Biorefining of Spruce TMP Process Water: Selective Fractionation of Lipophilic Extractives with Induced Air Flotation and Surface Active Additive

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Lignocellulose biomass plays an important role in reducing the dependency on fossil fuels and ameliorating the dire consequences of climate change. It is therefore important that all the components of lignocellulose biomass are exploited. These components include hemicelluloses and extractives that are liberated and sterically stabilized during the thermomechanical pulping and that form the dissolved and colloidal substance (DCS) in the process water. Biorefining of this process water can extract these substances, which have a number of promising applications and can contribute to the full exploitation of lignocellulose biomass. This paper presents a simple treatment of unbleached Norway spruce (*Picea abies*) process water from TMP (thermomechanical pulping) production using induced air flotation (IAF) and cationic surfactant, dodecyl trimethylammonium chloride (DoTAC) to refine the extractives and prepare the waters so that hemicellulose could be easily harvested at a later stage. By applying 80 ppm of DoTAC at a pH of 3.5 and 50 °C before induced air flotation, 94% of the lipophilic extractives were recovered from process water. Dissolved hemicellulose polysaccharides were cleansed and left in the treated process water. The process enabled efficient biorefining of lipophilic extractives and purification of the process water to enable more selective harvesting of hemicelluloses in subsequent steps.

Keywords: Biorefining; Lipophilic extractives; Thermomechanical pulping; Induced air flotation

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INTRODUCTION

Pollution from the extraction and burning of non-sustainable fossil fuels such as coal, petroleum, and natural gas is negatively affecting the natural world, diminishing the right of every living thing to a clean environment (Wang *et al.* 2016; Gustavsson *et al.* 2017). People in many countries suffer from the effects of airborne pollution. It is thus clear that industry and consumers need to reduce their dependency on fossil fuels and utilize renewable resources such as lignocellulose biomass as feedstock for industrial and consumer purposes (Brandt *et al.* 2013; Domínguez de María 2014).

There have been many recent efforts toward converting lignocellulosic biomass into a wide range of products and applications. Cellulose, the major component in lignocellulose biomass, has been the most investigated component and is found in various applications and products (Douglass *et al.* 2018), as it has been used extensively for many centuries (Hon 1994). Cellulose is present in pulp and paper products and is used in textile production. Lignin is another major component in lignocellulose biomass, and its derivatives are used mainly for energy generation in the mills, but are foreseen to be an important raw material for carbon fiber production and feedstock for automotive biofuels

(Norgren and Edlund 2014; Bhat *et al.* 2015). Hemicellulose and extractives, representing 20 to 30% and 1 to 3% of lignocellulose biomass (Zasadowski *et al.* 2012) respectively, are comparatively less exploited, even though a considerable number of promising applications have been identified, including their use as barrier materials in packaging, food ingredients, and pharmaceutical drugs (Lindqvist *et al.* 2013). The biorefining of these two families of components is therefore of great significance for developing sustainability and creating more value-added products from lignocellulose biomass.

Both hemicellulose and extractives can be recovered from side streams in mechanical pulping, such as thermomechanical pulping (TMP). The pulping process liberates wood components that are dissolved or dispersed in the TMP process water. These components are mainly hemicellulose and extractives of a hydrophilic or lipophilic nature that are known as dissolved and colloidal substances (DCS) (Ekman and Holmbom 1989; Ekman *et al.* 1990). The extractives consist of fatty and resin acids (FRAs), steryl esters (StE), sterols, triglycerides (TrG), and lignans. In the process water, the colloidal substances form droplets with a core-shell-structure, with triglycerides and steryl esters in the core and a surface layer of surface-active resin and fatty acids (Lee *et al.* 2011). The colloidal droplets are also known as pitch (Orsa and Holmbom 1994), and they often give rise to problems regarding paper strength, deteriorated optical properties of paper, and paper machine runnability (Sundberg *et al.* 1994; Nylund *et al.* 2007). Due to the anionic charge of the colloidal droplets, they also interfere with cationic retention aids and decrease the efficiency of effluent treatment (Sundberg *et al.* 1994). The colloidal substances are sterically stabilized by the dissolved hemicellulose polysaccharides, which prevents them from aggregating into pitch deposits (Holmbom and Sundberg 2003; Nylund *et al.* 2007). However, sterical stabilization can be affected by the ever-changing pulping condition. When simple electrolytes appear in the system, the loosely bound polysaccharides desorb from colloidal droplets, rendering the lipophilic extractives sensitive to the electrolytes (Sundberg *et al.* 1994; Nylund *et al.* 2007). This worsens the downstream effect of the extractives on the papermaking process and paper products. To reduce these negative effects, the colloidal substances and hemicellulose should be removed from the process water at an early stage.

