



Comparison of the ethylene production carbon footprint calculated with different allocation methods

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Abstract

Climate change affects the lives of millions of people every day. The main driver for the climate change is the increasing amount of greenhouse gases in our atmosphere. Industry is a large greenhouse gas producer on our planet. Therefore, it is important to find new ways to reduce the amount of greenhouse gas generated by industry. One way is to use more sustainable feedstocks in industry. In many industry sectors it is not possible to switch the fossil feedstock totally to sustainable feedstock. Switching totally to bio-feedstock often requires technical changes to the process. The availability of bio-feedstock does not meet the demand of the industry either.

Petrochemical industry falls into this sector. Plastic itself is still irreplaceable for us. Although plastic is associated as visible waste because of its poor recycling, its production generates fossil-based greenhouse gases. One way to reduce fossil-based greenhouse gases is to increase the amount of bio or circular feedstocks to steam crackers. Steam crackers produce olefins which are the main building blocks when producing plastic.

The aim was to count and illustrate the emission impact of producing ethylene from fossil- and bio-based feedstocks. The study aimed to find emission factors that best represent regional ethylene production. The recommendations were used to find the right allocation methods. Through these, the emission impact for both fossil- and bio-based feedstock was counted by using emission factors for bio-feedstock, naphtha-feedstock, and for the steam cracker.

Through the research questions, variations in the carbon footprints could be demonstrated, depending on the feedstock and allocation method. The climate impacts caused by both feedstocks were allocated using different allocation methods to enable their comparison.

The results indicated that the impact of biogenic carbon dioxide removal on the product's carbon footprint is significant. Different allocation methods also demonstrated substantial variability in product carbon footprints.

In conclusion, the transparency of calculations underlying the product's carbon footprint and the emission factors used is essential. Without background information, comparing carbon footprints might not be reliable.

Keywords/tags (subjects)

allocation, carbon footprint, ethylene, life cycle assessment, steam cracking

Miscellaneous (Confidential information)

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In Porvoo, 18th of August 2023

Toni Sundström

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Acronyms

AF	Animal Fat
CEN	European Committee for Standardization
CF	Conversion Factor
CFP	Carbon Footprint
CoC	Chain of Custody
CTO	Crude Tall Oil
dLUC	Direct Land-use Change
EF	Emission Factor
EFTA	European Free Trade Association
EN	European Norm
Eq	Equivalent
EU	European Union
FF	Feedstock Factor
GHG	Greenhouse Gas
GWP	Global Warming Potential
HVC	High Value Compounds
HVO	Hydrotreated Vegetable Oil
iLUC	Indirect Land-use Change
IPCC	Intergovernmental Panel on Climate Change
ISCC	International Sustainability and Carbon Certification
ISO	International Organization for Standardization
LCA	Life Cycle Assessment
LCI	Life Cycle Inventory Analysis
LCIA	Life Cycle Impact Assessment
LPG	Liquefied Petroleum Gas
MB	Mass Balance
NEXBTL	Neste's Renewable fuels and Chemicals Technology

PCR	Product Category Rules
PFAD	Palm Fatty Acid Distillate
PSA	Pressure Swing Adsorption
RED II	Renewable Energy Directive
SFS	Finnish Standards Association
SPIRIT	Sustainable Plastic Industry Transformation
UCO	Used Cooking Oil

Chemical compounds

C	Carbon
CO ₂	Carbon Dioxide
H ₂	Hydrogen
CH ₄	Methane
N ₂ O	Nitrous Oxide
O ₂	Oxygen

1 Introduction

This thesis has been commissioned by Borealis Polymers Oy as part of the Sustainable Plastic Industry Transformation (SPIRIT) program. Borealis is a key player in the global market, offering advanced and sustainable polyolefin solutions. As a pioneer in polyolefin recycling in Europe, Borealis stands at the forefront of innovation. Borealis is also a leading force in the European basic chemicals sector. Borealis's extensive polymer knowledge and decades of experience enable it to provide value-added, innovative, and environmentally conscious material solutions to critical industries such as consumer products, energy, healthcare, infrastructure, and mobility. (Borealis homepage, 2023.)

Climate change and global warming have become the world's most critical issues to be solved. Those have a huge effect on our living. The purpose of the Paris agreement is to constrain global warming to 1,5 degrees (United Nations, (n.d.)). In order to reach that target, it will demand huge modifications from the industry sector. Greenhouse gases (GHG) are those gases which cause the global warming. Typical GHGs which petrochemical industry generates are carbon dioxide, methane and nitrogen oxides. Different GHGs reflect thermal radiation differently and thus prevent the thermal radiation out of the atmosphere. This increases average temperature in the world above of normal. (VTT Technical Research Centre of Finland, 2018.)

Carbon footprint calculation is a method to calculate the GHG emission of a product. In addition, it is a good method to make research of various alternatives to decrease GHGs. In the sector of petrochemical industry, there has been much research about the methods to decrease the GHG emissions. The most important thing is to keep carbon in the cycle and not to release it to the atmosphere. There are several ways to do that: carbon capture and utilize, carbon capture and storage, and products that have been produced from biomass. In the last alternative, carbon cycle is based on photosynthesis where plants absorb carbon dioxide from the atmosphere. (IPCC, 2022.)

The plastic industry also has a big effect on climate change and thus it is important to move towards more sustainable plastic manufacturing. Most of the emissions which plastic industry causes are from cracking process because of its energy intensity. One option to decrease the emissions which the cracking process causes is to start using bio-based feedstocks and recycled raw materials instead of fossil ones.

Figure 1 presents a possible scenario for the plastic industry by 2050. It can be noticed from the figure that bio-based olefins are probably a part of plastic manufacturing also in the future. (IPCC, 2022.)

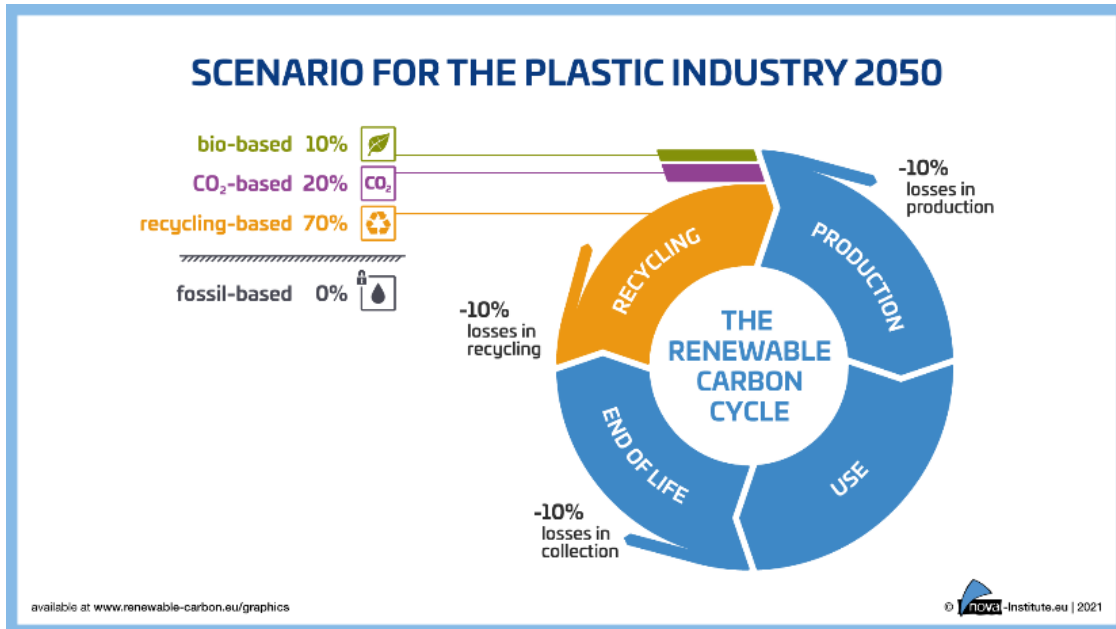


Figure 1 Scenario for the plastic industry 2050 (Scenario for the plastic industry, n.d.).

The purpose of this thesis is to compare the environmental impact of bio-based ethylene to fossil based one. In this context, the environmental impact is presented as carbon dioxide equivalent (CO₂-eq), which comprises carbon dioxide (CO₂), methane (CH₄) and nitrous oxide (N₂O) emissions of refining bio- or fossil-based feedstock by the steam cracking. The aim of this thesis is to answer three separate research questions:

1. What are the CO₂-eq emissions of the BIO-based ethylene in its totality when emissions are allocated to all cracker products, prime olefins or according to the PlasticsEurope recommendation (HVC)?
2. What are the CO₂-eq emissions totally if using fossil naphtha feed?
3. What are the CO₂-eq emissions of the BIO-based ethylene in its totality when using a proportional allocation or a non- proportional allocation?

The purpose is to present the impact variation at different allocation methods. All emission data in this thesis are based on the public literature and thus the results may vary from other studies.

2 Production of ethylene

2.1 Ethylene production via steam cracking

Ethylene is a raw material for the polyethylene production. In 2021, the world plastic production was 390,7 million tons and 90,2 % was produced by fossil based raw material. The rest of the plastics production was distributed as follows: 8.3 % recycled plastics and 1,5 % bio-based plastics. Plastic is, however, vital to the society. Plastic enables life which we are living. Packaging and building together with construction take over 50% of the plastic market. The mentioned amount of produced plastic includes plastic produced through polymerization as well as through mechanical recycling, excluding, however, the following: adhesives, sealants, coatings, paints, varnishes, or plastic used in the production of cosmetics, medicines, or chemical processes. Plastics used in textiles and textile waterproofing have also been removed from the given quantity, whereas thermoplastics and thermosets are included. (PlasticsEurope, 2022.) Without plastic packages food waste would be much larger than it is now. Plastic bottles are lighter than the glass ones, therefore it is possible to transport more at the time with the same environment impact.

Steam cracking is the main form of the production for olefins. There are three different types of steam crackers. Light feed crackers, naphtha feed crackers and mixed feed crackers. Basic principle is following, lighter feed produces lighter products. Main products from the steam cracking are methane, ethylene, propylene, butadiene, and heavier stream (C₅+). In addition, small amount hydrogen is releasing from the cracking reaction which is also categorized as a main product. In the cracking reaction, hydrocarbon chains are breaking due the heat. As a result of broken chains double bonds are generated. Double bonded hydrocarbons are often called olefins. (Matar & Hatch, 2001.) The following formula (1) shows the reaction formula for the ethane cracking.



