Life-cycle assessment of the production of cationized tannins from Norway spruce bark as flocculants in wastewater treatment

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Abstract: It will be necessary to make efficient use of our resources if our society is to be converted into a bio-based economy. Every year large side streams of bark are produced in sawmills and pulp mills. In addition to utilizing the bark for heat and electricity production, as happens today, high-value chemical components could be extracted prior to energy conversion. These components include tannins. Cationized tannins have already been indicated as promising renewable flocculants in wastewater treatment. However, today’s industrial production of tannins uses species from subtropical or temperate climates, and there has so far been little attention to the use of tannins from Norway spruce (Picea abies), an important species in forestry in the subarctic climate. The present life-cycle assessment (LCA) was undertaken to understand the environmental performance of the production of cationized tannins from the bark of Norway spruce and how the environmental impact is distributed along the production system. This work was connected to the Interreg Botnia-Atlantica TanWat research project, which studies the production and use of cationized tannins from Norway spruce for wastewater treatment at a pilot scale. The present LCA shows that the main environmental impact stems from the reagents used in the cationization step. The purification step could also be a significant issue depending on the possibility of reusing the eluent (ethanol) and the lifetime of the resin. The importance of running the processes with as concentrated streams as possible to minimize the need of process water and energy was also confirmed © 2020 The Authors. Biofuels, Bioproducts, and Biorefining published by Society of Chemical Industry and John Wiley & Sons, Ltd.

Supporting information may be found in the online version of this article.

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Introduction

In facing today’s environmental problems and converting our society to a biobased economy, it is of the greatest importance to use our resources as efficiently as possible. Biomass is a renewable resource, nevertheless the production is inherently restricted by available land and material. In addition sustainability constraints will limit resource outtake.

One important biomass-producing sector is the forest industry. In the European Union, Sweden and Finland are the two key producers of roundwood and in 2017 roundwood production was 74 million m³ under bark in Sweden and 63 million m³ under bark in Finland. This generates a side stream of millions of cubic meters of bark each year because most industries processing round wood, such as sawmills and pulp mills, mainly use the wood fraction, and 10–22% of the log volume consists of bark.

For political and economic reasons, most of the bark is converted to energy, such as process heat in industry or district heating. However, there are many interesting chemical compounds in bark that have a potentially higher value than just their energy content. These compounds could be a valuable resource for a growing bio-based chemicals market in the global chemical industry.

One of the dominant commercial tree species in Swedish and Finish forestry is the Norway spruce (Picea abies). Approximately 10% of the spruce bark are polyphenolic water-soluble compounds called tannins. Tannins have traditionally been used for leather manufacturing in the tanning process but are now also of potential interest in numerous other applications such as adhesives, foams (e.g., tannin-based polyurethane foam), food additive, ore flotation agents, cement superplasticizers, and medical and pharmaceutical applications. One area of particular interest in recent years has been the use of tannins in water and wastewater treatment as a way of providing a renewable and sustainable solution for processes requiring the addition of substantial amounts of chemicals each year.

Separation by coagulation-flocculation is one widely used chemical-intensive water treatment process. By adding either an inorganic salt, a polymer, or a combination of both, fine particles and colloids in the water are aggregated into larger particles that can be removed by subsequent sedimentation. There are several disadvantages in using inorganic coagulants. First, they need to be added in large amounts. Second, they only work within a limited pH range. Third, they cause corrosion problems.

Polymers for coagulation-flocculation have been used for at least 40 years. Compared with the traditional use of alum salt (aluminium sulfate), polymers are more cost effective, give a smaller sludge volume, and reduce the ionic load and the aluminium content in the treated water. Cationic acrylamide-based polyelectrolytes are available in a broad range of molecular weights and charge densities, and are therefore extensively used in industry including water and wastewater treatment. Every year, approximately 2500 metric tons of polyelectrolytes are used in Swedish municipal wastewater treatment plants.

However, today’s polyelectrolytes also have several serious drawbacks. The polyelectrolytes used have a low biodegradability leading to an accumulation in the environment and thus causing concern about negative long-term environmental effects. In response to potential environmental impacts, the German Fertilizer Ordinance (DüMV) will prohibit the use of polyacrylamide in wastewater and sewage sludge treatment if it is to be used for agricultural purposes. In addition both the polymers used and the inorganic salts are produced from non-renewable resources.