Common techniques for minimizing the impact of extractives include the use of retention agents or special pigments to retain them on the paper web (Wågberg and Ödberg 1991; Johnsen and Stenius 2007), or by adding a pulp-washing stage to the process (Käyhkö 2002). While those methods have reduced the problems caused by colloidal droplets, they also create new problems. For example, the retention agent may have a negative effect on paper quality (Holmbom and Sundberg 2003), and the pulp-washing stage requires extra water consumption and recovery of fines from the water (Käyhkö 2002). Thus, there is a need for a process that can remove the negative effects of DCS in TMP process water without creating new problems. One good option is the use of flotation to remove troublesome substances from the process water. The combination of induced air flotation (IAF) and a surface-active additive has earlier been proposed as a very effective set up (Zasadowski *et al.* 2012, 2014a).

Induced air flotation (IAF) has been applied for many years, and its first application in the water treatment field was in the flotation of suspended solids, fibers, ink particles, and other low density solids (Wang *et al.* 2010). More recently, induced air flotation has also been applied for the removal of pitch from TMP process water (Zasadowski *et al.* 2012). The mechanism of IAF starts with that induced air and liquid is mechanically mixed to generate bubbles in the process water. Then the lipophilic extractives attach onto the air bubbles containing cationic foaming agent. The combination of air/surface-active additive extractives rise to the surface where they could be collected. In the process, the IAF utilizes the differential densities in between the bubbles and extractives to affect the separation. Since the air-extractive agglomerates have a lower density than the medium in which they are immersed, they rise to the surface, where they are collected. The IAF method can achieve higher removal of lipophilic substances and low material loss during the flotation than the other flotation methods, for example, the dissolved air flotation. Besides the well-established mechanism, the key to the high process efficiency is the surface-active additive used in the flotation. Different surfactants were investigated by Zasadowski *et al.* (2012) for the removal of lipophilic extractives, including N,N-dimethyl dodecyl amine-N-oxide (DDAO), sodium dodecyl sulfate (SDS), and dodecyl trimethylammonium chloride (DoTAC). The DoTAC was shown to be the most effective surfactant tested in removing the lipophilic extractives; therefore it was applied in the present work. After the flotation, the subsequent step was to quantify the lipophilic extractives in the collected foam fraction, where the lipophilic substances need to be transferred from the collected foam into an organic solvent for further determination. The previously used method, liquid-liquid-extraction (LLE), is a mass transfer extraction based on the relative solubilities of lipophilic extractives in two different immiscible liquids. The driving force of the extraction is the chemical potentials of the analytes, where they are in a more stable conformation (Ahmad *et al.* 2015). However, LLE has certain drawbacks, such as emulsion formation, use of large sample volumes, and in many instances the loss of analytes (Rezaee *et al.* 2010). Another extracting method thus is needed to validate the removal of the lipophilic extractives, where the Soxhlet extraction is adapted for the purpose. The analytes in a Soxhlet extraction are constantly in contact with fresh portions of the extractant, thus facilitating the transfer equilibrium of the analytes into the organic solvent.

This paper describes the biorefining of lipophilic extractives from process water in a thermomechanical pulp mill using IAF treatment. This approach takes advantage of the negative charge from the double-layered colloidal droplets and the cationic charged DoTAC for the purpose of effective and selective removal of lipophilic extractives. It also enables the refining of hemicellulose in later stage from the accepted process water. The efficiency of the IAF treatment is verified and evaluated based on different extraction methods, in terms of the removal of lipophilic extractives from process water to the rejected foam and the concentrations of the extractives. The hemicellulose in the process water before and after IAF are also quantified and compared.

EXPERIMENTAL

Materials and IAF

The process water assessed in the work was collected from a thermomechanical pulp mill in the middle of Sweden, from the stage between pressing and hydrogen peroxide bleaching. The raw material in the mill was freshly harvested Norway spruce (*Picea abies*), which contained around 30% hemicellulose and 1 to 2% of lipophilic components. The process water was stored at 4 °C before IAF treatment and was heated to 50 °C to mimic the temperature condition of TMP production. The chosen flotation parameters were optimized previously with pH of 3.5, 50 °C, and 80 ppm dodecyl trimethylammonium chloride (DoTAC, China Innovation Group Co. Ltd., Beijing, China) (Zasadowski *et al.* 2012).

