Life cycle assessment of bio-based sodium poly-acrylate production from pulp mill side streams-Case at a TMP and sulphite pulp mill

Master's Thesis within Industrial Ecology programme

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Cover:
Photograph of Domsjo pulp mill

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Abstract

Sodium poly-acrylate is a super absorbent polymer which can be used in diverse hygiene products. The polymer is currently produced from fossil feedstock. The environmental issues and the depletion of fossil resources are the main drivers for exploring a more sustainable polymer product. Thus, integrating the production of the sodium-poly-acrylate in two different pulp mills (Ortviken pulp and paper mill in Sundsvall, and the Domsjö pulp mill in Örnsköldsvik) can potentially be a successful way to achieve sustainability. The main innovative part of the development is the conversion of the hemicellulose, derived from five diluted side streams into 3-hydroxypropionic (3-HP) acid by genetically modified yeasts developed at Chalmers.

In order to reveal the environmental tradeoffs between renewable, bio-based and non-renewable, fossil based sodium poly-acrylate a comparative, cradle-to-gate life cycle assessment (LCA) was conducted. For bio-based polymers, forestry activities, pulp and paper mills operations, acrylic acid production (including: concentration, hydrolysis, and detoxification of the side streams; fermentation of the free sugars; recovery, dehydration and distillation of 3-HP), and the polymerization of acrylic acid were the production steps considered in this study. The goals of the LCA study were: 1) to compare the renewable, bio-based and non-renewable, fossil based production of sodium poly-acrylate; 2) to identify the environmental hotspots at a very early stage of the development.

According to the results three of the bio-based polymers have a lower global warming potential (GWP) than the fossil-based polymer. However, the fossil-based polymer shows a lower environmental impact than its bio-based counterparts for three of the other environmental impact categories considered (acidification potential, eutrophication potential, and photochemical ozone creation potential). For the polymers produced at Ortviken, the concentration of the side streams is the hotspot identified. For the polymers produced at Domsjö, the hotspots identified are the detoxification, fermentation and recovery processes. Forestry activities, pulp mill operations, dehydration and distillation processes have very small contribution to the overall environmental impacts.

Key words: Sodium poly-acrylate, Pulp mills, Life cycle assessment, Biorefinery, Superabsorbent

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Abbreviation

3-HP	3 hydroxyproprionic acid
ALCA	Atributional life cycle assessment
AP	Acidification potential
BC	Base case scenario
C_3	Three atoms of carbon in a chemical compound
C_6	Six atoms of carbon in a chemical compound
CH_4	Methane
CLCA	Consequential life cycle assessment
CO_2	Carbon dioxide
CO	Carbon monoxide
EP	Eutrophication potential
FU	Functional unit
GWP	Global warming potential
HC	Hydrocarbons
LCA	Life cycle assessment
NO_x	Nitrogen oxides
N_2O	Dinitrogen monoxide
PCOP	Photochemical ozone creation potential
SO_2	Sulfur dioxide
SPA	Super absorbent
SS1	Sodium poly-acrylate produced from side stream 1 at Domsjo pulp mill
SS2	Sodium poly-acrylate produced from side stream 2 at Domsjo pulp mill
SS3	Sodium poly-acrylate produced from side stream 3 at Domsjo pulp mill
SS4	Sodium poly-acrylate produced from side stream 4 at Domsjo pulp mill
TMP-E	Sodium poly-acrylate produced from side stream thermo-mechanical pulping side stream concentrated via evaporation
TMP-UE	Sodium poly-acrylate produced from side stream thermo-mechanical pulping side stream concentrated via ultrafiltration

Contents

1. Introduction

The environmental issues and the scarcity of natural resources are the main drivers of exploring a more sustainable material production. The substitution of non-renewable materials with renewable ones is one solution to succeed achieving a sustainable society. Therefore, in the near future, bio-based fuels, chemicals and materials are expected to become a large share of these economic goods (Haveren et al., 2008). However, the current production of biomass based products (1st generation products) is in competition with the food and feed industry (corn, sugarcane, rapeseed, etc.). The competition raises ethical and environmental concerns regarding the sustainable production of these bio-products (Cherubini, 2010). Therefore, much effort is put into shifting to lignocellulosic feedstock (non-food crops) as the raw material for bio-products (2nd generation products). Lignocellulose is the most abundant renewable organic resource on Earth and is composed of carbohydrate polymers (cellulose (35-50%), hemicellulose (25-35%) and lignin (5-30%)) (Jäger and Büchs, 2012).

In this study the use of lignocellulosic residue biomass released, in the form of diluted side streams, from two different pulp mills are the feedstocks considered for the production of sodium poly-acrylate. Sodium poly-acrylate is a polymer with high absorbent properties which can be used in diverse products such as hygiene products. The polymer is currently produced from fossil feedstock in a conventional refinery. As the pulp industry is losing economic value because of the decrease in paper consumption there is a need for developing new value added products. Thus, the use of the side streams for producing poly-acrylates in an integrated biorefinery concept is a good way to increase the competitiveness of the pulp and paper industry. The concept of the biorefinery has been defined in different ways depending on the context in which it has been used. For instance, in a forest industry context, the biorefinery has been defined as the *"full utilization of the incoming biomass and other raw materials for simultaneous and economically optimized production of fibers, chemicals and energy."* (Berntsson et al., 2012). Biorefineries are very diverse and hard to be classified. For instance, depending on their input (feedstock), biorefineries have been classified into three types: the lignocellulose feedstock (LCF) biorefinery, the whole crop biorefinery (cereals and maize) and the green biorefinery (grassland and green crops) (Cherubini et al., 2009). Depending on their process design, biorefineries can be a single plant producing one or more products, or can be integrated with existing plants (such as pulp and paper mills) or other biorefineries. Thus, biorefineries can be characterized by their biomass feedstock inputs, large spectrum of products and their diverse and integrated processes.

Life cycle assessment (LCA) has been used to assess the environmental impacts of different types of biorefineries. A comparative life cycle assessment of renewable, bio-based and non-renewable, fossil-based sodium poly-acrylate production is the aim of this thesis. The fossil-based polymer is currently produced by using a conventional chemical process whereas for the bio-based polymer a bioprocess is in its early stages of development. Therefore, life cycle assessment is used, in this case, as a tool that can direct the technology development when comparing the two alternatives from an environmental perspective. By identifying environmental hotspots or energy intensive processes a better design of the new bioprocess technology can be made at a very early stage of the development.

2. Literature review

2.1. Biochemical conversion of lignocellulose

The conversion of lignocellulose into platform chemicals and biofuels can be done via two different process pathways: thermochemical (via gasification and catalytic synthesis) and biochemical (via hydrolysis and fermentation) (Mu et al., 2010). The biochemical conversion of lignocellulose follows three steps: pretreatment, hydrolysis and fermentation (see figure 1). The pretreatment process is intended to open up the structure of the biomass in order to have an easier access to the carbohydrates. In the (enzymatic or acidic) hydrolysis process, the carbohydrates (cellulose, hemicellulose, starch, etc.) are converted into sugars (glucose, galactose, mannose, etc.). Via fermentation (with genetically modified yeast) the sugars are converted to the desired product. Inhibitory compounds (e.g. organic acid or extractive) from the pretreatment or hydrolysis processes may decrease the reaction rates of the fermentation process. Therefore, in some cases a detoxification process should be applied prior to the fermentation (Jäger and Büchs, 2012).

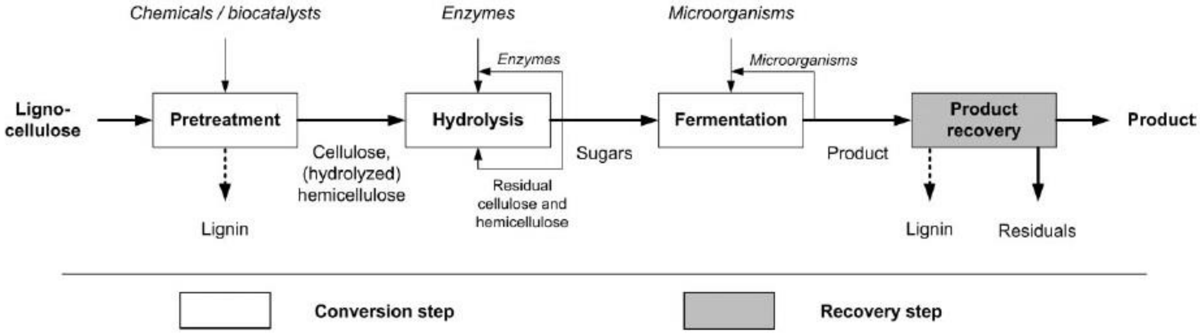

Figure 1: Scheme of bio-catalyst conversion of lignocellulose (Jäger and Büchs, 2012)

Product recovery is the next important step. In this study the desired product is the C_3 platform chemical 3-hydroxypropionic acid (3-HP), produced by the biochemical conversion of lignocellulose. In a report by the US Department of Energy, 15 platform chemicals (ranging from 2 to 6 carbon atoms), including 3-HP (see table A1), were selected as the most promising platforms for further development (Chaabouni et al., 2014). The selection was done based on involved processes, market size, economics, industrial viability and their potential to produce valued bulk chemicals such as, for instance, acrylic acid (Valdehuesa et al., 2013). Acrylic acid, which can be produced via the dehydration of 3-HP, can be polymerized into sodium poly-acrylate which is commonly applied as super-absorbent (SPA) in hygiene products.

2.2. Overview of biorefinery LCAs

By searching at the library of Chalmers University and the Google Scholar search engine (articles from 2007 to 2014), 32 relevant LCA peer-reviewed papers were found. The search terms used were: LCA biomass feedstock, LCA biomass waste, LCA biorefineries, LCA polymers, LCA chemicals, LCA acrylates and LCA 3-HP. Two additional conditions were defined for the screening process. First, the feedstock used in the process should be biomass and second, the technical system analyzed should be a biochemical process. The papers found through this screening were classified into: first generation biofuels (5 papers), second generation biofuels (12 papers), bio-materials/bio-chemicals (11 papers) and integrated bio-refineries (4 papers).

On the one hand, second generation biofuel LCAs are more relevant because they use lignocellulosic feedstock which is similar to the current study. Many other chemical and technical similarities exist like the lignocellulose which is converted to sugars via hydrolysis and subsequently used for fuels or chemicals production. On the other hand, it is interesting to look at the first generation biofuels' large scale production. First generation biofuels are produced nowadays at an industrial scale whereas the second generation biofuels (also lignocellulose-based chemicals) are not yet mass produced.

Because of the intended shift to sustainable platform and bulk chemical production, several LCA studies have been done to assess the environmental impacts of such bio-processes. Whole-crop biorefinerires for the production of polymers were most often assessed (7 articles out of 11). For example, Groot and Borén (2010) looked at poly-lactic acid production (from sugarcane) and Alvarenga et al. (2013) analyzed PVC production (from sugarcane). Fewer studies considered platform chemicals production from lignocellulosic feedstock. For instance, the production of poly-itaconic (Nuss and Gardner, 2013) or the production of propionic acid (Ekman and Börjesson, 2011) was assessed in an LCA study (see table 1).

Furthermore, another type of LCA studies investigated the integration of biorefineries with other production systems. For instance González-García et al. (2011) looked at bioethanol production (via fermentation) integrated at a pulp and paper mill. Cherubini and Ulgiati (2009) and Uihlein and Schebek (2009) investigated the multi-product output biorefinery concept in which several high valued products (bioethanol, electricity and chemicals) are produced (see table 1).

Finally, 16 out of the 32 LCAs were further detailed in order to analyze their methodological choices. Four LCA papers from each category were selected based on the relevance to the topic of the current study and different methodological choices (such as functional unit, feedstock type, and country of origin). For instance, for the chemicals/polymers category only 2nd generation production (4 papers) was selected as being relevant for the current study. For 1st generation biofuel the different functional units and the diversity of feedstocks for 2nd generation biofuels were the principles of selection. Finally, all four integrated biorefinery studies were included as being relevant for the current study. The presentation (see table 1) and analysis of the papers was based on the method developed at Fossil Free Fuels Center (2014). The methodological choices considered are: the aim of the study, functional unit, system boundaries, type of feedstock, type of LCA and allocation method. The quality of data used in this sample of LCA studies is not part of the analysis.

Table 1: Methodological choices for biorefinery LCAs

Study	Aim	F.U.	System boundaries	Feedstock type	Type of LCA	Type of Data	Allocation method
1st biofuels							
(Luo et al., 2009)	Compare the bio-ethanol and gasoline fuel with two blends fuels (E10, E85) used in a midsize car. Additionally, two ethanol processes were compared.	Power to drive a midsize car for 1 km	Cradle to Grave (sugarcane cultivation, ethanol production, blending process and use phase),Brazil	Sugarcane	Not specified	Average, Ecoinvent and EIPRO databases, literature	Economic allocation (for five sub-processes)
(Hussain et al., 2011)	Compare corn-based ethanol with conventional fuel in a Canadian context. With focus on GHG emissions and energy use in corn production.	1 L ethanol	Cradle to Gate (corn farming, production of ethanol, transportation),Canada	Corn	Not specified	Average Site specific, literature	No allocation
(Leng et al., 2008)	Identify environmental hotspots and energy efficiency in the production of cassava-based ethanol. For decision support for the Chinese Government	100,000 tonnes ethanol	Cradle to Gate (cassava cultivation, ethanol production, blending process,transportation (including transportation to use phase)), China	Cassava	Not specified	Average, Site specific, literature	Economic allocation and system expansion (mid value is used for electricity)
(Silalertruksa and Gheewala, 2009)	Identify the hotspots and compare the environmental burdens and energy usage for existing bio-ethanol production (four different production sites) in Thailand.	1000 L ethanol	Cradle to Gate (feedstock processing and cultivation, ethanol conversion and transportation), Thailand	Cassava and molasses (by-product from sugarcane processing)	Not specified	Average, Site specific, literature	Energy based allocation
2nd biofuels							
(Mu et al., 2010)	Compare the biochemical with thermochemical conversion of lignocellulose into ethanol. Focus on GHG, water consumption and fossil fuel used.	1 L of ethanol	Cradle to Gate (feedstock production, feedstock transportation and ethanol production), US	Wood chips, corn stover, waste paper, wheat straw	Not specified	Average, Sigma Pro, Ecoinvent databases, and literature	Substitution method (outputs) No allocation for feedstock
(González-García et al.,	Evaluate the environmental implications of the production	1 Kg ethanol,	Cradle to grave (feedstock cultivation, ethanol	Eucalyptus, Black locust,	Not specified	Average data. Research	No allocation

2012)	and use of ethanol in a flexi-fuel vehicle. The results were compared with conventional gasoline used in an equivalent car.	1 km driven	production, ethanol blend production transportation and final use), Spain/ Italy	Poplar		report, literature	
(Melamu and von Blottnitz, 2011)	Compare second generation ethanol production with industrial heat produced from bagasse residues. Seven case scenarios are investigated with focus on energy use and GWP.	MJ/ha (energy content in bio-ethanol or industrial heat in MJ per hectare)	Cradle to gate (sugar mill activities, bio-refinery, utility plant), South Africa.	Bagasse from sugarcane	CLCA	Marginal data, Site specific, ecoinvent database, literature	System expansion
(Roy and Dutta, 2013)	Evaluate the life cycle of ethanol production via enzymatic hydrolysis process of sawdust.	1 L anhydrous ethanol	Cradle to gate (collection and transportation sawdust, ethanol production, waste water management (biogas from sludge)), Canada.	Sawdust (residue from sawmill or forest activities)	Not specified	Literature data	Economic allocation
2nd generation chemicals/polymers							
(Ekman and Börjesson, 2011)	Investigate the environmental performance of propionic acid produced in a bio-refinery and compare it with its counterpart in a conventional refinery.	1 Kg of propionic acid	Cradle to gate (cultivation of raw material, bio-refinery activities and transportation), Sweden.	Agriculture waste (potato and rapeseed cultures)	ALCA	Average, site specific	Economic allocation
(Nuss and Gardner, 2013)	Assess the environmental burdens associated with softwood derived poly-iatonic acid and how this compare to current production practices.	1 kg of dry poly-itaconic acid	Cradle to gate (feedstock growth, production of poly-itaconic acid), US.	Softwood (Northeast US)	ALCA	Average, Ecoinvent and NREL database and,site specific	Mass allocation with economic allocation in sensitive analysis
(Liptow et al., 2013)	Assess the environmental impacts of producing ethylene from Swedish wood ethanol.	50.000 tonnes ethylene /year	Cradle to gate(forestry, ethylene production vie ethanol from wood, transportation), Sweden.	Sawmill residue	ALCA	Average, Literature and site specific	Economic allocation
(van Duuren et al., 2011)	Assess the possibility to reduce the environmental impact of the current petroleum based acidic acid production by comparing	1 tonne of acidic acid	Cradle to gate (crude oil extraction, refinery, beets cultivation, adipicacid production, transportation),	Benzoic acid , Impure aromatics, Toluene	Not specified /E-LCA ExergeticLC	Average, Gabi and Ecoinvent database and site specific	No allocation

	different feedstock (petrochemical and biomass) for the combined biological and chemical production of adipic acid.		The Netherlands.	(fossil based) and Phenol (lignin - sugar beets)	A		
Integrated biorefineries							
(Cherubini and Ulgiati, 2009)	Compare the production (in a bio-refinery) of ethanol, energy and chemicals from agriculture residues and compare them with their counterparts produced (in a conventional refinery) from non-renewable feedstock.	477 kilotonnes of biomass residue	Cradle to gate, (Residue collection, processing, transport, conversion and final use of products including land use change effects), Austria	Corn stover and wheat straw	ALCA	Average Databases and literature	No allocation
(González-García et al., 2011)	Assess environmental impacts of the production of cellulose (main product), ethanol and lignosulfonate (co-products) in an integrated pulp mill bio-refinery.	1 tonne of cellulose	Cradle to gate (forestry, pulp and paper mill activities, bio-refinery, transportation), Sweden	Soft wood (pine 20% and spruce 80%)	Not specified	Average Ecoinventdatabase and literature	Economic allocation
(Uihlein and Schebek, 2009)	Compare from an environmental perspective the products (ethanol, lignin, xylitol) produce in a lignocellulose feedstock (LCF) bio-refinery with their conventional counterparts (gasoline, acrylic binder, sugar).	1000 Kg dry straw	Cradle to gate (cultivation and harvest, bio-refinery processes, transportation)	Straw from agriculture	Not specified	Average Ecoinvent database	No allocation
(Cherubini and Jungmeier, 2010)	Assess environmental impacts of an integrated bio-refinery concept. Compare its diverse products/services (electricity, fuel, chemicals) outputs with the fossil-based counterparts.	477 ktoneswitch grass per year	Cradle to grave (Biomass cultivation, harvesting and processing, transportation, conversion and end use), Austria	Switchgrass	Not specified	Average, literature	No allocation

2.3. Methodological choices discussion

The most common approach (8 out of 16 articles) was to compare the bio-products and/or services with their fossil-based counterparts from an environmental perspective (see Table 1). Only few studies aimed at identifying the hotspots within the modeled production system in order to propose technological improvements or optimization of the system (Leng et al. (2008), Silalertruksa and Gheewala (2009)). Yet other studies compared two diferent alternative production systems (with one or two different products). For instance, Mu et al. (2010) compared biochemical with thermochemical production of ethanol whereas Melamu and von Blottnitz (2011) compared ethanol production (from bagasse residue) with industrial heat production from bagasse residues.

