.06E-01	2.54E-02
Ethylene	3.18E-02	1.00E+00	2.40E-01
Output to the environment			
Methane, trichlorofluoro-, CFC-11	1.20E-08	3.79E-07	9.05E-08
Biogenic Carbon Dioxide	1.55E-03	4.91E-02	1.17E-02
Ethylene oxide	3.06E-05	9.66E-04	2.31E-04
Hydrogen	5.40E-06	1.70E-04	4.07E-05
Nitrogen oxides	4.20E-07	1.33E-05	3.17E-06
Sulfur dioxide	1.82E-07	5.74E-06	1.37E-06
TOC, Total Organic Carbon	3.57E-07	1.13E-05	2.69E-06
HDPE	3.17E-02	1.00E+00	2.39E-01
Oils, unspecified	1.27E-05	4.02E-04	9.60E-05

3.3.5 Allocation

In this biorefinery complex several products are produced simultaneously. Therefore, it is important to allocate environmental burdens among them. Two scenarios are considered in this work:

1. Ethanol and HDPE are the only final products, that are obtained and sold.
2. Higher alcohols, that are co-produced during ethanol synthesis, are also considered as final products.

According to the Gustav Sandin and Francesco Cherubini, there are 3 ways of allocating environmental impacts: division into subprocesses; system expansion – approach, where system boundaries are expanded to include the alternative production route of the co-products and then environmental impacts, that are associated with this alternative route are subtracted from the total impact of the system; partitioning – approach, where environmental burdens are allocated to co-products based on their mass, energy or price. (Sandin et al., 2015)

In Sylvestre Njakou Djomo article it states, that system subdivision and expansion methods have a number of drawbacks, that can significantly affect the results of environmental assessment. Subdivision method can not be applied, because all the processed in biorefinery are highly integrated. System expansion is also not very suitable for life cycle assessment of biorefinery, as it doesn't show impact of individual product. (Ahlgren et al., 2015)

Therefore, in this study economic, mass and energy allocations were used. In Table 14 values, that were used for allocation for the first scenario can be found.

Table 14 Allocation basis scenario 1

	Bioethanol	HDPE	Reference
HHV MJ/kg	30	40.6	(Williams, 2017), (Statistics on the Plastic Resins Industry, 2020)
Economic USD	0.74	1.15	(Trading economics, 2020), (ICIS, 2020), (Echemi, 2020)
Mass kg	2.4777	1	(National Renewable Energy Laboratory, 2007)

In the next table the proportion of allocated impacts is summarized.

Table 15 Percentage of environmental impacts allocated to HDPE and Bioethanol

	Bioethanol	HDPE
Energy allocation	64.56	35.44
Economic allocation	61.45	38.55
Mass allocation	71.25	28.75

Propanol, butanol and pentanol were included as final products in the second scenario. In Table 16 and Table 17 new values for allocation are presented.

Table 16 Allocation basis scenario 2

	Bioethanol	HDPE	Propanol	n-Butanol	Pentanol	Reference
HHV MJ/kg	30	40.6	33.6	36.94	21	(Williams, 2017), (Statistics on the Plastic Resins Industry, 2020) (Shah, 2018)
Economic USD	0.74	1.15	50.9	37.9	58.8	(Trading economics, 2020), (ICIS, 2020) (Echemi, 2020)
Mass	2.4777	1	0.594	0.074	0.001	(National Renewable Energy Laboratory, 2007)

Table 17 Percentage of environmental impacts allocated to HDPE, bioethanol and higher alcohols

	Bioethanol	HDPE	Propanol	n-Butanol	Pentanol
Energy allocation	54%	30%	15%	1%	0%
Economic allocation	46%	29%	24%	1%	0%
Mass allocation	60%	24%	14%	2%	0%

3.3.6 Comparison with other production routes and sources of HDPE

For greater clarity of environmental assessment results, obtained data was compared with HDPE produced through biochemical pathway from sugar beet and fossil-based HDPE. Values for comparative analysis were taken from Sandra's Belboom and Angélique's Léonard research on biobased polymers. In this research authors estimated environmental impact, associated with production of one ton high density polyethylene from sugar beet and wheat in Belgium, using attributional LCA. The impact was calculated applying ILCD 2011 midpoint and ReCiPe 2008 methods. The considered biobased production process is presented below in Figure 7. It includes six steps: crop cultivation, crop transportation from field to plant, biochemical ethanol production, biobased ethanol dehydration, ethylene polymerization and end-of-life. The difference between system, considered in this thesis and system, that Sandra Belboom and Angélique Léonard have analyzed is the production of ethanol. In Sandra's Belboom and Angélique's Léonard research ethanol is produced via biochemical conversion, which includes following steps: liquefaction-saccharification, fermentation and distillation. (Belboom & Léonard, 2016) When in this thesis ethanol is obtained through thermo-chemical pathway via gasification and mixed alcohol synthesis. In addition, different types of raw material were used for HDPE production, what affects mostly cultivation stage and fertilizers requirements.

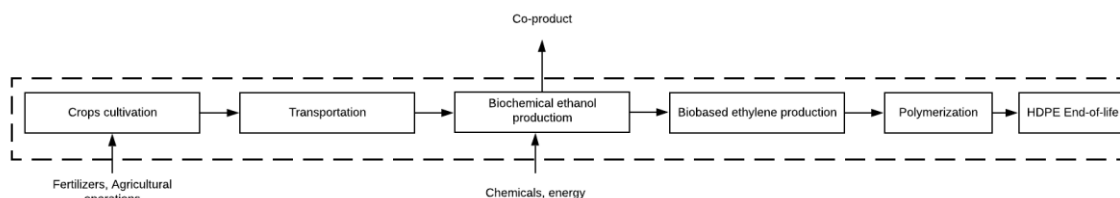


Figure 7 Reference biochemical production system

For the reference fossil-based system production of ethylene using steam cracking of naphtha was assessed with further ethylene polymerization and same end-of-life treatment. (Belboom & Léonard, 2016),

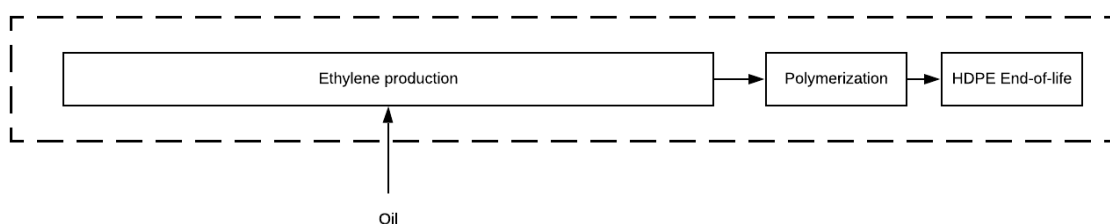


Figure 8 Reference fossil based production system

Since in Sandra's Belboom and Angélique's Léonard study end of life stage was included in the system and in this research it is not considered, environmental impacts from bio-ethylene and fossil ethylene production were used for comparative analysis. (Belboom & Léonard, 2016)

3.4 Impact assessment

For assessment the SimaPro 9.0 software (SimaPro, 2020) has been used. The life cycle assessment was conducted following the guidelines, described in Guinée et al. (Guinee, 2002) ReCiPe 2016 was used as life cycle impact assessment method. It is an update of ReCiPe 2008, that provides harmonized characterization factors at midpoint and endpoint levels. Characterization factors indicate the environmental impact per unit of stressor. There are two

ways of deriving characterization factors: at midpoint or endpoint. At midpoint level 18 impact categories, are considered, they are shown in Table 18 bellow. At endpoint level there are 3 areas of protection: damage to human health, damage to ecosystems, damage to resource availability. Interactions between midpoint and endpoint categories is shown in Figure 9. To estimate the fate of emissions in the environment 3 perspectives are used in ReCiPe 2016: individualistic, hierarchist, egalitarian. Individualistic perspective is characterized by short term interest, adaptive behavior and technological optimism. In egalitarian perspective long term effect, pessimistic technological and economic development and comprehensive behaviour is considered. Hierarchist perspective is an approach in between egalitarian and individualistic, where baseline scenario is assumed. (Huijbregts et al., 2016). In this work midpoint impact categories and hierarchist perspective is be considered.