As result of the reaction also coke is formed as shown in the formula 2. Coke is sticking on inner surface of the tubes and thus increasing the pressure difference over the tubes. Optimal conditions for the reaction are high temperature and low pressure. However, the high temperature increases the coke formation. Therefore, dilution steam is used to lower the partial pressure of

hydrocarbons and thus reducing the coke formation during the reaction. The reaction itself is highly endothermic and needs a large amount of energy. (Matar & Hatch, 2001.)



Mixture of preheated naphtha feed and dilute steam is fed into the pyrolysis furnace. The temperature of the outlet stream is approximately 800 degrees. The stream is cooled by producing high-pressure steam. After cooling, the C₅+ stream is separated from lighter stream in the primary fractionator. Lighter stream, which consists of butadiene and lighter products is led to the quench tower. After the quench tower, the feed must be pressurized, and acids must be removed in the caustic stripper. Before cooling the feed under zero degrees, it must be dried. Dry feed is fed to the demethanizer to separate methane and hydrogen from heavier products. Methane is used as an energy source on the pyrolysis furnaces. Hydrogen can be separated from methane to use it as a coproduct. (Matar & Hatch, 2001.)

C₂ to C₄ stream continues to the de-ethanizer. In the de-ethanizer, C₂ stream is separated from heavier components and led to the ethylene fractionator. The ethylene product is distilled as an overhead product from top of the ethylene fractionator. The bottom stream from the de-ethanizer, which consists of C₃ and C₄ components, is led to the depropanizer. In the depropanizer, C₃ stream is distilled from heavier C₄ stream and is fed to the propylene fractionator where the propylene product is distilled as an overhead product. The C₄ stream from the depropanizer can be fed to the butadiene unit or utilized as a crude C₄ product. (Matar & Hatch, 2001.) It's important to note that the steam cracking process according to this configuration is just one example of the existing configurations. Figure 2 presents simplified flow charter of steam cracker.

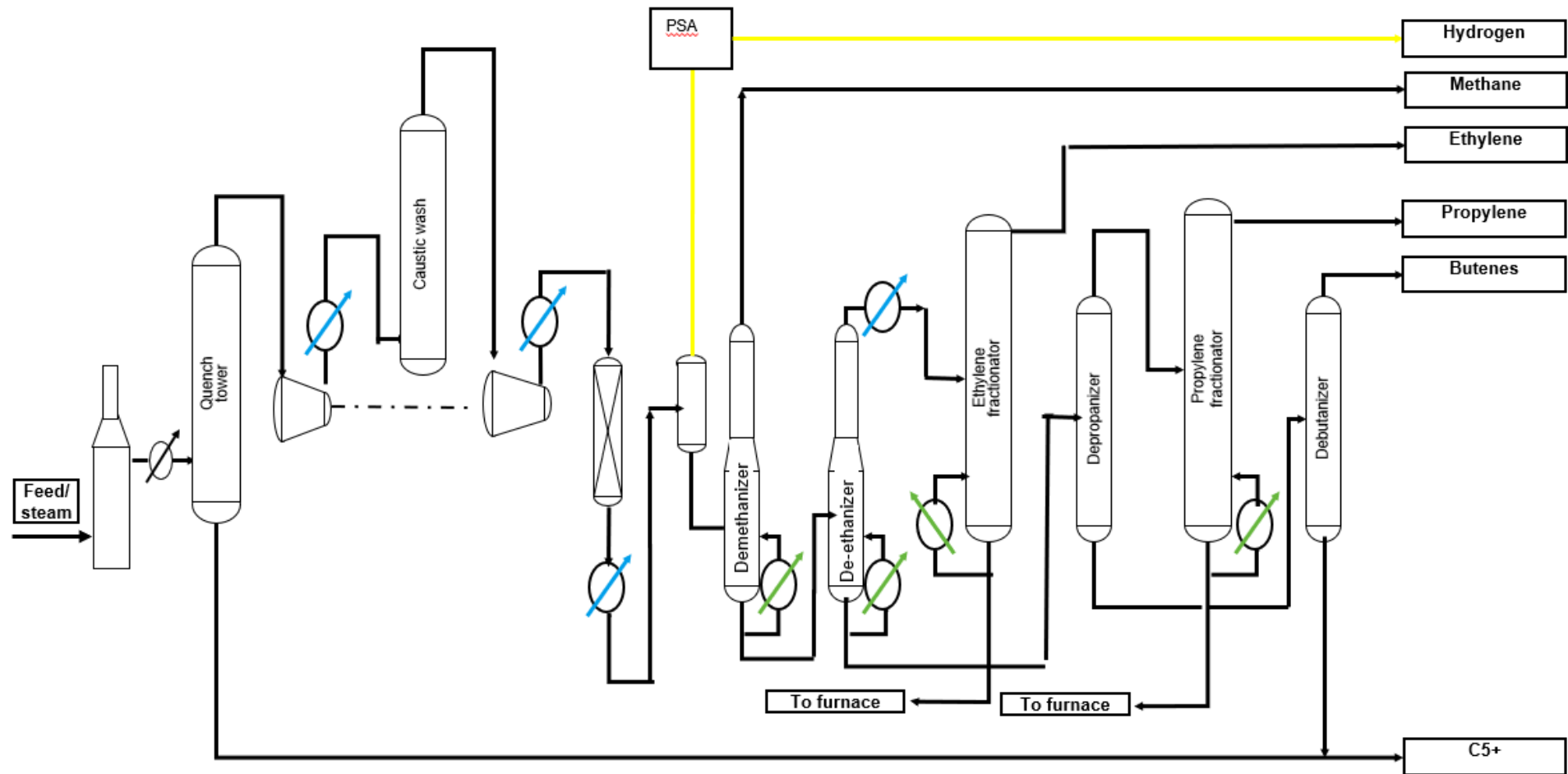


Figure 2 Simplified flow chart of steam cracker.

2.2 Yields of steam cracking with naphtha feedstock

Product yields vary in the steam cracking process depending on its feedstock. Lighter feedstock produce lighter products and vice versa. When comparing the fossil feedstock to a selected bio-based feedstock it is good to use naphtha as a reference feedstock. This is because the boiling point range of the bio feedstock reflects more to naphtha feedstock than the light ones. Table 1 presents the typical yields of steam cracker when using naphtha as a feedstock.

Table 1. Typical yields (w-%) of naphtha feedstock (Young et al., 2022).

Product	Yields
Hydrogen (H ₂)	1%
Fuel Gas (CH ₄)	14%
Ethylene (C ₂ H ₄)	30%
Propylene (C ₃ H ₆)	17%
Butene's (C ₄ H _n)	11%
C ₅ +	26%
Sum	99%

Fuel gas yield mainly consists of methane. Butene's yield includes butadiene and butene streams. C₅+ yield includes benzene, toluene, styrene, xylene, ethylbenzene, pyrolysis gasoline, and pyrolysis fuel oil. Minor streams are not included in the typical yields. More detailed yields are presented in Table 2.

Table 2. Detailed yields (w-%) of naphtha feedstock (Young et al., 2022).

Hydrogen	1,10 %
Methane	14 %
Ethyne	0,36 %
Ethylene	30 %
Propyne	0,60 %
Propylene	17 %
Butatriene	0,09 %
Butadiene	4,80 %
Butene	5,80 %
Benzene	6,40 %
Toluene	3,10 %
Styrene	1,10 %
Xylene	1,20 %
Ethylbenzene	0,79 %
Pyrolysis gasoline	11 %
Fuel oil	2,70 %
Sum	100.04 %

2.3 Alternative feedstocks for producing ethylene via steam cracking

There are several feedstock alternatives to produce ethylene. Naphtha is the most common feedstock for cracker in the European Union (Eco-profiles of the European Plastic Industry. ethylene). Other common feedstocks are ethane and liquefied petroleum gas (LPG). Methanol might be a future feedstock (LUT, 2021). Hydrotreated bio feedstock is one option. For hydrotreating there are many possible options of raw material, for example crude tall oil or vegetable oils. Chemically circulated plastic is also possible to use as a feedstock to a cracker. In this thesis, feedstocks which are used as a reference are fossil naphtha and hydrotreated vegetable oil.

Naphtha feedstock

Naphtha is a co-product of an oil refinery. Naphtha is used as a feedstock mainly in olefin production. Crude oil, which is drilled from oil fields include a wide range of hydrocarbons. In oil refinery crude oil is distilled to separate fractions. Fractions have different boiling ranges, therefore those can be separated by distillation. Naphtha fraction's boiling range is from 50°C to 190°C. (Eco-profiles of the European Plastic Industry. ethylene.)

Bio feedstocks

Bio-feedstocks can be divided in to three different generations. First-generation bio-feedstocks are typically from carbohydrate rich plants. These plants are often suitable for the food industry. Starch from different plants and edible seeds can be taken as an example. Seeds which consist of fatty acids and glycerol can be derived from plant sources, and starch in turn composed of glucose polysaccharides (Bardhan et al., 2015). Using edible crops as a feedstock to produce bio-chemicals is generally considered ethically wrong. It might increase the food price and affects its availability. (Wellenreuther & Wolf, 2020.)

Second-generation feedstocks, in turn, are non-edible ones. For example, cellulose or waste and by-products from the first-generation feedstock use. Used cooking oil and palm oil fatty acids can be taken as an example in this generation. (Wellenreuther & Wolf, 2020.)

Third-generation feedstocks are still in the early development stage. In this generation, biomass which is used as a feedstock, might be originated from municipal waste or industrial waste. Algae

can also be considered as a third-generation feedstock due to its high yield of lipids (Bardhan et al., 2015). Using these alternatives as feedstock for biochemicals is still quite expensive. In the future due to the advanced technology, these alternatives might be seriously considered feedstocks for biochemicals. (Wellenreuther & Wolf, 2020.) Figure 3 shows various biomass feedstocks in three different generations.