There are several commercially available tannin-based flocculation products, e.g. Acquapol, Silvafloc, and Tanfloc. These products have shown that it is feasible to use tannins for the production of coagulation-flocculation chemicals. The commercial products are produced from well-known sources for condensed tannins such as from quebracho (Schinopsis balansae) and black wattle (Acacia mearnsii). However, there are today no commercially available products based on tannins from tree species abundant in the subarctic climate, such as Norway spruce.

The EU TanWat project (www.tanwat.eu) is developing new methods to produce and use tannin-based flocculants from the bark of Norway spruce at pilot scale. Looking at new production routes, it is important to understand the environmental impact of different choices making the best decisions possible and focusing development on potential improvements. An established method to evaluate a system’s environmental performance is life-cycle assessment (LCA). There are several previous LCA studies on forest management and wood production. One LCA has been published on extraction of tannins from Norway spruce bark. However, as far as we are aware, there are no published LCA studies covering the production of grafted tannin-based flocculants.

This work provides a cradle-to-gate LCA of the production of a flocculation agent based on cationized tannins from the bark of Norway spruce – i.e., from the production of spruce...
trees to the finished flocculation product ready to leave the factory gate. The aim of the sustainability assessment is to identify the most promising pathways, to identify optimization potential, and to make a tentative comparison with the three conventional commonly used flocculants: polyacrylamide, aluminium sulfate, and iron(III)chloride.

Methods

Goal and scope

The sustainability assessment of the production of cationized tannins from the bark of Norway spruce was assessed according to the ISO 14044:2006 standard for life-cycle assessment. The goal of this sustainability assessment was:

- To identify the most significant environmental issues in the production of cationized tannins from the bark of Norway spruce.
- To identify potential for further process improvements.

The results are thus intended to be a guide for process development towards improved sustainability.

The system that was studied is shown schematically in Fig. 1. The end product in this study is a dried powder of cationized tannins ready to be used as a flocculant in water treatment. A preferred functional unit would be based on the function of treating wastewater. The TanWat project aims to study the use of the cationized Norway spruce tannins as flocculants in wastewater treatment. To facilitate future use of this LCA and comparison with other flocculants, the functional unit (FU) 1 kg of dried cationized tannins was chosen instead. In this LCA, the environmental impact of the production of 1 kg cationized tannins is tentatively compared with the production of the three conventional commonly used flocculants: polyacrylamide, aluminium sulfate, and iron(III)chloride, using data adapted from Ecoinvent 3.6.

Geographical area

The geographical area of this LCA is within the region around the Gulf of Bothnia in Sweden and Finland, as indicated in Fig. 2. This region was chosen as a result of the ongoing TanWat research project, focused on the extraction of tannins from bark in this area. The main activities – forestry, sawing, extraction, and cationization – are assumed to take place in Sweden or Finland. Chemicals and fuels other than wood fuels are assumed to come from a European or world market.

System description and inventory

In the following section the system and assumptions made are described in more detail. The LCA is calculated for an anticipated future industrial-scale process. The size of the equipment was scaled in relation to processing the bark from a medium sawmill generating 23 kt of dry bark per year. The life-cycle inventory (LCI) data for forestry, transportation, and sawmill operations comes from mature industrial processes. For the extraction, adsorption, evaporation, and cationization, the LCI is based on pilot and lab-scale experiments together with estimations based on literature values and physical properties.

An overview of the mass and energy flows in the system to produce the FU 1 kg of cationized tannins is presented in Fig. 3.

In the base process design, the liquid from the bark press was...
considered as waste. To reduce the raw material use and reduce the need of water and energy in the extraction process and in the bark press, an alternative process design where the liquid from the bark press was utilized in the same way as the main extract was also examined (indicated as a dotted line in Fig. 3).

Feedstock production

Bark is formed as a side stream in several different industries. In this LCA it is assumed that the bark for the process that is being studied comes from a sawmill. This bark is relatively uniform and free of soil contaminants, which should be beneficial for the optimization of extraction.

The environmental impact of the timber production was derived from the Econinvent 3.6 dataset, covering the production of spruce stem wood in Sweden with sustainable forest management. It includes all processes related to forest management such as site preparation, planting, thinning, and harvesting, including forest roads, according to regional practice.
The mean transportation distance of saw logs from forest to sawmill in the north of Sweden is 94 km. In this LCA a transportation distance of 100 km with a freight lorry is used.