Table 18 Environmental impact categories, assessed in this study

Midpoint Impact Category	Abbreviation
Global warming	GWP
Stratospheric ozone depletion	ODP
Ionizing radiation	IRP
Ozone formation, Human health	HOFP
Fine particulate matter formation	PMFP
Ozone formation, Ecosystems	EOFP
Terrestrial acidification	AP
Freshwater eutrophication	FEP
Marine eutrophication	MEP
Terrestrial ecotoxicity	ETP terra
Freshwater ecotoxicity	ETP fw
Marine ecotoxicity	ETP marine
Human carcinogenic toxicity	HT C
Human non-carcinogenic toxicity	HT noc
Land use	LCP
Mineral resource scarcity	MRP
Fossil resource scarcity	FFP
Water consumption	WCP

* Abbreviations (Li et al., 2019)

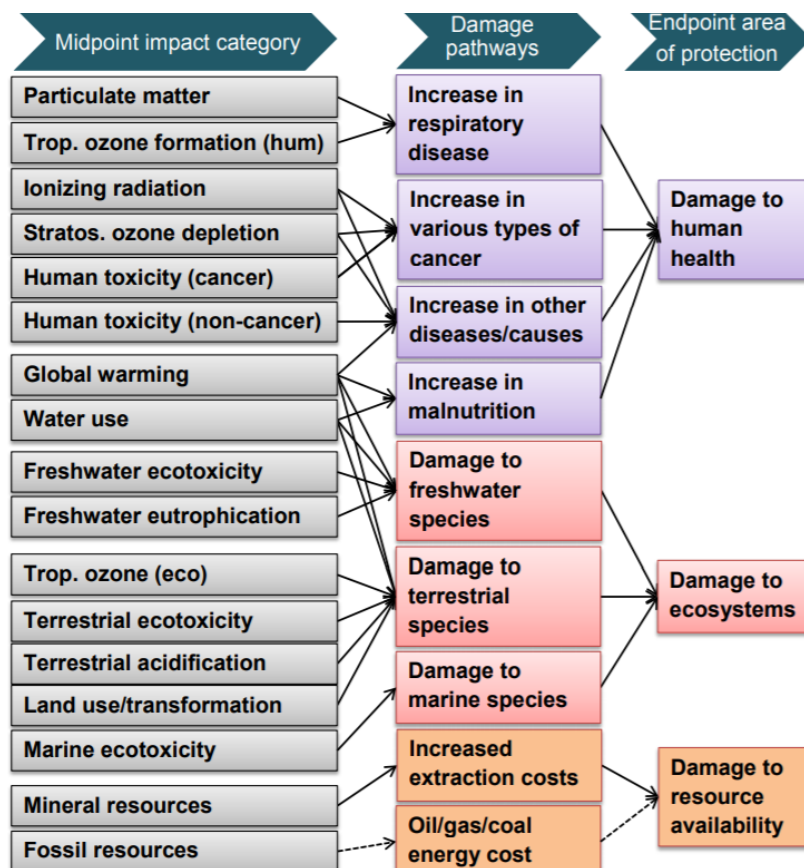


Figure 9 Relation between midpoint categories and areas of damage

Global warming

Climate change (global warming) is expressed in global warming potential. According to the ReCiPe 2016 report, it is the amount of additional radiative forcing integrated over time (here 20, 100 or 1,000 years) caused by an emission of 1 kg of GHG relative to the additional radiative forcing integrated over that same time horizon caused by the release of 1 kg of CO₂. The mechanism for temperature increase is the following: emission of a greenhouse gas (kg) cause an increase in atmospheric concentration of greenhouse gases (ppb) which, in turn leads to the higher radiative forcing capacity (w/m²) and this results in temperature change.

Stratospheric ozone depletion

Stratospheric ozone depletion is expressed in kg CFC-11 equivalents. Increase in concentration of Ozone Depleting Substances (ODSs) leads to damage to human health because of the resultant increase in UVB radiation.

Ionizing radiation

This impact category is expressed in Ionizing Radiation Potential (IRP), relative to the emission of reference substance Cobalt-60 to air. These type of emissions affects human health, causing cancer and other severe diseases.

Ozone formation, Human health, Ecosystems

Intake of NO_x and NMVOCs by humans and plant species lead to disappearance of plants and increase of mortality rate among humans. It is expressed in kg NO_x eq for humans and ecosystems.

Fine particulate matter formation

The impact of primary and secondary aerosols is measured in kg PM_{2.5} eq. These air pollutants have a substantial negative impact on human health.

Terrestrial acidification

In this impact category the effect of deposition of inorganic substances, such as sulphates, nitrates and phosphates is estimated. The effect is measured in kg SO₂ eq

Freshwater eutrophication

Eutrophication occurs due to emissions of P to waterbodies and soil and results in decrease in number of species.

Marine eutrophication

In this impact category effect of emissions of nitrogen on marine environment is measured.

Toxicity

Toxicity refers to environmental persistence (fate), accumulation in the human food chain (exposure), and toxicity (effect) of a chemical for humans and ecosystems. The effect is measured in kg 1,4-DCB.

Land use

Change of land cover and land use intensification negatively affects ecosystems, due to habitat loss and soil disturbance respectively.

Mineral resource scarcity

It is expressed in kg Cu eq and estimates effect of mineral resources extraction.

Fossil resource scarcity.

Fossil resources are not renewable and their extraction leads to decrease in resource availability. In the midpoint this effect is measured in kg oil eq.

Water consumption.

Water use results in reduction of freshwater availability, what in turns affects humans and ecosystems. (Huijbregts et al., 2016)

4 Results

In this section environmental impacts of HDPE produced from forest residues and poplar wood will be compared. First when energy, mass and economic allocation is used; ethanol and HDPE are the only final products. This will be followed by comparison of environmental impact of HDPE, when besides ethanol higher alcohols are considered as co-products. Results obtained in the first scenario and mass allocation will be compared with HDPE, produced from fossil fuels and through sugar beet fermentation. All values in figures refer to production of 1 kg of HDPE.

4.1 Comparison of feedstocks for biorefinery system

As it is shown in Figure 10 and Figure 11 when mass allocation is applied HDPE from forest residues is the best option among all impact categories. Relatively low difference between HDPE from forest residues from poplar wood is observed in such impact categories as land use, terrestrial acidification, fossil resource scarcity and water consumption. For the remaining categories impact of production of HDPE from poplar wood is way higher than from forest residues.

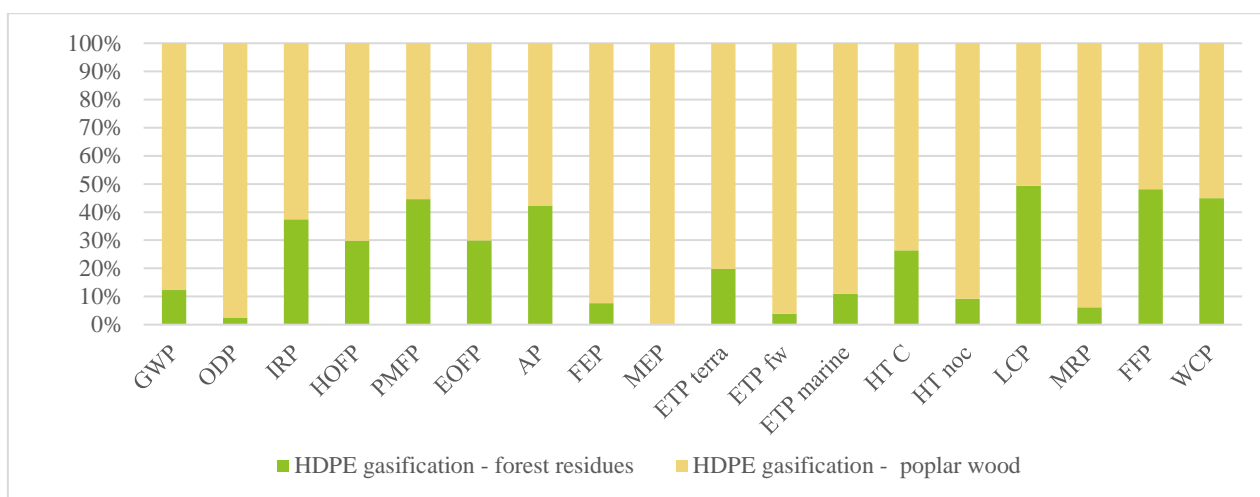


Figure 10 Life cycle environmental impacts of HDPE produced from poplar wood and forest residues for mass allocation