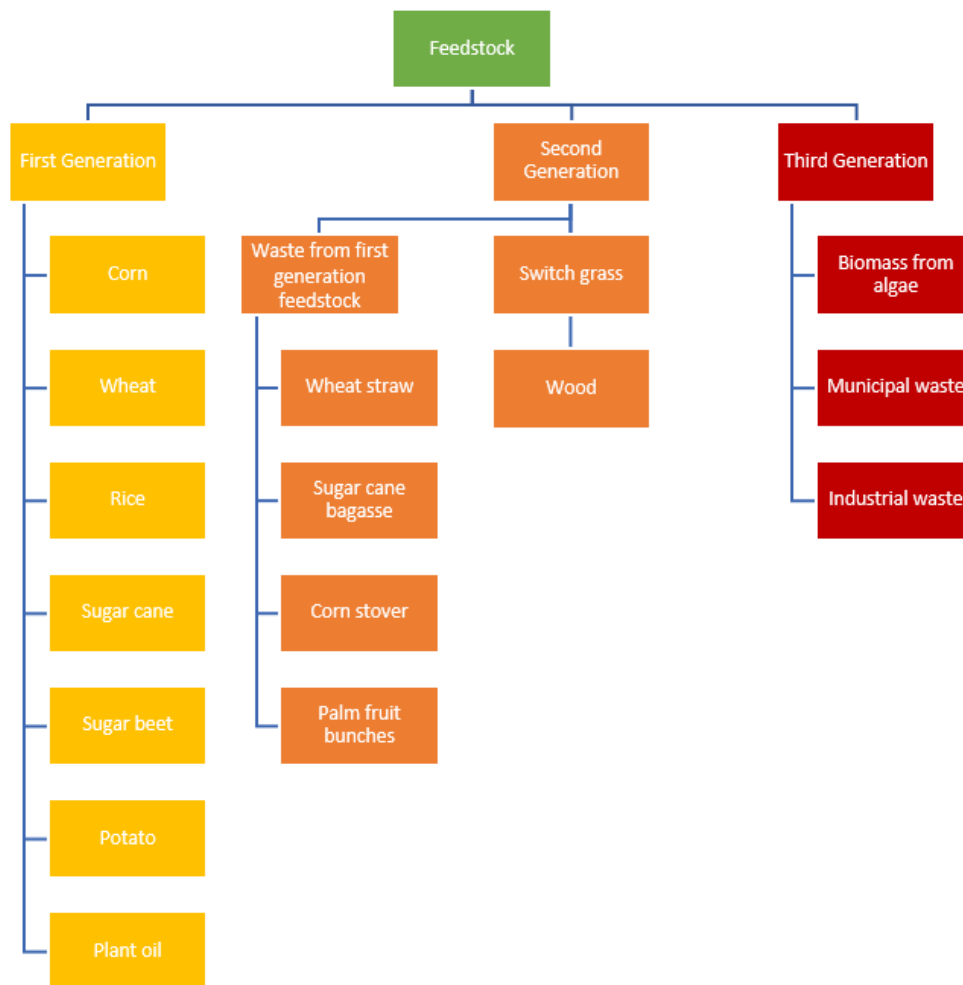


Figure 3 Examples of biomass feedstocks in three different generations (modified from Wellenreuther & Wolf, 2020.)

ISCC+ uses an alternative categorization for feedstocks. There are four categories. The first category is called bio and its feedstocks correspond to the feedstocks in the first-generation. The second category is called bio circular, and in this category, there are feedstocks such as tall oil, forestry residues, and used cooking oil. The third category which is called circular, includes waste materials of non-biological origin such as waste textiles, postindustrial CO₂, and mixed plastic waste. The fourth category is renewable-energy-derived. This category is for feedstocks which

have been derived by using renewable energy. However, biomass is not included as a renewable energy source. (ISCC Plus, 2021.) Figure 4 presents ISCC plus raw material categorization.

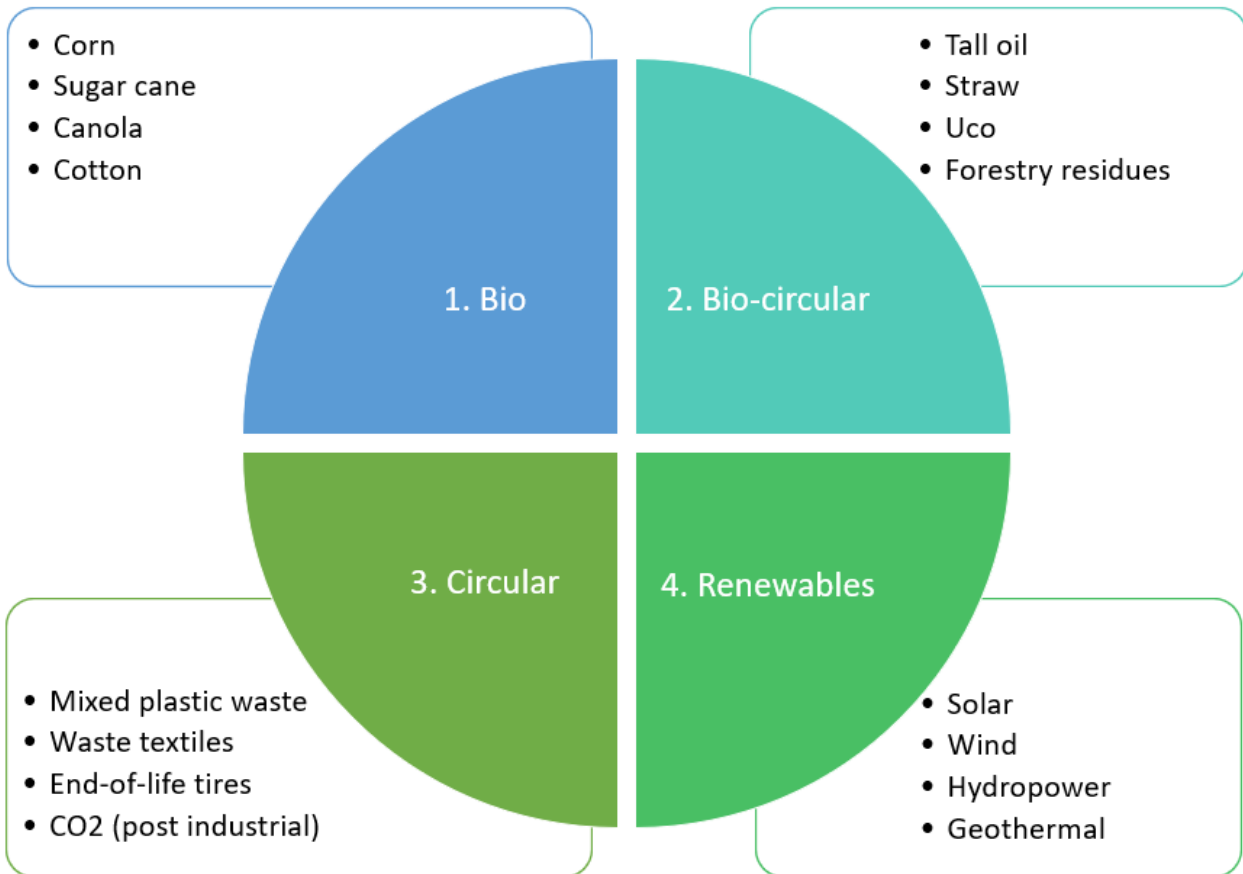


Figure 4 ISCC plus raw material categories (modified from ISCC PLUS, 2023)

Crude tall oil as a feedstock

Crude tall oil (CTO) is a by-product of pulp production. The CTO is a dark brown liquid with a sticky feature. Refined tall oil has a lighter color and oily features. (Aro & Fatehi 2017.) The CTO is used in the manufacture for example of inks, coatings and paints. It can also be used as a renewable raw material in energy production. (Cashman et al., 2016.) The CTO production is approximately around 2 million tons per year worldwide. In Europe, production is around 650,000 tons. (Rajendran et al., 2016.)

2.3.1 Hydrotreated Vegetable Oil

Hydrotreated Vegetable Oil known also as HVO is originated from time before 2010, when only vegetable oils were used as a feedstock. Nowadays HVO does not describe its origin, although change of the naming would be difficult because of its prevalence in the Europe. Today, HVO is primarily produced from the waste and residue fat fractions of the food industry, as well as non-edible vegetable oil fractions. (Neste Renewable Diesel Handbook, 2020.)

2.3.2 Bio feedstock hydrotreatment

Vegetable oils and animal fats contain impurities such as metals and those must be removed before the actual processing. Impurities are removed by using a separate pretreatment process. Vegetable oils and animal fats contain oxygen, and it must be removed before using the product for its purpose. Oxygen molecules are removed through the hydrogenation reaction. Thus, a pure hydrocarbon is obtained, which contains a high energy density. The hydrotreatment process produce the following substances: water, carbon dioxide, and renewable diesel as well as bio propane. (Neste Renewable Diesel Handbook, 2020.)

2.4 Bio feedstock GHG emissions sources and calculation method

As mentioned above, there are several different stages for producing bio-based feedstock. To obtain the total amount of generated emissions across all processing steps, it is essential to calculate the emission impact in each individual step. The GHG emission for the bio feedstocks can be calculated by following formula (3):

$$E = e_{ec} + e_l + e_p + e_{td} \quad (3)$$

Where:

E = total emissions

e_{ec} = emissions from the extraction or cultivation of raw material

e_l = annualized emissions from carbon stock changes caused by land-use change

e_p = emissions from processing

e_{td} = emissions from transport and distribution

Emissions from the cultivation of a raw material (e_{ec}) forms from related activities of agricultural and forestry. The related activities are as follows: production of fertilizers, plant protection products, seeds, fuel, electricity, collection, drying, and storage. If the raw material is waste or residue GHG emissions of the cultivation are zero. (ISCC EU 205, 2021.)

Annualized emissions from carbon stock changes caused by land-use change (e_l) are the emissions which are derived from the change of forest-, grass-, wet-land, settlements or other land to cropland or perennial cropland. Annualized emissions are calculated by subtracting the carbon stock of the actual land use from a referenced one. (ISCC EU 205, 2021.)

When counting emissions caused by processing (e_p) several emission sources should be considered. The following emission sources must be considered: electricity, heat energy, inputs, and wastewater. The total amount of the emissions consists of the sum of these emission sources. It is recommended to use the emission factors when calculating the emissions. There are several sources for the emission factors. (ISCC EU 205, 2021.)

The emissions of the transportation and distribution (e_{td}) are from the use of the fuel when transport raw materials or products. The calculation can be done by multiplying the transportation distance by the emission factor of the fuel that is used. (ISCC EU 205, 2021.)