The original pH value of the process water sample was about 5.1, and it was adjusted to 3.5 by adding hydrochloric acid before flotation. At pH 3.5 it has been reported that the RFAs associate with the colloidal droplets as a high flotation efficiency for collected lipophilic extractives (Sundberg *et al*. 2009). DoTAC was of analytical grade, and it was found to have the best performance as a surface active additive. A stock DoTAC solution was prepared by dissolving DoTAC in distilled water and directly adding it when the flotation commenced. 6L of process water was used in the flotation cell with a propeller rotational speed of 1340 rpm during the experiment. 5L/min of nitrogen gas was induced during the flotation. The concentration of the foaming agent was 80 ppm at the beginning of the flotation. The flotation proceeded for 60 min, and the foam fraction was collected from the top of the flotation cell shown in Fig. 1 below. The fiber and fine fraction in the collected foam fraction was removed by filtration through a fiber filter and stored at 4 °C for further analysis.

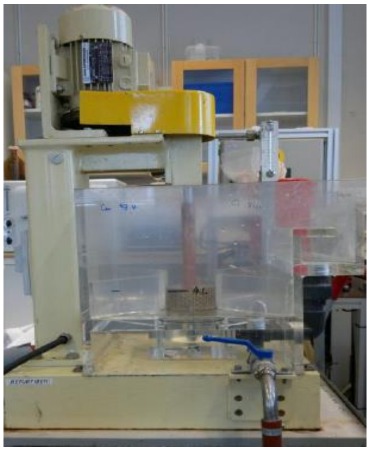

Fig. 1. The flotation cell in the induced air flotation (Zasadowski *et al.* 2012)

Gravimetric Determination of Lipophilic Extractives and Hemicellulose

The quantification of the total content of lipophilic extractives in the process water and the rejected foam was of significance in evaluating the efficiency of the IAF combining DoTAC method. To avoid the possible loss of the lipophilic extractives from the LLE method, the determination employed the Soxhlet extraction of the freeze dried process water and rejected foam. Methyl tert-butyl ether (MTBE, purchased from Sigma-Aldrich, Stockholm, Sweden) was used for extraction because of its effectiveness in solvent extraction of lipophilic extractives, as well as its high efficiency in extraction of lignans (Orsa and Holmbom 1994). As shown in Fig. 2, there were three different groups of extractive fraction. Fraction A and B were from the Soxhlet extractions of freeze-dried process water and rejected foam, respectively. For comparison with the Soxhlet extraction method, the liquid-liquid-extraction (LLE) of rejected foam, fraction C, was conducted. In the Soxhlet extractions, a specimen of about 1 g dry mass was taken from either the freeze-dried process water or the rejected foam. The dryness of the samples was measured by using a Mettler Toledo moisture analyzer (HC103, Stockholm, Sweden) after freeze-drying. The samples were then extracted with MTBE for 6 h with 15 circulations per h. When the extractions were finished, the flasks containing the extractives were put under nitrogen gas to evaporate the MTBE solvent. Then the residues were placed in an oven at 40 ± 1.5 °C overnight to ensure that the weight of the extractives had stabilized. The extractives obtained *via* LLE from the rejected foam (fraction C) were prepared by mixing 10 mL of foam samples with 5 mL of MTBE. The mixture was shaken vigorously for 1 min and then subjected to centrifugation at a relative centrifugal force of 1000 g for 10 min. Phase separation resulted in the lipophilic extractives and lignans being in the upper level, which was carefully pipetted out. The residual water phase was in the lower level for subsequent two more extractions. After all of the three extractions with MTBE, the three MTBE aliquots were combined. If an emulsion layer existed in the foam sample before mixing with MTBE, 1 g of sodium chloride was added to the 10 mL foam sample to break the emulsion and enhance the extraction. After the IAF process, the hemicellulose carbohydrates in the accepted water were further concentrated and freeze-dried for evaluation.