The mass balance for the amount of used timber in relation to products formed in the sawmill was based on a Swedish sawmill with an annual production of 370000 m³ sawn wood. The consumption of diesel for internal transports, heat, fuel oil and electricity was based on the same mill. All fluxes calculated for 1 FU are listed in Table S1 in the supplementary data. Construction of the sawmill and production of other equipment has not been included in this LCA.

Extraction

The tannin extraction unit is assumed to be co-located with the sawmill and the transportation between the sawmill and the extraction unit is therefore neglected. In sawmills in Sweden and Finland the logs are commonly debarked in a rotor-type debarker. As the bark exits, it is commonly shredded into smaller particles with a length less than 50 mm. This means that no further comminution is needed before tannin extraction, and the energy for comminution is included in the overall sawmill activity.

The mass balance for the extraction is based on data from studies of Norway spruce, as part of the TanWat project, in a pilot-scale pressurized hot water flow-through extraction system with a 300 L vessel at 2 MPa run in batch mode. The pilot extraction is analogous to conventional upright stationary cylindrical batch digesters used industrially for alkaline pulping. They normally have a working capacity of 70–350 m³, which is a reasonable scale for a full-scale tannin extraction process. The heat requirement depends on scale, so a theoretical value of the energy needed to heat the metal of the digester, the woodchips, and the added water was estimated within the scale of interest (supplementary data Table S2). Based on this, it was decided to use the value of 2.8 MJ kg⁻¹ dry bark extracted. The estimated energy requirement is probably an overestimation of the true value because a full-scale process is likely to include heat recovery. The heat is assumed to come from steam produced by incineration of wood chips in a co-generation unit. The electric energy for the pump is estimated as the maximum energy need of pumping all the process water at operating pressure. Constants and assumptions made for the mass and energy balance over the extraction are presented in Table S3 in the supplementary data.

After extraction, the bark is assumed to be pressed to the same dry matter content as the raw bark, in this case 0.38 kg kg⁻¹, and used as a fuel after additional dewatering. The electrical energy required for pressing the bark is estimated to be 18 kJ kg⁻¹ removed water. The heating value per dry weight is assumed to be the same before and after extraction.

In the base process design, the press liquid was treated as wastewater. In a second scenario it was assumed to have the same composition as the extract and to be used in the same way (indicated as a dotted line in Fig. 3).

Purification and drying

Before cationization, the tannin extract is upgraded in two steps: purification through adsorption and removal of solvent in an evaporation step.

Adsorption

After extraction, the water extract is passed through a bed with Amberlite XAD7HP, a non-ionic aliphatic acrylic polymer. The desired polyphenols are adsorbed while carbohydrates that might cause a problem in the final application of the cationized tannins pass through. After a wash cycle with water the polyphenols are desorbed using 70% ethanol. The mass balance for the adsorption is based on experimental data from treating 37 kg of extract in the TanWat project. The electrical energy needed for the pump was estimated for a worst case scenario of using a 8 m high column at the highest recommended flows, and pressure drop data were provided by the producer of the resin. Values used for the base process design are given in Table S4 in the supplementary data.

Evaporation

The ethanol is evaporated from the tannin extract (cf. Evaporation 1 – Fig. 3) to increase the concentration of tannins prior to cationization. The ethanol is regenerated and reused for desorption; however, in the pilot-scale experiments, 32% of the ethanol (calculated as water free) did not end up together with the collected extract and was not regenerated when drying the extract. There was also a dilution effect. The excess water is therefore removed, and makeup ethanol added to achieve the required amount of ethanol for subsequent elution. Thus, only the environmental burden of the production of 32% virgin makeup ethanol (calculated as water free) is included in the LCA. As the adsorption has not yet been optimized, calculations were also made for 2% makeup ethanol. The ethanol used is assumed to have been produced by dilute acid pre-hydrolysis and simultaneous scarification and co-fermentation (SSCF) of
Cationization