2.5 Biogenic carbon

Biogenic carbon is the carbon that is sequestered from the atmosphere during the photosynthesis. Biogenic carbon may origin from plants, trees, algae, and other forms of biomass. According to the ISO 14067:2018 removal of the CO₂ from the atmosphere is characterized with -1 kg CO₂/kg CO₂. According to this, the CO₂ uptake from the atmosphere can be calculated by using the biogenic carbon content of the product. The amount of the Biogenic carbon varies slightly depending on the molecule formula of the product. For the olefins the carbon ratio is always the same. Thus, the amount of the biogenic carbon is always the same in the same amount of olefin product. For example, in 1kg of ethylene product the biogenic carbon amount is 0,857kg. To calculate the amount of captured CO₂ from the atmosphere the amount of biogenic carbon is multiplied by the ratio of molecular weights of CO₂ (44 g/mol) and carbon (12 g/mol) as shown in the following formula (4). (Greenhouse Gas Protocol, 2011.)

$$kg CO_2eq = kg \text{ biogenic carbon} * \left(\frac{44}{12}\right) * GWP \quad (4)$$

3 Carbon footprint definitions

3.1 Carbon footprint

Climate change is one of the impact categories in the life cycle assessment (LCA). Carbon footprint is the main driver which affect to the climate change. The carbon footprint (CFP) discloses the amount of greenhouse gases emitted by the activity of something.

To understand what the CFP study consist to it is important to have good knowhow in the most common definitions behind the CFP. In the following chapters, a few common definitions that are linked to the CFP have been explained.

3.2 Standardization

“ISO (International Organization for Standardization) is an independent, non-governmental international organization with membership of 168 national standards bodies” (ISO homepage, n.d.).

ISO conducts standardization through around 250 technical committees. All organizations have the opportunity to propose participants for the work of these committees. Finnish standardization groups' members are allowed to participate in these committees. In Finland, the decision to adopt ISO standards as national standards is voluntary. In Europe, CEN (European Committee for Standardization) chooses certain ISO standards as EN (European Norm) standards, and they are required to be embraced as national EN ISO standards by all CEN member countries. In Finland, these standards are named as SFS-EN ISO standards. *(ISO homepage, n.d..)*

“CEN (European Committee for Standardization) is an association that brings together the national standardization bodies of 34 European countries” (CEN homepage, n.d.). CEN acts as the cooperation body for standardization organizations in both EU and EFTA countries. All CEN member countries have an obligation to adopt European standards nationally, ensuring their applicability throughout the region and the replacement of any conflicting standards. European standards issued by CEN are identified with the acronym "EN.". *(CEN homepage, n.d..)*

CEN operates with more than 300 technical committees, or European standardization groups, in which Finnish standardization groups also actively participate. All member organizations have the chance to get involved in the work of these technical committees (SFS homepage, n.d..)

3.3 Life cycle assessment

The purpose of the life cycle assessment (LCA) is to increase the knowledge of the environmental impacts. LCA is a mechanism to discover how the environmental impacts could be decreased during the life cycle of a product. Likewise, the LCA providing information for a decision-making. Currently, LCA is integrated into product marketing as it generates information about the environmental aspects and impacts of the product on nature.

A complete LCA contains four different phases, which are presented in a numbered list below. Chapter 3.2.1 present the LCA phases more specifically.

1. Goal and scope definition phase
2. Life cycle inventory phase (LCI)
3. Life cycle impact assessment (LCIA)
4. Life cycle interpretation

3.3.1 LCA phases

LCA could be implement as a complete assessment or likewise a partial assessment. The difference for these two assessments is in their scope. LCA have all four phases, whereas LCI assessment have only three phases, which are: goal and scope definition phase, inventory analysis phase, and life cycle interpretation phase. However, LCI assessment should not be apply to the public references. (SFS 14040, 2006.)

Goal and scope definition phase is for to define the boundaries of the analyzed target and similarly, how detailed assessment should be generated. The level of detail depends on the purpose of the assessment. Accuracy and scope can vary extensively depending on the purpose. (SFS 14040, 2006.)

The assessment purpose should be clarified in the goal description and additionally, the reasons that led to the assessment should be provided. To define the target audience for the

communication is part of the goal definition. It is important to define if the results of the assessment are used in the public comparison argument.

Scope definition phase includes detailed scope of the target. These examples must be included to the scope definition (SFS 14040, 2006):

- Sourcing of raw materials
- Transportations
- Use of electricity
- Possible re-use of product
- Waste handling

It is important to define the functional unit of the system. Purpose of the functional unit is to normalize the input and output data (SFS 14044, 2018). An example of the functional unit is one ton of product.

The purpose of the Inventory analysis phase (LCI-phase) is to complete the inventory of the input and output data. It is extremely important to collect all essential data. (SFS 14040, 2006.) It is important to explain the methods that brings the input and output data to a quantitative format.

This point of process knowledge of the evaluated system is increasing. Therefore, there might come a reason to collect data that we did not define at the beginning. It is possible that the goal definition must be updated due to this phase. It is effective to organize the collected data under main headings to make it clearer. (SFS 14040, 2006.)

The intention of the life cycle impact assessment (LCIA) is to generate additional information that helps us better understand the environmental impacts in the final phase of the assessment (SFS 14040, 2006). Impact categories should be selected in the impact assessment phase. Examples of the impact categories are climate change and acidification.

In addition, of impact categories, impact category indicators should be selected. In the carbon footprint calculation, climate change is the impact category. An impact indicator is carbon dioxide equivalent. The purpose of the carbon dioxide equivalent is to scale all greenhouse gases together by using their global warming potentials. The global warming potential (GWP) is a characterization factor for scaling different greenhouse cases together. For example, GWP100 shows different greenhouse gases warming potential during a 100-year period. In the warming potential table factor for carbon dioxide is one whereas factor for methane is 25. (Global Warming Potential Values, 2016.) Life cycle of carbon footprint is described more in ISO 14067 standard.

Task of the last phase in the life cycle assessment is to combine results of the inventory analysis and impact assessment. These results are utilized for the decision-making as described in the first phase. Results should be in line with the goal description of the first phase. For the decision-making the results should be understandable. (SFS 14040, 2006.)

3.3.2 Critical review

It is necessary to do critical review if it is intention to use results of the assessment in a public references. The life cycle assessment as the public reference will affect to the external stakeholders and can cause misunderstanding if the critical review has not been done. To aim of the critical review is to ensure that the impact categories are sufficient, and documentation is proper. Internal or external experts should do the critical review. Experts must know the requirements of 14040 standard and have adequate experience of the topic. Similarly, stakeholders can do the critical review. By acting like this the chairperson of the group should be external and choose impartial members to the group. (SFS 14040, 2006.)

3.4 Carbon footprint study

Carbon footprint calculation bases on to the ISO 14067 standard. The standard enables to create total carbon footprint study and partial carbon footprint study. It is possible to create a total study from the partial carbon footprint studies. However, studies shall represent the same time period and the same research method. Any overlaps or gaps shall not be occurred in the calculation. Separate process units form the system and units should be organized by life cycle order. The greenhouse gas emissions and possible removals shall be allocated to those system phases where they address. Carbon footprint study should have same all four phases as total life cycle assessment. (SFS 14067, 2018.)

3.4.1 Goal of a Carbon Footprint study

The goal of a carbon footprint study (CFP) is to calculate the impact that a product has on climate warming. The impact shall be reported as a carbon dioxide equivalent (CO₂e). Carbon dioxide equivalent contains all major greenhouse gas emissions harmonized by the emission factors. The delimitations of the study should be clearly defined in the goal i.e., which units are in the scope. In total CFP study the functional unit must be defined. Declared unit is for the partial carbon footprint study e.g., one kilogram of product. Those units that have major impact to the carbon footprint shall be clarified in the study. The primary information is not always possible to be found therefore it is allowed to use secondary information for others than major units. Some of the processes could be combined e.g., transportations in the same area. The principle is that the system boundaries should include all feed and product streams. Those streams that have found to be insignificant for the carbon footprint, may be excluded from the calculation. (SFS 14067, 2018.)

3.4.2 Life cycle inventory analysis for the Carbon Footprint Study

This phase is similar than the LCA inventory analysis (LCI). At this phase, all data from the process shall be collected. Data can be obtained by being measured, calculated, or estimated. (SFS 14067, 2018.) At this point, the limits of the process can be specified by means of sensitivity analysis. If necessary, processes or life-cycle steps could be excluded from the calculation if their effect to the outcome is irrelevant. Greenhouse gas emissions from the electricity consumption shall also be included to the calculation. Emissions from the electricity consumption shall include the life cycle greenhouse gas emissions of the electricity generation system, the greenhouse gas emissions during electricity generation, and possible greenhouse gas emissions at the end of the chain. When calculate the emissions of internally produced electricity it is mandatory to use life cycle data which is based to the actual production. For externally produced electricity that comes straight from the producer it is allowed to use the greenhouse gas emission factor provided by the electricity supplier. For electricity from the grid, the ISO standard allows to use life cycle information from the supplier. (SFS 14067, 2018.) According to the standard, it is mandatory to report certain greenhouse gas emissions and removals in the carbon footprint report. Table 3 shows these documented emissions.

Table 3. Specific GHG emissions and removals documentation (SFS 14044, 2018).

Specific Greenhouse gas (GHG) emissions and removals	Treatment in the Carbon Footprint (CFP) or the partial Carbon Footprint			Documentation in the Carbon Footprint study report	
	Shall be included	Should be included	Should be considered for inclusion	Shall be documented separately in the CFP study report	Shall be documented separately in the CFP study report, if calculated
Fossil and biogenic GHG emissions and removals	X			X	
GHG emissions and removals occurring as a result of Direct Land Use Change (dLuc)	X			X	
GHG emissions and removals as a result of Indirect Land-use Change (iLUC)			X		X
GHG emissions and removals from land-use		X			X
Biogenic carbon in products					X
Aircraft GHG emissions	X			X	

3.4.3 Impact assessment for Carbon Footprint Study

At this phase, the possible climate change impact of greenhouse gas emissions or removals in each process should be calculated. For this climate change, impact is calculated by multiplying the mass of the emission or removal by the heating potential of one hundred years. IPCC (Intergovernmental Panel on Climate Change) report define these emission factors. There is no evidence for the choice of a 100-year period, but it is based on the international agreement. (SFS 14067, 2018.)

Table 4 shows the global warming heating potentials (GWP) of the most common greenhouse gases over a period of one hundred years. The table shows the GWPs of the reports for the three different periods. GWPs comes from IPCC reports. The second evaluation report is from 1995, the fourth evaluation report is from 2007 and the fifth evaluation report is from 2014. (Global Warming Potential Values, 2016.)