In the majority of the papers, the functional unit was related to the output product (13 LCAs) and only three related to the input (feedstock) of the modeled system ((Cherubini and Jungmeier (2010), Uihlein and Schebek (2009), and Cherubini and Ulgiati (2009)). Furthermore, most of the LCAs used mass (kg, tonnes, ktonnes) or volume (in liters) as a functional unit. Some of them were related to a small or medium quantity output such as 1 kg, 1L , 1 tonne, 1000 L (González-García et al. (2012), Ekman and Börjesson (2011), Nuss and Gardner (2013), Hussain et al. (2011)), whereas others were related to the entire production in a year within a country or region in kilotonnes (Cherubini and Jungmeier (2010)**,** Liptow et al. (2013)**,** Cherubini and Ulgiati (2009), Leng et al. (2008)). Finally, in some bioethanol cases the functional unit was the energy needed for a car to drive 1 km (Luo et al., 2009) or the energy content of ethanol in MJ per hectare of biomass crop (Melamu and von Blottnitz, 2011).

Most of the LCA studies used a cradle to gate approach. The cradle to grave perspective was considered in only one study for biofuels production (Luo et al., 2009). Some of the papers focused on the hotspots during the production or compared two alternative technologies and therefore a cradle to gate perspective may be the best way to reach the goal of the study. The geopolitical context in which the studies were done was very diverse and covered all five continents with the majority of studies located in Europe.

The feedstocks considered in the studies were diverse. Four different types of biomass were analyzed: whole crops (e.g. corn, sugarcane), energy crops, virgin biomass and biomass residue (mostly from agriculture and forestry). All the first generation biofuel studies used whole crops biomass as the feedstock. Energy crops such as switch grass and fast growing trees were the feedstock investigated, for instance, by Cherubini and Jungmeier (2010) and González-García et al. (2012). Furthermore, González-García et al. (2011) and Nuss and Gardner (2013) examined the usage of softwood virgin biomass as the feedstock for a biorefinery. Finally, biomass residue from the forestry and agricultural industry was the most analyzed feedstock from the lignocellulosic biomass (e.g.Uihlein and Schebek (2009), Liptow et al. (2013), Cherubini and Ulgiati (2009), Roy and Dutta (2013), Melamu and von Blottnitz (2011), Mu et al. (2010)).

In most of the studies the practitioners did not specify what type of LCA they conducted. If the LCA is an attributional (ALCA) or a consequential (CLCA) is relevant for further methodological choices that need to be taken, like the type of data used (average or marginal) or the allocation method. Even if it is not specified, it can be understood from the type of data used or the allocation method adopted what type of LCA was conducted. Thus, it can be observed that the majority of studies have conducted an attributional LCA.

Since most of the studies conducted an attributional LCA, average data were used and only one study used marginal data (e.g. Melamu and von Blottnitz (2011)). All the studies used combined primary and secondary sources of data starting from site specific to databases and literature sources.

Some of the articles included in the literature review did not use any allocation procedure (6 articles). When allocation was done, an economic approach was the most common (6 articles). Few studies used mass allocation and only two studies used system expansion (Melamu and von Blottnitz (2011)and Mu et al. (2010)). Finally, in one study a mix of economic allocation and system expansion was used (Leng et al., 2008). Even all three studies applied system expension, only Melamu and von Blottnitz (2011) did an CLCA study.

2.4. Discussion and conclusions for literature review

Most of the reviewed LCA studies focused on second generation biofuels. Another popular topic investigated was the platform chemicals and polymers synthesized from whole crop biomass (1st generartion polymers/chemicals) In contrast, fewer studies looked at 2nd generation polymers/chemicals production. None of the studies investigated sodium poly-acrylate production from an environmental perspective. In one study a product (sodium poly-itaconic acid) with similar properties (absorbent) was assessed using LCA (Nuss and Gardner, 2013) where the environmental burdens were compared, as in the present case study, with fossil-based poly-acrylate.

As in the LCA carried out in this work, most of the studies compared the bio-based products with their fossil-based counterparts. The other aim of the current study is to identify the environmental hotspots in order to support technical development, an issue that was less examined in the reviewed studies.

The majority of the studies conducted a cradle to gate LCA using an attributional approach. That is also the case for the current study. The reason for why a cradle to gate perspective was chosen was not clearly expressed in the reviewed studies. However, the multitude of applications of chemicals/polymers may explain why this perspective was chosen. For instance, sodium poly-acrylate can be applied in diverse hygiene products, medicine applications, paint products, etc. Additionally, by doing a cradle to grave analysis for a final product (for e.g. diapers) would divert the current focus of the study (technical development of an integrated biorefinery).

Marginal data were used only in one study in which a consequential LCA was done. Because most studies carried out an attributional LCA, average data from several sources were most commonly used. The reason for using several data sources is the lack of site specific data sets from biorefinery plants, or as in the current case, when a technical system that is in its early stages of development is under investigation.

Most of the studies did not apply allocation or they used an economic approach when dealing with multi input-output issues. Mass allocation was used only in one study where economic allocation was tested in the sensitivity analysis. The reason for this choice was not specifically stated. However, the sensitivity analysis results showed insignificant difference when the two methods were applied.

Functional units and reference flows were also very diverse in the reviewed papers. They varied from small to large quantities and were most commonly expressed in mass or volume. Trying to compare the results of the reviewed papers based on the choice of functional unit is therefore quite difficult. That is due to the many other variables in the systems modeled such as the feedstock type, geographical boundaries, goal of the study, etc.

Although many of the papers looked at biomass residue feedstock (from agriculture and forestry), none of the papers investigated the production of the bio-products from diluted pulp mill side streams with one exception (González-García et al., 2011). In this paper, the integrated pulp mill biorefinery where cellulose, bioethanol, lignosulphonate, and energy carriers are produced was assessed using LCA. Black liquor, a hemicellulose and lignin side stream from chemical pulping, was used in this case for the production of bioethanol. The model was run for one tonne of cellulose as the reference flow where the bioethanol is a by-product of the system. This particular paper was a good source for data, deeper understanding of technical processes and the assumptions that could be made when building the models in the current study. However, in the current study the biorefinery concept is assessed for two different pulp mills (thermo-mechanical pulping and sulphite pulping), several side streams, and 1 kg of sodium poly-acrylate as the reference flow. Furthermore, due to the very diluted nature of the side streams investigated, the purification of the targeted product may be very energy intense when removing the water content.

3. Method

3.1. LCA framework

The method applied in this study is life cycle assessment. LCA has diverse applications and depending on its application some differences in the LCA methodology exist. They are very important factors for the consistency and comparability with other LCAs in the biorefinery field. The framework (see figure 1)consists of four main steps: goal and scope definition, inventory analysis, impact assessment, and interpretation(Baumann and Tillman, 2004).

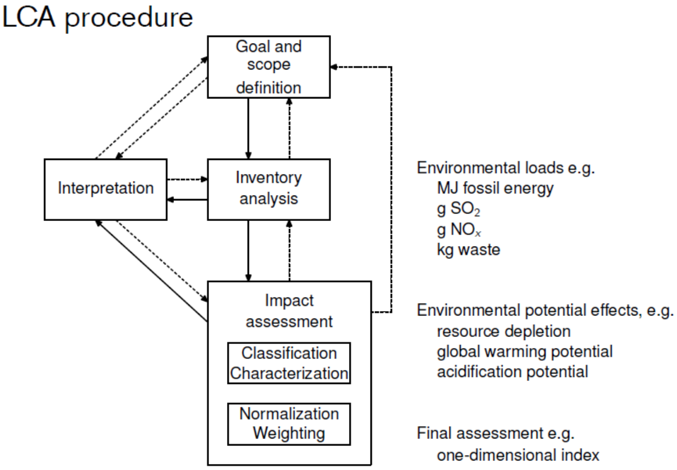

Figure 2: LCA framework(Baumann and Tillman, 2004)

The *goal and scope* definition of LCA defines many aspects of the analysis like the aim and purpose of the study or for whom such study is intended. Functional unit, system boundaries, allocation method, type of environmental impacts, level of detail of the study, type of data, type of LCA are the most relevant methodological choices that need to be made according to the aim and purpose of the study(Baumann and Tillman, 2004).

The *inventory analysis* (LCI) starts from building a flow model that fulfills the requirements described in the goal and scope definition. The model should include all the activities (processes, transportations, etc.) that a product has from raw material input to waste management ("cradle" to "grave") or to the gate of the manufacturing plant ("cradle" to "gate"). In order to gather all the input and output information, data should be collected for each activity from diverse sources. Raw materials used, energy used and emissions to water, soil and air are the data that are gathered during the inventory analysis. All the data collected should be related to the functional unit and if necessary, allocation issues should be solved(Baumann and Tillman, 2004).

The *life cycle impact assessment* (LCIA) deals at first with the classification of the flows into impact categories such as global warming potential, eutrophication etc. Furthermore, the different flows are characterized by using values that represent the cause-effect of the elements, substances or resource consumption in the natural environment. Thus, the approximate environmental impact can be established for each impact category. The impact categories can be even further aggregated into one index by using weighting procedures, an expert panel, etc. The level of aggregation of the data is directly dependent on the purpose of the study and who such study is intended for(Baumann and Tillman, 2004).

The *interpretation* handles the results of the analysis. The interpretation part is very important for the way the findings are communicated. They should be consistent with the goal and scope definition in order to reach valued conclusions. The results are often presented with bar diagrams or with a table in case the results of the LCIare presented. At this part of the LCA sensitivity or uncertainty analysis of the assumptions, type of data, allocation, etc., can be done for a more in-depth discussion of the results(Baumann and Tillman, 2004).

3.2. Goal of the study

The goal of the study is to analyze the environmental impacts of sodium poly-acrylate produced in a pulp mill biorefinery concept and to compare it with its counterpart produced from fossil feedstock. Five different side streams released from two different pulp mills are the biomass sources considered for the biopolymer production. Sodium poly-acrylate can be further applied as super-absorbent (SPA), in hygiene products. The objectives of the study are:

- To determine the environmental hotspots of the bio-based sodium poly-acrylate production for supporting technology development in order to optimize the overall process;
- To understand the possible environmental benefits and trade-offs of the new bio-process when compared to the current production of sodium poly-acrylate.

The LCA results are intended to be used by academic researchers, technology developers and decision makers from involved industries. The LCA is part of a larger project where industry (SCA, Domsjö) and academia (Chalmers University) are working together to achieve the proposed technology development.

3.3. Scope of the study

Functional unit

Although the polymers are made from different feedstocks (oil and lignocellulose) and via two different processes (fossil refinery and biorefinery) it is assumed that they have the same functionality and quality (e.g. chemical properties). The main function of the two technologies is to produce high quality sodium poly-acrylate. Therefore, to have the same functional unit for both processes is a reasonable choice. The functional unit is an amount of sodium poly-acrylate.

In addition to the functional unit, the reference flow needs to be established. The reference flow represents the amount of product used to satisfy the functionality of the system (which is described by the functional unit). Therefore, the reference flow chosen for the study is 1 kg of sodium poly-acrylate.

System boundaries

The production of sodium poly-acrylate is assessed using a cradle-to-gate approach. The technical system contains several main processes and they are different for the two cases (biorefinery and fossil refinery). However, they are classified into the same three categories: production of sodium poly-acrylate, auxiliary processes and transportation (see figures 3 and 4).

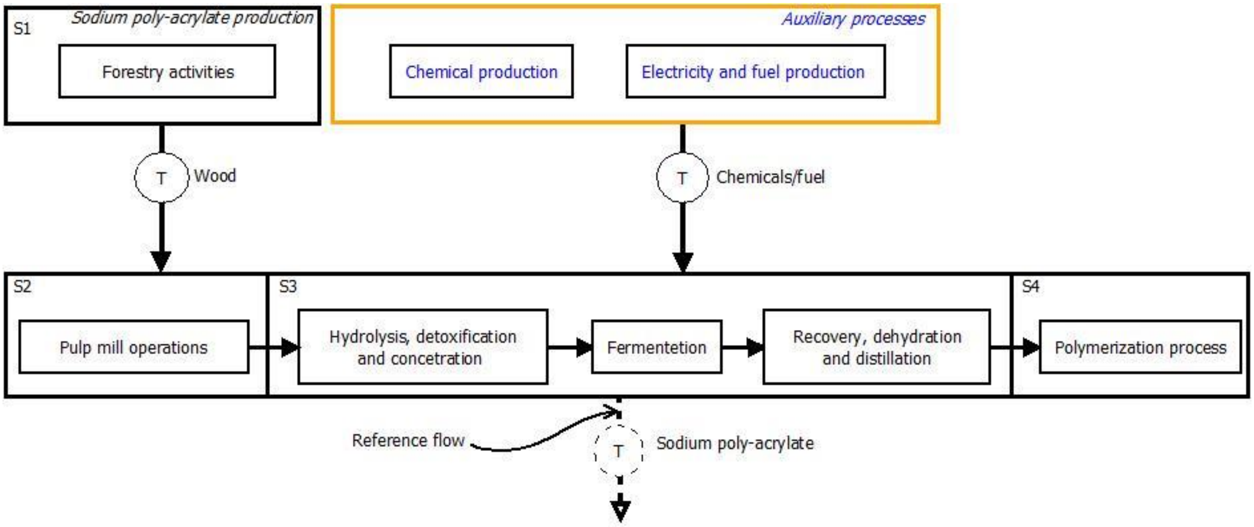

Figure 3: System Boundaries of bio-based sodium poly-acrylate

The first category is related to the *production of the sodium poly-acrylate* and for the bio-based sodium poly-acrylate it was divided into four distinctive subsystems (S): forestry activities (S1), pulp and paper mills operations (S2), acrylic acid production (S3) and finally the polymer production via polymerization (S4). The subsystem S3 is the focus of this study because this is where the development takes place, and it contains several steps: hydrolysis and detoxification of the side streams, fermentation of the free sugars, recovery, dehydration, and distillation of 3-HP (see figure 3). For fossil-based sodium poly-acrylate, the following activities are considered: acrylic acid production (including: crude oil extraction, refining of crude oil, cracking process of naphtha, two-step oxidation process of propylene) and polymerization of acrylic acid (see figure 4).

The *auxiliary processes* include the production of electricity, chemicals and fuel which are used in the polymer manufacture.

Transportation is needed for providing chemicals, fuels, and raw material (wood and crude oil) to the poly-acrylate production facilities.

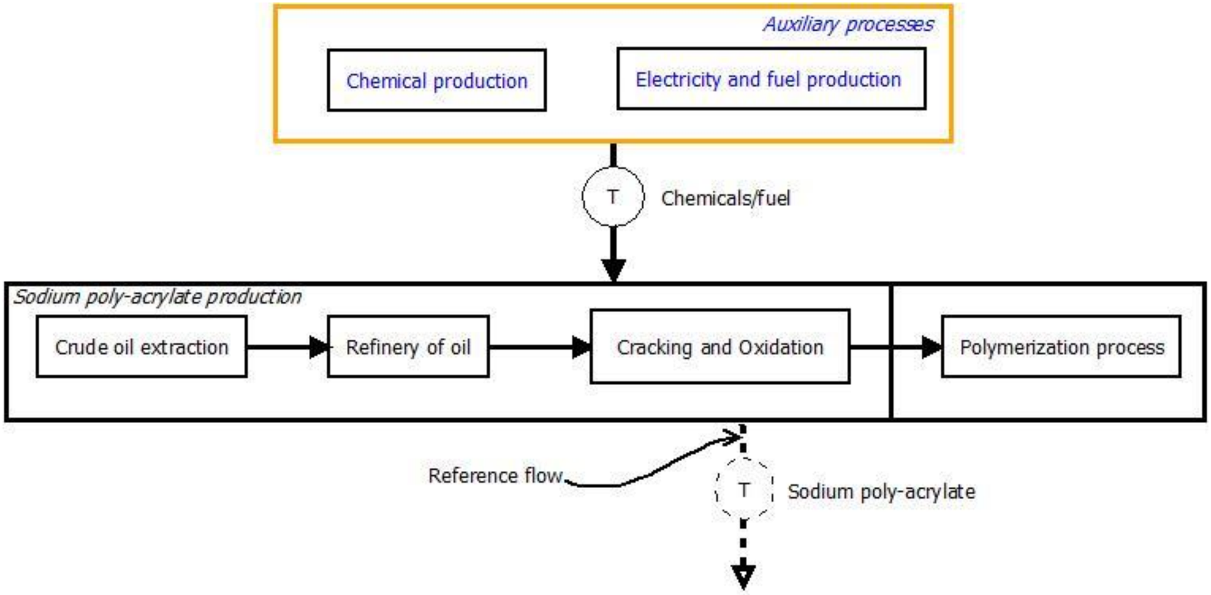

Figure 4: System boundaries of fossil-based sodium poly-acrylate

The Initial flowcharts (see figures 5 and 6) and a short technical description of the bio-based and fossil-based poly-acrylate production are given in the following paragraphs.