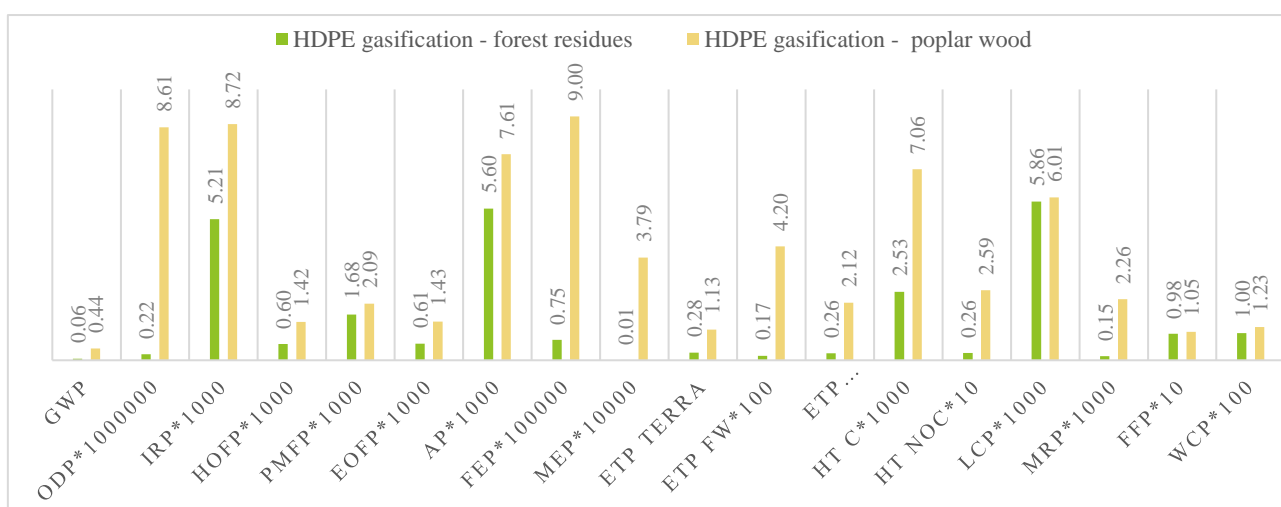


Figure 11 Life cycle environmental impacts of HDPE produced from poplar wood and forest residues for mass allocation

In Figure 12 and Figure 13 contribution of each process is presented. As it is shown in Figure 12 poplar wood supply (biomass supply) contributes the most to global warming potential, stratospheric ozone depletion, ionizing radiation, ozone formation (human health and ecosystems), marine and freshwater eutrophication, terrestrial ecotoxicity, freshwater ecotoxicity, marine ecotoxicity, human carcinogenic toxicity, human non-carcinogenic toxicity, mineral resource scarcity, fossil resource scarcity and land use.

In case with forest residues (biomass) supply stage contributes the most to such impact categories as freshwater and marine eutrophication, terrestrial ecotoxicity, human non carcinogenic toxicity, land use, mineral resource scarcity and fossil resource scarcity.

For both types of feedstock drying contributes the most to fine particulate matter formation and terrestrial acidification. This is a consequence of release of highly contaminated flue gas during this stage. The process is designed so that flue gas, that is formed during alcohol synthesis and gasification, is accumulated in the drying section, because biomass is dried by the hot flue gas. (National Renewable Energy Laboratory, 2007)

Gasification slightly affects water consumption, since for syngas clean-up water is used, what represents 3.3% of total water consumption for forest residues and 2.6% for poplar wood.

Polymerization and ethylene synthesis contribute to every impact category. For poplar wood polymerization process is responsible for around 25% emissions, that cause ionizing radiation, 22% - human carcinogenic toxicity and 40% water consumption. For the rest of impact categories contribution of polymerization is insignificant in comparison with poplar wood supply. Ethylene synthesis contributes a lot to ionizing radiation – around 20% of impact, to ozone formation – 35%, to fossil resource scarcity – more than 40% and to water consumption – around 32%.

For forest residues polymerization and ethylene synthesis have greater effect, because contribution of biomass supply process is not as significant as for poplar wood. Polymerization affects the most ionizing radiation (40%), stratospheric ozone depletion (55%), human carcinogenic toxicity (62%) and water consumption (48%) Polymerization and ethylene synthesis almost equally contribute to freshwater and marine ecotoxicity. Ethylene synthesis in turns, have the greatest effect on global warming and ozone formation.

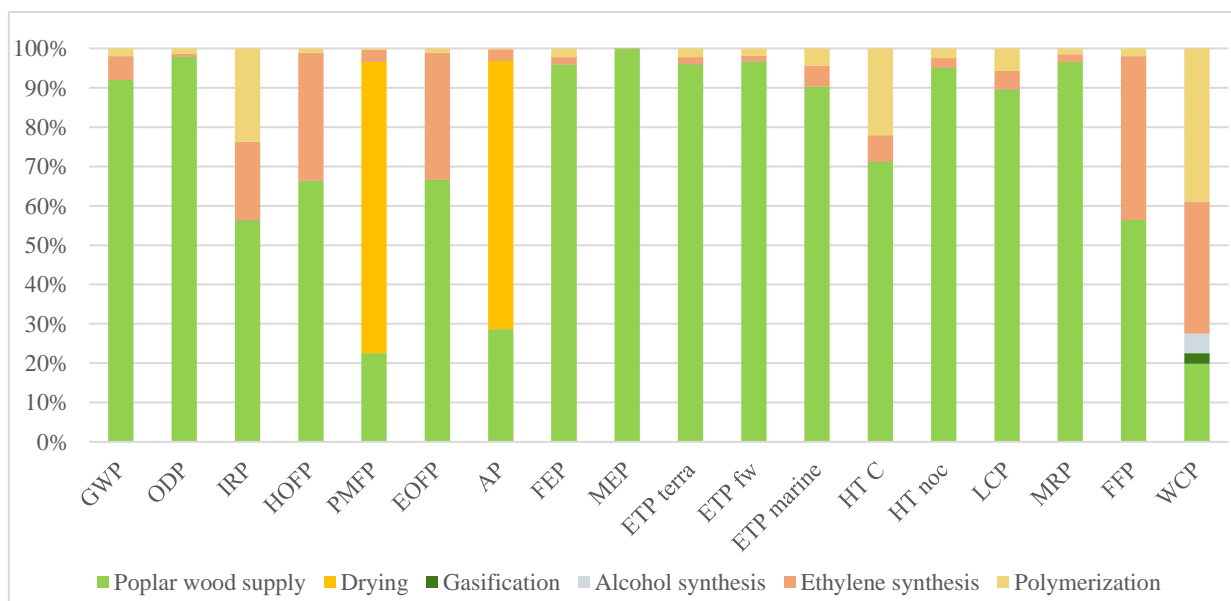


Figure 12 Life cycle environmental impacts of HDPE produced from poplar wood, process contribution

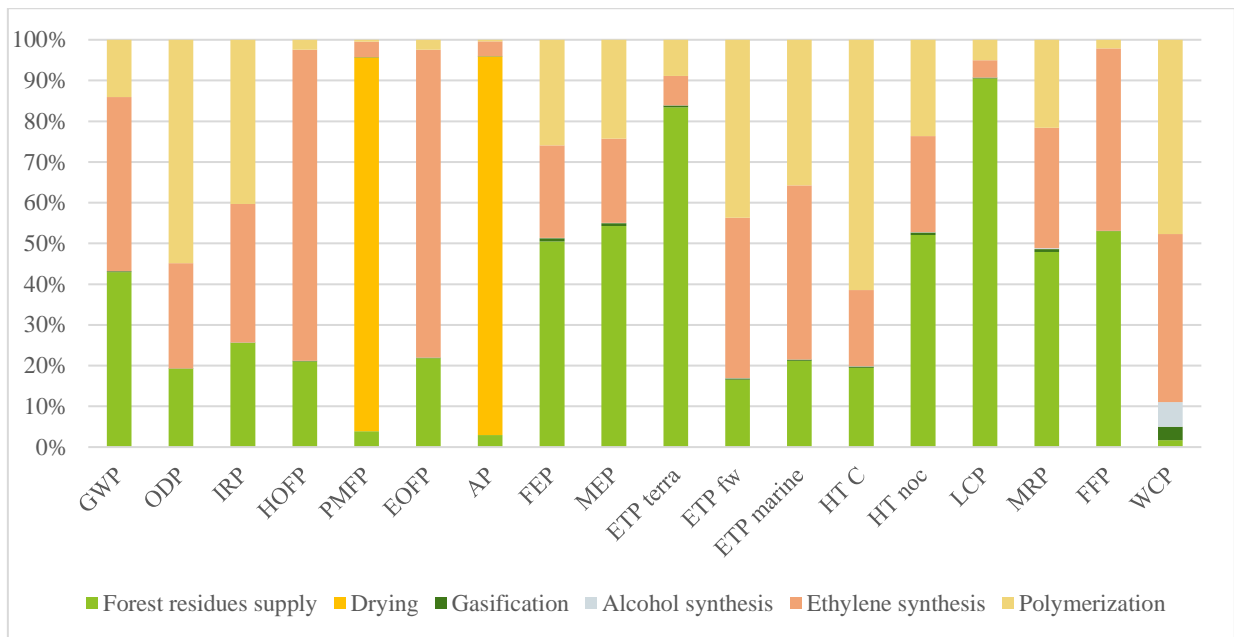


Figure 13 Life cycle environmental impacts of HDPE produced from forest residues, process contribution

To understand better environmental performance of biorefinery system, processes and emissions, that contribute to each impact category are explained in detail below.

