

Life cycle assessment of bio-based sodium polyacrylate production from pulp mill side streams: Case study of thermo-mechanical and sulfite pulp mills

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Abstract

Sodium polyacrylate (Na-PA) is a super absorbent polymer, which is commonly used in diverse hygiene products. The polymer is currently produced from fossil feedstock and its production consequently leads to adverse environmental impacts. Na-PA production from sugars present in pulp mill side streams can potentially be a successful way to achieve a more sustainable production of this polymer. In order to guide the development of a novel biochemical process for producing Na-PA, a life cycle assessment was done in which Na-PA produced from side streams of thermo-mechanical pulp (TMP) and sulfite pulp mills were compared. Furthermore, a comparison was made with Na-PA produced from fossil resources. The results show that the main determinant of the environmental impact of the bio-based Na-PA production is the free sugar content in the side streams. The lowest environmental impact is achieved by the least diluted side streams. More diluted side streams require larger amounts of energy for concentration, and, if the diluted streams are not concentrated, processes such as hydrolysis and detoxification, and fermentation are the environmental hotspots. Furthermore, the higher the yield of the fermentation process, the lower the environmental impact will be. Lastly, the production of bio-based Na-PA led to a lower global warming potential for some of the considered pulp mill side streams, but all of the other impacts considered were higher, when compared to fossil-based Na-PA production. Therefore, in parallel with efforts to develop a high-yield yeast for the fermentation process, technology developers should focus on low energy concentration processes for the side streams.

Keywords:

life cycle assessment, bio-based production, polyacrylate, sulfite pulp mill, thermo-mechanical pulp mill, side streams

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1. Introduction

The environmental issues pertaining to the fossil resources along with their increased scarcity are the main drivers of exploring new technologies for bio-based products manufacturing. As a consequence, in the near future, bio-based fuels, chemicals and materials are expected to achieve a larger market share ([van Haveren et al., 2008](#)). The substitution of non-renewable feedstocks with renewable ones and the reduction of the direct environmental impact during production are two relevant strategies for developing a sustainable product. However, the current production of bio-based products which is mostly based on 1st generation feedstocks such as corn, sugarcane and rapeseed, is in direct competition with the food and feed industry. This competition raises ethical and environmental concerns regarding the sustainability of bio-products ([Cherubini, 2010](#)) and much effort is put into shifting to lignocellulosic feedstock (non-food crops or second generation), which is very attractive since it is the most abundant and renewable resource on Earth ([Chen, 2015](#)). In this study the use of lignocellulosic residue, released in the form of diluted side streams discharged from pulp mills, is the feedstock considered for the production of sodium polyacrylate.

Sodium polyacrylate (Na-PA) is commonly applied as a super-absorbent polymer in hygiene products and is currently produced from fossil feedstock in conventional refineries. In parallel a new process is in its early stages of development where a bio-based polymer is engineered ([BASF, 2014](#)). The main innovative part of the process in development is the conversion of the fermentable sugars into 3-hydroxypropionic acid (3-HP) by genetically modified yeast. 3-HP was selected in a report by the US Department of Energy as one of the most promising platform chemicals for production of high-value bio-based chemicals or materials ([Valdehuesa et al., 2013](#)). Developing new added value products is highly relevant for the pulp and paper industry which is losing economic value due to, among other factors, high energy and fibre prices, and the decrease in paper consumption. This industry needs to explore new revenue streams ([Janssen et al., 2008](#)), and the use of the side streams for producing polyacrylates in an integrated biorefinery is an opportunity to increase its competitiveness. The production of Na-PA is also of interest for several hygiene companies situated in Sweden (e.g. SCA), which are currently importing the polymer.

Life cycle assessment (LCA) is a method used to determine the environmental burdens of multiple varied products and processes. It has been successfully applied to determine the environmental impacts associated with bio-based products that are typically manufactured in biorefineries. Most LCA studies in this field have focused on first and second generation biofuels, which can be explained by the high interest in replacing fossil fuel in the transportation sector ([Cherubini, 2010](#)). In contrast, fewer studies have considered biopolymer production based on second generation lignocellulosic feedstocks, with polyhydroxyalkanoate (PHA) being

one exception ([Koller et al., 2013](#); [Shahzad et al., 2013](#)). To the authors' knowledge, there are no studies analyzing bio-based Na-PA production from an environmental perspective. However, in one study poly-itaconic acid, which has properties similar to Na-PA, produced from wood and corn feedstock, was assessed using LCA ([Nuss and Gardner, 2013](#)). As in the present study, the environmental burdens were compared with fossil-based Na-PA. Additionally a more recent study analyzed acrylic acid produced from corn feedstock ([Nuss, 2015](#)). In the present assessment, acrylic acid is polymerized to form Na-PA, but it is produced from pulp mill side streams. Although many studies considered biomass residue from agriculture and forestry activities as the feedstock, few investigated the production of bio-products from industrial waste streams, such as diluted side streams from pulp mills. One relevant study is the assessment of ethanol and potassium acetate production from a diluted side stream released at a hardboard facility ([Liu and Shonnard, 2014](#)). The aim of the study was to compare the bio-products with their fossil-based counterparts and to account for the changes to the initial hardboard plant due to the presence of the integrated biorefinery. Another relevant study considered an integrated pulp mill biorefinery where several output products such as cellulose, lignosulfonate and bioethanol, which is a by-product derived from the diluted black liquor side stream, were assessed ([González-García et al., 2011](#)). The study was conducted in order to determine the environmental burdens of a dissolving pulp mill integrated biorefinery and the distribution of the environmental impacts of different value added products that are obtained together with the cellulose. LCAs of bio-based products have generally been done using data that describe industrial-scale processes, and thus assess the manufacturing of these products at a mature development stage. However, LCA can also be used to assess the environmental impact of processes that are still at an early development stage, as is the case in the current study. [Shibasaki et al. \(2007\)](#) developed a methodology to assess the environmental impact of such processes and pointed out that scale-up effects cannot be neglected when these are compared to processes that run at an industrial scale. This can, for instance, be done by considering the yield of the process in development. In this case, LCA is used as a tool that can direct the technology development when comparing the fossil-based and bio-based alternatives from an environmental point of view. By identifying environmental hotspots a more benign design of the new bioprocess technology can be achieved at an early stage of development ([Krotscheck and Narodslawsky, 1996](#)).

The purpose of the LCA in this paper is to compare the production of renewable, bio-based sodium polyacrylate and its non-renewable, fossil-based counterpart. The polymer is assumed to be produced in an integrated biorefinery concept from fermentable sugars present in diluted side streams derived from two different pulp mills a thermo-mechanical pulping mill and a sulfite pulp mill.