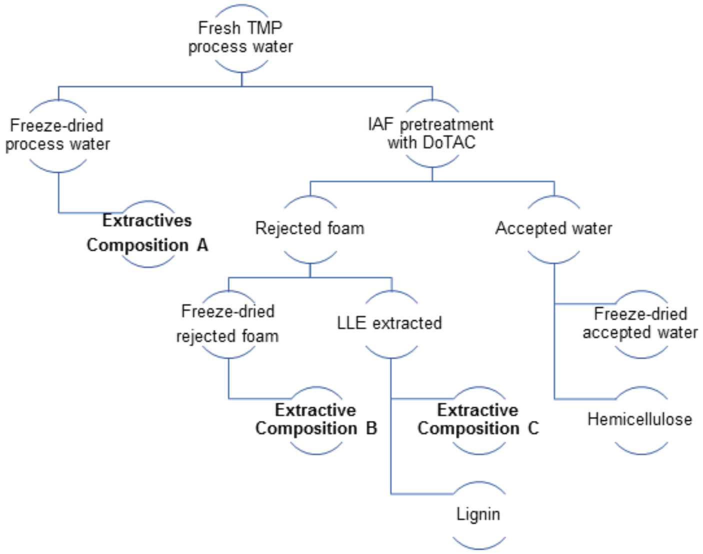

Fig. 2. Schematic diagram showing flows for substance separations in induced air flotation, and the analyzed substances from the sub-sections

GC-FID Analysis of Lipophilic Extractives

Extractives from the Soxhlet extractions of freeze-dried process water (fraction A) and the foam (fraction B) and extractives from LLE (fraction C) were silylated and then analyzed using a gas chromatograph equipped with a flame ionization detector (GC-FID). To prepare the lipophilic extractives and lignans for analysis using GC-FID, the components were silylated and assigned according to the internal standard mixture (IS) as follows: the IS was prepared by dissolving 0.1 mg of 1,3-dipalmitoyl-2-oleoylglycerol, cholesteryl heptadecanoate, heneicosanoic acid, and betulinol into 1 mL MTBE. A 1 mL sample from each extractive fraction, A, B, and C, was combined with 100 µL of IS (Orsa and Holmbom 1994). This mixture was dried in nitrogen gas. Next, 100 µL of N,O-bis-(trimethylsilyl)-trifluoro-acetamide (BSTFA) and trimethylsilyl chloride (TMCS) (99:1 by vol.) with an additional 50 µL of pyridine were added to the residual and sealed together in the reaction vial. The vial was kept in a 70 °C oven for 30 min for silylation. After cooling, the sample was ready for GC-FID injection. The trimethylsilyl esters of fatty and resin acids obtained after silylation are prone to hydrolysis, so testing is recommended within 12 h (Zinkel *et al.* 1968). The GC-FID (Varian 3400) and a DB-1 capillary column were used (Agilent J&W Technology, Santa Clara, CA, USA), 15 m x 0.53 mm x 0.15 µm, with 100% dimethylpolysiloxane as the stationary phase. The column was heated up from 70 °C to 340 °C at a rate of 16 °C/min and then held for 10 min. The running time was around 27 min in total. The injection temperature was 250 °C, while the temperature of the FID detector was set at 340 °C. Helium was used as a carrier gas with a flow rate of 12 mL/min.

GC-FID Analysis of Carbohydrates

The carbohydrates content in the accepted water was determined by gas chromatography (GC) after acid methanolysis. The sample was first filtered through a 0.2 µm nylon membrane to remove all the fines, and the sample was then freeze-dried. Previously prepared 2 M HCl in methanol was added to the dried sample. This mixture was kept at 70 °C in an oven for 3 h, and then pyridine was added to neutralize the extra acid in the solution. Sorbitol in methanol was added as the IS. The methanol was evaporated in a stream of nitrogen and the samples were further dried under vacuum in a desiccator. The samples were then silylated at room temperature using pyridine, hexamethyldisilazane (HMDS), and TMCS (Willför *et al.* 2009). The analysis of sugar units was conducted by long column GC (HP-1, 30 m x 0.25 mm x 0.10 µm) with split injection and equipped with a flame ionization detector (FID). The column was heated from 100 °C to 175 °C at a rate of 4 °C/min, followed by heating from 175 °C to 290 °C at a rate of 12 °C/min. The temperatures of the injector and detector were 260 °C and 290 °C, respectively.

Detection of Lignin

The residual water after LLE was kept for lignin content determination. Prior to testing, the water phase was first filtered with a 0.2 µm Teflon filter to remove any fines. The ultraviolet absorption of lignin at 280 nm was measured with a Shimadzu UV1800 spectrophotometer (Kyoto, Japan).

RESULTS AND DISCUSSION

Induced Air Flotation and Lipophilic Substances

As previously described, the pH value of the process water from the pulp mill was adjusted from 5.1 to 3.5 before flotation to maintain the association of fatty and resin acids with colloidal droplets. After the addition of DoTAC into IAF, the cationic surfactant first formed bubbles with the induced air and then contacted with the negatively charged colloidal droplets. The density difference in between the foam and the process water separated the lipophilic extractives from the medium, and then floated up the material for collection. Both the original process water and the harvested foam were analyzed for solid content as well as the extractive concentrations after Soxhlet extraction of the freeze-dried samples.