Global warming

As it was stated before, when poplar wood is used as raw material, biomass supply stage is the biggest contributor to global warming. This is due to emissions of dinitrogen monoxide, that occur from use of fertilizers for poplar wood cultivation. Emissions of fossil carbon dioxide, that come from production of fertilizers, transportation and electricity supply are the second biggest contributor to global warming potential. The remaining 15% of GHG emissions are: carbon dioxide from cultivation of poplar wood and methane, which is emitted during ethylene synthesis.

For forest residues contribution of biomass supply stage and ethylene synthesis is almost equal. Fossil carbon dioxide is the biggest contributor, it is emitted during the supply of forest residues, due to use of diesel and transportation. Emissions of fossil carbon dioxide also occur during the ethylene synthesis, since for production of ethylene electricity and natural gas is needed and their supply is partly associated with use of fossil fuels. Methane, which is emitted during the ethylene synthesis, also contributes to GWP, but less than fossil carbon dioxide.

However, it should be stated, that when assessment is conducted in SimaPro, the biogenic CO₂, that is emitted during the drying, gasification and further conversion of biomass is assumed to be carbon neutral, due to assumption that biomass-derived carbon emissions will be absorbed by plant regrowth through photosynthetic production effect. (Liu et al., 2019) Total amount of biogenic carbon dioxide, which is emitted during the HDPE production is 20.64 kgCO₂, with -15.3 kgCO₂, released during drying process, 4.52 kgCO₂ – gasification process, 0.492 kgCO₂, - ethylene synthesis and 0.329 kgCO₂, - polymerization. Issues, associated with accounting for contribution of biogenic carbon dioxide to global warming are discussed in the next chapter.

Stratospheric ozone depletion

In this impact category environmental impact of HDPE from poplar wood is 40 times bigger than from forest residues. This is a consequence of production of nitrogen, that is used as fertilizer during the poplar wood supply. Furthermore, during poplar wood supply polycyclic aromatic hydrocarbons are emitted, which directly contribute to stratospheric ozone depletion.

Ionizing radiation

For both types of feedstock emissions associated with electricity and heat production for polymerization and ethylene synthesis contribute a lot to this impact category. However, impact from HDPE from poplar wood is higher. Difference in values can be explained by production and use of nitrogen fertilizer for poplar wood supply.

Ozone formation, human health and ecosystems

Emissions of nitrogen oxides, that occur during the biomass supply stage and ethylene processing are responsible for around 98 % of impact in these categories for both types of feedstock. NMVOC, pentane, butane and propane contribution is negligible, compared to nitrogen oxide. Amount of nitrogen oxide, that is formed during the HDPE production from poplar wood is almost 20 times higher than from forest residue. This is a consequence of use of fertilizer, pesticides and emissions of nitrogen oxides during the poplar wood supply.

Fine particulate matter formation

Sulfur dioxide is the main contributor to this impact category. Flue gas, that is released into the atmosphere in the drying section contains 0.98 kg of sulfur dioxide/functional unit, what results in around 0.0008 kg PMeq/functional unit, depending on the allocation method. Nitrogen dioxide is another compound, that contributes to this impact category. It is also part of the exhaust gases, emitted in the drying section. Slight difference in impact of HDPE from poplar wood and forest residues can be explained by emissions of nitrogen dioxide, ammonia and nitrogen oxides during the poplar wood supply stage.

Terrestrial acidification

Biomass drying, as it was mentioned before, contributes the most to terrestrial acidification. This is due to 0.98 kg of sulfur dioxide/functional unit and 0.023 kg of nitrogen dioxide/functional unit, that are released as part of flue gas. Environmental impact of HDPE from poplar wood is higher in this impact category, because of the use of nitrogen fertilizer and emissions of nitrogen oxides during the poplar wood supply stage.

Freshwater eutrophication

In this impact category environmental impact of HDPE from poplar wood is almost 25 times higher than from forest residues. During the poplar wood supply stage emissions of phosphate and phosphorus occur, due to use of the fertilizer and pesticides. Application of glyphosate for cultivation of poplar wood, results in around 0.000007 kg P eq/functional unit emissions to water, when mass allocation is applied. In case with forest residues, just use of electricity and diesel significantly contribute to eutrophication.

Marine eutrophication

Marine eutrophication occurs due to increase of the concentration of nitrogen in water, which in this study is caused by emissions of nitrate, ammonium ion, ammonia and nitrogen. During the poplar wood supply stage 0.01941 kg of nitrate/functional unit is emitted to the water, what results in significantly higher impact of HDPE from poplar wood than from forest residues. Since forest residues supply contribute to marine eutrophication just by use of diesel.

Ecotoxicity

Copper, Nickel, Vanadium, Zinc and other toxic metals are the main contributors to terrestrial ecotoxicity. When poplar wood is used as feedstock, the biomass supply stage is associated with emissions of toxic metals to water and pesticides to the soil. This results in higher environmental impact value for HDPE from poplar wood than from forest residues. Nevertheless, transportation of biomass, which was assumed the same for both types of feedstock, also significantly

contribute to this impact category and therefore forest residues supply is the main contributor to terrestrial ecotoxicity. In case with freshwater and marine ecotoxicity impact of HDPE from poplar wood is way higher than of HDPE from forest residues, due to emissions, that come from use of pesticides for poplar wood cultivation and emissions of toxic metals to water. However, production of electricity during the ethylene synthesis and polymerization negatively affect these impact categories as well.

Human carcinogenic and non-carcinogenic toxicity

As it was stated before poplar wood supply affects the most these impact categories. This is a consequence of use of nitrogen as fertilizer. However, ethylene synthesis and polymerization process also negatively affect human health, due to emissions, associated with production of electricity and natural gas. During electricity and natural gas production emissions of toxic chemicals, such as zinc, chromium, nickel occur. Contribution of these processes is more significant for HDPE from forest residues, since forest residues supply stage in this case doesn't affect the results as much as poplar wood supply. However, emissions from diesel, that is used for collection of forest residues and transportation of biomass also have an impact on human health, and their contribution is more significant for non-carcinogenic toxicity.

Land use

Land use impact of HDPE from poplar wood and HDPE from forest residues is almost equal, because transportation and use of diesel mostly affect this impact category. Even though, more diesel is needed for forest residues supply, poplar wood supply requires electricity and fertilizer, what also affects land use and makes HDPE from poplar wood least preferable option.

Mineral resource scarcity

According to the results from SimaPro production of diesel and electricity leads to mineral resource scarcity for both types of feedstock and application of fertilizer affects mineral resources for HDPE from poplar wood. However, it should be noted, that olivine, which is used for gasification process, was not found in the database and sand was used instead. Therefore, results for this impact category can be inaccurate, since use of sand doesn't have a significant effect on mineral resource scarcity.

Fossil resource scarcity

Results in this impact category are almost equal for HDPE from poplar wood and HDPE from forest residues. This is a consequence of same use of diesel for biomass supply and natural gas for polymerization and ethylene synthesis. Even though more diesel is used for forest residues processing, difference is compensated by fossil fuels resources, which are used for production of fertilizers and pesticides for poplar wood cultivation.

Water consumption

Water consumption is almost equal for HDPE from poplar wood and for HDPE from forest residues, because most water usage is associated with use of electricity and in this project Norwegian energy mix was assumed, which is based on hydropower. Therefore, for production of electricity for obtaining 1 kg of HDPE 0.00896 m³ of water is needed. Contribution of other processes is insignificant compared to electricity production. (Energifakta Norge, 2020)

4.2 Sensitivity analysis of allocation approaches

4.2.1 Allocation methods

If the environmental burdens are allocated on the energy basis, as it is shown in Figure 14 bellow HDPE produced from forest residues is still the best option. As well as when economic

allocation is applied (Figure 15). Therefore, allocation method doesn't affect the choice of the best option.