2. Materials and methods

2.1. Description of the analyzed system

The technical system contains three main activities: production of sodium polyacrylate (Na-PA), auxiliary processes and transportation. The production of Na-PA is analyzed from cradle to the polymerization plant's gate, which includes forestry activities, pulp mill operations and polymer production (Fig. 1). Auxiliary processes are the production of energy and chemicals, which are used for the polymer manufacturing. The transportation is accounted for providing chemicals and raw material to the pulp mills where the polymer is produced. Two different pulp and paper facilities are investigated here: a thermo-mechanical pulp (TMP) mill in Sundsvall and a sulfite pulp mill in Örnsköldsvik, both located in Sweden.

2.1.1. Forestry activities

The round wood used in the pulp mills is harvested in Sweden where several forestry activities are considered: primary processes such as seedling production, silviculture operation, logging activities; secondary hauling and auxiliary processes such as fertilizer production, energy carriers and ancillary material (Liptow et al., 2013). Following the forestry activities, the round wood is transported to the pulp mill where the wood fraction is separated into cellulose and several by-products (Fig. 2).

2.1.2. TMP pulp mill

Spruce wood with a moisture content of 50 % is the feedstock used for pulp production. Approx. 7 % of the round wood is bark which is burned in a boiler to produce energy. The wood chips obtained from the chipping machine are sent to the thermo-mechanical pulping (TMP) process. The TMP process is energy intensive and consumes as much as 2.2 kWh kg^{-1} pulp wood (Fig. 2). Most of the energy (66 %) used in the TMP process is recovered in the form of low quality steam which is further cleaned with a yield of 95 % (Institute for Industrial Productivity, 2013). From the TMP process the pulp (99 % of the dry wood fraction) is further sent to the washing process, and the TMP side stream which contains 1 % of the dry wood fraction is used in the production of Na-PA. Due to its diluted nature, the TMP side stream is concentrated prior to the hydrolysis and detoxification process. Two methods have been tested: evaporation (TMP-E) and ultra-filtration together with evaporation (TMP-UE) (see Table 1 for the description of the side streams).

2.1.3. Sulfite pulp mill

Similar to the TMP pulp mill, the wood logs are debarked first (the bark is used for heat production) and then sent to the chipping machine. The wood logs used are 40 % spruce and 60 % pine with a moisture content

of 50 %. Next, the wood chips are sent to the cooking process where sodium hydroxide and sulfite are added to the process. From the cooking process, side stream 1 (SS1) which contains approx. 10 % of the wood fraction, is released (Fig. 2). The cooking broth is further washed and the cellulose is separated (approx. 48 % of the wood fraction). Black liquor from the washing process is recovered and sent to the evaporation process. From this process, a part of the black liquor (containing approx. 14 % of the total wood fraction) is used for bioethanol production. The same stream of black liquor, named here side stream 2 (SS2) (Fig. 2), is used for the production of Na-PA. Side stream 4 (SS4) with less than 0.1 % of the wood fraction, lignosulfonates (24 % of wood fraction), and sludge (approx. 4 % of the wood fraction) are also obtained from the evaporation process (Fig. 2). Following the ethanol production where most of the available feedstock is used in the production of ethanol, side stream 3 (SS3) with a content of approx. 5 % of the total wood fraction is released (Fig. 2). All the four side streams released are used for acrylic acid production.

2.1.4. Polymer production

The side streams enter the hydrolysis process where fermentable sugars are released. This process is the same for all the side streams. However, the concentration and detoxification procedures differ for the different side streams.

The TMP mill side stream is concentrated 50 times via either evaporation (TMP-E) or ultra-filtration and evaporation (TMP-UE) (see 2.1.2). Approx. 33 % of the sugars are lost from the streams when they are ultrafiltered. Next, the concentrated TMP side streams are chemically hydrolyzed with sulfuric acid. Additionally, the TMP-E side stream is detoxified with sodium dithionite in order to reduce the inhibitory conditions in the fermentation process. The TMP-UE side stream is not detoxified, because laboratory tests showed no improvement in the fermentation yields (personal communication). The four side streams from the sulfite pulp mill are not concentrated, and they are used as released from the pulp mill (Table 1). All the sulfite pulp mill side streams are chemically hydrolyzed by adding 2.5 % sulfuric acid to the medium. Finally, in order to reduce the amount of inhibitors during the fermentation the sulfite pulp mill side streams are detoxified with sodium hydroxide (personal communication, Chalmers University of Technology, March 2014).

Yeast metabolizes the fermentable sugars from the side streams in the fermentation process and converts them into 3-hydroxypropionic acid (3-HP). 90 % of the maximum theoretical yield of the β -alanine metabolic pathway (86 %) is assumed as the conversion yield (Borodina et al., 2015). The resulting 3-HP is recovered from the fermentation broth in a series of flash vessels. The recovered 3-HP is then sent to the dehydration process where phosphoric acid is added as a catalyst to convert 3-HP into acrylic acid with a yield of 97.5 % (Cie et al., 2012). Then, a three step-distillation process takes place from which purified acrylic acid (99.99 %) is obtained.

is obtained. Most of the bottom product (approx. 99 %) is recovered and sent back to the dehydration process.

The highly concentrated acrylic acid is polymerized in order to produce Na-PA. A solution polymerization process is assumed because it is the most common process used in the industry at the moment (Sanderson and Sadiku, 2003). Acrylic acid is first neutralized with sodium hydroxide, which is followed by the polymerization process that is initiated with a small quantity of ammonium peroxydisulphate $((\text{NH}_4)_2\text{S}_2\text{O}_8)$. 98 % of the total acrylic acid monomer is polymerized in the process (Sanderson and Sadiku, 2003).

2.2. LCA description

2.2.1. Set-up of the LCA

Although fossil-based and bio-based Na-PA are made from different feedstocks (fossil oil and lignocellulose), and two different processes for the production of the monomer, acrylic acid, are used, it is assumed that both have the same functionality and quality. Thus, the functional unit is an amount of Na-PA and the reference flow is 1 kg of Na-PA. The LCA follows an attributional approach due to the defined goals of the study which are: 1) to identify the environmental hotspots in order to direct the development, and 2) to compare the bio-based polymer from the different pulp mill side streams with the fossil-based polymer. A partitioning of the environmental impact based on the mass of the flows was used, where needed. The results of the LCA are intended for academic researchers, technology developers and decision makers from involved industries.