Bio-based sodium poly-acrylate production

The pulp mills use round wood as feedstock for the production of cellulose pulp which is the main product output. The side streams from two different pulp mills are further used for the sodium poly-acrylate production. The two pulp and paper mills are: Ortviken which uses a thermo-mechanical pulping process (TMP) and Domsjö pulp mill which uses a chemical (sulphite) pulping process. The synthesis of 3-hydroxypropionic acid (3-HP) via fermentation of biomass residue is the main innovative part of the production process. First, each side stream is chemically hydrolyzed and free sugars are formed. Then, the fermentation process, which is in development, converts the free sugars into 3-HP with a high yield. In order to reduce the inhibitory conditions the side streams are also detoxified prior the fermentation process. From the fermentation broth the 3-HP is recovered via evaporation. Finally, 3-HP is chemically converted into acrylic acid via dehydration which is subsequently used to produce sodium poly-acrylate.

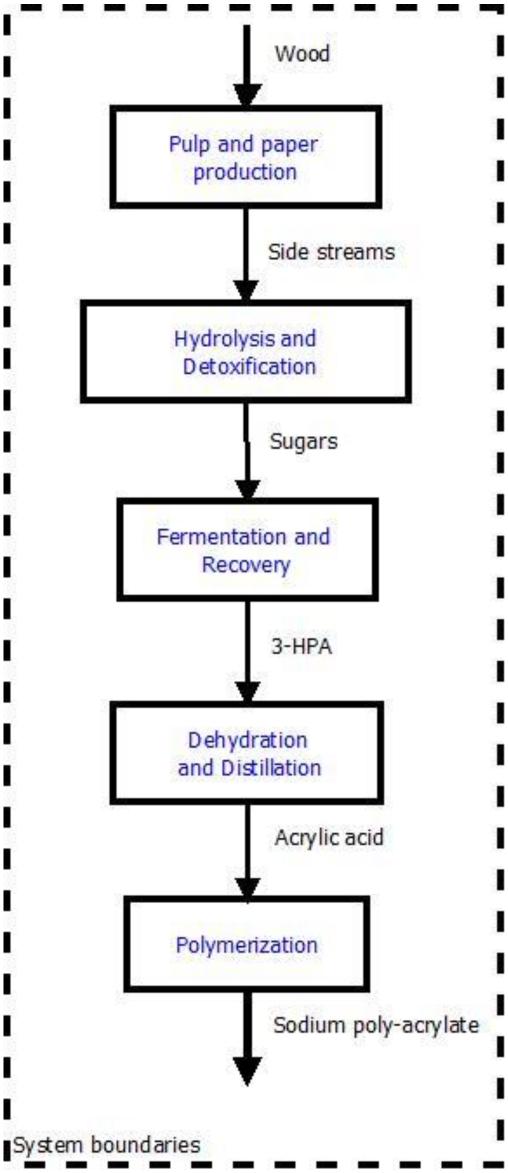

Figure 5: Initial flowchart of bio-based sodium poly-acrylates

Fossil-based sodium poly-acrylate production

Crude oil is the raw material used in the production of fossil-based poly-acrylate. After extraction from the ground, the crude oil is processed via refining where several compounds are obtained. Naphtha is one of them, and is further broken down by the steam cracking process into ethylene and propylene. Via a two-step oxidation process the propylene is oxidized to produce acrylic acid. Acrolein is a by-product of the oxidation process which can be further oxidized in order to increase the yields of acrylic acid. Finally, the acrylic acid is polymerized into sodium poly-acrylate which is subsequently used as SPAs for different products.

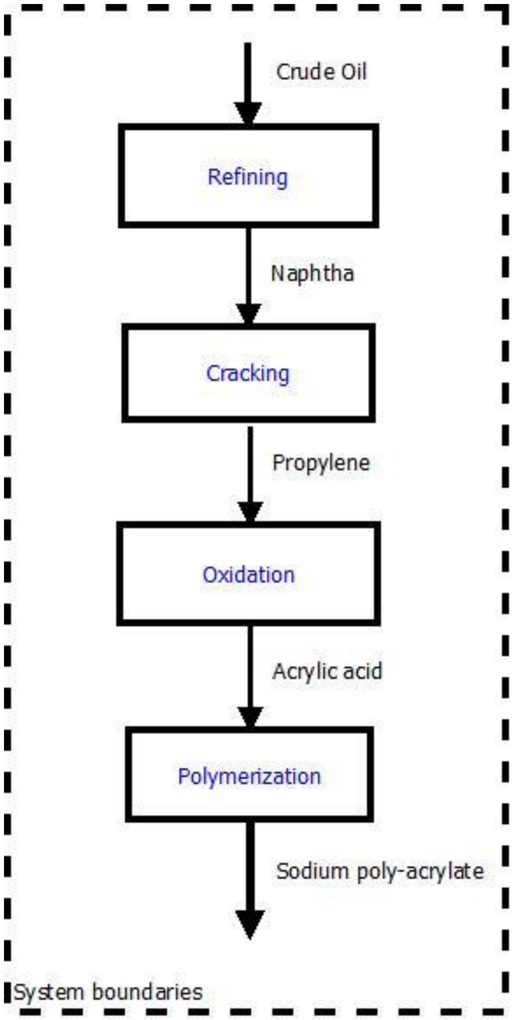

Figure 6: ***Initial flowchart of fossil-based sodium poly-acrylate***

Geographical boundaries

The production site of the bio-based sodium poly-acrylate is hypothetical because it is not yet produced at a large scale. The future location of the bio-refinery depends on the accessibility/availability to/of feedstock and the economy of scale. In this case it is assumed that the side streams released are large enough for producing economically viable poly-acrylate at the pulp mills. The lignocellulose residue originates from two Swedish pulp mills (Ortviken pulp mill (SCA) in Sundsvall and Domsjö pulp mill in Örnsköldsvik) and the transportation of the raw material should be as short as possible in order to reduce costs. Therefore, it is assumed that the bio-refinery is integrated at the pulp mill plants and the side streams are not transported. The entire production of the sodium poly-acrylate will take place at the mentioned mills.

The study is placed in a Swedish context. Therefore, the manufacturing of the fossil based sodium poly-acrylate is assumed to be in The Netherlands (BASF) which is the closest plant to Sweden. BASF is one of the largest chemical companies in the world and the largest producer of poly-acrylates in Europe (Nonwovens Industry, 2014). Poly-acrylates in form of SPAs are used in hygiene products by SCA which is the main consumer of sodium poly-acrylate in Sweden and one of the largest in Europe (Market Reports Online, 2014).

Temporal boundaries

The time horizon is examined in two perspectives: how long the results of the study are valid for and how far into the future the technical system is implemented.

The results of the study are valid for short to medium term period (10-20 years) as they are intended to support technology development. Furthermore, when considering the environmental impacts, the temporal boundaries may extend long into the future. For instance, greenhouse gases such as CO_2 have a long impact (100 years) on climate change.

Two scenarios are modeled when considering the temporal boundaries for technical system: first, the present year 2014 and second the year 2025 when the bio-refinery is expected to be implemented at industrial scale. The second scenario is relevant because the energy system is projected to change to some degree until the year 2025 (European Commission, 2014).

Type of LCA

The results of the study should indicate the hotspots of the bio-refinery for supporting technical development. Additionally, they should indicate which of the alternatives performs better from an environmental perspective. Considering the described goals of the study the intended LCA is an attributional LCA (ALCA).

All the data collected is implemented in the model described in the goal and scope. For an easier modeling of the data, the free, open source software OpenLCA is used.

Allocation method

Some allocation problems related to multi-output and multi-input processes need to be solved when conducting the analysis. A mass partitioning of the inputs (raw material, energy) and outputs (emissions, by-products) is the method used. The economic partitioning is avoided in this study due to lack of data. However, in the sensitivity analysis the model is run using an economic allocation. The allocation methods are further stated when used in the life cycle inventory (LCI) for each process.

Type of data

Foreground data

The foreground data are site specific and primary source data. For the bio-process, lab-scale data from Chalmers laboratory are used for the hydrolysis, detoxification and fermentation (yields and nutrients only). For the recovery of 3-HP, fermentation (energy use only), distillation and dehydration of acrylic acid all the data needed were collected from a simulation report (Cie et al., 2012). Additionally, most of the data for the pulp mill operations are collected from the industrial partners involved in the project (SCA and Domsjö). The types of data are:

- Yields for each of these processes;
- Resources used during production (e.g. water, chemicals);
- Types and quantities of energy used.

Background data

The main source of background data is the Ecoinvent database. The database is reliable and relevant for this study and for the geographical boundaries that have been defined (Swedish context). The database is used for the fossil-based acrylate production, transportation and auxiliary processes. Moreover, where data are missing, other secondary sources such as literature data can be used. In case no direct measurements have been done for bio-based polymers production (e.g. polymerization, forestry etc.) such sources can be used.

Impact categories

The purpose of environmental impact assessment is to make the inventory results more relevant for decision making by linking these to impacts to the environment and/or human health (Baumann and Tillman, 2004). Here, a midpoint assessment is done by using the CML characterization method (Guinée, 2002).

When choosing the impact categories, their relevance to the study should also be considered. For instance, global warming potential, eutrophication, acidification and direct/indirect land use change are relevant impacts when biomass is the feedstock used. However direct and indirect land use change are omitted from this study. The former one is omitted because the Swedish forestry has been well managed for more than a hundred years (Swedish Wood, 2014) and no virgin forest is used for the production of poly-acrylates. Furthermore, since indirect land use change accounts for marginal effects on the system modeled (here an ALCA is intended, where average data is used) this impact category is also excluded.

In this case study the impact categories considered are:

- *Renewable and non-renewable energy used (REU and NREU)*;
All the energy used during the production of the poly-acrylates is accounted for. Then the energy mix is divided into renewable and non-renewable sources.

-*Global warming potential* (GWP);
For GWP, carbon dioxide, methane and nitrous oxide are the main compounds considered. They all affect the radiative forcing and thereby heat the atmosphere. This fact has further adverse consequences on global climate. The use of biomass instead of petroleum reduces the global warming

impact. However, to what extent depends on many factors, such as land management, land use change, geographical boundaries of the study, etc.

The biogenic carbon is considered as climate neutral and is not accounted for in this study, although several recent studies contested the climate neutrality of biomass. The carbon sequestrated in the final product is also omitted, even for some products (such as diaper) the time period after which the carbon is released back in the natural cycle is substantially longer than if the hemicellulose is burned for heat recovery (the present procedure).

-*Eutrophication potential* (EP);
The use of fertilizers is the main cause of eutrophication of land and water. The imbalance of the nitrogen and phosphorus biogeochemical cycle has further consequences on climate change and human health.

-*Acidification potential* (AP);
Similar to the eutrophication potential the nutrients used in the fermentation process and in the energy production have direct impact on the acidity of water and soil. SO_2, NO_x, NH_3 are the main compounds that contribute to pollution of air and water. They have further effects on human and ecosystem health.

-*Photochemical ozone creation potential (POCP)*;
The ozone is created in the presence of NO_x and sunlight. It is formed in the troposphere due to incomplete combustion of fossil fuels and biomass and also from the use of nutrients. The potential increases when there are other organic substances in the lower atmosphere (e.g. various hydrocarbons). This affects human health and damages vegetation.

Assumptions

Several assumptions were made when the LCA was conducted:

-The lab scale data (nutrients, chemicals and yields) for hydrolysis, detoxification and fermentation process are used without considering any possible scale-up effects;

- Much of the data for the biorefinery were collected from a simulation study of a large scale (160 ktonnes/year) acrylic acid production process (Cie et al., 2012). However, in our case the quantity of biomass feedstock availability maybe much smaller and it is restricted to the amount of biomass residue available from the mills.

- The entire heat required for the bio-refinery comes from biomass in a cogeneration plant. Alternative sources of heat are tested in the sensitivity analysis.

- The electricity used in both cases is assumed to be from the grid. For the bio-refinery the Swedish electricity mix is used. Whereas, for the fossil-refinery (for the polymerization process only) the electricity mix for The Netherlands is used. These differences in energy mix sources may be very sensitive for the overall outcome of the LCA when comparing the two products.

LCA limitations

Some of the most important limitations are:

- Some of the important environmental impacts such as impacts on biodiversity are not accounted for in this study

- The lab scale data used in this model may not be relevant when scaling up the sodium poly-acrylate production. This fact may reduce the reliability of the LCA results. However, some of the variables (e.g. fermentation yields) of the model are tested in the sensitivity analysis.

3.4. Scenarios description

Base case (BC) model

In the base case (BC) model, sodium poly-acrylate production is assumed to be integrated at the pulp mills' locations. The concentrations of the side streams investigated in the LCA study are the same as the ones tested in the laboratories at Chalmers. For the fermentation process a yield of 90% from 85.77% the theoretical yield was assumed. The BC model is analyzed for the present year of 2014 with the current electricity mix (from ecoinvent database). Finally, all the extra heat required for the production of sodium poly-acrylate is assumed to be produced from biomass in a cogeneration plant[1].

Explorative scenarios

Starting from the BC model, several explorative scenarios are tested: (1) concentrating (hypothetically) side streams 3 and 4 from the Domsjö pulp mill (SS3 and SS4) prior the hydrolysis process, (2) testing different yields linked to other metabolic pathways for the fermentation process, (3) substituting biomass with fossil heat, (4) exploring electricity system changes for the year 2025 and (5) applying an economic allocation to the BC scenario.

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[1] 'heat, at cogen 6400kWth, wood, allocation heat' from Ecoinvent database is used as extra heat needed in the BC model.

4. Life cycle inventory

The inventory for sodium poly-acrylate production is done separately for bio-based and fossil-based production. Transportation operations (see also table B1) and auxiliary processes are discussed when needed within the bio and fossil based poly-acrylate inventories. Each process is presented in detail including technical description, allocation method and the source and type of data used.

4.1. Bio-based poly-acrylate

For bio-based production of poly-acrylates the four subsystems considered are: forestry activities, pulp and paper mill operations, acrylic acid production in an integrated biorefinery, and the polymerization process. The final inventory results for each biopolymer are presented in the appendix B (see tables B3 to B7).

4.1.1. Forestry activities

The forestry data were collected for Sweden, the location for which the study was modeled. The emissions and energy used related to forestry differ depending on the forest management, climate, and latitude (Berg and Lindholm, 2005). As Sweden expands from 56 to 68 degree latitude three separate regions (south, central and north of Sweden) were considered by Berg and Lindholm (2005). It was shown that the energy consumption and related emissions increase from southern to northern regions of Sweden. However, because the forestry activities have no major impact on the overall environmental performance of pulp mills (González-García et al., 2011) average data for the whole country is used.

The data have been collected for 1 m^3 s.u.b. (cubic meter solid under bark) (see table 2). The processes included in the study are: seeding production, silviculture operation, logging activities and secondary hauling and transportation to the paper mill (see figure 6). Other auxiliary processes included are the fertilizer production, energy carriers and ancillary materials (Liptow et al., 2013).

Table 2: Inventory for forestry activities

Forestry inventory	Quantity	Unit	References
Input			(Liptow et al., 2013)
Primary energy	183.90	Mj/m^3s.u.b	
Output			(Liptow et al., 2013)
S.U.B.	1	m^3s.u.b.	
Emissions (*to air*)			(Liptow et al., 2013)
CO_2	12.52	Kg/m^3s.u.b.	
NO_x	0.12	Kg/m^3s.u.b.	
SO_2	$4.9 \cdot 10^{-4}$	Kg/m^3s.u.b	
HC	0.01	Kg/m^3s.u.b.	
CO	0.03	Kg/m^3s.u.b.	
CH_4	$1 \cdot 10^{-3}$	Kg/m^3s.u.b.	
N_2O	$8.8 \cdot 10^{-4}$	Kg/m^3s.u.b.	