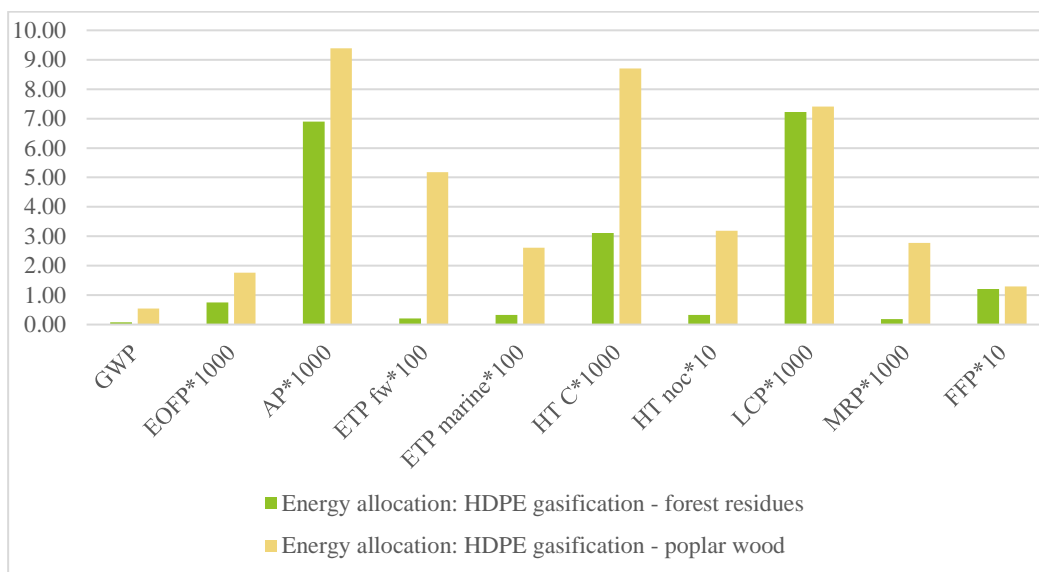


Figure 14 Life cycle environmental impacts of HDPE produced from poplar wood and forest residues for energy allocation

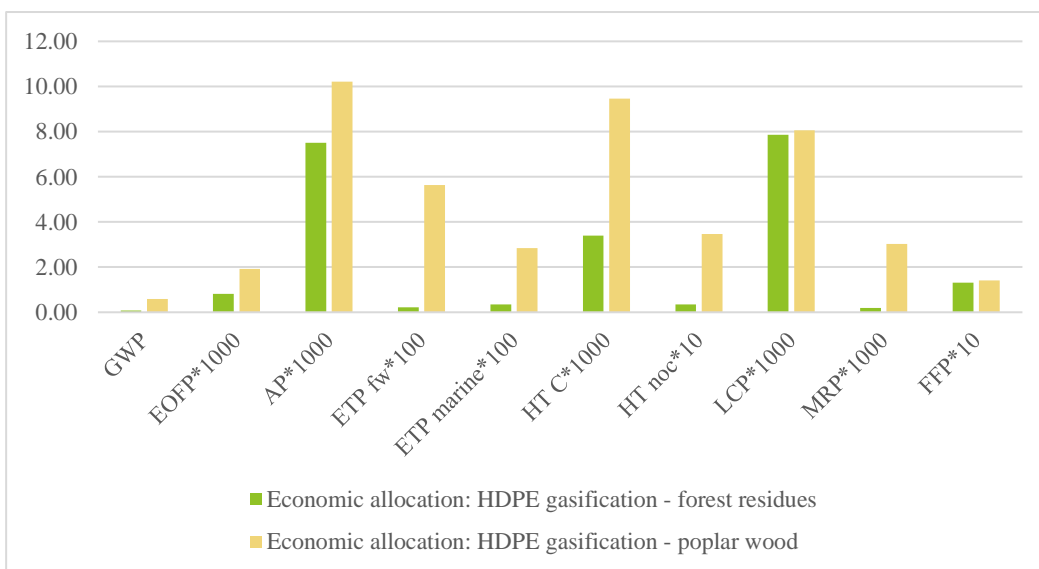


Figure 15 Life cycle environmental impacts of HDPE produced from poplar wood and forest residues for economic allocation

However, if we compare all 3 allocation methods (Figure 16), we can see, that the absolute values have changed. If the environmental burdens are allocated on the mass basis, impacts associated with HDPE production are the lowest. This is a consequence of difference in production volume of ethanol and HDPE. Mass of ethanol is 2,47 kg, when HDPE is – 1 kg. Hence just 28.75% of impact is allocated to HDPE. When energy allocation method is used, 19% more impact is allocated to HDPE, because HHV of HDPE is higher than of ethanol, therefore higher allocation percentage was used compared to mass allocation. Environmental impact of HDPE increases by additional 8%, when economic allocation is applied. Market price of 1 kg of HDPE is 41 cents higher than of 1 kg of ethanol, therefore 38.55% of impact is allocated to it.

Therefore, the highest impact is observed, when environmental burdens are allocated on the economic basis.

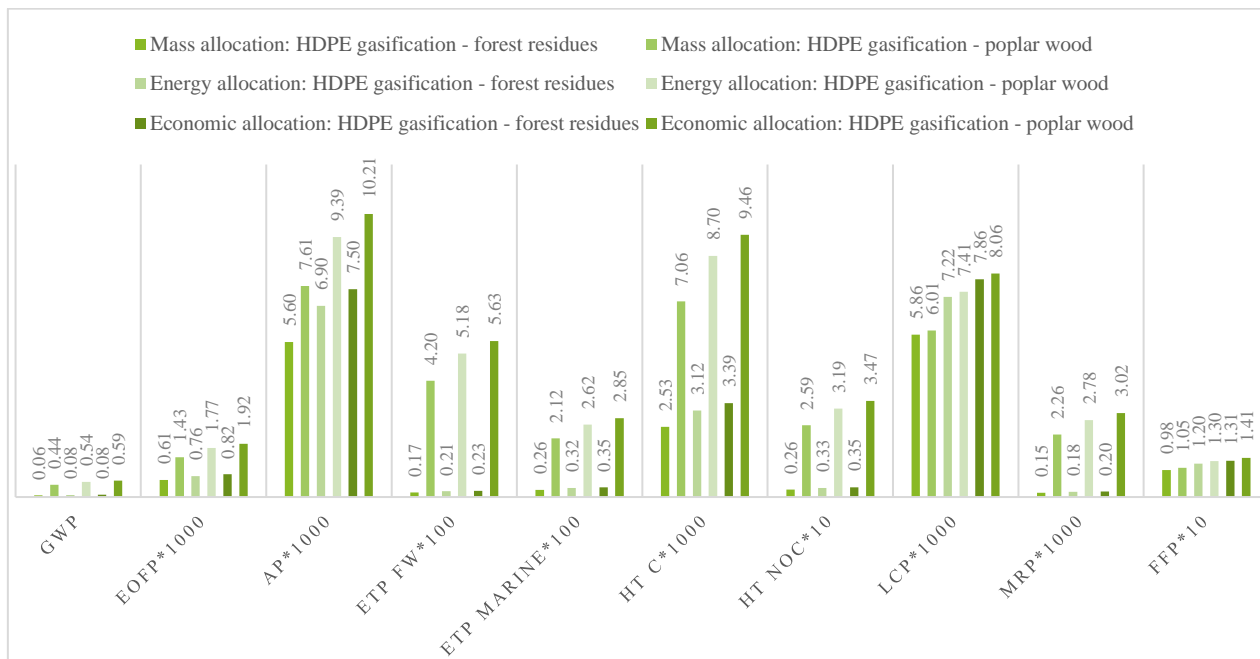


Figure 16 Comparison of environmental impact of HDPE from forest residues and poplar wood for mass, economic and energy allocation methods

4.2.2 Additional co-products

During the alcohol synthesis besides ethanol higher alcohols, such as propanol, n-butanol and pentanol are produced. When these products are included in the system, environmental impact of the biorefinery is allocated between HDPE, ethanol, butanol, propanol and pentanol. In this scenario, when mass allocation is applied, environmental impact of HDPE production decreases by 19.79% regardless of feedstock, compared to the first scenario (Figure 17). This is the consequences of addition 0,594 kg of propanol/functional unit, 0,074 kg of n-butanol/functional unit and 0,001 kg of pentanol/functional unit to final products and therefore decrease of impact allocated to HDPE from 28.75% to 24%

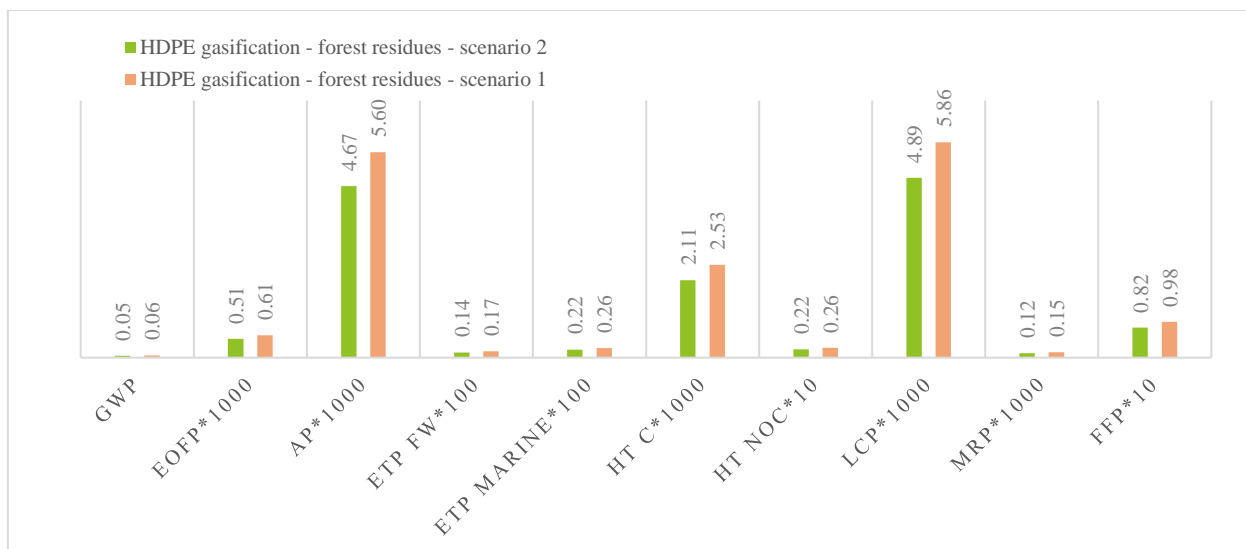


Figure 17 Comparison of environmental impact of HDPE from forest residues for scenario 1 and 2, based on mass allocation