The life cycle impact assessment was carried out using the CML characterization method (Guinée et al., 2002) and the impact categories examined in this study are:

- Global warming potential (GWP)

The use of biomass instead of petroleum as feedstock for polymer production can reduce global warming. However, to what extent depends on many factors, such as geographical boundaries of the study, technology used, type of feedstock, etc. Therefore, it is highly relevant to consider this impact category. It should be noted that biogenic carbon emissions are considered as climate neutral and are not accounted for in this study, although several recent studies have contested the climate neutrality of biomass (McDermott et al., 2015; McKechnie et al., 2011).

- Eutrophication potential (EP)

The use of nutrients, which contain nitrogen and phosphorus and are used in the fermentation process, may lead to increased eutrophication of soil and water.

- Acidification potential (AP)

The release of SO_2 and NH_3 is due to incomplete combustion of biomass and fossil fuel, which has an impact on the acidity of water and soil.

- Photochemical ozone creation potential (POCP)

The ozone is created in the presence of NO_x, emitted due to incomplete combustion of fossil fuels and biomass, and sunlight.

Renewable and non-renewable energy used (REU and NREU) (Frischknecht et al., 2007) during the production of Na-PA are also accounted for. Direct and indirect land use change are omitted from this study. The former one is omitted because the Swedish forest has been well managed for more than a hundred years and no significant land use change has taken place any more (Swedish Wood, 2012). Indirect land use change is due to marginal effects on the system modeled, and here an attributional approach is used. Nevertheless, it is important to underline that the land area required will be considerably higher for the bio-based polymer than for the fossil-based counterpart.

A baseline model was constructed, and the major assumptions considered in this model were 1) that 90 % of the maximum theoretical yield of the β -alanine metabolic pathway (86 %) was achieved, and 2) that all the extra heat required in the process was produced from wood which was modeled using the 'heat, at cogen 6400kWth, wood, allocation heat' process (cogen stands for cogeneration of heat and electricity) (Bauer, 2007) from the ecoinvent database (Frischknecht et al., 2005).

2.2.2. Data collection

The emission data for the forestry activities were collected for 1 m³ s.u.b. (solid wood under bark) of wood from Liptow et al. (2013). Operating data of the pulp mills (yields, chemicals and energy) were collected from the industrial partners involved in the project through personal communication. Data for the concentration of the TMP pulp mill side streams were gathered from lab experiments (personal communication, Chalmers University of Technology, March 2014). The energy needed to evaporate one liter of water was assumed to be 0.47 MJ heat (Cie et al., 2012). For the hydrolysis, detoxification and fermentation processes (nutrients only), most of the foreground data originated from lab experiments (personal communication, Chalmers University of Technology, March 2014). It was assumed that these data also apply at an industrial scale process. Data related to recovery of 3-HP, energy required in the fermentation process, distillation and dehydration were collected from a simulation of the acrylic acid production process done by Cie et al. (2012). The data for the polymerization process were collected from literature (Sanderson and Sadiku, 2003).

In a sensitivity analysis, the malonyl-CoA metabolic pathway, which is another pathway to produce 3-HP and has a maximum theoretical yield of 67 % (Chen et al., 2014), was tested for the system under study. For both metabolic pathways (β -alanine and malonyl-CoA), the fermentation yield for which bio-based Na-PA has a lower environmental impact than the fossil-based Na-PA, were determined. Furthermore, in order to

determine what would be the impact of concentrating the highly diluted side streams from the sulfite pulp mill side streams (SS3 and SS4, Fig. 2 and Table 1), similar to the TMP side stream, they were assumed to be concentrated prior to the fermentation process in another sensitivity analysis. It was assumed that SS3 was concentrated 6 times prior to the hydrolysis process whereas SS4 was concentrated 50 times. When concentrated via ultra-filtration a 33 % sugar loss was also assumed, as was the case for the TMP-UE side stream. An increase of inhibitory conditions due to the applied concentration process which may also require a detoxification process, was not considered in this analysis. Lastly, it was assumed in the baseline that only biomass heat is used for the extra heat required in the bio-based polymer production. This may however not be attainable. Therefore, several cases in which fossil fuel was used as an additional fuel were constructed (see results in sensitivity analysis). Theecoinvent process ‘heat, heavy fuel oil at industrial furnace 1 MW’ (Jungbluth, 2007) was used to model this.

The ‘acrylic acid, at plant’ ecoinvent process was used to model the fossil-based acrylic acid production (Althaus et al., 2007). The fossil-based N-PA was assumed to be produced in The Netherlands (NL) and thus the energy mix for NL was employed from the ecoinvent database. The bio-based Na-PA production was assumed to be co-located at the pulp mills and therefore the energy mix for Sweden (SE) was employed. The polymerization process used for both types of Na-PA was assumed to be the same. The only difference is the energy mix applied due to different locations of the plants (NL and SE). Processes from the ecoinvent database were also used to model the production and transportation of the chemicals needed in the bio-based acrylic acid production process, and for the auxiliary processes (electricity and heat production and use). Most of the chemicals needed in the processes were found in the ecoinvent database whereas for the missing chemicals stoichiometry or literature data were used (see Supplementary data). The chemicals were assumed to be produced at the nearest location to the pulp mills (see Supplementary data). All the data collected were used for calculation of the mass and energy balances in a spreadsheet. The resulting inventory data (see Supplementary data) were then implemented in the open source LCA software openLCA (Ciroth, 2007), and the life cycle impact assessment was run.

3. Results and discussion

The results for the baseline are shown in Figs. 3 and 4 for all the four environmental impact categories considered (GWP, AP, EP, POCP), and REU and NREU, respectively. Each bar chart shows the results for the bio-based Na-PA produced from the side streams co-located at the two pulp mills, and for their fossil-based counterpart. At first glance, the results show that Na-PA produced from four of the side streams (TMP-E,

TMP-UE, SS1 and SS2) have a lower GWP than the fossil-based Na-PA. However, fossil-based Na-PA shows a lower environmental impact for the other environmental impact categories considered (EP, AP, and POCP). Furthermore, the impacts of biogenic carbon emissions were not included in the analysis, and these emissions may increase the GWP of the biopolymer production from the side streams. It stands to reason that due to the slow growth rate of trees in a Nordic forest (from which the sugars in the pulp mill side streams originate), the bio-based polymer should be applied in a product with a longer life span in order to minimize the impact of biogenic carbon emissions. Na-PA produced from three side streams (TMP-UE, SS1 and SS2) have a lower NREU than the fossil-based Na-PA, and Na-PA produced from all side streams have a much higher REU than their fossil-based counterpart. Regardless of the side stream used for the production of Na-PA and the possible changes in energy mix, the total energy use (REU+NREU) in the production of the bio-based polymers is always higher than in the production of the fossil-based polymer. The interpretation of the results is detailed in the next sections.