Table 1 shows that the solid content of the harvested foam was increased to 1.5 times that of the process water. Considering the fact that some fines and fibers were filtered away from the foam fraction, this indicates that more extractives were collected in the flotation. Comparing the concentrations of the extractives in the process water and the harvested foam, the concentration in the foam fraction was almost four times higher than in the process water. This shows that the flotation setup was effective in refining lipophilic extractives from TMP process water.

Table 1. Comparison of Process Water and Foam Fraction Before and After IAF

	Solid Content (g/L)	Extractive Concentration (g/L)
Process Water	7.23	0.268
Foam Fraction	11.20	0.959

The extractives were concentrated from 0.268 g/L in the process water to about 1 g/L in the foam fraction. Considering that 0.262 L of foam fraction were collected for 1 L of process water in the IAF treatment, this means that about 94% of the extractives were transferred from process water into the foam fraction.

GC Analysis of Extractives of Process Water, Rejected Foam, and the Foam Fractions

As shown above, IAF combined with DoTAC offers an efficient, single-stage method of recovering the extractives from the TMP process water. It is also important to know the compositional changes of the extractives before and after treatment. The total concentrations of the extractives before (Extractives A) and after IAF treatment (Extractives B and C) are shown in Fig. 3 below. The graph shows that the extractives were enriched from the original process water into the foam fraction during the IAF process. During the IAF process, the cationic DoTAC was able to effectively bind the anionic pitch droplets and enrich the components in the foam fraction (Zasadowski *et al.* 2014a). The processing with DoTAC also cleaned and enabled the reuse of the process water. To compare the effect of the extraction method on the results, fractions B and C were extracted with Soxhlet extraction and LLE, respectively. A comparison of the total concentrations in Extractive B and C revealed that the concentration in Extractive B was about 70 mg/L higher than the concentration in C. This could be attributed to the thorough extraction with the Soxhlet method, where the extractives were constantly contacting the fresh extractant and pushing the transfer of the analytes into the MTBE phase. The higher volume of extractant and possible loss of the analytes in the LLE method can also contribute to lowered concentration in Extractives C (Orsa and Holmbom 1994).

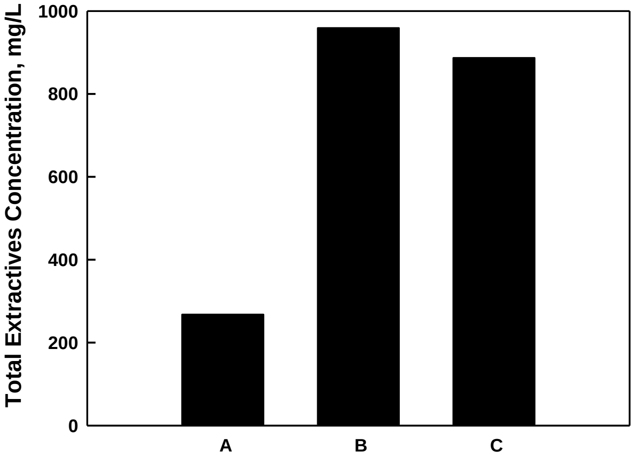

Fig. 3. The total extractives concentrations in the process water (Extractives A), foam fraction (Extractives B), and MTBE extractives (Extractives C)

The specific changes before and after IAF treatment for each extractive component from process water, foam fraction, and LLE were measured and compared. **Fig.** Figure 4 shows that the extractives from the spruce TMP process water were triglycerides, sterol esters, fatty acids, resin acids, sterols, and some lignans. About 56% of the extractives were composed of neutral substances such as steryl ester and triglycerides, which agrees with previous trials conducted by the authors (Zasadowski *et al.* 2012). Triglycerides were the main component of the lipophilic extractives. Fatty and resin acids constituted about 25% of the lipophilic extractives in the process water. When comparing the extractive compositions of the foam fraction with process water, the percentages of neutral components changed slightly. This is because the neutral steryl ester and triglycerides were in the core of the double-layer colloidal droplets during flotation. Therefore, they were less affected by the flotation condition (Lee *et al.* 2011). However, the content of lignans, fatty acids, and resin acids showed more variance before and after IAF. The percentage of lignans in the extractives decreased from 11% in the process water to 4% in the foam fraction. Lignans are hydrophilic rather than amphiphilic, which favors solubility in the water phase rather than transfer to the foam fraction (Sihvonen *et al.* 1998). A comparison of the total fraction of the fatty and resin acids and sterol in the process water revealed that this number from the rejected foam fraction increased about 24% statistically. The increment of the percentage of fatty and resin acids can come from the decrement of lignans in the rejected foam, which leads to a higher percentage of FRAs in fraction B. Furthermore, the hydrolysis of the triglycerides can generate more fatty acids, thus leading to the increment of the percentage of the FRAs in the rejected foam. Some researchers have reported that nearly 30% of fatty and resin acids are dissociated and dissolved in the water phase at the process water condition of pH = 5, while at the pH adjusted to 3.5 for flotation they are barely dissociated (Sundberg *et al.* 2009).