Condensed tannins are natural anionic polyelectrolytes (with ionized phenol groups depending on pH), and natural tannins have been investigated for use as flocculants in water treatment.26 However, cationic properties are usually desired. Cationic polymers are widely used in coagulation-flocculation processes for water treatment because most of the target particles in natural waters and in a wide range of industrial suspensions are negatively charged.27 Tannins can be grafted in many ways to achieve the properties required for different applications.28 A common way to introduce cationic properties to tannins is by adding a protonated tertiary nitrogen through a Mannich reaction29–33 as shown in Fig. 4. In addition to the introduction of cationic groups there is a crosslinking between formaldehyde and the Mannich base, resulting in higher molecular weight of the cationized tannins. The resulting polymers will be ampholytic with both cationic (tertiary ammonium) and anionic (ionized phenols) groups.32

In the scenario considered in this LCA, tannins in the liquid extract are modified to quaternary ammonium tannate as described in Fig. 5. First, primary, and secondary amines are created by mixing 37% formalin with ammonium chloride and concentrated hydrochloric acid. The reaction mixture is heated to 65 °C for 5 h. The tannin extract is then added and the reaction mixture is heated for another 8 h.

The mass balance over the cationization step in this LCA (Fig. 3) is based on lab-scale experiments in the TanWat project.34

The energy requirements for the cationization step will depend on the future scale of the process. A smaller reactor will require more energy, both as heat and as electricity for agitation, per kg cationized tannins produced. To find a reasonable value for the energy requirements, calculations were made with a scale of 1–40 m³ (supplementary data Table S6). The cationized product is a viscous liquid, with a viscosity of approximately 100 cP.29 In addition to volume, therefore, the effect of a viscosity change in the interval of 1–200 cP was also evaluated. Values used for these calculations are summarized in Table S7 in the supplementary data.

In the interval that was studied, the heat requirement varied between 211–214 MJ and the electric energy requirement was 3–11 MJ per cubic meter of cationized product. In the 1–200 cP interval the change in viscosity had a negligible effect on the energy consumption. To avoid underestimating the energy requirements of the cationization process, the values of 11 MJ of electricity and 214 MJ of heat per cubic meter of cationized product were used in the base-case calculations.

Drying of final product

To increase the shelf life of the product, it is dried after cationization (cf. Evaporation 2 – Fig. 2). The energy for evaporation is approximated here with the energy needed to heat the total liquid product after cationization from 65 °C to 100 °C and the latent heat for vaporization of the water in the liquid. The heat capacity of the liquid product was approximated with the heat capacity of water. The water content in the liquid product was calculated as the original water plus one mole of water formed per mole of formaldehyde added (assuming 100% turnover). Only the water was assumed to evaporate. Values used in the calculations are presented in Table S8 in the supplementary data.

Electricity

It was shown previously that the choice of electricity production system has a significant effect on the overall environmental impact. In a cradle-to-gate LCA of sawn wood in Norway, a 30% increase in the potential climate change was seen if a Nordic instead of Norwegian electricity mix was used.
used. Environmental data for several electricity mixtures were therefore evaluated in this LCA. The most relevant should be a Nordic electricity mixture (Nordic Countries Power Association) with 52 g CO₂-eq kWh⁻¹ because electricity in Sweden and Finland is traded on a common Nordic electricity market and there is a large exchange of electricity between the countries. Environmental data for electricity mixtures representing production in Sweden, Finland, and Central Europe (the Central European Power Association) was used as a comparison, with 24 g, 214 g and 840 g CO₂-eq. kWh⁻¹ respectively. The electricity mixture from Central Europe was of limited practical interest because it is from outside of the geographical scope of this LCA study, but it indicates a worst case scenario since it is mainly based on fossil fuels.

### Life-cycle impact assessment

The Ecoinvent 3.6 database was used for the life-cycle impact assessment (LCIA) using allocation at the point of substitution as system model. Used datasets are listed in Table S9 of the supplementary data.

Impact categories and characterization factors were obtained from the ReCiPe midpoint Hierarchist v 1.13 method as listed in Table S10 of the supplementary data. In this method the same impact factors are used for emissions in the near future as for emissions after 100 years. This means that there will probably be an overestimation of the environmental impact of long-term emissions. The ReCiPe model is well adapted to European conditions, which is consistent with the geographical scope of this LCA.

### Allocation

Several of the process stages in the production of cationized tannins are multiple output systems. In round wood production, forestry will generate co-products, such as wood chips from tops and branches, in addition to the saw logs and pulpwood. In the sawmill, sawn wood, pulp chips, sawdust and bark are produced. In the tannin extraction process, the extraction liquid is the main product and the extracted bark residue the co-product.