If the environmental burdens are allocated on energy basis, the impact of HDPE is decreasing by 18%, compared to the first scenario, regardless of feedstock. This is due to the fact, that HHV of propanol and butanol is higher than HHV of ethanol. Therefore, less impact is allocated to HDPE and ethanol. (Figure 18)

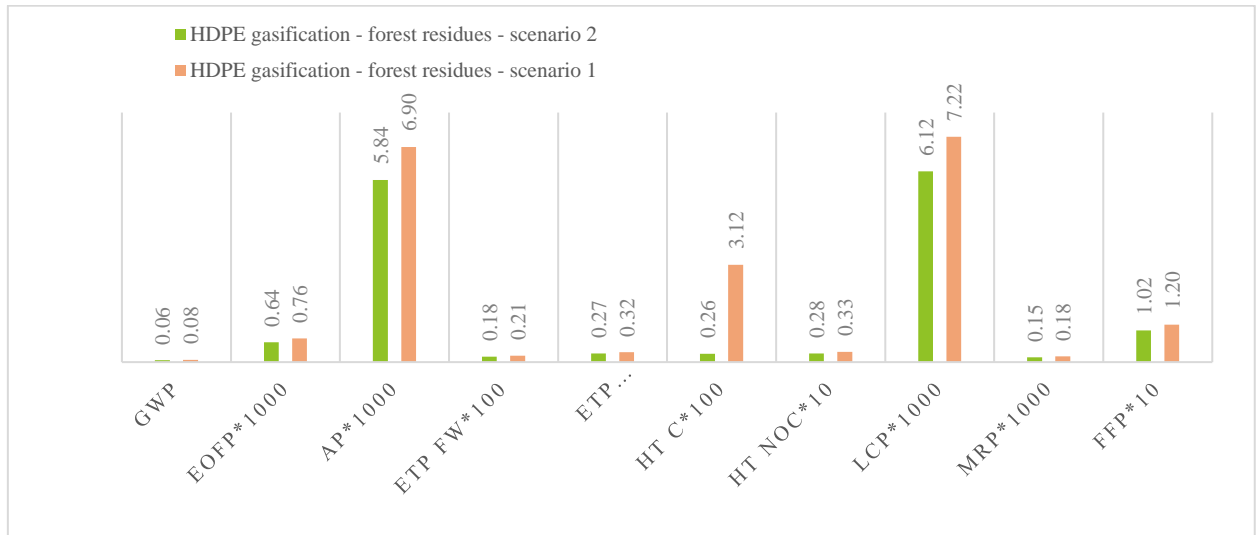


Figure 18 Comparison of environmental impact of HDPE from forest residues for scenario 1 and 2, based on energy allocation

When economic allocation is applied, reduction compared to the first scenario are even more significant. From the Figure 19 bellow it is obvious, that environmental impact of HDPE with co-production of ethanol, propanol, n-butanol and pentanol is almost 33% lower than environmental impact of HDPE in the first scenario. This is a consequences of high propanol price, which was assumed to be 1.575 \$ per kg (Echemi, 2020). The higher price can be explained by the rapid growth of propanol market. This alcohol is used in paints, coatings, pharmaceuticals, and cosmetics and in the last few years consumption in these industries increased, what in turns drives the propanol market. (Market Research Reports, 2020)

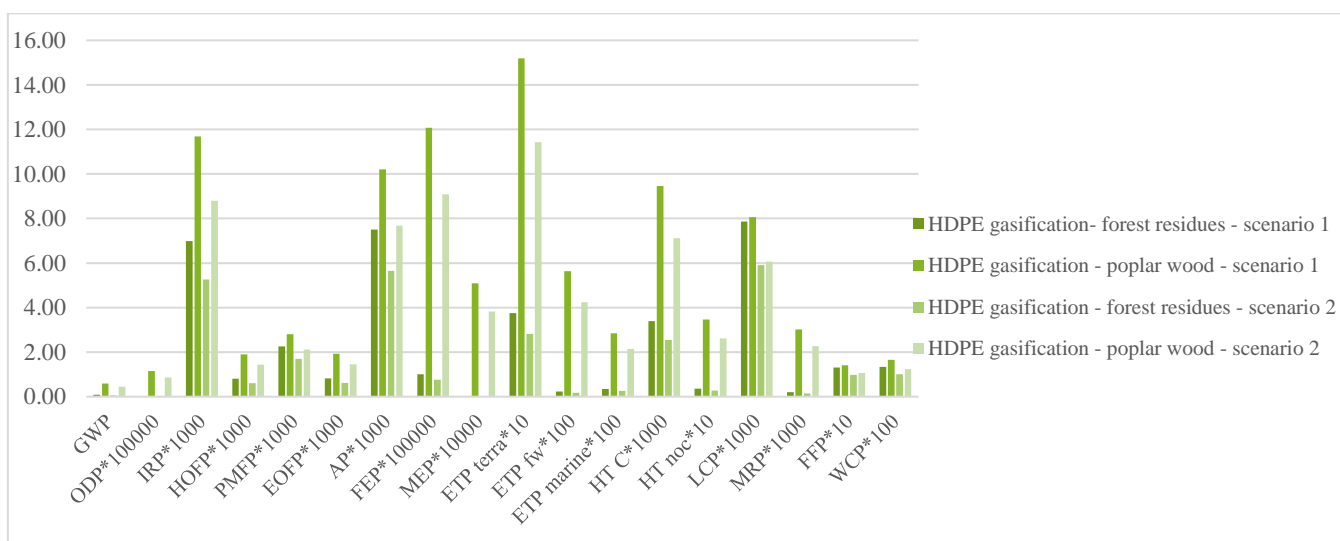


Figure 19 Comparison of environmental impact of HDPE from forest residues for scenario 1 and 2, based on economic allocation

Among all the allocation options, the lowest values were obtained for both types of feedstock when 5 co-products were considered, and environmental burdens were allocated on mass basis. Economic allocation for the second scenario (5 co-products) showed slightly higher values, than mass allocation for the same scenario, but the reduction compared to the first scenario and economic allocation approach are greater than for any of others. However, as it was mentioned before, allocation approach and even change in number of final products doesn't affect the choice of best feedstock option, it affects just the absolute values.

4.3 Comparison of thermochemical and biochemical ethylene

For comparison of the environmental impact, associated with production of ethylene from poplar wood, ethylene from forest residues via gasification and ethylene from sugar beet via fermentation ILCD 2011 and ReCiPe methods were used. (Figure 20) As it was stated in methodology part ethylene is chosen for comparison, due to difference in system boundaries between this research and research, made by Sandra Belboom and Angélique Léonard. (Belboom & Léonard, 2016)

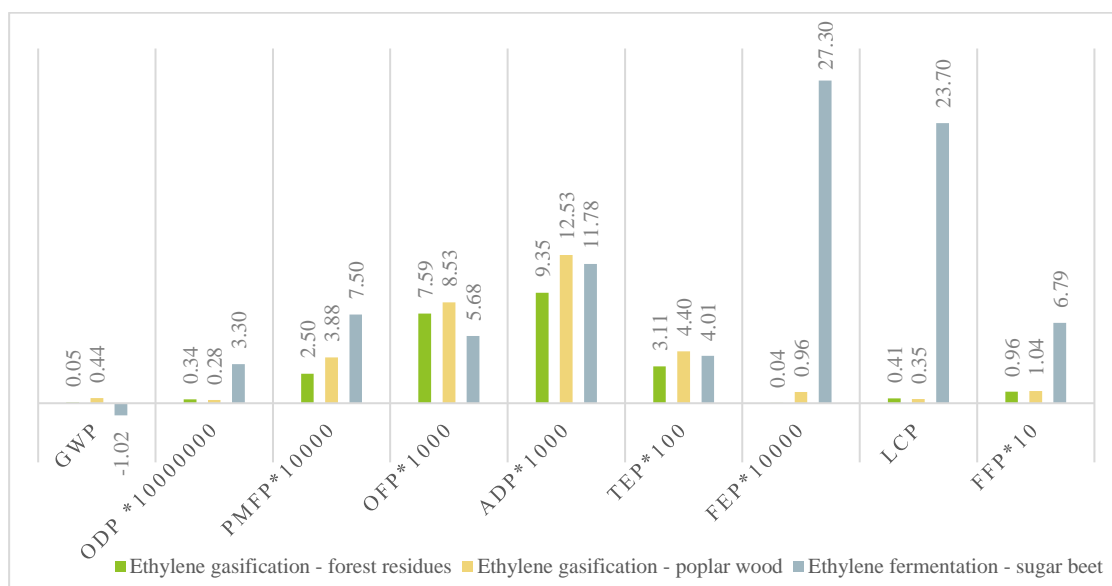


Figure 20 Comparison of thermo-chemical and bio-chemical ethylene for mass allocation