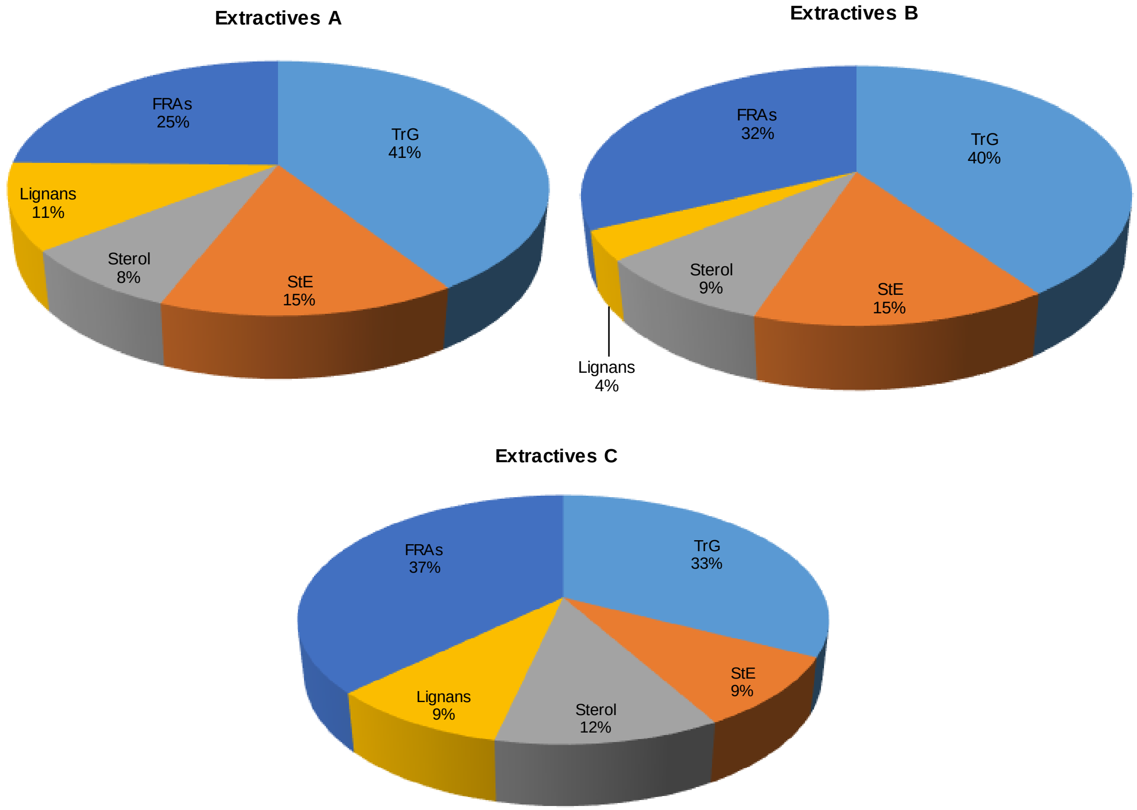

Fig. 4. Composition of the lipophilic extractives and lignans from process water (Extractives A), foam fraction (Extractives B), and MTBE extractives (Extractives C). FRAs = fatty & resin acids, StE = steryl ester, TrG = triglyceride, diglycerides, and monoglycerides