Table 4. Common Greenhouse gases and Global warming potential factors (Global Warming Potential Values, 2016).

Common name	Chemical formula	Global warming potentials-100 values		
		Second assessment report (SAR)	Fourth assessment report (AR4) (REDII)	Fifth assessment report (AR5)
Carbon dioxide	CO ₂	1	1	1
Methane	CH ₄	21	25	28
Nitrous oxide	N ₂ O	310	298	265

3.4.4 Interpretation of Carbon Footprint Study

In the final phase, final step is to present the main factors that have influenced to the results of the study, such as processes and flows. In the interpretation phase, presentation shall include conclusions as well as limitations. At this phase, it is important to highlight possible recommendations. The information shown in Table 5 shall be included in the carbon footprint study report. (SFS 14067, 2018.)

Table 5. Required information for the CFP study report (SFS 14067, 2018).

Required information for the Carbon Footprint study report
Functional or declared unit and reference flow
System boundary
List of important unit processes
Data collection information, including data sources
The list of GHGs taken into account
The selected characterization factors
The selected cut-off criteria and cut-offs
The selected allocation procedures
Timing of GHG emissions and removals
Description of data, decisions concerning data and assessment of data
Result of sensitivity analyses and uncertainty assessments
Treatment of electricity, which should include information on the grid emission factor calculation and relevant grid specific constraints
Result of the life cycle interpretation, including conclusions and limitations
Disclosure and justification of value choices that have been made in the context of decisions within the CFP study
Scope and modified scope
Description of the stages of the life cycle
The assessment of influence of alternative use profiles and end-of-life scenarios on the final results
Time period for which the CFP is representative
Reference of the PCR applied, or other supplementary requirements used in the study

3.5 Greenhouse gas protocol

Greenhouse gas protocol corporate standard was published in 2001. It has been built up with several different stakeholders beginning already in 1998. The GHG protocol contains two standards: GHG Corporate Accounting and Reporting Standard and GHG Protocol Project Quantification Standard. The GHG protocol provides standards and guidance to help companies to make their GHG calculations and reporting. The GHG protocol includes six different GHGs: Carbon dioxide, methane, nitrous oxide, hydrofluorocarbons, perfluorocarbons, and sulphur hexafluoride. However, it is good to note that companies may have additional requirements regarding the accounting or reporting by other programs. It is important to note that the GHG protocol provides guidance only for emission accounting and reporting parts, not for example to verification process. (Greenhouse Gas Protocol, 2015.)

4 Techniques to track and verify carbon footprint of ethylene production

4.1 Chain of custody

Purpose of this chapter is to illuminate the techniques which are mainly used to define the carbon footprint in the petrochemical industry. It is important that the generated greenhouse gas emissions can be calculated over the entire product's life cycle. Tracing the product's life cycle acts a really important role when calculating the carbon footprint.

Chain of custody (CoC) is a general term that is used of models which creates transparency and thrust of the entire value chain. It is an overall process which tracks very precisely all the origin evidence movements in the life cycle of the product. All persons who have handled these evidences are documented. Through the CoC it is possible to track afterwards the origin of every step in the life cycle. Mass balance is one of the five chain of custody models. Chain of custody models have been generated to enable traceability of sustainable produced materials. (Beers et al., 2022.)

Mass balance

Using a mass balance (MB) as to proof the sustainability in the polymer sector in the Europe is common. The MB-system is in use because of the complexity of the processes and the processes are typically fully integrated, thus the MB is the simplest way to track the inputs and outputs. Due to the complexity of the processes, it is not possible to make fully transition to the sustainable feedstock. Therefore, the MB-system enables the partial transition to the sustainable feedstocks. The MB system also ensures for the petrochemical companies the possibility to verify that the sustainable product regulations are meet. Six different certification programs in the world uses the MB system to certify circular, recycled and sustainable polymers. The MB-system has been designed to track the desired content through to the production system. The desired content might be for example bio feedstock. The MB-system ensures that bio feedstock is allocated correctly to the products based on a bookkeeping which is audited by the external parties. The MB-system enables to blend circular feedstock and fossil feedstock together. Circular feedstock which is fed to the production system generates credits by mass basis. Credits are then uncoupled during the production phase and reassigned to the products. The MB-system ensures that outputs of the process does not exceed the original inputs. (Beers et al., 2022.)

4.2 ISCC

“The International Sustainability and Carbon Certification (ISCC) is an independent multistakeholder initiative and leading certification system supporting sustainable, fully traceable, deforestation-free and climate-friendly supply chains” (ISCC homepage, n.d.).

ISCC certificate covers several bio-based materials for example forest biomass, biogenic waste and residues, and recycled carbon-based ones. ISCC focus to reduce the GHGs in the value chain and more sustainable land use. The companies which are certified by ISCC can proof to their customers that their products have been produced from the sustainable raw materials. ISCC uses chain of custody MB model to track the amount and sustainability of the bio based or circular based material in the value chain. ISCC has several different certification schemes. For example, ISCC EU controls compliance of GHG savings criteria for the raw materials and fuels which have been mentioned in RED II directive. (ISCC EU 102, 2021.)

ISCC+ is part of ISCC certification system. ISCC+ is certificate for the markets and sectors which are not covered by REDII directive. ISCC+ certificate covers all types of wastes and residues as well as agricultural and forestry raw materials. Three different raw material categories can be certified by ISCC plus. These are bio feedstocks, circular feedstocks, and renewable feedstocks. With the chain of custody mass balance system, it is possible to track the amount of different feedstocks and their allocations to products. ISCC+ certification system prevents double counting of used sustainable feedstocks and produced products. (ISCC Plus, 2021.)

For attributing the correct output of sustainable product ISCC+ uses a conversion factor (CF). The conversion factor ensures that the outgoing sustainable product does not exceed the incoming volume of sustainable feedstock. (ISCC Plus, 2021.) Conversion factor can be calculated by the following formula (5):

$$CF = \frac{\text{Total amount of output}}{\text{Total amount of input}} \quad (5)$$

5 Allocation as an instrument on Carbon Footprint

In allocation, all inputs and outputs are split between products by using one of the allocation parameter. It is forbidden to allocate any share of emissions to the waste or residues. There are several sources that provide the standards for products, co-products and intermediates allocation methods. ISO 14040:2006 and ISO 14044:2006 allocation methods can be summarized in the three different categories. Prior one is to use the system subdivision. It means that if it is possible, the process should be divided in the separate sub processes. The input and output data can then be collected for each sub-process. Or another way is to use the system expansion. The system expansion shall take in place if it is possible to include co-product facilities in the boundaries. Prior two is to use the physical relationship allocation. The most used physical relationship allocation parameters are mass, energy and stoichiometry. If neither of previous methods are valid economic allocation can be utilized. (SFS 14067, 2018.) Figure 5 illustrates the physical allocation of steam cracking based on mass. In the figure, the proportions of different fractions relative to the feed are depicted in percentages based on Young et al., (2022). The figure also displays typical reaction equations for the cracking process.

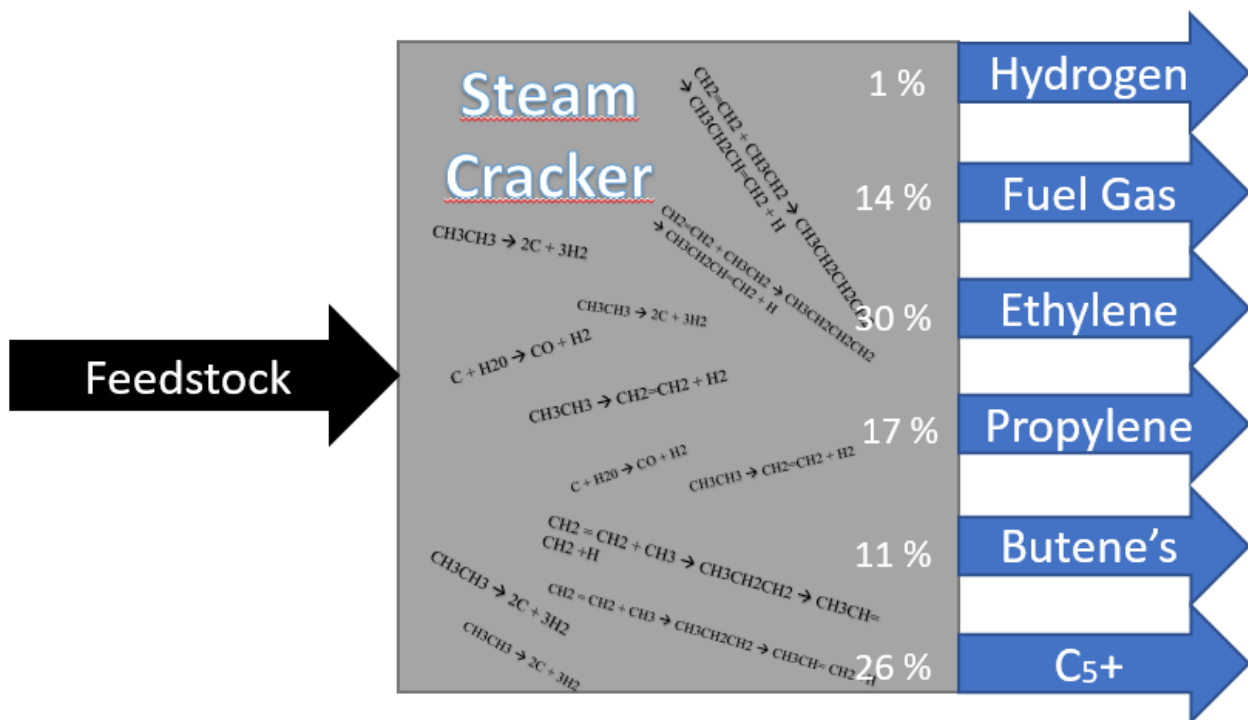


Figure 5 Mass yields of steam cracker

PlasticsEurope has made recommendation on a steam cracker allocation. It has been made by the PlasticsEurope sustainability working group and other experts. Main points of the recommendation are linked to the main- and co-product allocation. It is important to allocate the GHG emission only to the main products. It ensures that the different studies are comparable. The recommendation also guides to use mass allocation when the GHGs are allocated to the main products. According to the PlasticsEurope, the main products of the cracker are as follows. (PlasticsEurope, 2017.)