3.1. TMP pulp mill

Except for GWP, the environmental impacts of TMP-UE Na-PA (Na-PA produced from the TMP-UE side stream) are up to approx. 4 times lower than those of TMP-E Na-PA. For example, the AP of TMP-UE and TMP-E Na-PA are 2.2×10^{-2} kg SO₂-eq and 8.0×10^{-2} kg SO₂-eq, respectively. The difference in GWP is not as big, but still significant at 3.7 kg CO₂-eq for TMP-UE Na-PA and 2.0 kg CO₂-eq for TMP-E Na-PA, respectively. The GWP of fossil-based Na-PA is 3.8 kg CO₂-eq, (Fig 3a), and Na-PA produced from the TMP side stream thus performs better from a climate impact point-of-view. The results for REU and NREU show similar trends as in the case of the impact categories (Fig. 4), and it can be concluded that combining ultra-filtration and evaporation is the better method to concentrate the TMP side stream. However, the environmental gains of using ultra-filtration as the concentration process are reduced due to the loss of fermentable sugars by 33 % from the side stream. The loss of sugars affects the environmental performance of TMP-UE due to an increase of wood required to produce 1 kg of Na-PA (TMP-UE needs approx. 0.33 m³ s.u.b. and TMP-E needs approx. 0.22 m³ s.u.b. of wood). Nevertheless, this loss of sugars is not high enough to cause an increase in the impact that would exceed the impacts related to the evaporation process in the case of TMP-E Na-PA.

The concentration process is the main environmental hotspot due to its significant energy use (Fig. 3). There is however one exception, the GWP of TMP-UE Na-PA, in which case the environmental hotspots are the fermentation process (37 %) followed by the polymerization process (32 %). This is due to the increased use of nutrients and chemicals required to overcome the loss of fermentable sugars (33 %). The polymerization process has a significant contribution and is discussed separately in section 3.3 for all the side

streams. In the case of TMP-E Na-PA, the detoxification process contributes significantly to the AP and POCP impact categories (8 % and 19 %, respectively). This is due to the use of sodium dithionite ($\text{Na}_2\text{S}_2\text{O}_4$) in the detoxification process.

The highest contributor to REU is the concentration process for both TMP-E (95 %) and TMP-UE (74 %) Na-PA, because all process energy needed is generated from biomass in the baseline (Fig. 4). The TMP process is energy intensive and contributes significantly to the NREU results. However, only 1 % of the total electricity used in this process is allocated to the TMP side stream. The pulping process contributes 31 % to TMP-UE Na-PA and 23 % to TMP-E Na-PA. Nevertheless, the contribution to the environmental impact categories (GWP, EP, AP and POCP) is insignificant, because non-renewable energy in Sweden consists to a large extent of nuclear energy which contributes little to these impact categories.

3.2. Sulfite pulp mill

At the sulfite pulp mill, the side streams are not concentrated prior to the fermentation process. Na-PA that is produced from the side streams with a relatively high concentration of fermentable sugars (26 g L⁻¹ for SS1 and 41 g L⁻¹ for SS2) has an environmental impact that is 2 to 3 times lower than Na-PA produced from SS3 (8.9 g L⁻¹ of fermentable sugars). For instance, the GWP of SS1 Na-PA and SS2 Na-PA are 2.9 kg and 2.1 kg CO₂-eq, respectively, compared to a GWP of 7.1 kg CO₂-eq for SS3 Na-PA (Fig. 3). The production of Na-PA from SS4, which has a GWP of 138 kg CO₂-eq, is an extreme case because the fermentable sugar concentration in this stream (0.45 g L⁻¹) is very low compared to the other side streams. The environmental impact of SS4 Na-PA is two orders of magnitude higher than that of Na-PA produced from the other side streams and their fossil-based counterpart. The results for all the other impact categories (AP, EP, POCP), and REU and NREU, follow the same pattern (Figs. 3 and 4). These results underline that more diluted side streams require larger quantities of wood feedstock, chemicals and energy in order to produce 1 kg of Na-PA (see Supplementary data), and this consequently increases the environmental impacts.

The main hotspots are the hydrolysis and detoxification, and fermentation processes for all the environmental impact categories. In the case of GWP, these two hotspots contribute 30 % and 41 % to the impact of the SS1 polymer, 25 % and 36 % to the impact of the SS2 polymer, 37 % and 49 % to the impact of the SS3 polymer, and 41 % and 54 % to the impact of the SS4 polymer, respectively (Fig 3a). The contribution of these processes is within the same range for all other impact categories (from 20 % to 58 %). The production of sulfuric acid (used in the hydrolysis process), sodium hydroxide (used for detoxification of the side streams) and ammonium sulfate (used as nutrient in the fermentation process) which cause emissions of carbon dioxide, sulfur dioxide, phosphate, and nitrogen oxide, contribute most to all impact categories considered.

The process for recovering the 3-HP from the fermentation broth is the main contributor to REU for Na-PA produced at the sulfite pulp mill. This is due to the large quantities of biomass energy required in this recovery process (Fig. 4a). The contribution of the recovery process in case of SS3 and SS4 Na-PA to GWP is approx. 3.2 % and 3.7 %, respectively. It should be noted however that this contribution is higher for EP, AP and POCP (11 %, 15 % and 7 % for SS3, respectively; 14 %, 18 % and 8 % for SS4, respectively).

3.3. Polymerization process

The polymerization process contributes to all impact categories for Na-PA produced from most side streams. Its contribution to the GWP of TMP-E, TMP-UE, SS1, and SS2 Na-PA is 17 %, 32 %, 22 % and 29 %, respectively. For the highly diluted side streams (SS3 and SS4, Table 1) the contribution of the polymerization process is less significant: it contributes 9 % to SS3 and only 0.1 % to SS4 (Fig. 3a). The results for the GWP of the polymerization process are reflected in the results for the NREU (Fig 4b). The high contribution to GWP and NREU is primarily related to the use of sodium hydroxide and the energy mix used in the process (see Supplementary data). For the other impact categories (AP, EP and POCP) as well as the REU, the contribution of the polymerization process follows the same trend but it is lower than in the case of GWP and NREU.