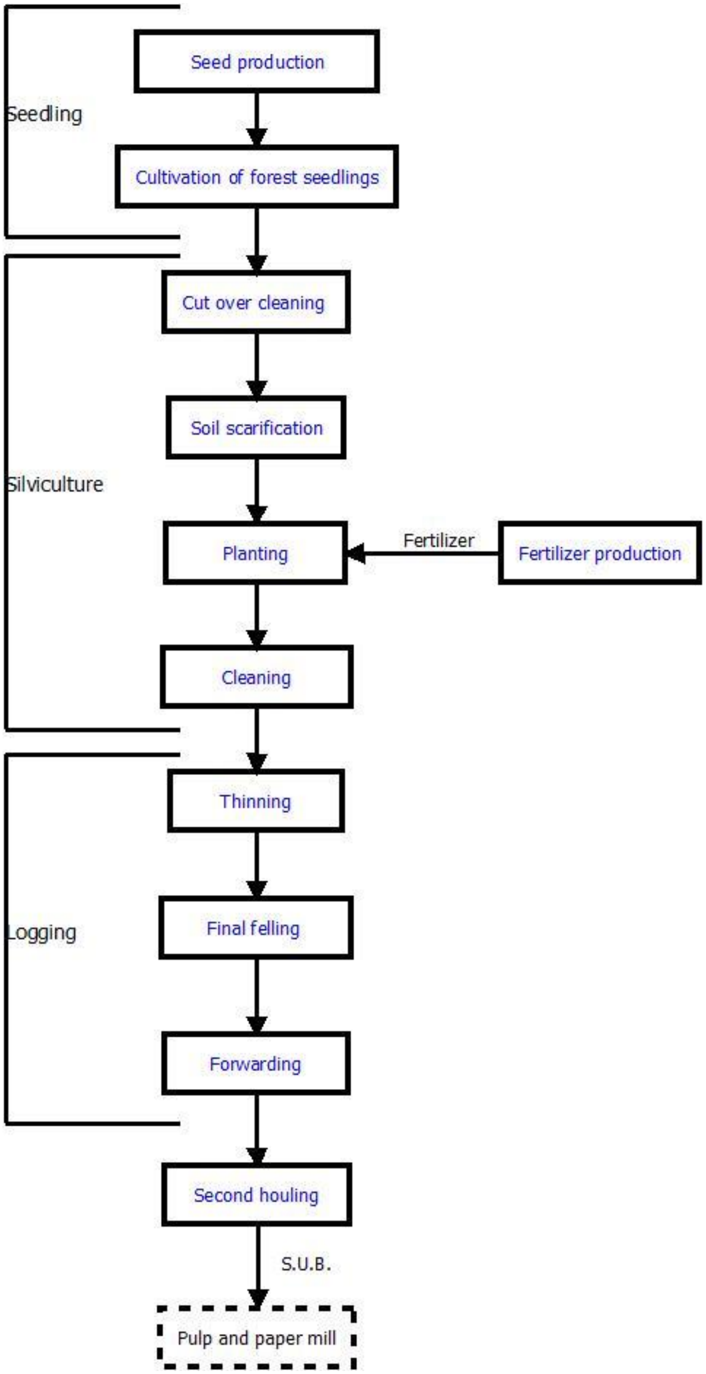

Figure 7: Forestry activities - a simplified flowchart

4.1.2. Pulp and paper mill operations

In pulp and paper mills the wood fraction is separated into hemicellulose, cellulose and lignin. Cellulose is the main product extracted. The side streams released from pulp mills are high in hemicellulose content and are further used for acrylic acid production.

For pulp and paper mills, with few exceptions, primary data was collected from the companies involved. Two different pulp and paper facilities are investigated here: the Ortviken pulp and paper mill (SCA) in Sundsvall and the Domsjö pulp mill (Domsjö) in Örnsköldsvik. The former one uses a thermo-mechanical pulping process (TMP) and the latter one uses a chemical (sulphite) pulping process.

Ortviken pulp mill (TMP)

After transferring the logs to the mill the wood is debarked. Spruce wood with a moisture content of 50% is the type of feedstock used for cellulose pulp production. Circa 7% of the round wood is bark which is sent to a boiler to produce energy[2]. The wood chips (97% after screening) obtained from the chipping machine are sent to the thermochemical pulping (TMP) process.

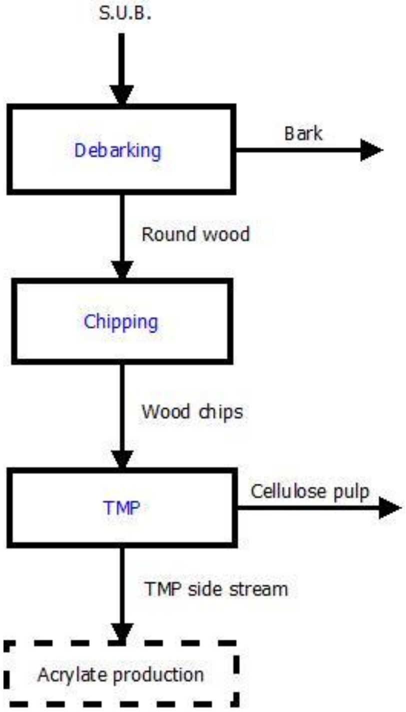

Figure 8: Ortviken pulp mill- a simplified flowchart

The TMP process is energy intensive and consumes as much as 2.18 kWh/kg pulp wood. Most of the energy (66%) used in the TMP process is recovered in form of dirty steam. The steam is further cleaned with a yield of 95% from where the turpentine is also recovered (Industrial Efficiency Technology Database, 2009). The cellulose pulp (99% of the dry wood fraction) is further sent to the washing process. The TMP side stream which contains 1% of the dry wood fraction (hemicellulose) is used in the production of acrylic acid. The multi output and input processes are allocated based on their mass. However, an economic allocation is tested in the sensitivity analysis.

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[2] The energy recovered (in form of heat) is allocated to the polymer production based on the percent of wood fraction in the side stream. In this case only 1% of total recovered heat is allocated. See total recovered energy before allocation in table B4.

Domsjö pulp mill (sulphite pulping)

As in the TMP pulping, the wood logs are debarked first and then sent to the chipping machine. In this case the wood logs used are 40% spruce and 60% pine with a moisture content of 50%. The bark and screened wood chips are used for heat recovery[3]. Next, the wood chips are sent to the cooking process in a digester where sodium hydroxide and sulphite[4] are added to the process (data collected from González-García et al. (2011)).

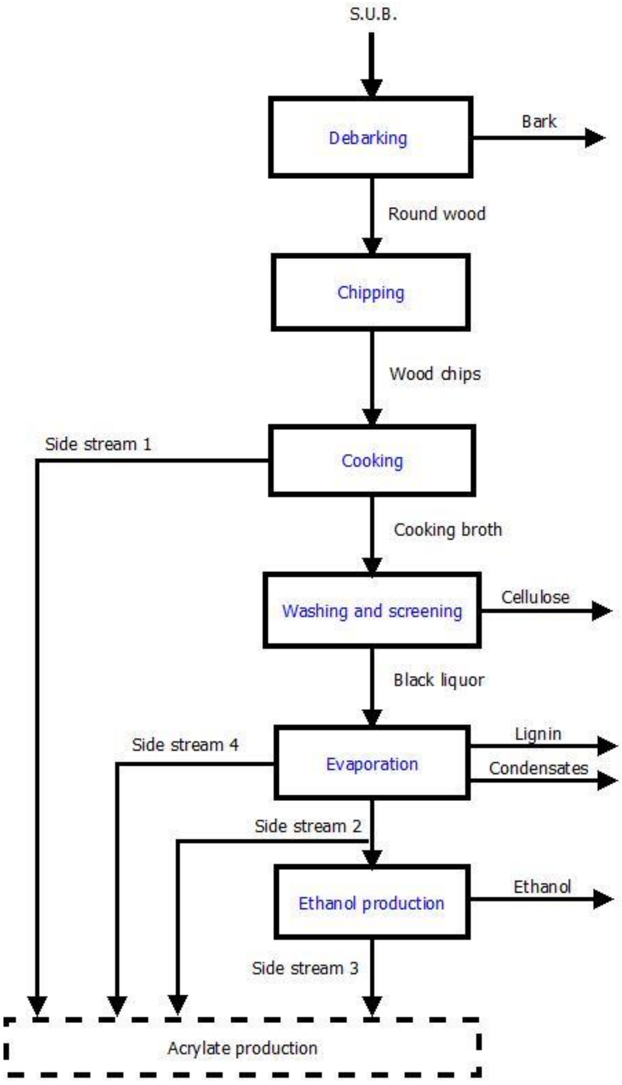

Figure 9: Domsjo pulp mill – simplified chart

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[3] The heat recovered is allocated to the sodium poly-acrylate production based on the percent of dry wood fraction found in each side stream. See total recovered heat before allocation for each side stream in table B5.

[4] The transportation of the chemicals to the pulp mill is presented in appendix table B1.

From the first cooking step the first side stream (which contains circa 10% of the wood fraction) of the wood fraction is released (see figure 9). The cooking broth is further washed in a batch diffuser from where the cellulose is collected (48% of the wood fraction). Black liquor from the washing process is recovered and sent to the evaporation process. A part of the concentrated liquor stream (side stream 2 with 14% of the wood fraction) is sent to the fermentation process where ethanol is produced. The same side stream 2 is also tested for the production of sodium poly-acrylate. The lignin content (24% of wood freaction) and the fourth side stream (less than 0.1% of the wood fraction) are also obtained from evaporation process. The resulting sludge (4 % of the wood fraction) is sent to the waste water treatment plant where biogas is produced and chemicals are recovered. From the ethanol fermentation process the third side stream is released (side stream 3). Most of the wood fraction from side stream 2 is used in the ethanol production and only circa 5% content can be found in the resulting stream 3[5]. Finally, all the four side streams are sent to the acrylic acid production. The allocation method used was based on the mass of wood fraction for each side stream and by-products resulted from the processes.

4.1.3. Acrylic acid production in an integrated bio-refinery

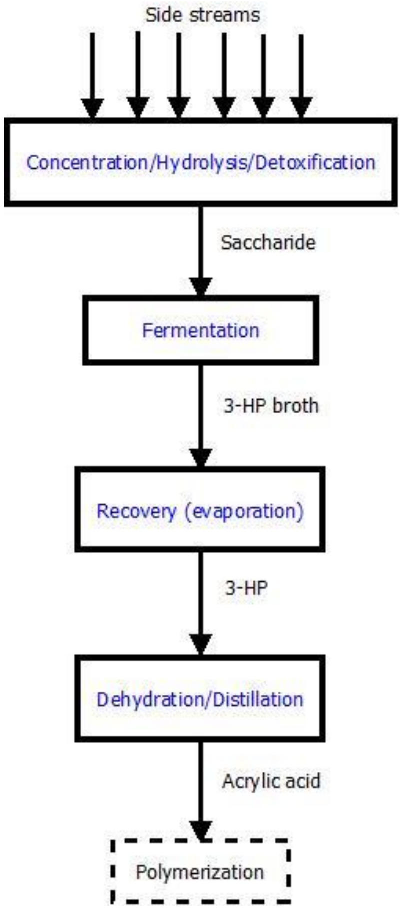

Figure 10 : Acrylate production - a simplified flowchart

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[5] See abbreviations of the side streams in table 8

Initially each side stream is chemically hydrolyzed and in most cases detoxified. Some of the waste streams are very diluted and they need to be concentrated via evaporation or ultrafiltration prior to the hydrolysis process. Next, the hydrolyzed sugars are fermented where 3-HP is synthesized. From the fermentation broth the 3-HP is recovered (via evaporation) and is chemically converted into acrylic acid via dehydration and distillation processes (see figure 10).

The data for the fermentation (energy use only), recovery, dehydration and distillation were collected from a study in which large scale production of acrylic acid in a biorefinery was simulated (Cie et al., 2012). For concentration, hydrolysis, detoxification and fermentation (yields and nutrients used) the data was collected from Chalmers.

Hydrolysis/Concentration/Detoxification

The hydrolysis process (acidic hydrolysis) is the same for all the streams. However, the detoxification and concentration procedures are different for each side stream. The transportation of chemicals (used in these processes) to the pulp mill are presented in table C1.

Ortviken side streams

Prior to the hydrolysis process the TMP side stream is (50 times) concentrated via two different procedures: evaporation (TMP-E) where water is evaporated under vacuum at a temperature of 80 ^{O}C; ultra-filtration (TMP-UE[6]) where the side stream is ultra-filtrated with two different kDa filters and then 6 times concentrated via evaporation under vaccum at a temperature of 80 ^{O}C. Different concentration methods lead to different sugars content in the TMP side stream (see table 3). Circa 33% of the sugars are lost from the streams when TMP side stream is ultra-filtrated. For the evaporation process 0.47 MJ of heat was assumed to be used when evaporating one liter of water from the side stream(Cie et al., 2012). This value includes the heat recovery and the reuse of it in the process.

Next, both concentrated TMP side streams (TMP-E and TMP-UE) are chemically hydrolyzed with sulfuric acid (2.5 % concentration in the side stream). In the hydrolysis process, the carbohydrates are converted into free sugars (glucose, galactose, mannose, etc.) (see table 3). Then TMP-E is detoxified in order to reduce the inhibitory conditions in the fermentation process. Sodium dithionite (1.54 g/L) was tested for the TMP-E side stream. TMP-UE showed better results without detoxification and therefore no detoxifying agents were applied.

Domsjö side streams

Compared to the side streams from the Ortviken mill the four side streams from Domsjö are not concentrated[7]. Next, the side streams are chemically hydrolyzed by adding 2.5% sulfuric acid to the medium. Finally, different detoxification procedures were tested in order to reduce the amount of

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[6] See abbreviations of the TMP side stream in table 8.

[7] A hypothetical scenario where side stream 3 and 4 are concentrated prior to the hydrolysis is tested in the sensitivity analysis.

inhibitors during the fermentation. The alkali pretreatment where 10%(w/v) NaOH is added to the streams showed the best results.

Table 3: Carbohydrates (sugars) composition of the side streams after hydrolysis and concentration (g/L) (Chalmers University)

Side stream	Ortviken		*Domsjö*			
Composition	TMP-UE	TMP-E	SS1	SS2	SS3	SS4
Arabinose (C5)	1.29	3.28	0.42	0.63	0.3	0.81
Galactose (C6)	6.79	11.77	3.15	4.92	1.2	0.23
Glucose (C6)	7.87	14.17	6.95	11.3	1.9	0.11
Xylose (C5)	0.29	0.57	7.91	10.9	10.8	0.21
Mannose (C6)	29.36	39.63	16.4	24.5	5.8	0.105
Total C6 sugars	44.02	65.57	26.45	40.7	8.9	0.445

Fermentation

Via fermentation, genetically modified yeasts metabolize the fermentable sugars from the side streams and convert them into 3-HP. The fermentation yield data were collected from the laboratories at Chalmers where different biosynthetic pathways are tested. At the moment only C_6 sugars pathways are investigated. In the base case (BC) model a yield of 90% of the theoretical yield of 85.77% was assumed. Thus, approximately 1.4 kg of sugars are needed for producing 1 kg of sodium poly-acrylate. In the sensitivity analysis several different yields and another pathway (malonyl-CoA intermediary with 66.88% theoretical yield) are explored.

The heat and electricity required for powering the fermentation, seeding and mixing processes are assumed to be constant regardless the dilution level of the side streams (see table 4). However, more diluted streams in practice would require larger quantities of energy. On the other hand the quantity of yeasts and other nutrients that are added to the fermentation process (g/kg sodium poly-acrylate) are assumed to be dependent on sugar concentration of each side stream. Thus, more diluted side streams require larger quantities of nutrients and yeasts in the fermentation process (see table B6).

It was also assumed that the yeasts are transported from Sollentuna, Sweden to the pulp mills by medium truck and the nutrients are transported by large truck from Ludwigshafen, Germany and Engis, Belgium respectively to the pulp mills (see also table B1).

Table 4: Fermentation process inventory for 1 kg 3-HP in broth

Fermentation	Quantity	Unit	References
Yield	77.4	%	Chalmers University
Input			
Fermentable sugars	1.291	Kg	
Electricity	1.457	MJ	(Cie et al., 2012)
Heat	11.181	MJ	
Yeast	2	g/L	Chalmers University
$(NH_4)_2SO_4$	5	g/L	

Na_3PO_4	3	g/L
$MgSO_4$	0.5	g/L
Output		
3-HP in broth	1	Kg

Recovery

The 3-HP is recovered from the fermentation broth by using the evaporation process. Through heating in a series of flash vessels, 98.8% of the water is evaporated and 91.4% of the 3-HP is recovered from the broth (see table 5). The energy used in the evaporation process differs depending on the concentration level of sugars in the side streams. Each liter of water evaporated requires circa 0.47 MJ heat(Cie et al., 2012).

Table 5: Recovery process inventory for 1 kg 3-HP

Recovery	Quantity	Unit	References
Yield	91.4	%	(Cie et al., 2012)
Input			(Cie et al., 2012)
Electricity	0.472	MJ/L	
3-HP in broth	1.094	Kg	
Output			
3-HP	1	Kg	

Dehydration/Distillation

The recovered 3-HP is sent to the dehydration process where a strong acid catalyst (phosphoric acid) is added. Next, a three step-distillation process takes place from where the purified acrylic acid (99.99%) is obtained. Most (99%) of the bottom product (which contains 3-HP and the acid catalyst) resulted from the third step distillation process is recovered and sent back to the dehydration process. In the closed-loop dehydration and distillation process, 97.5% of the 3-HP is converted to acrylic acid. The energy required for the production of 1 kg acrylic acid can be seen in the table 6. The phosphoric acid production and transportation were added to the model from the ecoinvent database (see table B1).

Table 6: Inventory for dehydration and distillation processes for 1 kg acrylic acid

Dehydration and Distillation	Quantity	Unit	References
Yield	97.5	%	(Cie et al., 2012)
Input			(Cie et al., 2012)
3-HP	1.282	kg	
Electricity	0.023	MJ	
Heat	1.515	MJ	
H_3PO_4	$2.0\cdot10^{-4}$	kg	
CO_2	$2.1\cdot10^{-5}$	kg	

Output		
Acrylic acid	1	kg

4.1.4. Polymerization process

The highly concentrated acrylic acid is sent to the polymerization process from which the sodium poly-acrylate results (see figure 11). A solution polymerization process is used here as being the most common procedure practiced at the moment by the industry(Sanderson and Sadiku, 2003). The acrylic acid is initially neutralized with sodium hydroxide (NaOH) followed by the polymerization process which is initiated with a small quantity of ammonium peroxydisulphate ($(NH_4)_2S_2O_8$).As much as 98 % of the total acrylic acid monomer is polymerized in the polymerization process(Sanderson and Sadiku, 2003).

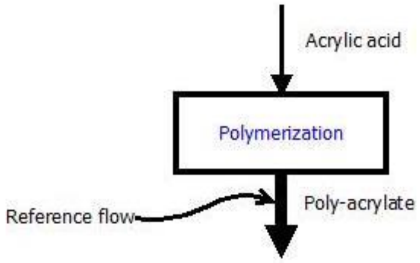

Figure 11: Polymerization process

The transportation of NaOH by barge from Rotterdam to the pulp mill in Sweden was also considered in the model. 7.830 MJ of electricity per kg of sodium poly-acrylate (see table 7 and C7) was used to power the heating, cooling and evaporation systems needed in the process (Sanderson and Sadiku, 2003). For energy mix in Sweden, the ecoinvent database was used in the model.