Ethylene from forest residues is the best option for 6 out of 9 impact categories, such as ozone depletion (ODP), fine particulate matter formation (PMFP), acidification potential (ADP), terrestrial eutrophication (TEP), freshwater eutrophication (FEP), and fossil resource scarcity (FFP). However, in such important impact category as global warming (GWP) ethylene produced through gasification has higher impact than ethylene, that is obtained from fermentation of sugar beet. This is a consequence of considering CO₂, that is emitted during the production of ethylene from sugar beet, as well CO₂. Sandra Belboom and Angélique Léonard assumed, that cultivation of sugar beet compensates emissions during the production and even lead to negative net emission. In case with ethylene from poplar wood and forest residues, carbon dioxide, that was emitted during production process, was considered as carbon neutral, due to its biogenic origin, but positive contribution of feedstock cultivation to climate change was not considered. Therefore, production of ethylene via gasification doesn't lead to negative net emissions. This is discussed in more detail in next chapter. (Belboom & Léonard, 2016)

Impact in photochemical oxidation (OFP) of ethylene obtained through fermentation is also lower than ethylene, that is produced through gasification. This can be explained by high concentration of nitrogen dioxide in flue gas, which is released during the drying stage and leads to photochemical oxidation.

Ethylene from poplar wood has the highest values in acidification and terrestrial eutrophication. This is due to nitrogen dioxide and sulfur dioxide emissions, that occur during the biomass drying stage. Even though, same amount of NO₂ and SO₂ is emitted, when forest residues are used as a feedstock, impact of ethylene from poplar wood is higher, since cultivation stage also significantly contribute to these impact categories.

Due to use of different method, values have changed and ethylene from forest residues appeared to be worse than ethylene from poplar wood in such categories as ozone depletion (ODP) and land use (LCP). The reason behind it is use and production of diesel. According to the inventory data for poplar wood supply less diesel is needed.

4.4 Comparison of thermo-chemical and fossil-based HDPE

ILCD 2011 and ReCiPe were applied to estimate environmental impacts of thermo-chemical ethylene and fossil ethylene. (Belboom & Léonard, 2016) Results are presented in Figure 21 below.

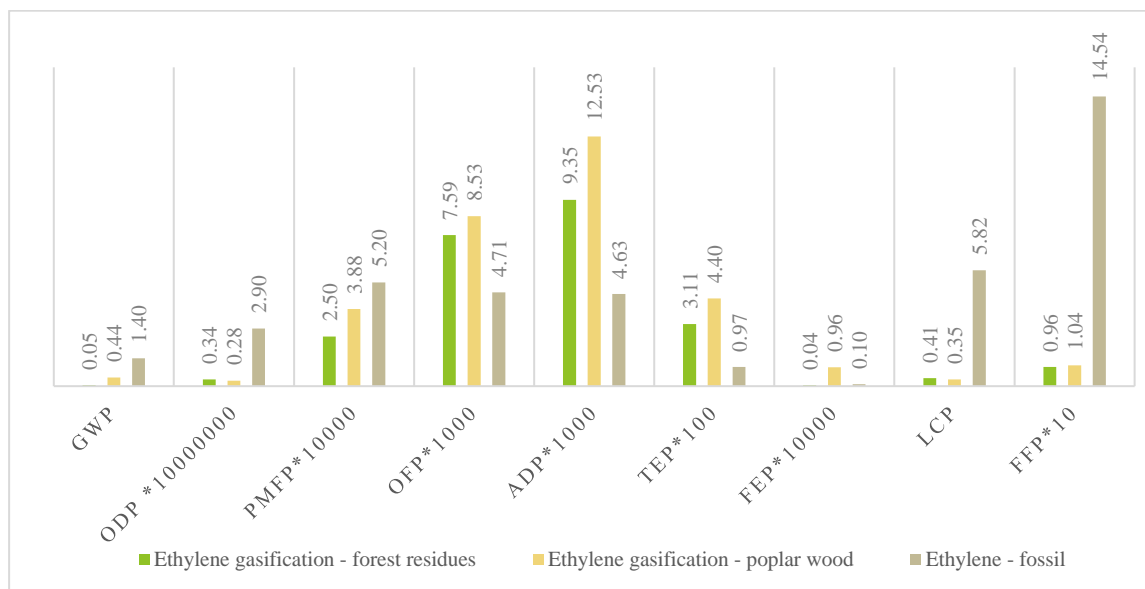


Figure 21 Comparison of thermo-chemical and fossil based HDPE for mass allocation

For 3 out of 9 impact categories: photochemical oxidation (OFP), acidification (ADP), terrestrial eutrophication (TEP) ethylene produced through gasification is the worst option. Flue gas, that is released during the drying stage and consists of biogenic carbon dioxide, nitrogen dioxide and sulfur dioxide, is the biggest contributor to these impact categories. Ethylene from poplar wood has higher values than the others for freshwater eutrophication, because of the cultivation stage and use of fertilizers. However, for the remaining 5 categories: global warming, land use, fossil resource scarcity, ozone depletion and fine particulate matter formation thermo-chemical ethylene showed good results. Fossil resource scarcity and land use is more than 10 times lower for ethylene from poplar wood/forest residues. Particulate matter formation and ozone depletion is higher for fossil ethylene, since steam cracking of naphtha is associated with more emissions of sulfur dioxide, particulates and chlorofluorocarbons respectively.

Impact on global warming is 3 times lower, when poplar wood is used as raw material for ethylene production and 28 times lower, when ethylene is obtained via gasification of forest

residues. This is due to origin of CO₂, which is emitted during the production. As it was stated before biogenic carbon dioxide, which is released to the atmosphere in biorefinery is considered carbon neutral, when fossil carbon dioxide, which is emitted during steam cracking of naphtha, significantly contribute to global warming.

5 Discussion

5.1 Key findings

As it was stated in introduction the main objective of biorefinery concept, suggested in this study is to minimize environmental impact from plastics and fuels production. Especially in such categories as global warming and fossil resource scarcity. LCA results of this study, showed that switch from fossil to biobased HDPE can contribute to significant reduction in consumption of fossil resources and is a promising solution for climate change mitigation. Furthermore, production of ethylene via gasification has lower environmental impact than production of its fossil equivalent in such impact categories as: ozone depletion, particular matter formation and land use. When forest residues are used as feedstock for ethylene production contribution to freshwater eutrophication is lower compared to fossil ethylene and ethylene from poplar wood. However, for such categories as acidification, terrestrial eutrophication and photochemical oxidation bio-ethylene is worse than fossil ethylene. What indicates shift in pollution between categories.

Thermochemical production pathway was also compared with biochemical. Comparative analysis showed, that biochemically produced ethylene has higher environmental impact than ethylene, obtained via gasification from forest residues in most of the impact categories considered. Forest residues and poplar wood for thermo-chemical HDPE production were also compared between each other and forest residues appeared to be the best option for all impact categories. These conclusions verify, that first and second research questions have been answered: *environmental impact from biorefinery system was assessed; bioethanol and bioplastic production from forest residues and poplar wood via gasification can be considered as the best configuration.*

Sensitivity analysis of allocation approaches showed, that regardless of allocation method HDPE from forest residues is the best option. However, absolute values of impact categories have changed, and the lowest values were obtained, when burdens were allocated on mass basis. In addition to applying variety of allocation methods two scenarios were compared: 1. Ethanol and HDPE as final products 2. Ethanol, HDPE and higher alcohols as co-products. Second scenario showed reduction in impacts compared to the first, but it should be stated that inventory data for separation and distillation of higher alcohol was not included in the study. (Luk et al., 2017) Hence, decrease in environmental impact from HDPE production can be overestimated.