According to ISO 14044, allocation must be avoided as far as possible by using system expansion. If allocation is needed it should preferably be based on physical properties (e.g., mass or volume) when the difference in revenue from the co-products is low. In such cases, allocation should preferably be based on economic value. However, for wood products, allocation based on both energy and economic value may introduce uncertainties because there is a great variation in the moisture content, heating value, and price of round wood. In this LCA all data adapted from Ecoinvent was calculated using allocation at the point of substitution as the system model.

The emissions from round-wood production, transportation to the sawmill, and sawmill activity were all added together. Three different allocation factors were calculated to assign the impact of the upstream activities to the bark leaving the sawmill based on the mass flow in a Swedish sawmill with an annual production of 370 000 m³ sawn wood. Table 1 shows that allocation by volume will assign 9% of upstream environmental impact to bark. If energy is used, 7% will be allocated to bark, and if economic allocation is used only 2% will be allocated to bark. To avoid underestimating the possible burden of the bark production volumetric allocation was used in the base case.

The residual bark after extraction is assumed to be pressed to the same water content as the raw bark and used as a fuel to produce heat in the same way as it is used today. An equal amount of raw material is subtracted in the LCA. The net use of bark with a dry matter content of 0.38 kg kg⁻¹ to produce 1 FU is 2.2 kg in the base process design and 1.9 kg in the alternative process design where press water is used.

### Table 1. Calculated allocation factors (AF) for the different co-products in the sawmill based on their volume, energy content, and economic value.

| Input timber          | Volume | AF | Energy content | Energy content | Economic value | Economic value |
|-----------------------|--------|----|----------------|----------------|----------------|----------------|
|                       | Amount |    | Amount         | AF             | Amount         | AF             |
|                       | 10⁵ m³ |    | TJ            |                | 10⁶ SEK        |                |
| Sawn wood             | 740    | 0.48 | 3135           | 0.50           | 649            | 0.83           |
| Sawdust/raw chips     | 390    | 0.38 | 2360           | 0.38           | 102            | 0.13           |
| Bark                  | 71     | 0.09 | 439            | 0.07           | 19             | 0.02           |
| Dry chips/cutter dust | 49     | 0.05 | 303            | 0.05           | 15             | 0.02           |
Results and discussion

In this section the principal findings concerning process hotspots are discussed first. This is followed by a tentative comparison of the overall process impact compared with the production of conventional flocculants. The method used for the LCIA includes 18 impact categories. Of particular concern, based on the current focus on environmental and sustainability goals, is the potential impact on climate change and the use of fossil resources. These categories will therefore be evaluated first in detail and the others summarized in

![Figure 6. Potential impact on climate change as global warming potential (GWP) for the different process steps for the production of 1 FU. Blue bars represent the base case in which press liquid is treated as waste. The red bars show the GWP if the bark press liquid is used as a source of extractives (alternative process design).](image)

![Figure 7. Potential impact on climate change as global warming potential (GWP) in the adsorption step for the production of 1 FU. The lighter parts of the makeup ethanol and adsorbent bars indicate the potential improvement if 2%, instead of 32%, virgin makeup ethanol is needed and if the adsorbent can be reused 1000 times instead of 100 times.](image)

![Figure 8. Potential impact on climate change as global warming potential (GWP) in the cationization step for the production of 1 FU.](image)
an overview. The energy performance of the production system is also evaluated.

**Process environmental hotspots for contribution to climate change**

An overview of the potential impact on climate change, calculated as global warming potential (GWP), for the different process steps is shown in Fig. 6. The process-step feedstock represents the environmental burden from forestry, transportation, and sawmill activity allocated to bark based on the volume fraction produced. Both the adsorption and the cationization steps appear to have high GWP. These are the two steps that demand a substantial input of chemicals and are discussed further below. The benefit of re-using the bark press liquid, as in the second process alternative, is, however, limited from a GWP point of view. The net use of bark with a dry matter content of 0.38 kg kg$^{-1}$ to produce 1 FU is 2.2 kg in the base process design and 1.9 kg in the alternative process design where press water is used. That corresponds to a 15% reduction in bark use and also heat and water used in the extraction. However, since the contribution to GWP for these steps is already low, the effect on the overall system is limited.