Table 7: Polymerization process inventory for 1 kg of sodium poly-acrylate

Polymerization	Quantity	Unit	References
Yield	98.0	%	(Sanderson and Sadiku, 2003)
Input			(Sanderson and Sadiku, 2003)
Electricity	7.830	MJ	
Acrylic acid	0.782	kg	
NaOH	0.468	kg	
Initiator [$(NH_4)_2S_2O_8$]	0.005	kg	
Water	1.753	kg	
Output			
Sodium poly-acrylate	1	kg	

4.2. Fossil-based sodium poly-acrylate

4.2.1. Conventional acrylic acid production

After the extraction from the ground, the crude oil is processed via refining where several compounds are obtained. Naphtha is one of the compounds obtained, and is further broken down by the steam cracking process into ethylene and propylene. Via a two-step oxidation process propylene is oxidized to produce acrylic acid. Acrolein is a by-product of the first step oxidation process which is further oxidized in order to increase the yields of acrylic acid production (see figure 12).
As the site specific data for industrial production of fossil-based acrylic acid is hard to find at the moment, the ecoinvent database is used.

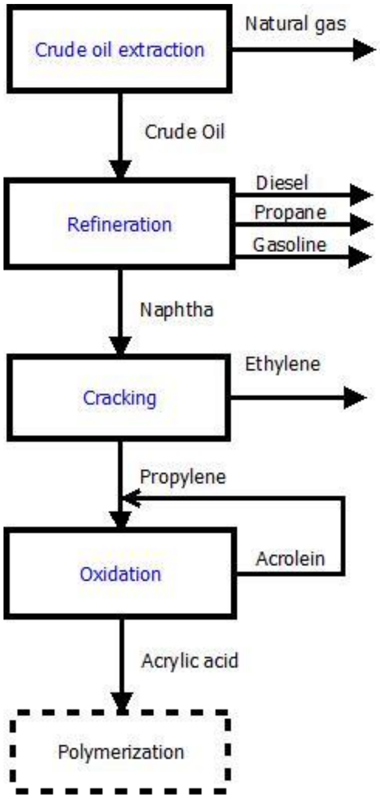

Figure 12: Fossil-based acrylic acid production

4.2.2. Polymerization process

The polymerization process used for fossil-based sodium poly-acrylate production is assumed to be the same as the one used for the production of bio-based sodium poly-acrylate. The only difference is the source of the energy mix used in the production. Because fossil-poly-acrylate is currently manufactured in The Netherlands (NL) the energy mix for NL is employed from the ecoinvent database.

5. Results and discussion

The results are presented for the base case (BC) model, where sodium poly-acrylate production is assumed to be integrated at the pulp mills' locations. The concentrations of the side streams investigated in the LCA study are the same as the ones tested in the laboratories at Chalmers. For the fermentation process a yield of 90% from 85.77% the theoretical yield was assumed. The model is analyzed for the present year of 2014 with the current electricity mix. Finally, all the extra heat required for the production of sodium poly-acrylate is assumed to be produced from biomass in a cogeneration plant. For the presentation of the results for the different side streams the following abbreviations are used (see table 8).

Table 8: Abbreviations for sodium-poly-acrylate produced from the different side streams.

Abbreviation	Description	Pulp mill
TMP-E	Sodium poly-acrylate produced from TMP side stream concentrated via evaporation	Ortviken
TMP-UE	Sodium poly-acrylate produced from TMP side stream concentrated via ultrafiltration	
SS1	Sodium poly-acrylate produced from side stream 1	Domsjö
SS2	Sodium poly-acrylate produced from side stream 2	
SS3	Sodium poly-acrylate produced from side stream 3	
SS4	Sodium poly-acrylate produced from side stream 4	

5.1. Global warming potential (GWP)

The global warming potentials (GWP) of three of the bio-based polymers (TMP-UE,SS1, and SS2) are lower than the GWP of the fossil-based polymer (see Figure 13). Specifically, the bio-based polymer produced from side stream TMP-UE shows the lowest GWP. The GWP for the biopolymers varies mainly due to the difference in sugar concentration in the side streams (see table 3). More diluted side streams require more energy in order to get rid of the water, and require more chemicals for e.g. detoxification and fermentation. For the Ortviken pulp mill, the side stream is 50 times concentrated prior the hydrolysis process via evaporation (TMP-E) and ultrafiltration (TMP-UE). For TMP-E, the environmental hotspot is the concentration process which is energy intensive (in the form of biomass heat) and contributes 64% to the total GWP. The transportation and the energy input for the biomass production used for extra heating are the main contributors to the concentration process. The biopolymer production from the TMP-UE side stream requires four times less energy in the concentration step and therefore has a significantly lower GWP than the biopolymer produced from the TMP-E side stream. As a result, for the TMP-UE biopolymer the fermentation process is the hotspot, mainly due to higher (33%) losses of sugars during the ultrafiltration. This leads to the use of larger quantities of chemicals and nutrients in the process which implies a larger GWP. Additionally, the polymerization process contributes to a relatively large extent of total GWP. This is due to the use of sodium hydroxide and the electricity mix used in the process. Domsjö's side streams are not concentrated prior the hydrolysis process which results in the fermentation, detoxification and polymerization processes to contribute the most to the overall GWP. The electricity mix used in the production of sodium hydroxide (used in detoxification and polymerization processes) and ammonium sulphate (used as nutrient in the fermentation process) contributes the most to GWP. For SS1 and SS2 the GWP is lower than for their fossil based counterpart and they have a 2-3 times lower GWP than SS3. SS4 is an outlier because it has a very low concentration of fermentable sugars in the side stream (0.445 g fermentable sugars per liter side stream). This results in a very high use of energy and chemicals during the downstream processing and thus it has a very high GWP.

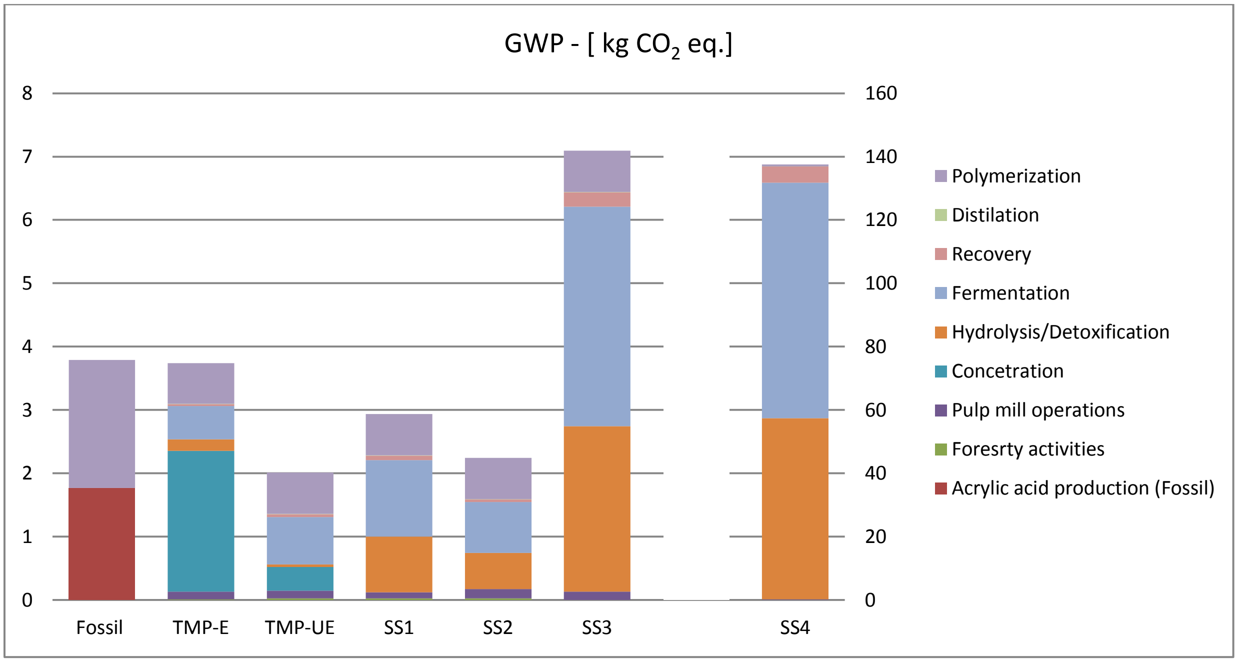

Figure 13: Global warming potential for base case scenario (BC)

5.2. Acidification Potential (AP)

As shown in figure 14, the acidification potential (AP) is smaller for the fossil based sodium poly-acrylate than for all the bio-based counterparts. The SS2 biopolymer produced from side stream 2 has the lowest AP from the bio-based polymers. For TMP-E and TMP-UE, the concentration process has the largest AP. This is due to nitrogen oxides (NO_x) related to the fossil fuel used in the transportation and energy used for biomass production. The TMP-UE polymer has circa 6 times lower acidification potential than TMP-E polymer because of the two different concentration methods used (ultrafiltration and evaporation). Additionally, TMP-E is detoxified with sodium dithionite which also has a significant impact.

SS1, SS2 and SS3 require less chemicals than SS4 due to higher concentration of fermentable sugars in the side streams and thus have lower acidification potential. The fermentation and detoxification activities followed by the polymerization process are the hotspots identified when producing SS1 and SS2 polymers. For the SS3 and SS4 polymers the recovery process is also a hotspot due to large quantities of biomass heat required to evaporate the water when 3-HP is recovered from the fermentation broth. Domsjo's polymers (SS1, SS2, SS3 and SS4) require large quantities of nutrients and sodium hydroxide. The electricity used for producing these chemicals and high emissions of sulfur dioxide are the main contributor to the AP. The sulphuric acid used in the hydrolysis process also has a high contribution to the acidification potential (between 10% and 15%).

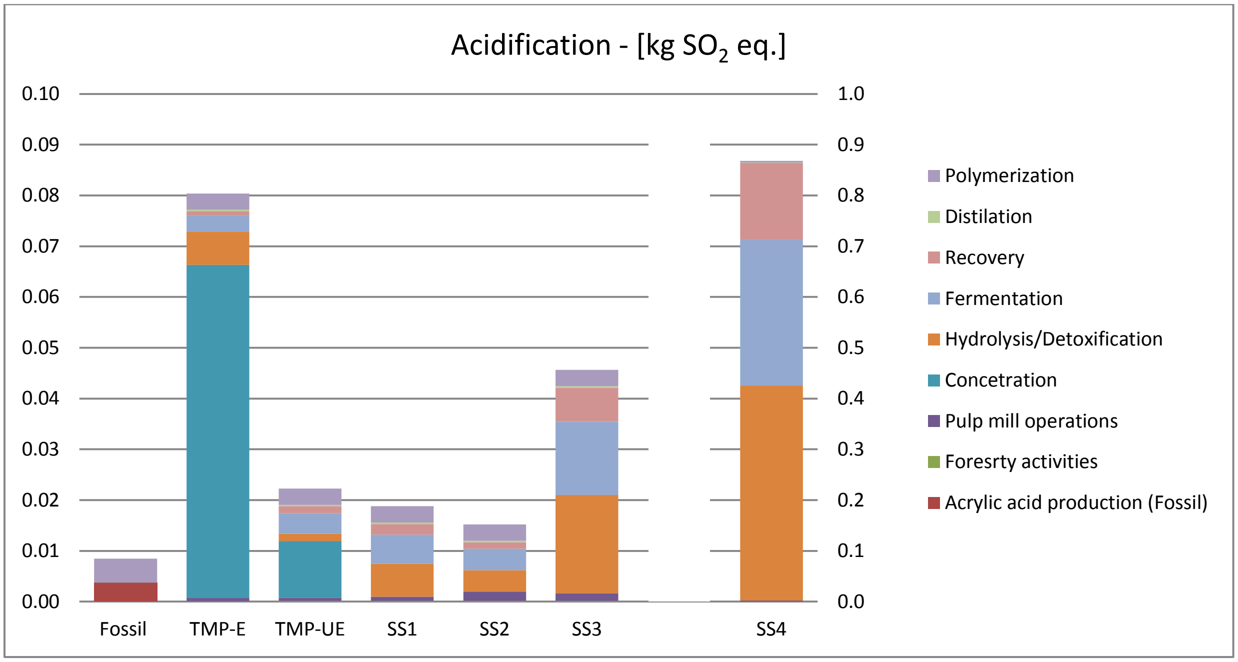

Figure 14: Acidification potential (BC)

5.3. Eutrophication potential (EP)

Similar to the acidification potential all the bio-polymers have a larger eutrophication potential (EP) than the fossil based polymer (see figure 15). SS2 again shows the best results from all the bio-based polymers. For TMP-E the concentration process is the hotspot identified contributing with 82% to the overall eutrophication potential due to NO_x released when transporting and producing the biomass. For TMP-UE the concentration process has a much lower impact on the polymer production (circa 40%).

For the Domsjö polymers, the detoxification process has the largest impact. For SS1 and SS2 polymerization process has also a large contribution to the AP results. Sodium hydroxide used in these two processes is the main contributor. Phosphate and nitrogen oxides are the most relevant emissions during the production of this chemical. For the fossil-based polymer the contribution of the polymerization to the eutrophication potential is as much as 77%. This is a result of the use of fossil based electricity from The Netherlands which is mostly fossil-based but also because of sodium hydroxide used in the polymerization. Finally, it can be seen that the forestry activities, the pulp mill operations and distillation process contribute less to the impact compared to other processes.

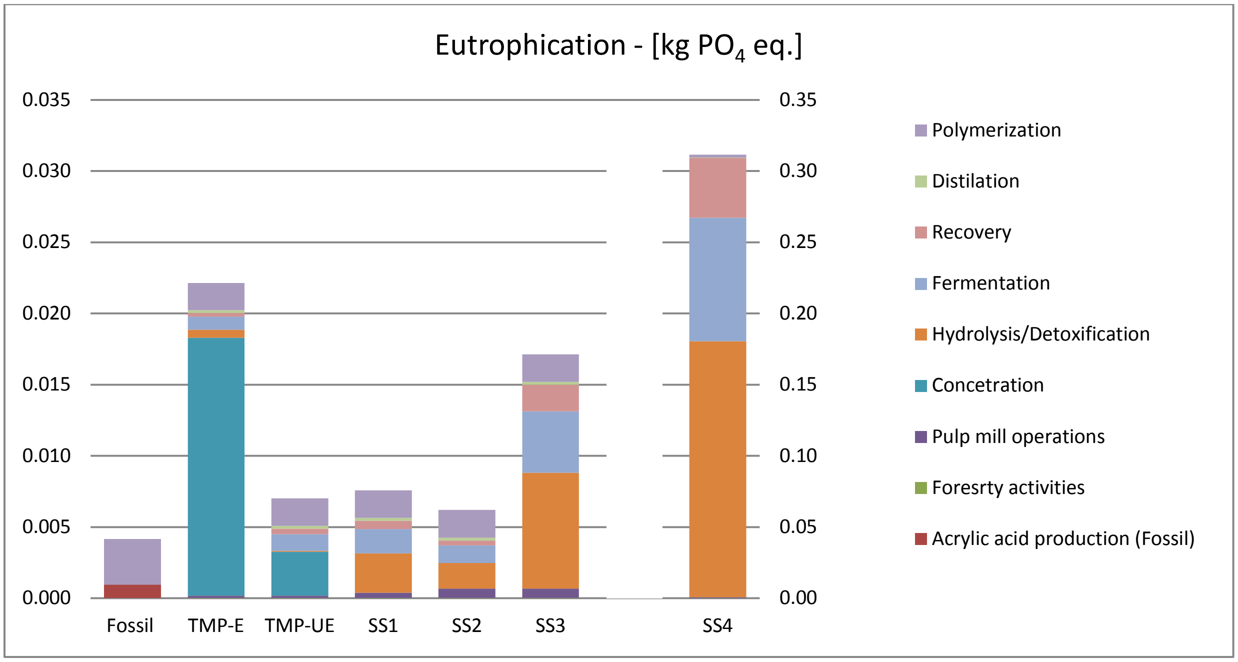

Figure 15: Eutrophication potential (BC)

5.4. Photochemical ozone creation potential (POCP)

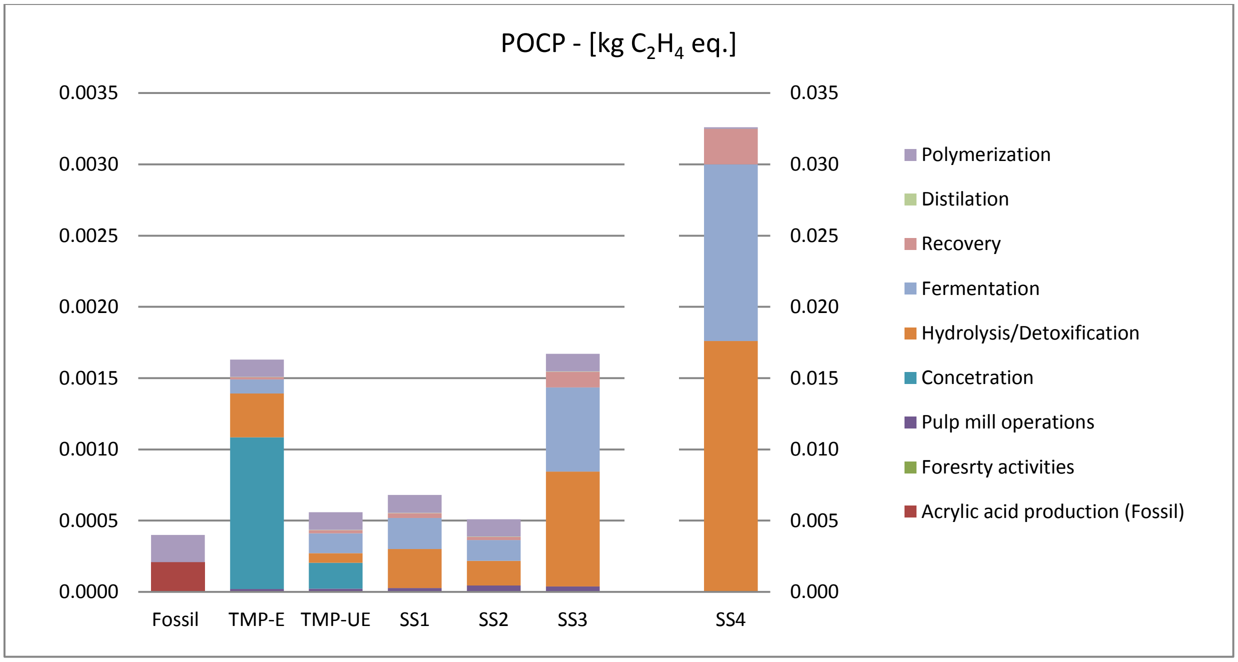

Figure 16: Photochemical ozone creation (BC)

Fossil-based poly-acrylate shows better results than the bio-based counterparts. From the bio-polymers the SS2 and TMP-UE show the best results (see figure 16). As in the previous impact categories the largest contribution for the Ortviken's polymers is the concentration process where a large share of biomass heat is needed. However, for TMP-UE polymer the concentration process is by far not as dominant as for TMP-E polymer. For the Domsjö's polymers the nutrients and chemicals used are the largest contributors to the photochemical ozone creation potential. The production of ammonium sulphate (used for the fermentation process), sulphuric acid (used for the hydrolysis process) and sodium hydroxide (used for the detoxification process) have the largest share to the overall POCP.