In the case of the fossil-based polymer, the contribution of the polymerization process is much higher than in the case of the bio-based polymers (for GWP it contributes with 53 %). For EP, the polymerization process contributes up to 77 %. The bio-based and fossil-based production processes use the same amount of energy in the polymerization process (7.8 MJ) for producing 1 kg of Na-PA. The difference in the results is related to the different locations of these processes (Sweden and the Netherlands, respectively), and consequently to the energy mix used in these countries. The Netherlands has a larger share of fossil power in the energy mix. In other work, the energy mix employed in different countries was also shown to have a large influence on the environmental impacts in biopolymer production (Shahzad et al., 2013). It should be noted that when the production of the bio-based polymer becomes viable at an industrial scale, the energy mix for the Netherlands may have changed and have a larger share of renewable energy and thus have a lower environmental impact. Furthermore, it is relevant to understand the importance of defining the system boundaries when comparing bio-based and fossil-based Na-PA with regards to the high contribution of the polymerization process. If the gate product had been set to the acrylic acid product instead of Na-PA, only TMP-UE and SS2 Na-PA would have better GWP results than their fossil-based counterpart. However, this would not be the case for all the other impact categories, and REU and NREU.

In a study of the production of poly-itaconic acid (Nuss and Gardner, 2013), the Itaconix polymerization process was employed which showed a lower contribution to the environmental impact when compared to

the results for the polymerization process in the current study. In the study by [Nuss and Gardner \(2013\)](#), the data regarding the process were collected through personal communication and these data were not further specified in the paper. Thus, a direct comparison cannot be made between the two types of polymerization processes. What can be concluded is that the Itaconix process appears to have a lower environmental impact than the polymerization process that was employed in the current study ([Sanderson and Sadiku, 2003](#)).

3.4. Sensitivity analysis

3.4.1. Fermentation yields and metabolic pathways

Several metabolic pathways for converting fermentable sugars into 3-HP have been mentioned in the literature ([Valdehuesa et al., 2013](#)), of which two were considered here. The β -alanine intermediary pathway ([Borodina et al., 2015](#)) with a maximum theoretical yield of 86 % was assumed for the baseline. In the sensitivity analysis the malonyl-CoA intermediary pathway ([Chen et al., 2014](#)) with a maximum theoretical yield of 67 % was considered. In both cases, it was assumed that the fermentation yield is 90 % of the maximum theoretical yield.

The GWP of TMP-UE and SS2 Na-PA is lower than the GWP of fossil-based Na-PA in case of the malonyl-CoA pathway (Fig. 5). In the baseline case, TMP-E and SS1 Na-PA also had a lower GWP (Fig 3a). This result shows the importance of obtaining high yields in the fermentation. The minimum acceptable yield of the fermentation process, that is, the fermentation yield at which bio-based Na-PA has a lower GWP when compared to fossil-based Na-PA, was determined in case of both metabolic pathways. The results show that overall TMP-UE Na-PA production can be run at lower yields using both pathways, and still have a lower GWP than the fossil-based polymer (Table 2). TMP-E Na-PA production needs to be run at nearly maximum theoretical yield in the baseline, and SS1 Na-PA production can be run at a somewhat lower yield. Finally, SS2 Na-PA production can, as is the case for the TMP-UE polymer, be run at lower yields for both metabolic pathways.

The metabolic pathways used in this analysis were developed and tested for processing C_6 sugars only. It is important to underline that there is a potential to also use C_5 fermentable sugars ([Novy et al., 2014](#); [Oreb et al., 2012](#)). Although most of the research is focusing on developing C_6 sugars metabolic pathways ([Valdehuesa et al., 2013](#)), the concentration of C_5 sugars in some of the side streams is high enough to be relevant in the future. To what extent the C_5 sugars would contribute to lower environmental impacts is hard to assess at this moment as no such metabolic pathway and its yield could be found in the literature. However, an increase in fermentable C_6 sugars in the side streams showed a lower environmental impact, and a lower impact thanks to the use of C_5 sugars can be expected.

The dry matter content or the concentration of fermentable sugars in the fermentation broth was also discussed in previous studies (Janssen et al., 2014, 2016). The sugar content in the broth can be much higher than in the present study, from 100 g L^{-1} to 300 g L^{-1} of fermentation broth. It was observed that at a higher sugar (or dry matter) content in the fermentation broth, the yield may decrease and that consequently the environmental impacts may increase (Janssen et al., 2014, 2016). In contrast, the current study indicates that highly diluted side streams lead to high environmental impacts as well. This indicates that an optimal sugar concentration (or dry matter content) should be found in order to minimize the environmental impact. The results presented for the baseline are optimistic because the assumed fermentation yield is close to the maximum theoretical yield.

3.4.2. Fossil energy use

In the baseline, it was assumed that all the process energy needed is generated by combustion of biomass (Harding et al., 2007). However, the availability of this biomass may be limited. Therefore, several cases were explored where the energy required to produce 1 kg of bio-based polymer is produced partially from fossil fuel. In the case of SS2 Na-PA, 43 % of the heat needed in the process can be produced from fossil resources without causing a higher GWP than fossil-based Na-PA (Table 3). The results also show that Na-PA produced at the TMP mill are more sensitive to changes in the type of energy source used. Especially, TMP-E Na-PA production shows a very low tolerance to fossil energy. This is explained by the high energy demand in the concentration process (Fig. 4a).

3.4.3. Concentration process

SS3 and SS4 Na-PA had the highest environmental impacts in the baseline due to the highly diluted nature of these side streams (Table 1). Therefore, in order to assess to what extent applying a concentration process to these streams would result in lower environmental impacts, they were concentrated prior to the fermentation process, similar to TMP-E and TMP-UE Na-PA, using evaporation, and evaporation and ultra-filtration.

By concentrating the SS3 and SS4 side streams via evaporation, the GWP decreased 3.2 times and 12.6 times, respectively, when compared to the baseline (Fig. 6a). This decrease is due to the lower use of chemicals and energy in the detoxification and fermentation processes, and due to lower energy demand to recover the 3-HP from the fermentation broth. Moreover, it is important to underline that, in this case, SS3 Na-PA shows an overall better result than the fossil-based alternative whereas SS4 Na-PA still has a higher GWP. For SS4 Na-PA, the concentration process via evaporation and ultra-filtration showed an even greater improvement in GWP (21 times) compared to the baseline results (Fig. 6b). On the contrary, the GWP of SS3 Na-PA decreased

2.9 times compared to the baseline result for GWP. This lower improvement can be explained by the 33 % loss of sugars from the side stream due to ultra-filtration. Nevertheless, SS3 Na-PA still attains a lower GWP than fossil-based Na-PA.