The adsorption step has the largest potential impact on climate change in the present analysis, and is the main hotspot in the overall process for many of the ReCiPe impact categories as will be shown later in the summary of all 18 impact categories. An explanation is seen in Fig. 7 where the consumption of makeup ethanol and adsorption resin is shown to be the main reason for the high GWP value, even though bioethanol (based on lignocellulose) is assumed to be used. However, the adsorbent calculations have a considerable uncertainty because the lifetime of the resin is not known for the present application. In the base case, it was assumed that the resin can be regenerated 100 times. If it can instead be regenerated 1000 times, the impact would be significantly reduced. The consumption of resin also depends on its adsorption capacity. In the base case, this capacity was taken to be 140 mg g$^{-1}$ based on a literature value for total polyphenols from black chokeberries (*Aronia melanocarpa*). However, the actual value for Norway spruce tannins is not known and could be significantly different from this value. A lower adsorption capacity would require more electricity due to a greater pressure
drop, but the main effect would be an increase in the resin use. Nevertheless, the uncertainty of the resin lifetime probably has a greater impact on the result, with a larger probable span.

The amount of makeup ethanol needed is also uncertain. The pilot experiments of the adsorption step are still at an early stage and it was estimated that only 68% of the water-free ethanol added could be reused. Optimization will likely show that a higher share of the ethanol can be reduced. Calculations were therefore also made for the scenario in which 98% of the ethanol could be reused. A completely different option is to cationize the bark extract directly without purification. The cationized additional compounds are primarily carbohydrates and may also confer some flocculating properties. The environmental impact of the adsorption step could be decreased in this case.

For the second main hotspot, the cationization, the different contributors to climate change impact are presented in Fig. 8. The process of cationization has a long reaction time and requires heating. The product also has a high viscosity. However, even though some potential overestimations of the required heat and electricity were made in the LCI, the impact from these steps is negligible compared to the potential impact on the climate change from the chemicals used. All the three chemicals used – formalin, ammonium chloride, and concentrated hydrochloric acid – stem from energy-intense production processes based on fossil resources for both material and energy. Thus, a potential future improvement will be for chemical suppliers to start to develop fossil-free production systems for these chemicals. This is outside of the tannin producers’ control.

**Process environmental hotspots for contribution to fossil depletion**

Another important goal in using cationized tannins instead of conventional alternatives is to use renewable raw
materials instead of fossil resources. The profile in Fig. 9, showing the potential impact on fossil depletion (FDP), is qualitatively very similar, including the difference for the two process alternatives, to that for the potential impact on climate change shown in Fig. 6. This stems from the use of fossil oil both for chemicals and fuels used. It is perhaps initially surprising that the evaporations, only fueled with wood chips, have an impact on climate change. No fossil carbon is released in the combustion. In Ecoinvent, biogenic carbon and fossil carbon are treated separately and hence it is not the carbon dioxide released during incineration that is the source in Fig. 6. The contribution to climate change and fossil depletion is mainly due to the use of fossil fuels in the production and transportation of the wood chips. The same is seen in the other upstream processes involving the use of wood as a material or energy resource. These contributions could be lowered by using more biofuels in forestry operations, transportation and in forest industry. Today, a small fraction of the timber transports is fueled with hydrogenated vegetable oil (HVO), and this is not accounted for in this LCA. However, as for the potential impact on climate change, the dominating source of potential impact on fossil depletion is the use of chemicals in the cationization.

Even though the overall profiles of potential climate change and fossil depletion are qualitatively very similar, a difference in the cationization step can be seen by comparing Figs 8 and 10. The release of nitrogenous gases during the production of ammonium chloride contributes to a high potential impact on climate change, although the use of fossil resources is considerably lower than formalin.

The relative contribution to additional impact categories

In a broader perspective, the relative contribution to the impact categories of ReCiPe for the overall production of cationized tannins is shown in Fig. 11. The pattern of the burden distribution is similar in many of the impact categories discussed previously, including GWP and fossil depletion – i.e., dominated by the adsorption and cationization steps.

Energy performance

The two processes requiring most heat are the extraction and the drying of the purified extract (cf. Evaporation 1 in Fig. 12). This is due to the very dilute system with a high water content. Utilizing the liquid from the residual bark only gives a minor energy saving in the extraction. A more important improvement would be to reduce the water used in the extraction.