5.5. Renewable and non-renewable energy

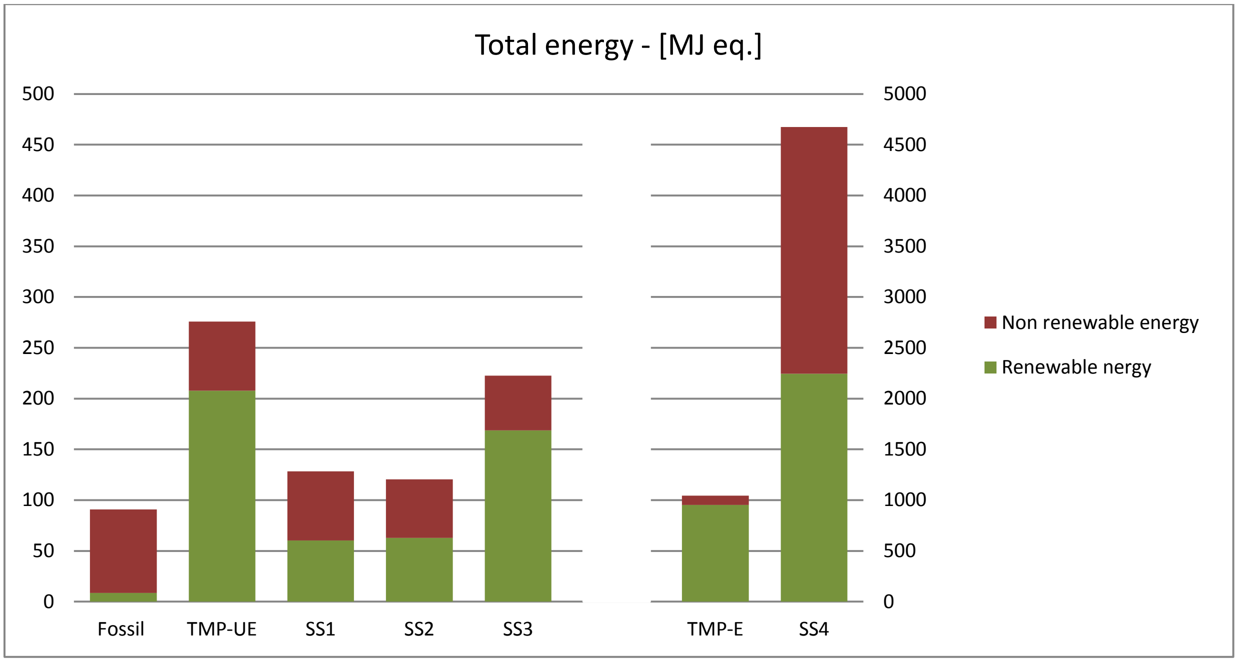

Figure 17: Renewable and non-renewable energy (BC)

The least energy intensive choice is the fossil-based polymer followed by the SS1 and SS2 polymers produced at the Domsjö pulp mill. However, the SS1 and SS2 use less non-renewable energy (NREU) than their fossil-based counterpart of which 90% of the total energy use is in the form of non-renewable energy. The Dutch electricity mix used in the polymerization process and the propylene production have a large impact on the NREU of fossil polymer production.

The high renewable energy use (REU) during the production of sodium poly-acrylate at the Ortviken pulp mill is due to the heat needed for the evaporation of the water when concentrating the streams. TMP-E has 4 times higher energy consumption than TMP-UE. This high difference in results between the two polymers can be observed also for other impact categories (AP and EP). For GWP the difference is much smaller even though the use of energy is considerably higher in the TMP-E case. This is due to the use of biomass (which has a very low GWP compared to other fossil sources) as a source of heat.

For the Domsjö polymers, most renewable energy (REU) is used during the recovery of 3-HP from the fermentation where water is evaporated. The NREU originates from nuclear electricity produced in Sweden and from the fossil energy used for chemical production (see appendix, Figure C1). The largest share for fossil energy is due to sodium hydroxide and ammonium sulphate production which are used in the different processes. The use of these chemicals and their impact is reflected in all the other impact categories under study.

5.6. Sensitivity analysis

Based on the hotspots identified and also the assumptions made during the modeling, several relevant scenarios are tested: (1) concentrating side streams 3 and 4 from the Domsjö pulp mill (SS3 and SS4) prior the hydrolysis process, (2) testing different yields linked to other metabolic pathways for the fermentation process, (3) substituting biomass with fossil heat, (4) exploring electricity system changes for the year 2025 and (5) applying an economic allocation to the BC model. The results are presented here only for the global warming potential due to the importance of GWP impact category and similarities with GWP in the results trends of all the other impact categories under study.

5.6.1. Concentrated streams scenario

Based on the results of the base case model, two hotspots were identified for the Domsjö pulp mill: the fermentation and detoxification processes. The highest impact can be seen for the biopolymers produced from side stream 3 and side stream 4 due to their very diluted nature (see table 3). Therefore, similar to the Ortviken side stream (TMP-E and TMP-UE), Domsjö side streams 3 and 4 are hypothetically concentrated prior to the hydrolysis process. Side stream 3 is concentrated 6 times prior the hydrolysis process whereas side stream 4 is concentrate 50 times. In the first scenario the side streams are concentrated via evaporation and in the second scenario they are concentrated via ultrafiltration. Further increase of inhibitory conditions due to the applied concentration process (which may require extra detoxification chemical compounds) is not considered in the scenario.

5.6.1.1. Evaporation

By concentrating side streams 3 and 4, GWP decreases 3.2 times and 12.6 times respectively when compared with the BC scenario (see figure 18). This is related to the decrease of chemicals used in detoxification and fermentation processes but also the energy required to extract the 3-HP from the broth. Moreover, the SS3 polymer shows an overall better result than its fossil-based counterpart. The same decrease of the environmental impacts can be seen for all the other impact categories.

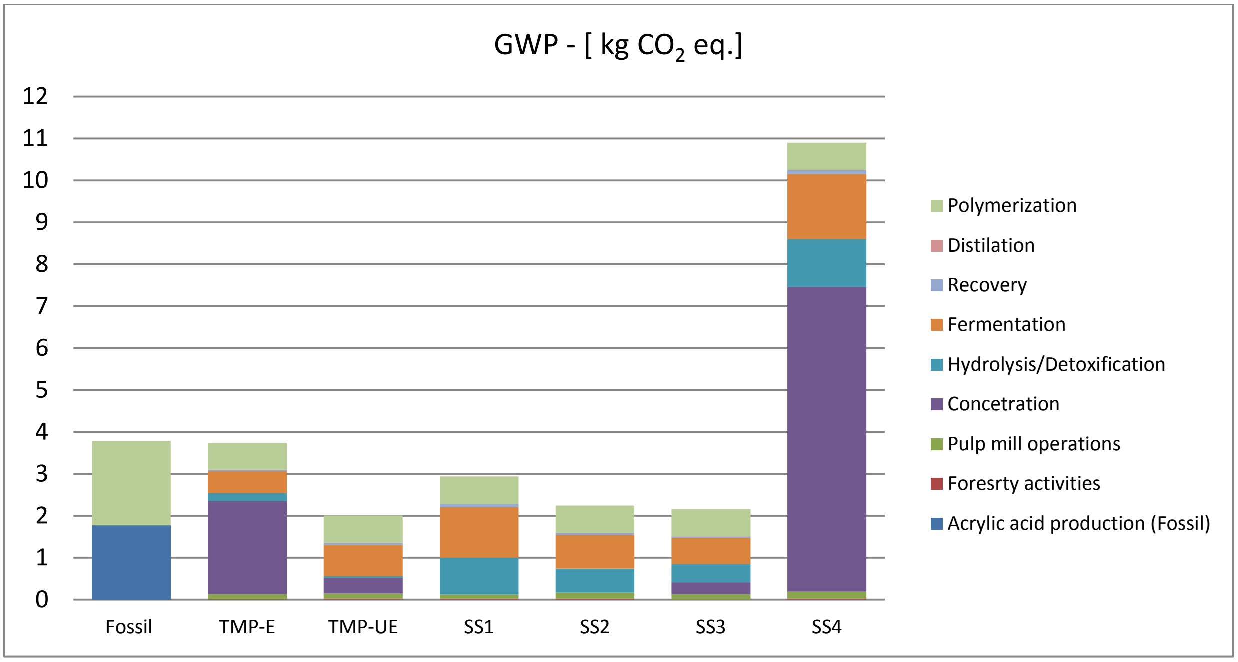

Figure 18: GWP for concentrated streams scenario (via evaporation)

5.6.1.2. Ultrafiltration-Evaporation

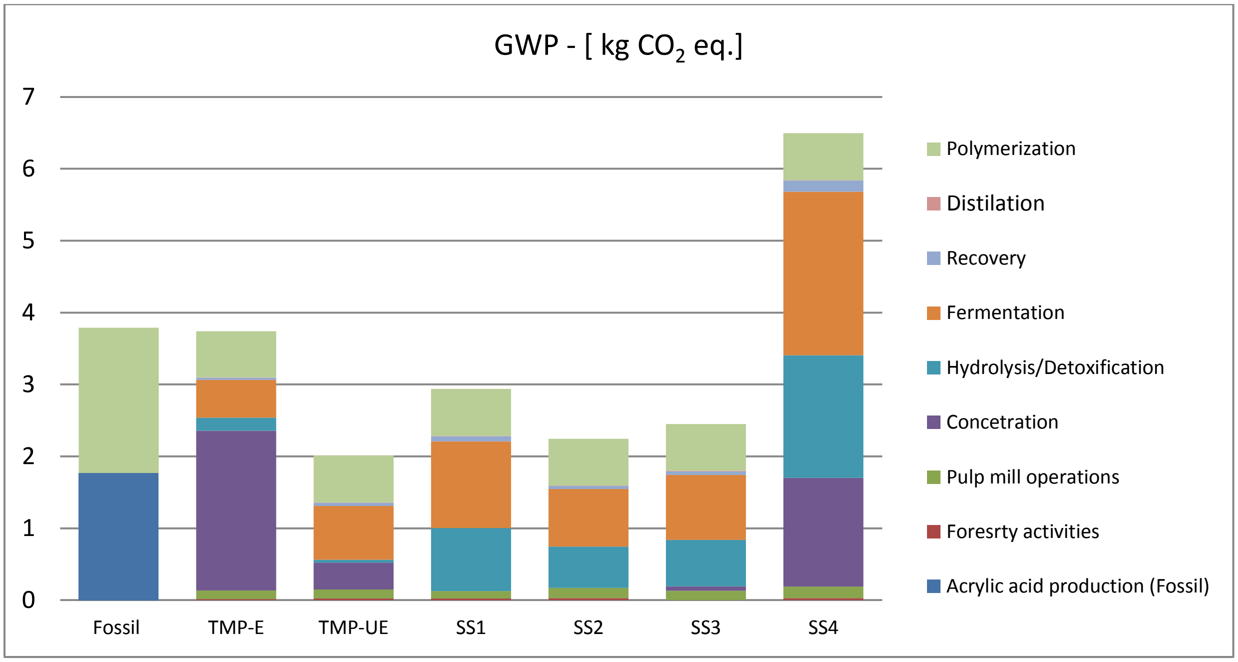

Figure 19: GWP for concentration scenario (via ultrafiltration)

The ultrafiltration scenario showed an overall improvement of 21 times compared with base case scenario for SS4 biopolymer (see figure 19). However for SS3 the improvement decreased from 3.2 times for the evaporation scenario to 2.9 times for the ultrafiltration scenario. The decrease is related to the 33% loss of sugars from the side streams and as a consequence there is an increase of chemicals used in the detoxification and fermentation processes.

5.6.2. Fermentation yields scenarios

In the fermentation process genetically modified yeast produced 3-HP from sugars. In the Chalmers laboratories several pathways have been tested, including the malonyl-CoA intermediary pathway (Chalmers University) with a maximum theoretical yield of 66.88 %. The scenario analyzed here is 90 % from 66.88% (maximum theoretical yield) pathway.

In this scenario circa 1.8 kg (compared with 1.4 kg for BC scenario) of sugars are needed for producing 1 kg of bio-based sodium poly-acrylate. This trend can be seen for all the impact categories and for all the side streams considered in this study. As can be seen in figure 20, two biopolymers (TMP-UE and SS2) show better results when compared to fossil-based polymer. When compared to the BC model it can be see that SS1 no longer showes better results than the fossil-based counterpart. The highest increase in GWP is observed in the concentrations processes for the Ortviken polymers and fermentation and detoxification for the Domsjö polymers. The distillation and polymerization processes are not affected by the changes in the pathways because they are not related to the upstream processes such as the fermentation process.

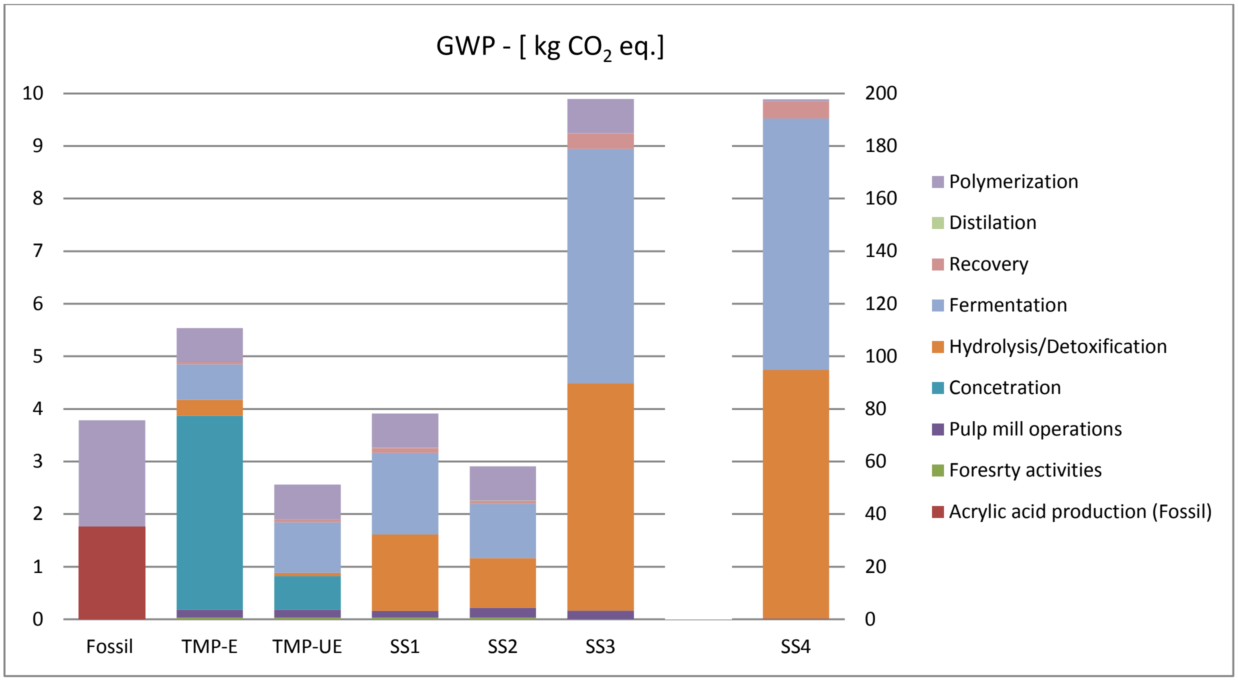

Figure 20: GWPfor 90% yield of 66.88% pathway

Two other scenarios were further explored: 75% yields of 66.88% metabolic pathway and 60% of the 86% pathway, respectively. The graphs are presented in the appendix (see figures C2 and C3). The outcome demonstrates that a lower overall yield results in a higher GWP.

5.6.3. Fossil heat sources scenarios

Integrating the production of sodium poly-acrylate at a pulp and paper mill does not necessarily mean that all the heat needed comes from biomass combustion (as it was assumed in the BC scenario). Therefore, two scenarios in which 15% and 25%, respectively, of the total heat required to produce 1 kg bio-based polymer is substituted with a fossil energy source. The ecoinvent process "heat, heavy fuel oil at industrial furnace 1 MW" was used for these scenarios. The largest quantities of heat are required for the concentration process (for the Ortviken mill) and for the recovery of 3-HP from the fermentation broth (for the Domsjö mill). Therefore, the fossil heat was added to these processes when running the model.