- Ethylene
- Propylene
- Benzene (*)
- Butadiene (*)
- Hydrogen
- Toluene (*)
- Xylene (*)
- Butene's

(*) if it is separate stream

In addition to this, one method is to allocate the GHG emission only to the prime olefins which are Ethylene and Propylene.

5.1 Feedstock factor (*FF*)

Feedstock factor describes by mass-based product relation to the feedstock. The feedstock factor is needed to point out the feedstock related incoming GHG emissions. When the feedstock emission factor is in of kgCO₂eq/kg feedstock form it is necessary to use the *FF* to show the total amount of emission related to the products. (ISCC EU 205, 2022.)

The feedstock factor can be calculated by using yields. Formula (6) describes the calculation of the feedstock factor.

$$FF = \frac{\text{Total amount of feedstock (ton)}}{\text{Total amount of product (ton)}} \quad (6)$$

5.2 Emission factors (EF)

Emission factors (EF) help the calculation when calculate the GHG emissions for the complex entities like petrochemical plant. As mentioned in ISO 14067 standard it is allowed to use the secondary data if primary data is not possible to use. Therefore, it is allowed to use the EFs from reliable sources for example RED II, Ecoinvent or other peer reviewed literature. Various emission sources have different EFs. The EFs show the amount of emission in relation to amount of selected input. There are several sources where to find different EFs. The result of the calculation can vary a lot depending on the chosen EFs. The chosen EFs should reflect to the target. If the target scope is in the Europe, then the chosen EF should reflect to the European situation. EFs for the energy supply must include both direct and indirect emissions. Direct emissions mainly consist of emissions from combustion. Indirect emissions are from upstream. A few EFs from different sources are listed in Table 6, these are useful when calculating emissions to petrochemical industry. (ISCC EU 205, 2022.)

Table 6. Emission factors for petrochemical industry

Process water	0,3418	kgCO ₂ eq/M3	Europe without Switzerland	Ecoinvent v. 3.7 2020 market for tap water
Electricity	383	kgCO ₂ eq/MWh	EU	JEC Well to tank report v5, 2020
Electricity	99	kgCO ₂ eq/MWh	Finland	Finnish Energy agency. 2020:
Electricity	285,32	kgCO ₂ eq/MWh	Finland	AIB. 2021: residual distribution
Heat from boiler (NG)	250,2036	kgCO ₂ eq/MWh	Europe without Switzerland	Ecoinvent v. 3.7, 2020: heat production, natural gas, at industrial furnace >100kW
Ethylene from fossil source	1,44	kgCO ₂ eq/kg product	Allocation to HVC only	PlasticsEurope Ethylene Ecoprofile
Ethylene from fossil source	1,3	kgCO ₂ eq/kg product	USA hydrogen as a by-product	Young et al., 2022
HVO	0,45	kgCO ₂ eq/kg hvo	Raw material UCO,PFAD,AF,Fish fat	Tähkämö, et al., 2022
Naphtha	0,345	kgCO ₂ eq/kg naphtha	Fossil based naphtha	PlasticsEurope Naphtha Eco-profile
Cracker	0,485	kgCO ₂ eq/kg product	Industrial average	Young et al., 2022
CTO	0,74	kgCO ₂ eq/kg	CTO distillation product Europe	Cashman, et al., 2016

6 Comparison carbon footprint of different feedstocks by different allocation methods

6.1 Goal and scope definition

The aim of this study is to compare the different allocation methods. By the comparison, it is aimed to illustrate the CFP variation of these feedstocks and allocation methods. The purpose is to demonstrate step by step how the CFP calculation is done for a certain entity by using the emission factors from the literature sources.

The study has been done by using the gate-to-gate system boundaries. Inside of the boundaries are bio feed production, naphtha production, and steam cracker process. Direct emissions are the emissions from the cracker process. Indirect emissions are the emissions from the energy generation by external supplier and the emissions from feedstock facilities. Figure 6 presents which facilities are included to the study.

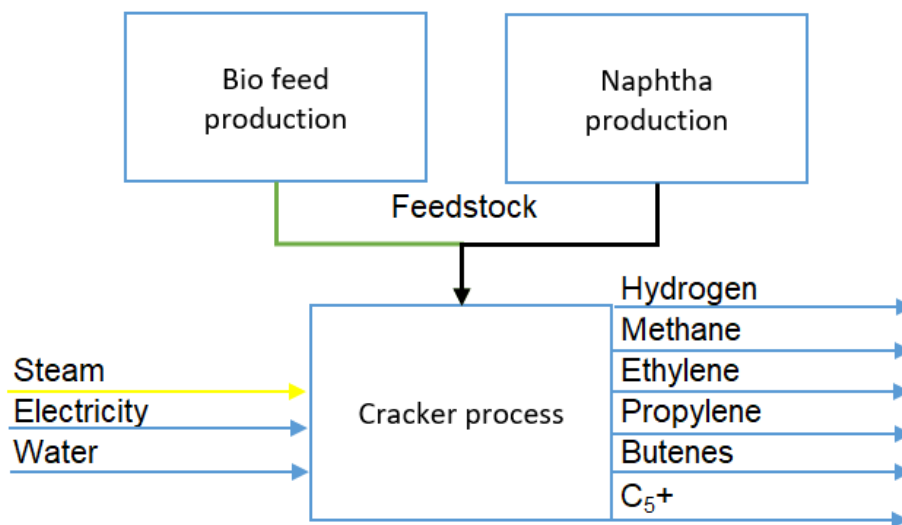


Figure 6 Boundaries of the study

6.2 Allocation alternatives for steam cracker products

In this study the purpose is to compare three different allocation methods. These different allocation methods are based on Young et al., 2022 typical yields of the naphtha feedstock. One method is to allocate the generated emissions to all-products. The all-product allocation contains typical cracker products, however the streams which are used as a fuel like fuel gas and fuel oil has been

extracted from the list. According to the PlasticsEurope recommendation an additional products such as fuels shall not take any environmental burdens. (PlasticsEurope, 2017.) The prime olefins allocation includes only ethylene and propylene. These allocation methods are presented in Table 6. All the numbers are calculated by supposition that feedstock is 100 kg.

Table 7. different allocation alternatives

	All-Product	Prime Olefins	PlasticsEurope recommendation (HVC)
Hydrogen	1		1
Ethylene	30	30	30
Propylene	17	17	17
C4	11		11 (butene + butadiene)
C5+	23		10 (Benzene+Toluene+Xylenes)
Sum	82	47	69

By using assumption that feed is 100 kg it is possible to calculate the feedstock factor of this study. The feedstock factor can be calculated as shown previously. According to the following formula (7) the feedstock factor of this study is 1,22.

$$FF = \frac{100 \text{ kg}}{82 \text{ kg}} = 1,22 \quad (7)$$

6.3 Functional unit/declared unit

The declared unit of this study is 1 kg of steam cracker product. In this study, 100 kg feedstock is used to calculate both the incoming emissions and the emissions emitted by the cracker process.

6.4 Emission factors used in this study

The required emission factors for calculating total emissions of producing 1 kg of product at steam cracker are listed in table 6. These emission factors are collected from different literature sources. Emission factors vary somewhat depending on their source.

The emission factor for HVO is calculated based on the emissions generated during the HVO production steps. This factor is based on the LCA of renewable hydrocarbons which are derived from bio-based waste and residues. Shares of used feedstock in this LCA study was as follows: 33% of used cooking oil (UCO), 33% of animal fat (AF), 33% of palm fatty acid distillate (PFAD), and 1% of fish fat. UCO, AF, and fish fat considered as waste in this LCA study so burden of production those feedstocks is zero. The hydrotreating process selected for this LCA study was Neste's patented technology known as the NEXBTL process. (Tähkämö et al. 2022.)

Functional unit in this LCA study was 1 kg of renewable liquid hydrocarbons. Allocations have been made in several points. The emissions from PFAD production have been allocated economically between palm oil and PFAD. The products from the NEXBTL process have been allocated based on energy content. Conclusion of this LCA study was that the cradle-to-gate climate impact of renewable liquid hydrocarbons is 0,45 kg CO₂-eq / kg, without the biogenic GHG removal. Cradle to gate climate impact was -2,65 kg CO₂-eq / kg with the biogenic GHG removal. (Tähkämö et al. 2022.)

Naphtha emission factor is based on PlasticsEurope naphtha eco profile. The naphtha eco profile includes emissions from the crude oil feedstock production and delivery to the refinery. Oil refinery emission data itself is from seven different oil refinery and from Internal Energy Agency's world data. CO₂ and CH₄ emission data have been converted to CO₂ equivalent using the GWP-100 values from the Second Assessment Report. The emissions from producing naphtha consists of four distinct steps. 0,134 (kgCO₂eq/kg naphtha) from the fuel production, 0,092 (kgCO₂eq/kg naphtha) from the fuel use, 0,006 (kgCO₂eq/kg naphtha) from the transportation, and 0,113 (kgCO₂eq/kg naphtha) from the process. (PlasticsEurope, 2005.)

Cracker emission factor is calculated from the data which is based on PlasticsEurope ethylene eco profile. Cracker emission factor consists of emissions from the cracker process and from the used

electricity. According to the PlasticsEurope ethylene eco profile emission factor per 1 kg of product is 1,21 kg CO₂eq if emissions are allocated to the all-cracker products. (PlasticsEurope, 2012.)

Based on the ethylene eco profile, the emission factor comprises a distribution of 64 % from the cracker and 36 % from the naphtha production. Cracker share of the total emission is 0,774 (kg CO₂eq/kg product) and the naphtha share is (0,436 kg CO₂eq/kg product). In the ethylene eco profile allocation method for the total emission impact 1,21 (kg CO₂eq/kg product) was all-product. If the feedstock factor from this study is utilized, which was 1.22, the naphtha emission factor is 0,357 (kg CO₂eq/kg feedstock). This value is comparable to the naphtha eco profile's emission factor of 0,345 (kg CO₂eq/kg naphtha). (PlasticsEurope, 2012.)

Feedstock related emission factor for the cracker, when using feedstock factor of this study, is 0,635 (kg CO₂eq/kg feedstock). All the emission factors used in this study are presented in Table 8.

Table 8. Emission factors used for calculations according to different allocation methods.