As shown in Fig. 13, the energy use in form of electricity is very low compared with the total energy use in form of heat and electricity (see Fig. 12), even though the values are probably somewhat overestimated. As the electricity use is low, the choice of electricity mixture between electricity from Finland, Sweden, the Nordic Countries Power Association, or the Central European Power Association had little influence on the environmental impact assessment (data not shown).

Comparison of cationized tannins with conventional alternatives

The dose that is required of a flocculant depends on the application and the agent used. Too little is known about the required dose of cationized tannins from Norway spruce for different applications, so a tentative comparison was made of the potential environmental impact of the production of 1 kg cationized tannins and the production of 1 kg of the three conventional commonly used flocculants – polyacrylamide, aluminium sulfate, and iron(III)chloride. An overview of the comparative environmental profiles for all 18 impact categories in the ReCiPe midpoint method is presented in Fig. 14.
The environmental performance of the conventional alternatives is based on data from Ecoinvent 3.6.

It is important to remember that the development of the process for producing cationized tannins from Norway spruce bark is still at an early stage and that more work will be done on process optimization. There are also some values with high uncertainties included in the calculations. Figure 14 therefore contains two bars describing the environmental impact of cationized tannins. One bar is for the base process design. The other shows a lower reasonable value, utilizing the liquid in the bark press (instead of treating it as waste), re-using 98% (instead of 68%) of ethanol in adsorption, and regenerating the adsorbent 1000 times (instead of 100 times).

It can be seen that even though the higher value of the base case in general is the highest for all impact categories, the lower value for the production of cationized tannins is within the same range as the conventional alternatives.

It should be remembered that the comparison here is not based on a practical functional unit, but simply the production of the same mass of the compound. The properties of the sludge, and their environmental impact, may also be affected by the flocculant used.

**Choice of allocation method**

As described above, it is possible to use different allocation methods in LCA. In this study the generation of bark in a sawmill (including timber production, transportation, and sawmill activity) was modeled as one single process and the total environmental burden of the system was allocated to all products and co-products. The share allocated to the bark could be 9%, 7%, or 2% depending on whether the allocation is based on volume, energy, or economic value, respectively. In this study volumetric allocation was chosen to avoid underestimating the environmental burden of the raw material but if economic allocation had been chosen the environmental burden of bark production would have been reduced by as much as some 75%. However, since the impact from production of the feedstock is rather limited in relation to the overall impact from the complete production system (see Fig. 11) a change in allocation method will have a minor effect on the result in this LCA.

**Conclusions**

In this study the environmental impact of the production of cationized tannins from Norway spruce bark was investigated from a cradle-to-gate perspective. Of the seven process steps in the production system that were assessed, the adsorption (i.e., purification) and cationization steps were identified as the main sources of the environmental impact of the whole system.

The most important action to improve the environmental performance of the system is to improve the environmental profile of the chemicals used in the cationization step. The reagents used today – formalin, ammonium chloride and hydrochloric acid – all have high energy requirements for production. Their precursors are also based on fossil resources, thus leading to high climate impact. To reduce the environmental impact of the cationization it could be of interest to evaluate the use of formalin based on renewable methanol or to find alternative chemicals.

The data for the adsorption step are less certain but point towards the importance of re-using the ethanol for elution and using a resin with a long lifetime. Another potential option to be explored could be cationization of the bark extract directly, without purification. The cationized crude product might still be effective in the required flocculation application, and the environmental impact of the adsorption step can be eliminated. This LCA also points towards a reduction in water consumption in the extraction as a way to reduce the environmental impact of the process. Both the extraction and evaporation steps have high energy demands and by reducing the water content the energy demand will be reduced.
Compared with today’s conventional alternatives, the environmental impact of the production of cationized tannins is higher in several categories, expressed per kilogram of product. However, it is important to remember that the development of this process for producing cationized tannins is still at an early stage, and that variations in the flocculation efficiency between the alternatives were not considered. This LCA shows the most important steps to take to facilitate a process development towards a lower environmental impact.

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Figure 14. Comparative environmental profiles (%) of the potential environmental impact for the production of 1 kg of cationized tannins, polyacrylamide, aluminium sulfate, and iron(III) chloride, respectively.
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Modeling and Analysis: LCA of cationized tannins from Norway spruce

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