The results show an overall increase of the GWP for all the biopolymers (see figure 21). SS1 and SS2 have the best results followed by the fossil based polymer. The TMP-UE biopolymer, which had the lowest GWP in the BC scenario, is now the fourth best option and it has a higher GWP than the fossil based polymer. The Ortviken polymers are the most affected by this change in the system modeled. TMP-E has 3.5 times larger GWP impact than in the BC scenario and TMP-UE circa 2 times larger GWP. For the Domsjö polymers the use of fossil heat has a lower impact in the overall process when compared with TMP polymers. This is due to lower heat requirements in the production of the polymers.

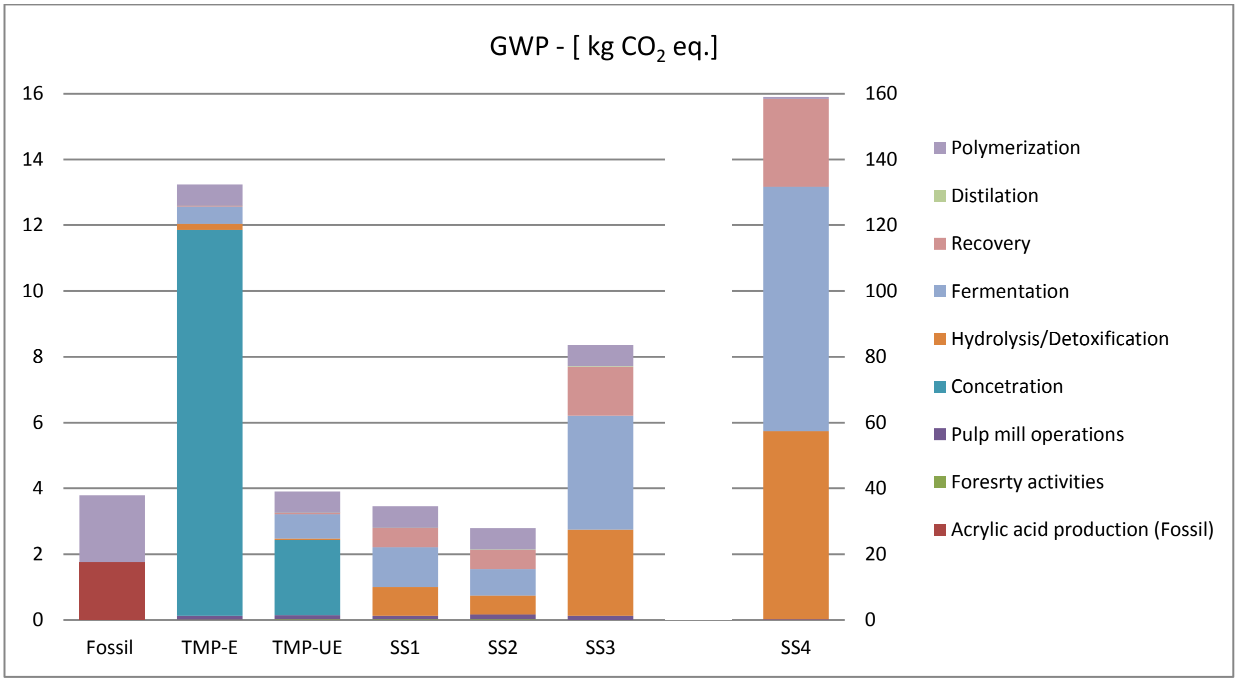

Figure 21: GWPfor 15% fossil heating system

As in the previous case the 25% fossil heat was added to the concentration and recovery processes. As a result in this scenario only SS2 polymer show a better GWP than the fossil-based polymer (see figure C4).

5.6.4. 2025 electricity scenario for direct electricity input

As the polymerization process takes up 50 % of the total GWP for fossil-based sodium poly-acrylate, changes in the future energy system may play a major role when comparing the two alternatives, especially because the current European electricity system is in transition from non-renewable to renewable sources. For this reason the electricity changes have been implemented only in the polymerization processes. Also, for all the biopolymers the 2025 electricity mix is also implemented only in the polymerization process because it is the most electricity intensive.

Data was collected from future energy scenarios for the year 2025 for Sweden and The Netherlands (the countries where the polymers are/will be produced). For Sweden the electricity mix production is projected to become: hydro - 38 %,nuclear - 44 %, wind - 10 %, biomass – 6 %, oil – 1 %, natural gas – 1 % (Gustavsson, 2011). For The Netherlands no concrete future scenario of electricity supply could be found in the literature. However, 30 % renewable energy should be implemented in the current system by 2025 in order to meet the European policies. Since most of the studies indicate that biomass and wind electricity will have the biggest potential for development, in this scenario, it is assumed that 15% of the future electricity system is biomass and 15% is wind electricity. The rest of the needed electricity for The Netherlands comes from natural gas (53%), coal (14%) and nuclear (3%) (International Energy Agency, 2012).

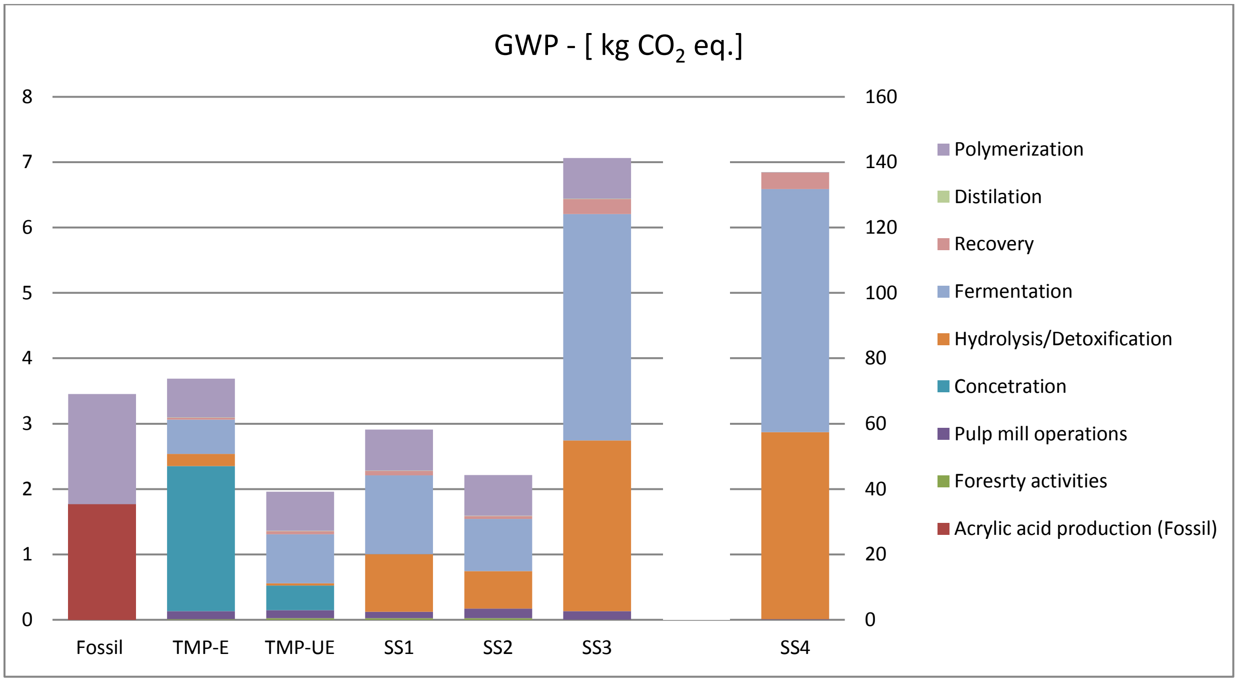

Figure 22: GWP for 2025 electricity scenario

All the investigated polymers showed a decrease in the environmental impacts. A more evident decrease (of 1.1 times) in the GWP (compared to the BC scenario) can be seen for the fossil-based polymer (NL electricity mix). For the biopolymers the change in the GWP is small. This is because the production of the bio-based polymer requires small quantities of electricity, thus such changes do not affect the environmental impacts. Similar to the base case scenario, in this scenario three biopolymers (SS1, SS2 and TMP-UE) have a lower GWP impact than the fossil based polymer.

5.6.5. Economic allocation scenario

The economic allocation has been tested only for the Ortviken polymers (TMP-E and TMP-UE) based on economic heating value because of the easy access to relevant data. The economic allocation was based on the value of 35$/tonne wood pulp. With the heating value of the wood pulp of 15MJ/kg, 13.6 MJ/kg for hemicellulose and 25 MJ/kg for lignin the resulting economic value of the hemicellulose is 32$/tonne (Nuss and Gardner, 2013). Finally the wood chips and bark are assumed to have the same price of 25$/tonne.

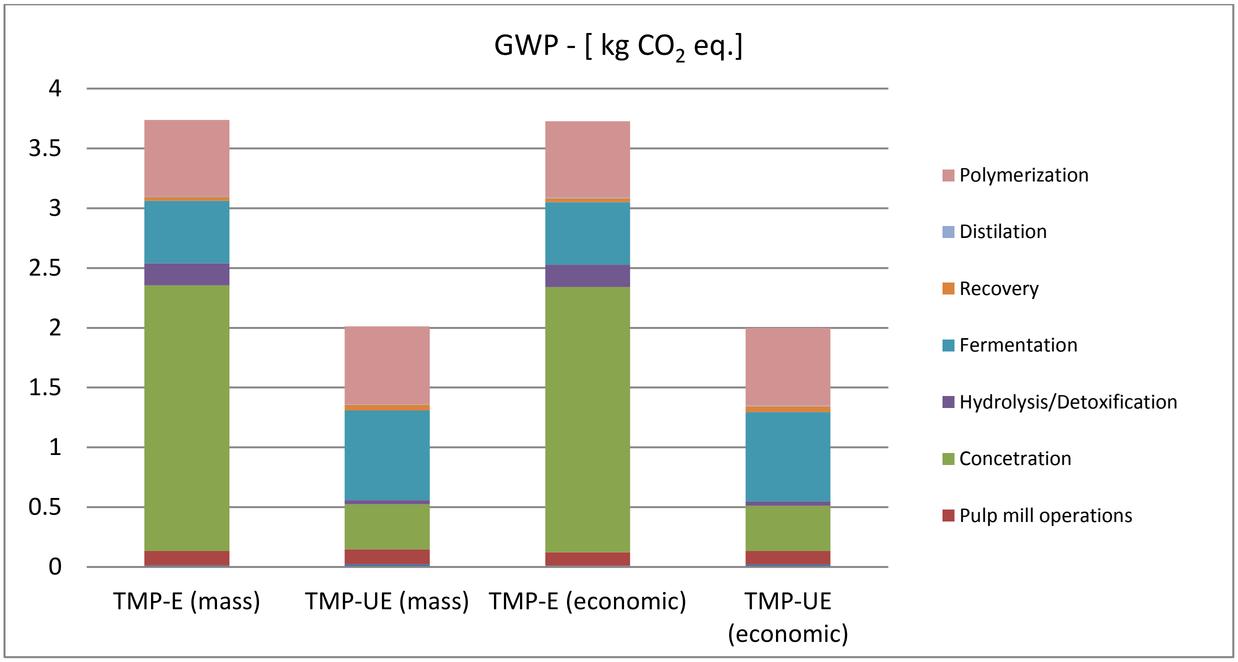

Figure 23: GWP for economic allocation scenario

The results show that the economic allocation applied to the model has very little effect on the Ortviken polymers. This is mainly because the side streams contain very little of the overall wood fraction and therefore pulp mill operations have a little impact on the overall production of the biopolymers. This is relevant also for all the other polymers investigated (SS1, SS2, SS3 and SS4 from Domsjo pulp mill).

6. Conclusions

The first goal of this LCA study was to compare the six bio-based polymers production with the fossil-based polymer production. The results of the BC model showed that for the GWP impact category, three of the biopolymers (SS1, SS2 and TMP-UE) have a lower environmental impact than the fossil-based counterpart. However, the fossil-based polymer showed better results than the bio-based polymers for three of the impact categories under study (AP, EP, PCOP). In the end, four of the biopolymers have a lower NREU than fossil polymer and all the biopolymers show much higher REU than their counterpart.

The second goal of the LCA was to identify the hotspots in the newly developed biopolymers production. For Ortviken polymers the concentration process is the hotspot identified. However, when compared the two concentration methods, the ultrafiltration (TMP-UE) show significantly lower environmental impact than the evaporation (TMP-E). For the Domsjö polymers (SS1, SS2, SS3, and SS4) the hotspots identified were the detoxification and fermentation processes. In addition, for the SS3 and SS4 polymers the recovery is a hotspot identified due to the very diluted nature of these side streams. The polymerization process has a relative large contribution to all the biopolymers, except for SS4 which is an outlier. Finally forestry activities, pulp mill operations, dehydration and distillation processes have very small contribution to the environmental impacts.

The overall performance of each biopolymer is dependent on the concentration of the sugars in the side streams. More diluted side streams require larger quantities of energy and chemicals which lead to larger environmental impacts. Therefore, to find very low energy intensive ways to concentrate the sugar content in the side streams is an important step for future development. Furthermore, the conversion yield of the fermentable sugars into 3-HP is a very sensitive point of the development. Thus, exploring different metabolic pathways (including pathways for C5 sugars) and achieving high yields should be the continuous focus of future research. Based on the sensitivity analysis results, TMP-UE and SS2 show the largest tolerance to lower fermentation yields thus, being the most promising alternatives from all biopolymers investigated.

The chemicals and nutrients used in the detoxification, hydrolysis, fermentation and polymerization processes should be reduced prior large scale production of the biopolymers. The reduction of chemicals is especially relevant when producing the biopolymer from the very diluted side streams. Furthermore, the model developed showed high sensitivity when fossil energy is used in the production of the polymer. Thus, the fossil energy should be avoided and the extra heat produced at the pulp mill should be further allocated to the sodium poly-acrylate production.

Future LCA analysis can potentially investigate: (1) the use of the biopolymers in final products such as hygiene products (in a cradle to grave perspective); (2) the use of the side streams in other bio products such as ethanol and to compare the results with the current study; (3) the biopolymer production in a different model with different methodological choices such as: feedstock's, countries (different forestry management), functional unit, et.

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Appendix

Appendix A: Introduction

Chemicals name and molecular formula

Table A1: Names and molecular formulas of chemical compounds

Chemicals name	Molecular formula
3- hydroxyproprionic acid	$C_3H_6O_3$
Acrolein	C_3H_4O
Acrylic acid	$C_3H_4O_2$
Arabinose	$C_5H_{10}O_5$
Galactose	$C_6H_{12}O_6$
Glucose	$C_6H_{12}O_6$
Mannose	$C_6H_{12}O_6$
Sodium poly-acrylate	$(C_3H_3NaO_2)_n$
Xylose	$C_5H_{10}O_5$

Appendix B: Inventory

Transportation of chemicals from the manufacturing plant to the pulp mills in Sweden

Because the pulp mills are relatively close to each other (100 km difference) it was assumed that the chemicals are transported the same distance for both cases. For each chemical compound the closest manufacturing plant to Sweden was considered. In table B1 the manufacturing location, the distance in km, and type of transportation assumed are presented for each chemical compound used in the model.

Table B1: Transportation of chemicals to the pulp mills

Chemical compound	Manufacturing location	Distance [km]	Type of transportation
NaOH	Rotterdam, The Netherlands	1850	Barge
H_2SO_3	Hamburg, Germany	1350	Lorry , 16-32tonnes
H_2SO_4	Hamburg, Germany	1350	Lorry , 16-32 tonnes
$Na_2S_2O_4$	Hamburg, Germany	1350	Lorry , 16-32 tonnes
Yeast	Sollentuna, Sweden	350	Lorry, 3.5-7 tonnes
$(NH_4)_2SO_4$	Ludwigshafen, Germany	1900	Lorry , 16-32 tonnes
KH_2PO_4	Engis, Belgium	1900	Lorry , 16-32 tonnes
$MgSO_4X\ 7H_2O$	Engis, Belgium	1900	Lorry , 16-32 tonnes
H_3PO_4	Engis, Belgium	1900	Lorry , 16-32 tonnes

Creating new processes for chemical compounds in open LCA

Some of the chemicals or nutrients used in the production of sodium poly-acrylate could not be found directly in ecoinvent database. Therefore, new processes were created by using open LCA software based on the stoichiometry of the chemicals or literature papers. The input data have been implemented in the new processes from ecoinvent database. Three chemical compounds have been created in open LCA: ammonium persulphate ($(NH_4)_2S_2O_8$), potassium phosphate (KH_2PO_4 fertilizer grade), magnesium phosphate $MgSO_4X\ 7H_2O$ (see table B2).

Table B2: Input data for the new chemical compounds created in open LCA

Chemical compounds	Quantity	Unit	Reference
Input			(Jakob et al., 2000)
H_2SO_4	0.578	kg	
$(NH_4)_2SO_4$	0.429	kg	
Electricity	2	kwh	
Output			
$(NH_4)_2S_2O_8$	1	kg	
Input			(Haifa Group, 2014)
P_2O_5	0.52	kg	
K_2O	0.34	kg	
Output			
KH_2PO_4	1	kg	
Input			Stoichiometry
$MgSO_4$	0.488	kg	
H_2O	0.512	kg	
Output			
$MgSO_4X\ 7H_2O$	1	kg	

Life cycle inventory results

The following tables present the inventory results for all the biopolymers under study. The data are presented distinctively for all the four subsystems of the sodium poly-acrylate production: forestry activities (table B3), pulp mill operations, acrylic acid production (table B6), and polymerization process (table B7). For the pulp mill activities, due to different pulping process used, the inventory results are presented in two separate tables (see table B4 and B5).