5.2 Comparison with previously conducted studies

Obtained results supports findings from, LCA conducted by Bernabé Alonso-Fariñasa et al., where bio-ethylene produced via gasification showed 66-105% reductions in global warming, compared to fossil ethylene. In research made by Bernabé Alonso-Fariñasa et al. global warming potential was 0.68 kgCO₂ eq/functional unit and obtained value in this study – 0.44 kgCO₂eq/functional unit, when same ethylene production method and type of feedstock was considered. The difference is not remarkable and can be explained by distinct inventory data and considered co-products. Researches also provided comparative analysis of ethylene obtained via gasification and via fermentation. They concluded, that thermochemical pathway leads to bigger emission reduction than biochemical, especially in such categories as global warming, eutrophication, acidification, ozone depletion and fossil resource depletion. What agrees with findings in this study. (Alonso-Fariñas et al., 2018)

Christin Liptow et al. assessed environmental performance of bio-ethylene production from wood chips via gasification and further MTO synthesis. Even though, the production chain was not identical to the one, examined in this study, results of Christin Liptow's et al. research are in line with Bernabé Alonso-Fariñasa et al. findings and results, obtained in this study. Findings in this thesis confirm Christin Liptow's conclusion that production of ethylene via gasification is the best option for reducing the fossil resource consumption. (Liptow, Tillman & Janssen, 2015) Another key finding, regarding shift in pollution between impact categories, when HDPE is

produced from biomass, can be confirmed by conclusion, which many other researchers have made. Their comparison of bio-based and fossil ethanol, showed that for such categories as terrestrial acidification and freshwater eutrophication fossil ethanol is preferable option. (Wang, Littlewood & Murphy, 2013) (Jeswani, Falano & Azapagic, 2015), (Piemonte, 2011) Therefore, it is important to minimize contribution not just to global warming and fossil resource depletion, but to other impact categories as well. Findings of this research indicates, that use of forest residues as raw material reduces impact across many categories, including freshwater eutrophication. However, issues associated with increased acidification potential still have to be solved.

Data obtained in this thesis indicated, that use of forest residue as feedstock for biorefinery is the best choice. This finding goes in line with conclusions made by Handler et al., and Jeswani in their work. Scientists agreed that forest residues as raw material minimize contribution of production process to such categories as eutrophication and acidification, because the feedstock supply doesn't require use of fertilizers and pesticides. (Handler, Shonnard, Griffing, Lai & Palou-Rivera, 2015) (Jeswani, Falano & Azapagic, 2015)

In results section comparison between bio-ethylene, produced via gasification and fermentation was presented. As it was already stated, values for bio-ethylene produced through fermentation were taken from study, made by Sandra Belboom and Angélique Léonard. Comparative analysis demonstrated higher values in global warming potential for thermo-chemically produced ethylene. This is a consequence of assumption in Sandra Belboom and Angélique Léonard research, that amount of CO₂ well is higher, than amount of CO₂, which is emitted during the ethylene production. In other words, more CO₂ is absorbed during sugar beet cultivation, than emitted during the production stage. (Belboom & Léonard, 2016) In this research, poplar wood cultivation was assumed to take place in already existing plantation. Hence, obtained values for GWP were not negative.

5.3 Limitation and future work

One of limitations of this study is that, land use change effect was not considered, because poplar wood is already cultivated in that area and forest residues are not energy crops and do not affect the land use. Nevertheless, if direct conversion of land was examined, as it was done in research, conducted by Temitope Falano, Harish K. Jeswani and Adisa Azapagic, possible reductions could be higher or lower, depending on the land, which is converted. Since for poplar wood significantly higher GHG savings can be achieved if the grassland is converted, because carbon sequestration by the poplar wood is higher than the emissions released during the grassland conversion. However, if the cultivation takes place in current forest, GWP increases a lot, because carbon is more effectively absorbed by forest than poplar wood. (Jeswani, Falano & Azapagic, 2015) Hence, it is important to consider effect of land use, when energy crops are chosen as feedstock for biofuels and biochemicals production, because inappropriate land management can lead to increase of GHG emissions.

In methodology part an essential assumption was made. Efficiencies, materials usage and emissions of HDPE from poplar wood and forest residues were assumed to be the same, due to almost identical elemental composition. This assumption has led to unfair comparison between poplar wood and forest residues, since according to the inventory data, made by Jeswani et al., for life cycle assessment of ethanol production via gasification, significantly higher amount of forest residues is needed for 1 liter of ethanol. This is a consequence of higher moisture content in forest residues. Furthermore, slightly higher amount of magnesium oxide and olivine is applied for gasification of forest residues. (Jeswani, Falano & Azapagic, 2015) That is why in future work difference in feedstock should be taken into account.

Another uncertainty, that affects the results is choice of allocation method. In this research allocation on economic, mass and energy basis was applied. To avoid inaccuracy of results system expansion method was not used, despite the fact that in many researches, when credits were given for avoiding production of co-products environmental impact of the main product

was way lower. (Falano, Jeswani & Azapagic, 2014) However, this method was found not suitable for this study, due to the high uncertainty concerning which product systems are affected by changes in the system under study. (Ahlgren et al., 2015) In addition, according to Edivan Cherubini et al., this method introduces a broad range of scenarios, since the avoided products can bring a positive impact to the product system. (Cherubini, Franco, Zanghelini & Soares, 2018) In case of considered production system in this study application of system expansion (extraction of impacts, associated with bioethanol production) would lead to unfair comparison between fossil ethylene, ethylene, produced via fermentation and ethylene, produced in thermo-chemical biorefinery. Therefore, choice of partitioning as allocation method for this particular study seems to be adequate. Nevertheless, author of thesis aware of difficulties, associated with these allocation methods, when for example electricity or heat are considered as co-products. (Cherubini, Strømman & Ulgiati, 2011) In future research system expansion for allocating environmental burdens should be examined for better understanding benefits of biorefinery system.

As it was already discussed, notably reduction in global warming potential are achieved for bio-based HDPE, due to assumption, that biogenic carbon, which is emitted during the production is carbon neutral. This assumption is based on hypothesis, that biogenic carbon dioxide will be absorbed by plant regrowth through photosynthetic production effect. (Liu et al., 2019) Even though this theory is supported by current guidelines, many scientists don't agree with it. Liu et al. claim that supposition of carbon neutrality leads to inaccurate results, due to disregard of carbon uptake dynamics, carbon decay in the atmosphere and land use change impact. (Liu et al., 2018) Cherubini et al. also state that, emissions of biogenic carbon should be taken into account, since biomass-derived CO₂ is emitted by a one-time combustion of biomass and requires years to be compensated by regrowth. (Cherubini et al., 2011) Liu et al. emphasize, that accounting for biogenic carbon is especially important, when forest bioenergy system is considered. In this study poplar wood and forest residues were examined as raw materials for biorefinery, therefore biogenic carbon should have been taken into account. According to the Liu et al. research there are several reasons for accounting for biogenic carbon, they were already stated earlier: 1. Emissions of biogenic carbon requires years to be compensated by forest regrowth 2. Assuming, that there are no carbon emissions during the biomass supply stage 3. Emissions, associated with land use change effect 4. Loss of carbon sequestration 5. Negative effect of forest residues removal. (Liu et al., 2018) Christin Liptow et al. in their research examined 3 accounting methods: the GWP_{bio} method, the GWP_{netbio} method and the WF method. First two calculate characterization factor to assess the climate impact of biogenic CO₂ flows. In WF method first weighting factor (WF) is calculated, which is further applied to the inventoried amount of biogenic CO₂ and then to CFs commonly used for fossil CO₂. (Liptow, Janssen & Tillman, 2018)

In this report, as it was already mentioned, issue of land use change and therefore its contribution to global warming was overcome by considering, that poplar wood cultivation takes place in already existing plantation. Biomass supply stage and its contribution to global warming was also taken into account. Accounting for biogenic carbon dioxide should be done in next work, since due to the lack of comprehensive information about carbon uptake dynamic and loss of forest residues, results of this research are inaccurate. For the future work one of the previously described methods can be used. This is essential for fair comparative analysis between oil refinery and biorefinery.

6 Conclusion

This research aimed to identify the most promising biorefinery system and assess its environmental performance. The process for production of bioethanol and HDPE was designed. Based on literature review and life cycle assessment it was concluded that thermo-chemical conversion of biomass into high density polyethylene and ethanol is beneficial and sustainable solution for climate change mitigation and reduction of fossil resource consumption. Its implementation will help to reduce GHG emissions in plastic production and transportation sector, since according to the finding bio-based HDPE and ethanol have lower global warming potential than their fossil equivalent. Results of life cycle assessment indicated that forest residue is preferable type of feedstock, its use as raw material contribute to large emission reductions in all impact categories considered. Comparison of bio-chemical and thermo-chemical production pathways showed, that last is the better option, it had lower values in 6 out of 9 impact categories. Nevertheless, there is room for development that would be worth looking into, since results of research indicate shift in pollution, when biomass is used as raw material for fuel and plastic production.

Implication of life cycle assessment for estimating environmental performance of biorefinery system provides a good insight into the origins of impacts and is a useful tool for decision making. However, it is not very suitable for bioenergy systems. The program used for analysis underestimates contribution of biogenic carbon, what leads to unfair comparison between oil and biorefinery. Future research is needed to determine the effect of biogenic emissions and understand better the consequences of use of biomass for biofuels and bioplastics production. Findings from this thesis address the research gap in life cycle assessment of thermo-chemical biorefinery, where biofuel and bioplastic are co-produced.

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