	Emission factor	Unit	Comments	Source
HVO	0,45	kgCO ₂ eq/kg hvo	UCO, PFAD, AF, Fish fat	Leena Tähkämö. et al., 2022
Naphtha	0,345	kgCO ₂ eq/kg naphtha	Fossil based naphtha	PlasticsEurope naphtha eco-profile
Cracker	0,635	kgCO ₂ eq/kg feedstock	Calculated from ethylene eco profile	PlasticsEurope ethylene eco profile

6.4.1 Naphtha feedstock

100 % naphtha as a feedstock carries the emission impact which has been incurred as stated above. 100 kg of naphtha feed carries 100 times of emission impact comparing to the emission factor. Thus, total emission impact of the naphtha feed is calculated by using the following formula (8).

$$100(kg_f) * 0,345 \left(\frac{kgCO_2eq}{kg \text{ feedstock}} \right) = 34,5(kgCO_2eq) \quad (8)$$

Generated emissions from the cracker process itself can be calculated by using the emission factor for cracker. Cracking 100 kg of feedstock generates emissions as calculated in the following formula (9).

$$100(kg_f) * 0,635 \left(\frac{kgCO_2eq}{kg \text{ feedstock}} \right) = 63,5 (kgCO_2eq) \quad (9)$$

34,5 kg impact of CO₂eq when using the naphtha emission factor. Cracker process itself gives 63,5 kg impact of CO₂eq. Totally 100 kg of cracker feedstock generates 98 kg impact of CO₂eq when using literature-based emission factors.

The following formula (10) shows the impact if emissions are allocated to all cracker product:

$$\frac{98(kgCO_2eq)}{82(kg_p)} = 1,20 \left(\frac{kgCO_2eq}{kg_p} \right) \quad (10)$$

When comparing the results of this study with the ethylene eco profile, a slight difference can be noticed. The slight difference is due of using different naphtha emission factor than in the ethylene eco profile.

Allocation of the emissions from naphtha feedstock

The total emission impact can be allocated using the selected allocation method. Total amount of emissions is divided by the total amount of product in the chosen allocation method.

PlasticsEurope recommendation

$$\frac{98(\text{kgCO}_2\text{eq})}{69(\text{kg}_p)} = 1,42 \left(\frac{\text{kgCO}_2\text{eq}}{\text{kg}_p} \right) \quad (11)$$

Prime olefins

$$\frac{98(\text{kgCO}_2\text{eq})}{47(\text{kg}_p)} = 2,09 \left(\frac{\text{kgCO}_2\text{eq}}{\text{kg}_p} \right) \quad (12)$$

When emissions are allocated regarding to the recommendation of plasticsEurope the result is 1,42 (kg CO₂eq/kg product). Allocation only to the prime olefins gives result of 2,09 (kg CO₂eq/kg product). The CFP is 74 % higher if the emissions are allocated to prime olefins only than if the emissions are allocated to all-product. The CFP is 18% higher when emissions are allocated according to the plasticsEurope recommendation compared to the all-product allocation method.

6.4.2 Bio feedstock

Emissions for the bio-based ethylene can be calculated similarly to naphtha-based emissions. 100 % HVO as a feedstock carries the emission impact which has been incurred as stated above. 100 kg of HVO feedstock carries 100 times of emission impact comparing to the HVO emission factor. Thus, the total emission impact of HVO feedstock can be calculated by using emission factor of the HVO feedstock.

$$100(kg_f) * 0,45 \left(\frac{kgCO_2eq}{kg \text{ feedstock}} \right) = 45 (kgCO_2eq) \quad (13)$$

The assumption is that the cracker process generates the same amount of emissions despite its feedstock when emissions are allocated to the products. It is also stated above that the naphtha and the bio feedstock are similar regarding the boiling point range.

$$100(kg_f) * 0,635 \left(\frac{kgCO_2eq}{kg \text{ feedstock}} \right) = 63,5 (kgCO_2eq) \quad (14)$$

Feedstock carries 45 kg impact of CO₂eq when using the HVO emission factor. The cracker process itself gives 63,5 kg impact of CO₂eq. Totally 100 kg of HVO based cracker feedstock gives 108,5 kg impact of CO₂eq when using the literature-based emission factors. It is important to notice that this result is without the biogenic GHG removal.

The following formula (15) shows the impact if emissions are allocated to all cracker product:

$$\frac{108,5 (kgCO_2eq)}{82(unit_p)} = 1,32 \left(\frac{kgCO_2eq}{unit_p} \right) \quad (15)$$

When comparing the result without biogenic GHG removal it can be noticed that it is slightly larger than the fossil based one. This is due to its slightly larger EF than the naphtha one.

Allocation of the emissions from the bio-feedstock

Total emission impact can be allocated similarly as above in naphtha case.

PlasticsEurope recommendation (16)

$$\frac{108,5 \text{ (kgCO}_2\text{eq)}}{69 \text{ (kg}_p\text{)}} = 1,57 \left(\frac{\text{kgCO}_2\text{eq}}{\text{kg}_p} \right) \quad (16)$$

Prime olefins (17)

$$\frac{108,5 \text{ (kgCO}_2\text{eq)}}{47 \text{ (kg}_p\text{)}} = 2,31 \left(\frac{\text{kgCO}_2\text{eq}}{\text{kg}_p} \right) \quad (17)$$

In order to calculate how much carbon dioxide is bound in the 1 kg of bio-based ethylene, it is necessary to know the proportion of the biogenic carbon in the product. At this case feedstock was 100 % bio based, thus the biogenic carbon proportion of the product is also 100%. Content of the biogenic carbon can be calculated using the atomic weights of carbon and hydrogen. Atomic weight for carbon is 12 g/mol and for hydrogen 1 g/mol. Ethylene molecular formula is C₂H₄, thus the molecular weight for the ethylene is 28 g/mol. Carbon content can be calculated by following formula (18):

$$C \% = \frac{C_2}{C_2H_4} = \frac{24}{28} = 0,857\% \quad (18)$$

In order to further calculate the amount of bounded carbon dioxide, it is necessary to calculate molecular weight for the carbon dioxide. Carbon dioxide molecular formula is CO₂. Atomic weight for oxygen is 16 g/mol, thus molecular weight for the carbon dioxide is 44 g/mol. The amount of sequestered carbon dioxide can be calculated by using the following formula (19) and using carbon dioxide to carbon ratio.

$$C \% * \frac{CO_2}{C} = 0,857 * \frac{44}{12} = 3,14 \text{ kg } CO_2 \quad (19)$$

Emission impact for the 100% bio-based feedstock produced ethylene was 1,57 (kg CO₂eq/kg ethylene) when allocated according to the PlasticsEurope recommendation and 2,31 (kg CO₂eq/kg ethylene) when emissions was allocated only to the prime olefins. With biogenic GHG removal emission impact is -1,57 (kg CO₂eq/kg ethylene) when allocation is according to the PlasticsEurope recommendation and -0,83 (kg CO₂eq/kg ethylene) when emissions are allocated only to the prime olefins. For the all-cracker products with the biogenic GHG removal the impact is -1,82 (kg CO₂eq/kg ethylene).

6.4.3 Bio feedstock allocations using mass balance approach

If using the mass balance, there are three different methods to allocate the bio share of the feedstock to the products. First method is called a proportional allocation and it means that the GHG emissions are allocated to all-product by the yields (Beers et al., 2022.) Example of proportional allocation is presented at figure 7.

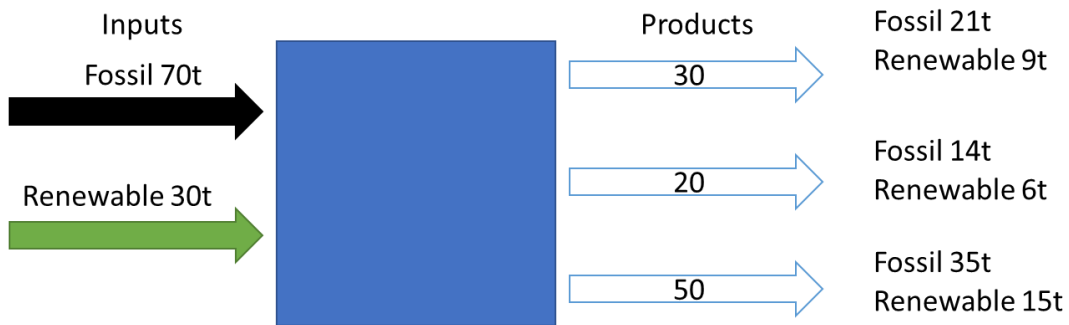


Figure 7 Illustration of proportional allocation (modified from Beers et al., 2022)

Second method is called a non-proportional or a free allocation and it means that GHG emissions can be freely allocated to the end-products. For example, it is possible to allocate all GHG emissions to a single product. Of course, if 100% of the emissions are allocated to the single product only 0% can be allocated to the other products. (Beers et al., 2022.) Example of non-proportional allocation is presented at figure 8.

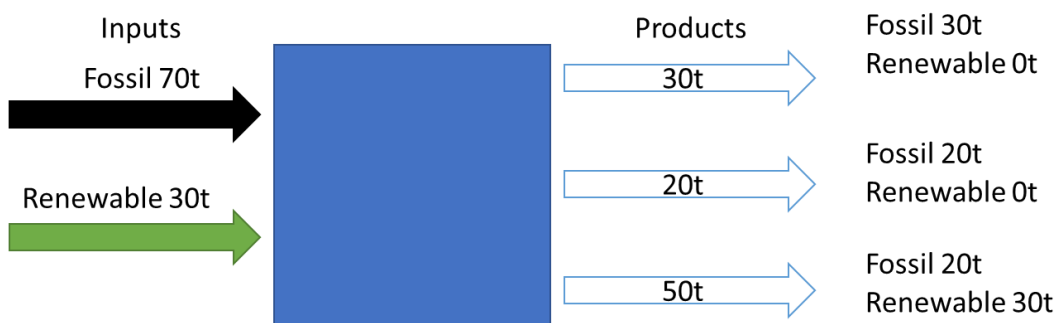


Figure 8 Illustration of non-proportional allocation (modified from Beers et al., 2022)

Third method to allocate bio share is non-proportional fuels exempt method also called a free allocation fuel exempt. This method enables to allocate the bio based GHG emissions to the fuel gas. Though the method ensures that no double counting have been made. (Beers et al., 2022.) Example of free allocation fuels exempt is presented at figure 9.