3.5. Comparison with relevant studies

The environmental impacts of producing Na-PA of the tested pulp mill side streams were compared with those published in two other studies (Nuss and Gardner, 2013; Nuss, 2015). The analysis by Nuss and Gardner (2013) resulted in a lower GWP (1.32 kg CO₂-eq) for the manufacturing of poly-itaconic acid than the GWP of producing Na-PA from all of the side streams tested in the current study (Fig. 3). The GWP of Na-PA produced from the more concentrated side streams (TMP-UE and SS2) are however in the same range. The main hotspot in the system analyzed by Nuss and Gardner (2013) was the recovery of itaconic acid from the fermentation broth which is due to the use of NaOH. In the present study, the recovery process of 3-HP from the fermentation broth has a minor contribution in all cases, and other processes contribute significantly (see sections 3.1, 3.2 and 3.3). Nuss (2015) assessed the production of acrylic acid from corn feedstock. This process, which was based on a process flow diagram from Straathof et al. (2005), resulted in a GWP of 4.9 kg CO₂-eq which is significantly higher than for the production of acrylic acid from side streams SS1, SS2, TMP-UE and TMP-E in the present study (Fig. 3). The hotspots identified by Nuss (2015) were steam production and consumption in the distillation process and the glucose extraction in the corn wet milling process. The energy needed in both these hotspots was mostly generated by burning fossil resources (natural gas and coal), whereas the energy in the present study was generated by burning biomass.

4. Conclusion

In this study an LCA was done of a novel bio-based process for the production of sodium polyacrylate (Na-PA) from sugars present in pulp mill side streams. The polymer was produced from five different side streams released at two different pulp mills (a thermo-mechanical and a sulfite pulp mill) in Sweden. The environmental impacts of the production of bio-based Na-PA were compared with fossil-based Na-PA, and the environmental hotspots of their production were identified.

The main determinant of the environmental impact of the bio-based production of Na-PA is the concentration of the fermentable sugars in the pulp mill side streams. The side streams with the highest concentration of sugars showed the best results when compared to the fossil-based counterpart. For more diluted side streams, which were concentrated to increase their sugar content, the concentration process was identified as the environmental hotspot in the process. Applying a concentration process to the highly diluted side streams prior

to the fermentation process lowered the environmental impacts significantly. Combining ultra-filtration and evaporation to concentrate the side streams resulted in the lowest environmental impacts due to its lower energy use. When the side streams were not concentrated, considerable amounts of chemicals, nutrients and energy were required in the detoxification, fermentation and 3-HP recovery processes. Another important determinant of the environmental impact was the fermentation yield. A higher yield of the fermentation process lowers the environmental impact. Therefore, yeast strains should be developed to obtain such high yields.

The production of sodium polyacrylate based on pulp mill side streams does not always lead to a better environmental performance when compared to its fossil-based counterpart. Moreover, of the environmental impacts considered, only the global warming potential shows a better performance for some of the pulp mill side streams considered. In further developing the bio-based process, the efforts to develop a high-yield yeast for the fermentation process should be complemented with the consideration of low energy processes to concentrate the pulp mill side streams.

Supplementary data

Supplementary data are available as an electronic annex.

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Table captions

Table 1

Description of the pulp mill side streams and their concentration of C₆ fermentable sugars (see also Fig. 2). The abbreviations shown in the table are also used to name the sodium polyacrylate produced from the respective side stream.

Table 2

Minimum yields (in percentage of the max. theoretical yield) for which the biopolymers have a lower GWP than their fossil-based counterpart

Table 3

Maximum percentage of fossil heat used in the integrated biorefinery for which the biopolymers have a lower GWP than their fossil-based counterpart

Figure captions

Fig. 1. Cradle-to-gate system for the evaluation of the sodium polyacrylate production. T denotes transportation.

Fig. 2. Simplified flowchart of the production of sodium polyacrylate in two different integrated pulp mill biorefineries: a TMP pulp mill and sulfite pulp mill; S.U.B. - solid wood under bark; 3-HP – 3 hydroxypropionic acid; TMP-E - TMP side stream concentrated via evaporation, TMP-UE - TMP side stream concentrated via ultra-filtration; SS1 - side stream 1 ; SS2- side stream 2 SS3 - side stream 3; SS4 - side stream 4

Fig. 3. Environmental impacts of the production of the polyacrylate from the selected pulp mill side streams: a. global warming potential (GWP), b. eutrophication potential (EP), c. acidification potential (AP), and d. photochemical ozone creation potential (POCP)

Fig. 4. Renewable (REU) and non-renewable energy use (NREU) of the production of the polyacrylate from the selected pulp mill side streams

Fig. 5. Global warming potential (GWP) results for malonyl-CoA metabolic pathway (90 % of the maximum theoretical yield)

Fig. 6. Global warming potential results (GWP) results for: a. concentrating side streams 3 and 4 via evaporation; b) concentrating side stream 3 and 4 via ultra-filtration. The values depicted for the other streams (fossil, TMP-E, TMP-UE, SS1 and SS2) are the same as in Fig. 3a.

Tables

Table 1

Pulp mill	Description	Abbreviation	C ₆ fermentable sugars [g L ⁻¹]
TMP	TMP side stream concentrated via evaporation	TMP-E	44
	TMP side stream concentrated via ultra-filtration and evaporation	TMP-UE	66
Sulfite	Side stream 1	SS1	26
	Side stream 2	SS2	41
	Side stream 3	SS3	8.9
	Side stream 4	SS4	0.45

Table 2

Metabolic pathway	Side stream			
	TMP-E	TMP-UE	SS1	SS2
β -alanine	<89 %	48 %	71 %	55 %
Malonyl-CoA	n/a	62 %	n/a	71 %