Table B3: Inventory for forestry activities (for 1 kg sodium poly-acrylate before allocation)

Forestry	TMP-E	TMP-UE	SS1	SS2	SS3	SS4	Unit
Input							
Primary energy	40.452	60.196	3.489	2.581	6.741	828.260	Mj
Output							
S.U.B.	0.220	0.327	0.019	0.0140	0.036	4.503	m^3
Emissions							
CO2	0.0264	0.0393	0.00228	0.00168	0.00440	0.5405	Kg
NOx	2.7539	4.0982	0.23759	0.17573	0.45894	56.3884	Kg
SO2	0.0001	0.0002	0.00001	0.000007	0.00002	0.0022	Kg
HC	0.0022	0.0033	0.00019	0.00014	0.00037	0.0450	Kg
CO	0.0066	0.0098	0.00057	0.00042	0.00110	0.1351	Kg

CH_4	0.0002	0.0003	0.00002	0.00001	0.00004	0.0045	Kg
N_2O	0.0001	0.0003	0.00002	0.00001	0.00003	0.0040	Kg

Table B4: Inevetory for Ortviken pulp mill operations (for 1 kg sodium poly-acrylate before allocation)

Debarking/Chipping	TMP - E	TMP-UE	Unit
Input			
S.U.B.	173.77	258.59	kg
Electricity	12.12	18.04	MJ
Output			
Bark	11.27	16.77	kg
Recovered heat from bark	175.73	261.50	MJ
Recovered heat from chips	72.74	108.25	MJ
Wood chips	156.80	233.34	kg
Thermo-mechanical pulp			
Input			
Wood chips (dry)	156.80	233.34	Kg
Heat	40.95	61.12	MJ
Electricity	1220.32	1821.37	MJ
Output			
Recovered heat from TMP	765.14	1211.21	MJ
Cellulose (dry) pulp	109.670	231.92	kg
TMPside stream	1.41	1.41	kg

Table B5: Inventory for Domsjo pulp mill operations (for 1 kg sodium poly-acrylate before allocation)

Debarking/Chipping	SS1	SS2	SS3	SS4	Unit
Input					
S.U.B. (kg)	15.14	11.19	29.24	3593.54	kg
Electricity	1.05	0.78	2.04	250.73	MJ
Output					
Bark	0.98	0.72	1.89	233.08	kg
Recovered heat (bark)	15.31	11.32	29.57	3634.03	MJ
Recovered heat (chips)	6.33	4.68	12.24	1504.34	MJ
Wood chips	13.66	10.10	26.39	3242.70	kg
Cooking					
Input					
Wood chips	13.66	10.10	26.39	3242.70	kg
Heat	23.97	17.73	46.31	5690.95	MJ
Electricity	0.70	0.52	1.36	167.86	MJ
NaOH	0.69	0.51	1.34	164.8	kg
SO_3	0.021	0.015	0.041	5.1	kg
Output					
Cooking Broth	12.24	9.05	23.65	2906.42	kg
Side stream 1 (hemi)	1.41	1.04	2.45	301.40	kg
Washing					

Input					
Cooking broth	-	9.05	23.65	2906.42	kg
Electricity	-	0.77	2.02	248.51	MJ
Heat	-	3.54	9.26	1138.44	MJ
Output					
Cellulose	-	4.76	12.44	1529.32	kg
Black liquor	-	4.29	11.2	1377.09	kg
Filtration/Evaporation					
Input					
Black liquor	-	4.29	11.2	1377.09	kg
Electricity	-	3.48	4.3	1118.63	MJ
Heat	-	27.76	34.34	8907.49	MJ
Output					
Side stream 2 (hemi)	-	1.41	3.7	454.63	kg
Side stream 4 (hemi)	-	0.0044	0.011	1.41	kg
Lignin	-	2.36	6.18	759.91	kg
Hemi (Condensates)	-	0.5	1.31	161.12	kg
Ethanol production					
Input					
Side stream 2 (hemi)	-	-	3.7	-	kg
Electricity	-	-	0.55	-	MJ
Heat	-	-	12.62	-	MJ
Output					
Hemi (ethanol)	-	-	2.27	-	kg
Side stream 3 (hemi)	-	-	1.41	-	kg

Table B6: Inventory for acrylic acid production (for 1 kg sodium poly-acrylate)

Concentration	TMP-E	TMP-UE	SS1	SS2	SS3	SS4	Unit
Input							
Heat	635.12	107.81	-	-	-	-	MJ
Side steam	1390.30	2074.11	-	-	-	-	L
Fermentable sugars	1.41	1.41	-	-	-	-	kg
Output							
Fermentable sugars	1.41	1.41	-	-	-	-	kg
Concentrated side stream	27.80	41.48	-	-	-	-	L
Water	1362.49	2032.63	-	-	-	-	L
Hydrolysis/Detoxification							
Input							
Side stream	27.91	41.48	69.21	44.97	201.02	4030.9	L
Fermentable sugars	1.41	1.41	1.41	1.41	1.41	1.41	kg
H_2SO_4	0.069	0.103	0.173	0.112	0.514	10.284	kg
NaOH	-	-	0.692	0.449	2.056	41.137	kg
$Na_2S_2O_4$	0.042	-	-	-	-	-	kg
Output							
Fermentable sugars	1.41	1.41	1.41	1.41	1.41	1.41	kg
Fermentation							

Input							
Side stream	27.918	41.48	69.21	44.97	205.68	4030.9	L
Fermentable sugars	1.41	1.41	1.41	1.41	1.41	1.41	kg
Electricity	1.598	1.598	1.598	1.598	1.598	1.598	MJ
Heat	12.262	12.262	12.262	12.262	12.262	12.262	MJ
Yeast	0.043	0.064	0.107	0.069	0.318	6.368	kg
$(NH_4)_2SO_4$	0.108	0.161	0.267	0.174	0.796	15.920	kg
KH_2PO_4	0.064	0.096	0.160	0.104	0.477	9.552	kg
$MgSO_4$X $7H_2O$	0.011	0.016	0.026	0.017	0.079	1.592	kg
Output							
3-HP in broth	1.096	1.096	1.096	1.096	1.096	1.096	kg
Broth	27.918	41.48	69.21	44.97	205.68	4030.9	L
Recovery							
Input							
Electricity	0.014	0.021	0.035	0.023	0.106	2.135	MJ
Heat	9.034	13.45	20.26	12.31	65.00	1348.5	MJ
3-HP in broth	1.096	1.096	1.096	1.096	1.096	1.096	kg
Broth	27.918	41.48	69.21	44.97	205.68	4030.9	L
Output							
3-HP		1.002	1.002	1.002	1.002	1.002	kg
Water	1.002 26.81	40.2	67.27	43.53	204.02	4028.3	L
Dehydration/Distillation							
Input							
3-HP	1.002	1.002	1.002	1.002	1.002	1.002	kg
Electricity	0.018	0.018	0.018	0.018	0.018	0.018	MJ
Heat	1.185	1.185	1.185	1.185	1.185	1.185	MJ
H_3PO_4	0.00017	0.00017	0.00017	0.00017	0.00017	0.00017	kg
CO_2	0.00002	0.00002	0.00002	0.00002	0.00002	0.00002	kg
Output							
Acrylic acid	0.782	0.782	0.782	0.782	0.782	0.782	kg

Table B7: Inventory for acrylic acid polymerization (for 1 kg sodium poly-acrylate)

Polymerization	TMP-E	TMP-UE	SS1	SS2	SS3	SS4	Unit
Input							
Electricity	7.830	7.830	7.830	7.830	7.830	7.830	MJ
Acrylic acid	0.782	0.782	0.782	0.782	0.782	0.782	kg
NaOH	0.468	0.468	0.468	0.468	0.468	0.468	kg
Initiator [$(NH_4)_2S_2O_8$]	0.005	0.005	0.005	0.005	0.005	0.005	kg
Water	1.753	1.753	1.753	1.753	1.753	1.753	L
Output							
Sodium poly-acrylate	1	1	1	1	1	1	kg
Water	1.953	1.953	1.953	1.953	1.953	1.953	L

Annex C: Results

Detailed renewable and non-renewable energy usages for the BC model

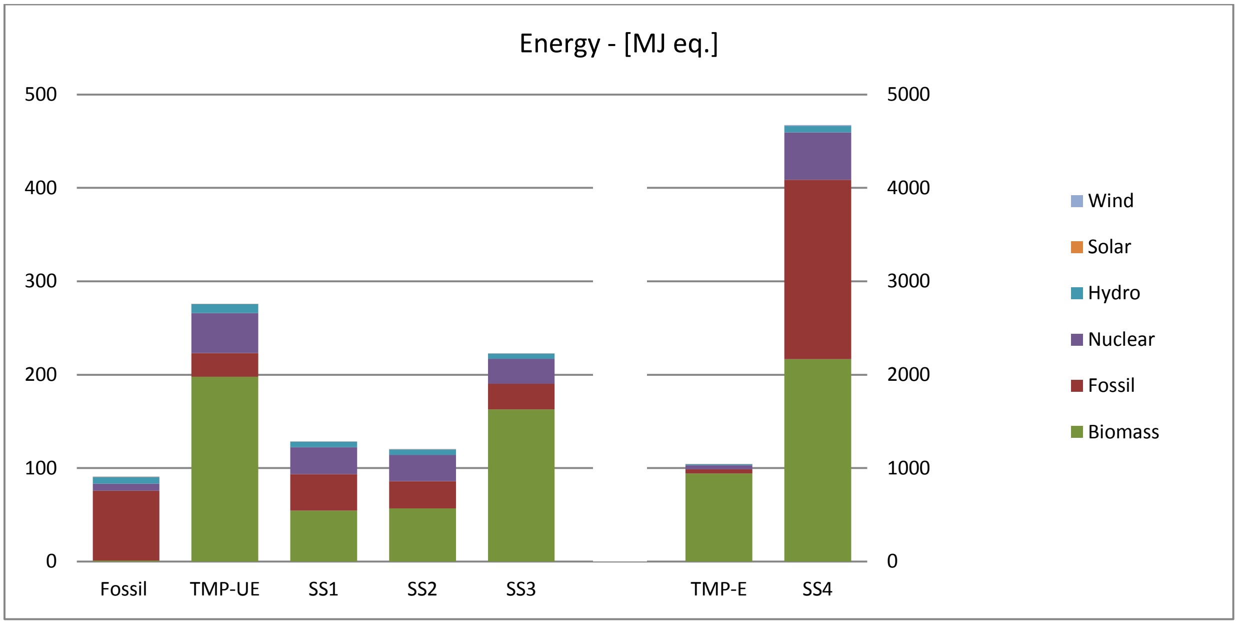


Figure C1: Detailed renewable and non-renewable energy usages for the BC model

75% yield of 66.88% pathway and 60% yield of 86% pathway scenarios

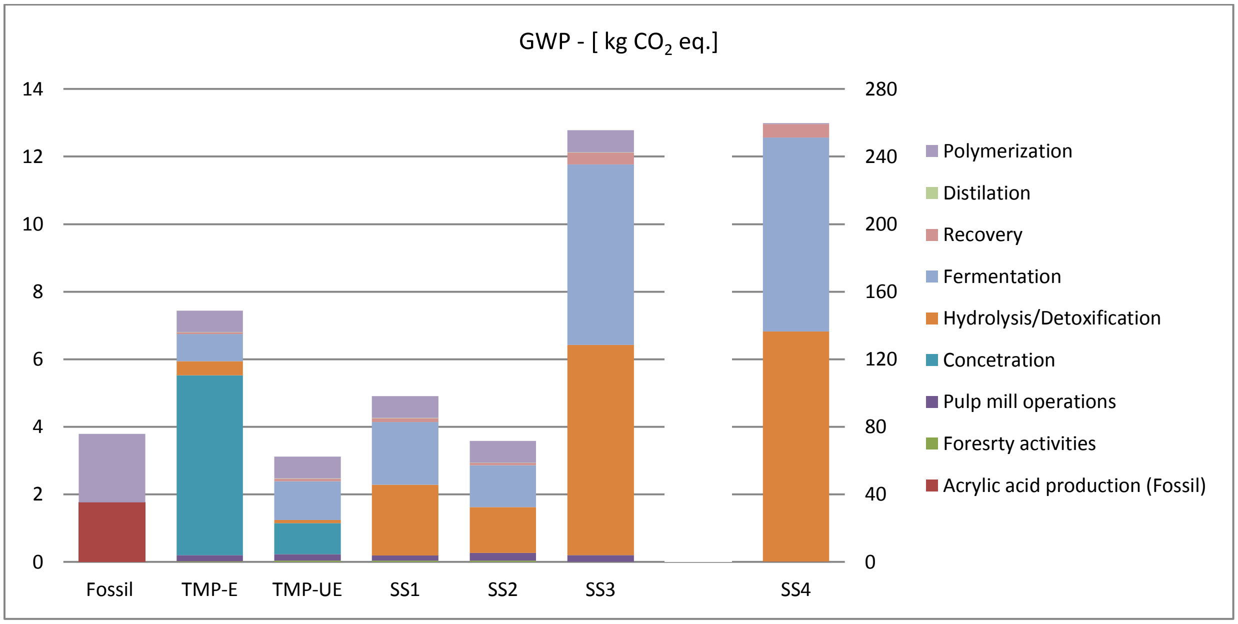


Figure C2: 75% yield of 66.88% pathway scenario

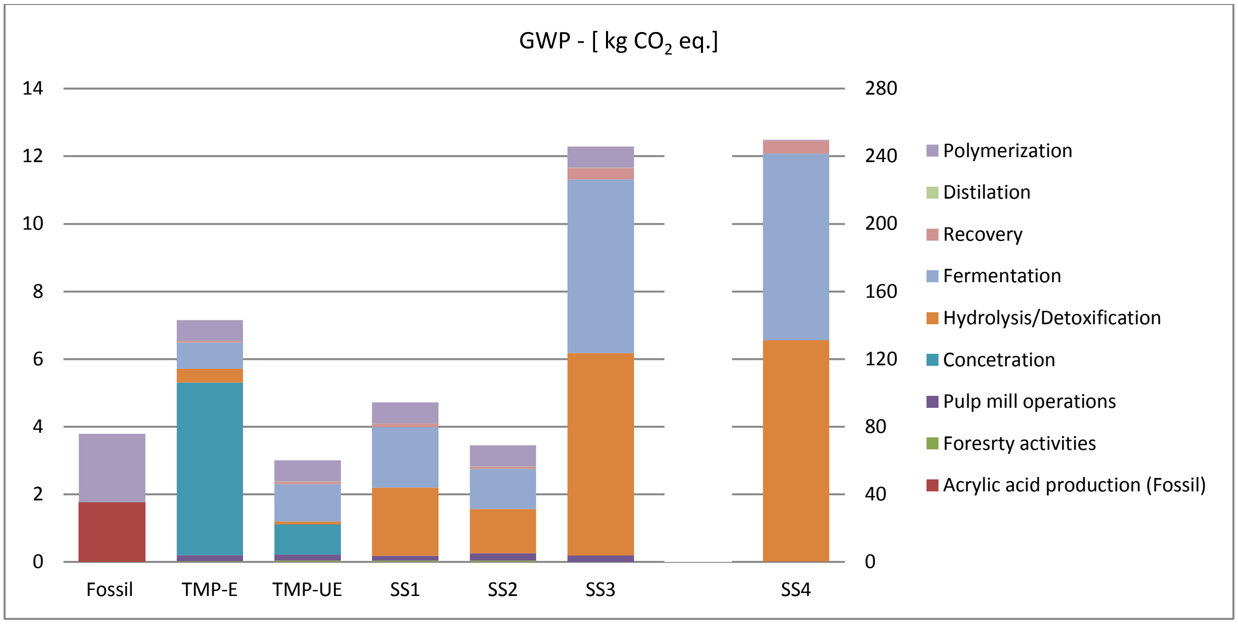
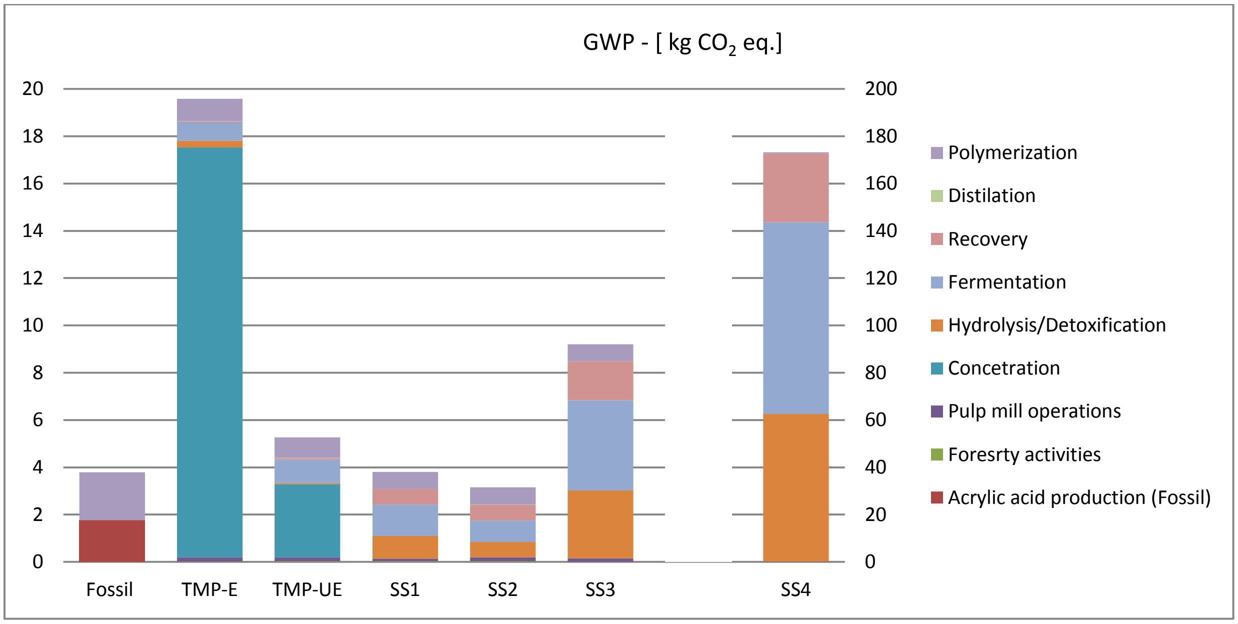


Figure C3: 60% yield off 86% pathway scenario

GWP for 25% fossil heating scenario



FigureC4: GWP for 25% fossil heating system