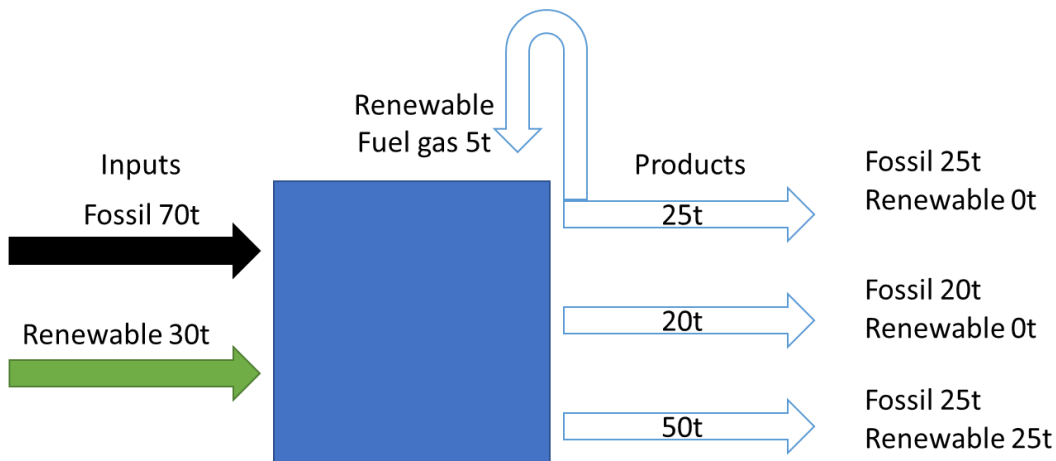


Figure 9 Illustration of non-proportional fuels exempt allocation (modified from Beers et al., 2022)

Through these examples it is possible to calculate the emission impact when 30% of feedstock is bio based and 70% is naphtha based. Total emission impact of the mixed feedstock can be calculated by following:

Bio feedstock:

$$30(kg_f) * 0,45 \left(\frac{kgCO_2eq}{kg\ feedstock} \right) = 13,5(kgCO_2eq) \quad (20)$$

Naphtha feedstock:

$$70(kg_f) * 0,345 \left(\frac{kgCO_2eq}{kg\ feedstock} \right) = 24,15(kgCO_2eq) \quad (21)$$

Cracker:

$$100(kg_f) * 0,635 \left(\frac{kgCO_2eq}{kg\ feedstock} \right) = 63,5 (kgCO_2eq) \quad (22)$$

Formula (23) is shown the result if allocation is for the prime olefins and using the proportional allocation for the bio share.

$$\frac{101,5 \text{ (kgCO}_2\text{eq)}}{47(\text{kg}_p)} = 2,15 \left(\frac{\text{kgCO}_2\text{eq}}{\text{kg}_p} \right) \quad (23)$$

In this case 1 kg of ethylene product the biogenic carbon content is 30 %, which correspond 0,257 kg of biogenic carbon in 1 kg of product. if calculate the corresponded CO₂ amount, it is 0,942 kg. With the biogenic GHG removal emission impact is 1,21 (kg CO₂eq/kg ethylene).

If allocation is done according to the PlasticsEurope recommendation and whole bio content is allocated to the ethylene which the non-proportional allocation allows.

$$\frac{101,5 \text{ (kgCO}_2\text{eq)}}{69(\text{kg}_p)} = 1,47 \left(\frac{\text{kgCO}_2\text{eq}}{\text{kg}_p} \right) \quad (24)$$

If the whole bio content is allocated to the ethylene. In this case 1 kg of ethylene product biogenic carbon content is 100%, which correspond 0,857 kg of biogenic carbon in 1 kg of ethylene product. The calculated corresponded CO₂ uptake amount is 3,14 kg. With biogenic GHG removal emission impact is -1,67 (kg CO₂eq/kg ethylene). If using the proportional allocation, the biogenic carbon content is the same as in the prime olefin case. Thus, with the biogenic GHG removal impact is 0,53 (kg CO₂eq/kg ethylene).

6.5 Comparison of the footprints

In this chapter the purpose is to compare footprints with different allocation methods and footprints from different feedstock. All the footprints differ depending on their feedstock and the chosen allocation method.

First, comparing the 100% naphtha feedstock case and its allocation methods. The CFP increases from 1,42 (kg CO₂eq/kg ethylene) to 2,09 (kg CO₂eq/kg ethylene) when allocation method was changed from the PlasticsEurope to prime olefins. The difference is due to the different mass content of the allocation methods. In the PlasticsEurope case a larger mass of products carries the same burden, thus the emission per kilogram is lower.

When comparing the 100% bio-based feedstock case and its allocation methods. The CFP increases from 1,57 (kg CO₂eq/kg ethylene) to 2,31 (kg CO₂eq/kg ethylene) when allocation method was changed from the PlasticsEurope to prime olefins. If comparing the naphtha-based and bio-based CFP, bio-based CFP is 11% higher without the biogenic GHG removal than naphtha-based one. This is due to slightly higher emission factor for the bio-based feedstock than naphtha-based one.

With the biogenic GHG removal the CFP from the bio-based feedstock decreases from 1,42 (kg CO₂eq/kg ethylene) to -1,57 (kg CO₂eq/kg ethylene) if comparing naphtha-based feedstock and bio-based feedstock in the PlasticsEurope allocation. In prime olefins allocation the CFP decreases from 2,09 (kg CO₂eq/kg ethylene) to -0,83 (kg CO₂eq/kg ethylene).

If examine CFPs from the 30% bio-based feedstock case and PlasticsEurope allocation where total bio share has been allocated to the ethylene product it can be noticed that the CFP with biogenic GHG removal is slightly lower than from the 100 % bio-based feedstock.

When comparing the proportional and non-proportional allocation methods it can be noticed that the emission impact per 1 kg of ethylene product varies from 0,53 to -1,67 depending how the bio share is allocated.

7 Conclusions

The objective of this thesis was to provide answers to the three separate research questions and thus illustrate the factors behind the CFP that affect the final outcome of the CFP. Due to the big effect to the climate change which plastic industry have, it is very important that the CFPs are comparable with each other. Through the comparable CFPs it can be truly find those solutions which helps to reduce the emissions. The transparency and critical review of the CFP study is necessity so that customers can really choose the more sustainable choices. However, in this thesis, no critical evaluation was conducted, as the emission factors are derived from LCAs where critical evaluation has been performed.

First research question was to calculate the CFP for bio-based ethylene and present the results with three different allocation method. The thesis was able to demonstrate the difference between these three allocation methods by using literature-based emission factors. The emission impact for bio-based ethylene by different allocation methods with and without the biogenic GHG removal is presented in Table 9.

Table 9. Calculated CFP for bio-based ethylene.

Allocation method	100% HVO (without biogenic GHG removal)	100% HVO (with biogenic GHG removal)	
All-Product	1,32	-1,82	(Kg CO ₂ eq/kg ethylene)
PlasticsEurope	1,57	-1,57	(Kg CO ₂ eq/kg ethylene)
Prime Olefins	2,31	-0,83	(Kg CO ₂ eq/kg ethylene)

The CFP from naphtha-based feedstock was able to be calculated by using literature-based emission factors. The CFP from naphtha-based feedstock corresponded the literature one. Thus, the counted CFP is assumed to be correct. The CFP for naphtha-based ethylene is presented in Table 10.

Table 10. Calculated CFP for naphtha-based ethylene.

Allocation method	100% Naphtha	
All-Product	1,2	(Kg CO ₂ eq/kg ethylene)
PlasticsEurope	1,42	(Kg CO ₂ eq/kg ethylene)
Prime Olefins	2,09	(Kg CO ₂ eq/kg ethylene)

The thesis was able to answer also to the last research question which concerned the CFP from bio-based feedstock by using proportional and non-proportional (free) allocation methods. Through the mass balance approach, it was possible to show the difference of CFP in proportional allocation and non-proportional allocation. Table 11 presents the emission impact by using proportional and non-proportional allocation methods.

Table 11. Calculated CFP for mixed feedstock

Allocation method	30% Bio proportional (with biogenic GHG removal)	30% Bio non-proportional (with biogenic GHG removal) *	
PlasticsEurope	0,53	-1,67	(Kg CO ₂ eq/kg ethylene)

*Bioshare is allocated totally to the ethylene

The results of this thesis do not significantly differ from the ethylene ecoprofile's findings. The emission impacts per kilogram of ethylene are approximately the same for both all-product and when allocated according to the PlasticsEurope recommendation. During the data collection process, a surprising variation in emission factors and carbon footprints was observed, possibly due to regional and process-specific differences.

Reliability assessment

In the thesis, life cycle assessments that have been critically evaluated and regionally represent Europe have been used as sources. The product distribution of the cracking process has been based on the typical product distribution of the cracking process with naphtha feedstock, as indicated by the source. The sources used in the work are primarily peer-reviewed, and efforts have been made to utilize the most current sources available. Each process is unique, resulting in distinct carbon footprints; therefore, the results are not directly comparable to those of other studies.

8 Discussion

As shown in this study, the results of the carbon footprint analysis vary significantly depending on the feedstock and allocation method. Bio-based feedstock can be produced from various sources and all different sources have different footprint. In addition, the current legislation of wastes and residues affects to the CFP of bio-based feedstock. The biggest difference for the CFP of bio-based feedstock in comparison to fossil one is that the carbon which contain in the products is from the atmosphere and thus not increase the amount of carbon dioxide in the atmosphere.

A wide range of literature sources made difficulties to complete this study. In my opinion, the standards and guidelines are still too permissive, which means a very widespread in carbon footprints, depending on which emission factors and allocation methods have been used. From an ethical standpoint, the more transparently the emission factors and the calculations behind the allocations are presented, the easier it is for the reader to evaluate the outcome from their own perspective. According to the current legislation and guidelines feedstock from the waste and residues seems to carry the smallest burden of environment impact. More precise regulations regarding the use of the emission factors and the allocation of emissions would standardize the results of the carbon footprint calculations.

Next, it would be interesting to calculate in more detail what kind of effects the bio-feed has in terms of the cracker's direct emissions, if part of the bio-feedstock were allocated to the fuel gas. However, this would require more precise calculations regarding the cracker's energy consumption. However, I would believe that there are currently no economic grounds that would support the allocation of emission reductions to fuel gas instead of the products, due to the free emission rights distributed to the companies.

During this thesis I have learned a lot about the guidelines and regulations related to the carbon footprint calculation. With the knowledge that I have gained by doing this thesis work, it is easier to understand the background of various carbon footprint calculations.

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