Table 3

Side stream	TMP-E	TMP-UE	SS1	SS2
% fossil heat	<1 %	15 %	25 %	43 %

Figures

Figure 1

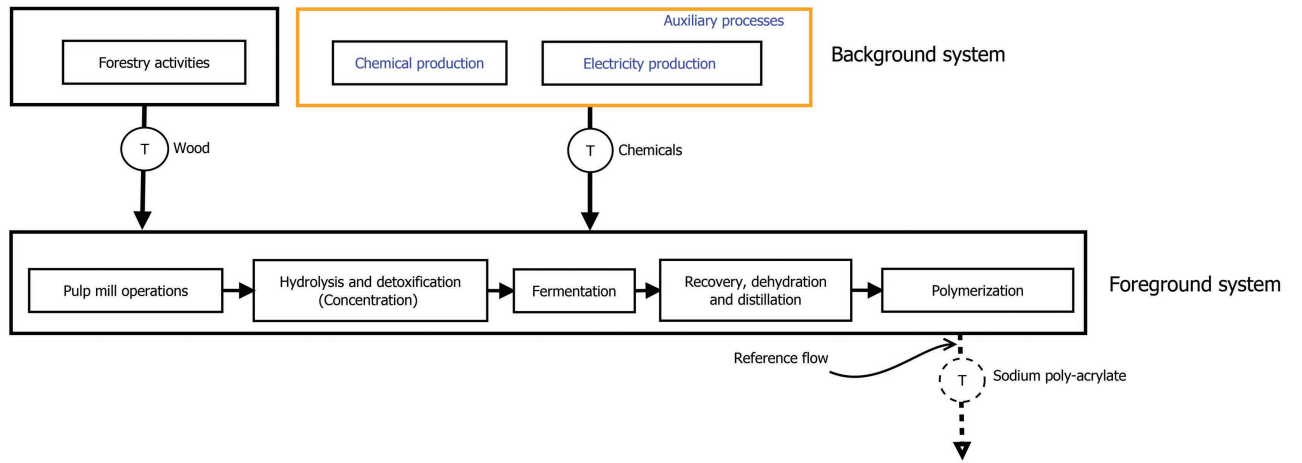


Figure 2

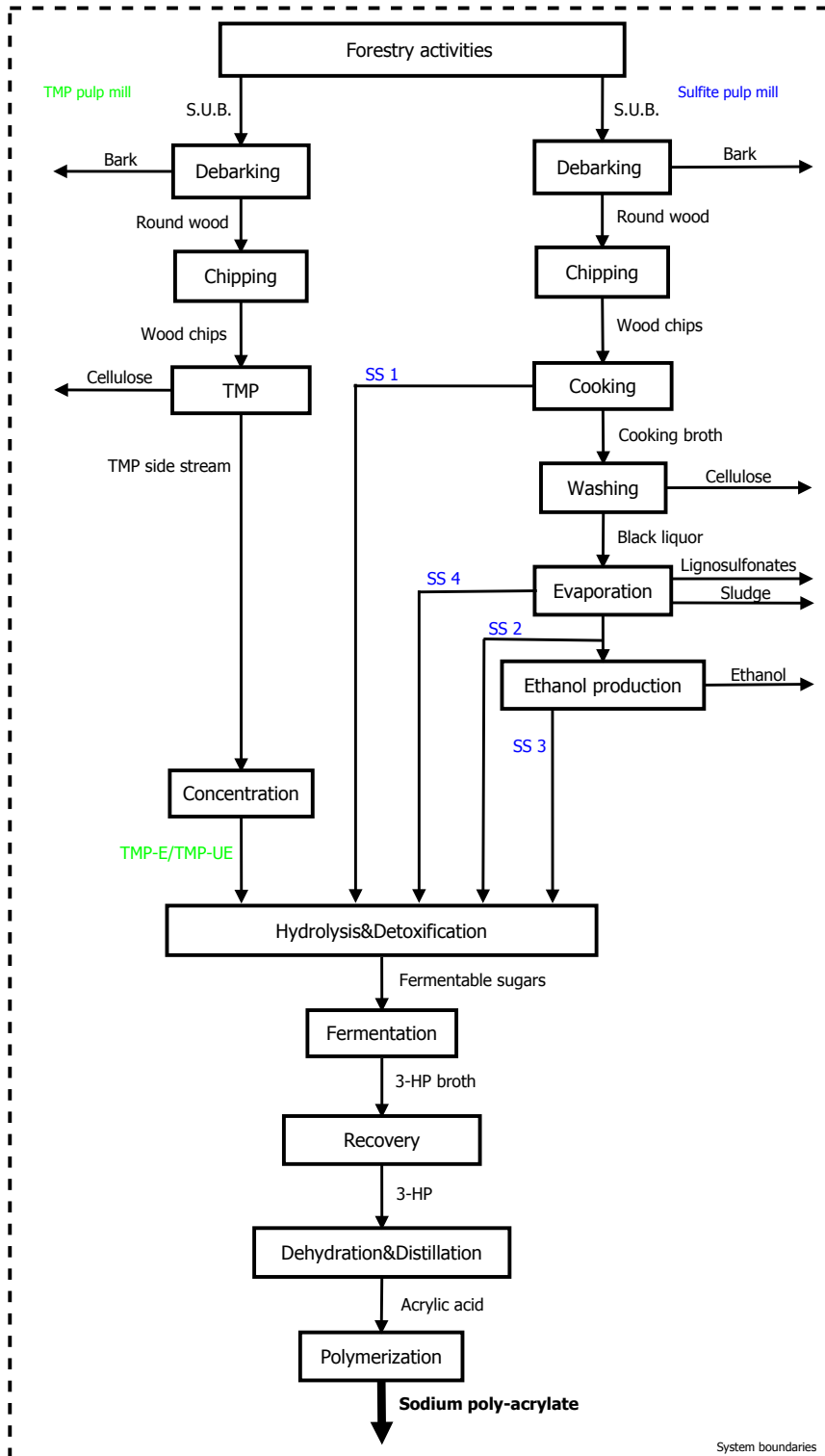