The compositions of the lipophilic extractives in Extractives B and C after different methods are also compared in Fig. 4. As stated in the experimental setup, the LLE extraction of the sample was tripled to obtain a better extraction yield of lipophilic extractives and lignans, and then the extract was silylated before GC analysis. The comparison shows that the fatty and resin acids increased from 32% to 37% in the LLE fraction. During the LLE treatment, the fatty and resin acids and sterol were mostly transferred into the MTBE solution, which could explain the high fraction of the components in the extract. The pH changes during the extraction possibly affected the phase distribution of triglyceride and sterol ester, and thus rendered lower percentages of the neutral components in extractive fraction C (Sundberg *et al.* 2009). The percentages of the triglycerides and steryl ester decreased from 40% to 33%, and from 15% to 9%, respectively. The percentage of lignans increased from 4% in the foam fraction to 9% in the LLE. The hydrophilic nature of the lignans led to the low removal from the process water, but the MTBE enabled efficient extraction of lignans (Orsa and Holmbom 1994). Comparing the results from LLE with Soxhlet extraction, 92.5% of the lipophilic extractives after the Soxhlet extraction were detected with the LLE method, while the Soxhlet extraction enabled 94% of the lipophilic extractives to be transferred from process water to the foam fraction. This indicates that the expression of the lipophilic extractives removal with LLE was lower than what it really was. In the two methods of extracting the lipophilic components in the foam fractions, Soxhlet extraction of freeze-dried foam achieved high yield in extracting the refined lipophilic extractives from the rejected foam. This might be attributable to the favourable mass transfer equilibrium when the foam fraction constantly meets the fresh MTBE. IAF combined with DoTAC is thus an efficient way of removing the lipophilic extractives from TMP process water, minimizing the downstream effects of pitch components on the process and products.

Composition of the Hemicellulose, and Lignin from the Accepted Water

The effective removal of the pitch compounds using IAF combined with DoTAC from the process water enabled the return of benign accepted water back to the process. However, it is also necessary to know how the dissolved hemicellulose and lignin are affected by flotation. The accepted process water was freeze-dried, and acid methanolysis was performed for quantification analysis. As shown in Table 2, the concentration of dissolved hemicelluloses changed only slightly after the IAF process, which indicates that IAF combined with DoTAC is a selective process in refining the lipophilic extractives from the TMP process water.

Table 2. Carbohydrate Analysis of the Process Water, Before and After Flotation

	Original TMP Process Water	Purified TMP Process Water
Lignin (mg/L)	1279	611
Carbohydrates		
Mannoses (mg/L)	1270	1300
Glucoses (mg/L)	354	356
Galactoses (mg/L)	554	410
Arabinoses (mg/L)	119	107
Xyloses (mg/L)	38.8	37.0
Rhamnoses (mg/L)	80.6	62.2
Galacturonic Acid (mg/L)	97.7	86.0
Glucuronic Acid (mg/L)	60.9	51.7

Of the detected monosaccharides, the major ones in the water samples both before and after IAF treatment were galactoses, mannoses, and glucoses. This agrees with the fact that galactoglucomannan is the major hemicellulose polysaccharides in Norway spruce. The lignin content in the treated process water was decreased compared to the original process water. This indicates that some of the lignin was also removed by the IAF treatment.

CONCLUSIONS

1. Induced air flotation in combination with DoTAC is an effective way of refining lipophilic extractives from TMP process water. By applying 80 ppm DoTAC at a pH of 3.5 and 50 °C, 94% of the lipophilic extractives were removed from the process water into the foam fraction. This significantly reduced pitch droplet formation in the process water, which could minimize negative effects on paper machines and paper products.
2. Compositional analysis of the lipophilic extractives from both the process water and the collected foam fraction showed only minor compositional changes to triglycerides and steryl ester, but large changes in the composition of fatty and resin acids and sterol. This indicates that the lipophilic extractives have a core-shell structure, where the core of the droplets is less affected by the flotation process than the shell. Due to the hydrophilic nature of lignans, they were mostly dissolved in the aqueous phase. Soxhlet extraction of the reject foam achieved higher yield of extraction than the LLE method due to the favourable mass transfer equilibrium during the extraction, thus giving accurate efficiency of recovering lipophilic extractives with IAF method.
3. The dissolved hemicelluloses in the TMP process water were almost unaffected by the IAF treatment, allowing for the relatively easy recovery of hemicellulose from the accepted process water.

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REFERENCES CITED

Ahmad, W., Al-Sibaai, A. A., Alwael, B. H., and El-Shahawi, M. S. (2015). “Recent advances in dispersive liquid-liquid microextraction for pesticide analysis,” *Trac-Trend. Anal. Chem.* 72, 181-192. DOI: 10.1016/j.trac.2015.04.022

Bhat, A. H., Dasan, Y. K., and Khan, I. (2015). “Extraction of lignin from biomass for biodiesel production,” in: *Agricultural Biomass Based Potential Materials*, K. R. Hakeem, M. Jawaid, and O. Alothman (eds.), Springer International Publishing, pp. 155-179.