Figure 3

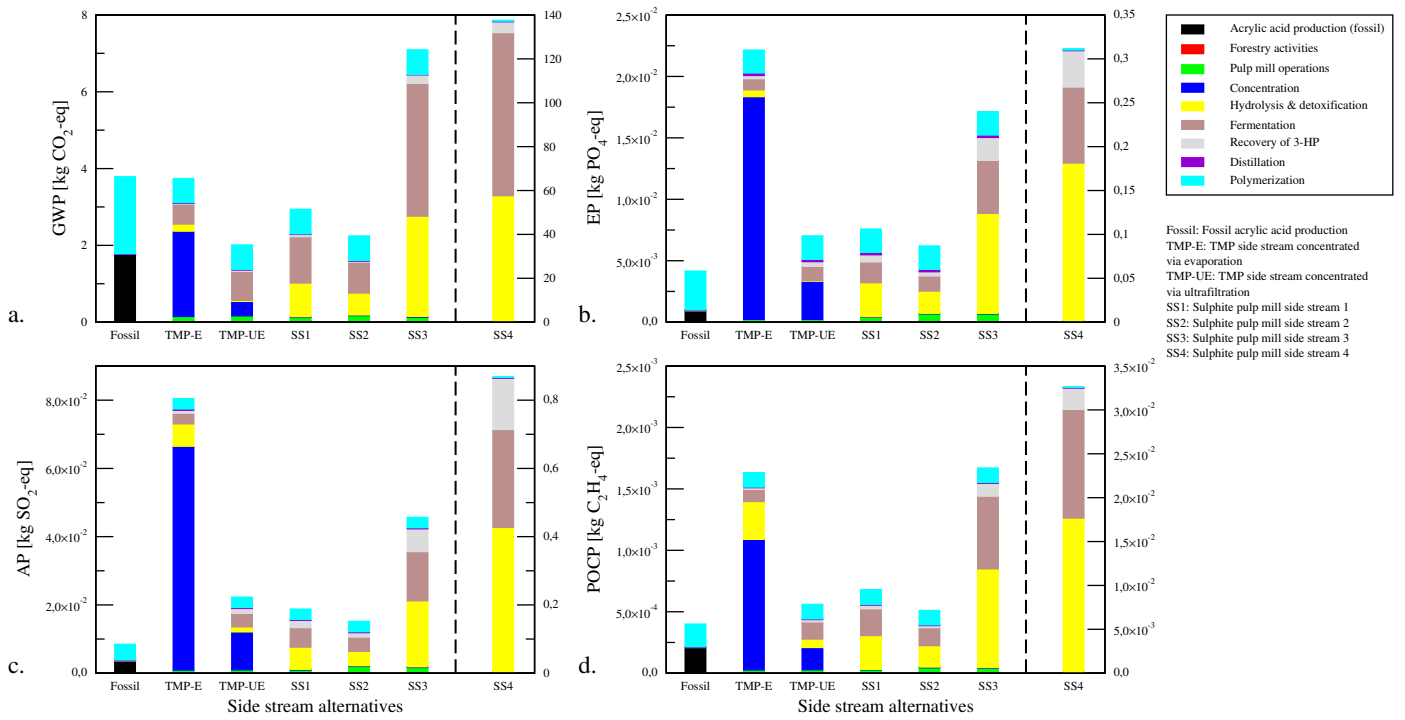


Figure 4

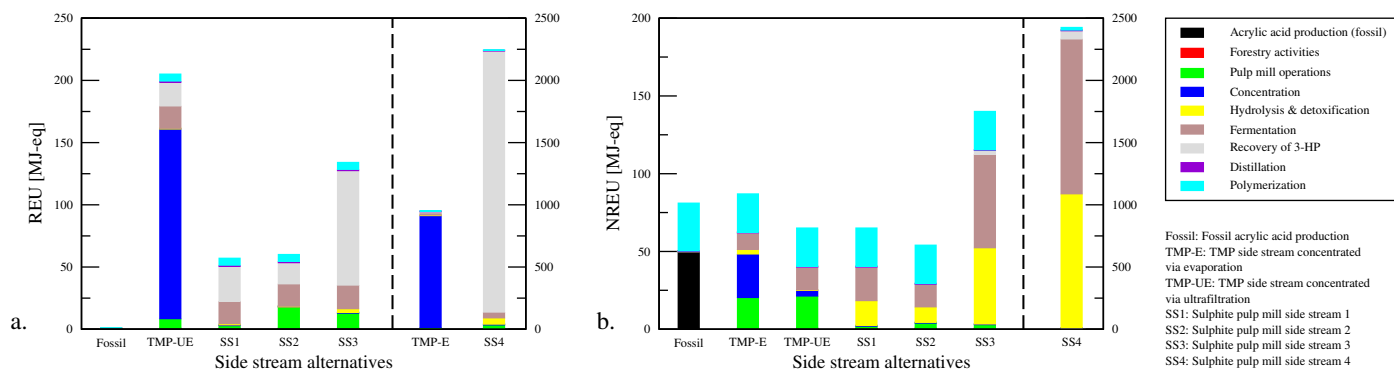


Figure 5

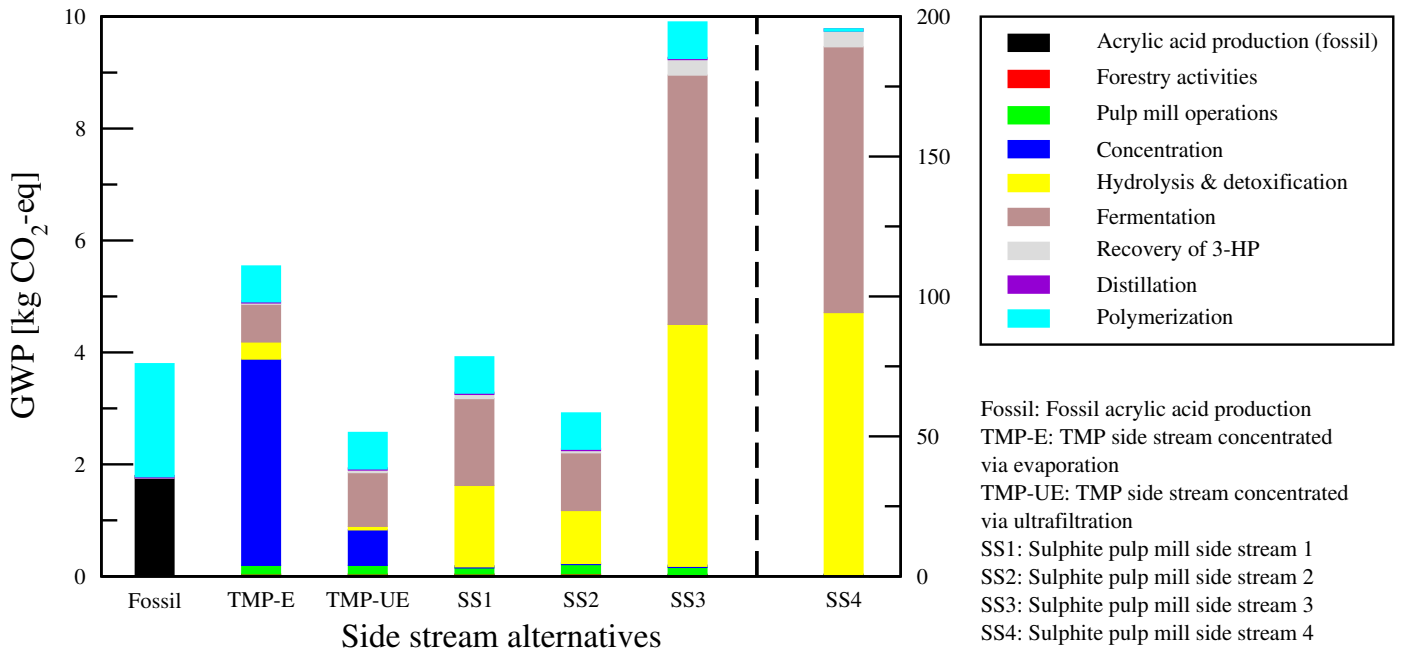


Figure 6