Brandt, A., Grasvik, J., Hallett, J. P., and Welton, T. (2013). “Deconstruction of lignocellulosic biomass with ionic liquids,” *Green Chem.* 15(3), 550-583. DOI: 10.1039/C2GC36364J

Domínguez de María, P. (2014). “Recent trends in (ligno)cellulose dissolution using neoteric solvents: Switchable, distillable and bio-based ionic liquids,” *J. Chem. Technol. Biot.* 89(1), 11-18. DOI: 10.1002/jctb.4201

Douglass, E. F., Avci, H., Boy, R., Rojas, O. J., and Kotek, R. (2018). “A review of cellulose and cellulose blends for preparation of bio-derived and conventional membranes, nanostructured thin films, and composites," *Polym. Rev.* 58(1), 102-163. DOI: 10.1080/15583724.2016.1269124

Ekman, R., and Holmbom, B. (1989). "Analysis by gas chromatography of the wood extractives in pulp and water samples from mechanical pulping of spruce," *Nord. Pulp. Paper Res.* 4(1), 16-25. DOI: 10.3183/npprj-1989-04-01-p016-024

Ekman, R., Eckerman, C., and Holmbom, B. (1990). "Studies on the behavior of extractives in mechanical pulp suspensions," *Nord. Pulp. Paper Res.* 5(2), 96-103. DOI: 10.3183/npprj-1990-05-02-p096-103

Gustavsson, L., Haus, S., Lundblad, M., Lundström, A., Ortiz, C. A., Sathre, R., Truong, N. L., and Wikberg, P.-E. (2017). "Climate change effects of forestry and substitution of carbon-intensive materials and fossil fuels," *Renewable and Sustainable Energy Reviews*, 67, 612-624. DOI: 10.1016/j.rser.2016.09.056

Holmbom, B., and Sundberg, A. (2003). "Dissolved and colloidal substances accumulating in papermaking process waters," *Wochenblatt für papierfabrikation* 131(21), 1305-1311. DOI:

Hon, D. N.-S. (1994). "Cellulose: A random walk along its historical path," *Cellulose* 1(1), 1-25. DOI: 10.1007/bf00818796

Johnsen, I. A., and Stenius, P. (2007). "Effects of selective wood resin adsorption on paper properties," *Nord. Pulp. Paper Res.* 22(4), 452-461. DOI: 10.3183/NPPRJ-2007-22-04-p452-461

Käyhkö, J. (2002). "The influence of process conditions on the deresination efficiency in mechanical pulp washing," PhD Dissertation, Lappeenranta University of Technology, Lappeenranta, Finland.

Lee, R., Garnier, G., Lewis, T., Richardson, D., Van De Ven, T. G. M., and Stack, K. (2011). "Pitch deposition at the solid–liquid interface: Effect of surface hydrophobicity/hydrophilicity and cation specificity," *Colloid. Surface. A.* 388(1-3), 84-90. DOI: 10.1016/j.colsurfa.2011.08.019

Lindqvist, H., Holmback, J., Rosling, A., Salminen, K., Holmbom, B., Auer, M., and Sundberg, A. (2013). "Galactoglucomannan derivatives and their application in papermaking," *BioResources* 8(1), 994-1010. DOI: 10.15376/biores.8.1.994-1010

Norgren, M., and Edlund, H. (2014). "Lignin: Recent advances and emerging applications," *Curr. Opin. Colloid. In.* 19(5), 409-416. DOI: 10.1016/j.cocis.2014.08.004

Nylund, J., Sundberg, A., and Sundberg, K. (2007). "Dissolved and colloidal substances from a mechanical pulp suspension—Interactions influencing the sterical stability," *Colloid. Surface. A.* 301(1-3), 335-340. DOI:10.1016/j.colsurfa.2006.12.068

Orsa, F., and Holmbom, B. (1994). "A convenient method for the determination of wood extractives in papermaking process waters and effluents," *J. Pulp. Paper Sci.* 20(12), 361-365. DOI:

Rezaee, M., Yamini, Y., and Faraji. M. (2010) . "Evolution of dispersive liquid-liquid microextraction methods," *J. Chromatogr. A* 1217, 2342-2357. DOI: 10.1016/j.chroma.2009.11.088

Sihvonen, A., Sundberg, K., Sundberg, A., and Holmbom, B. (1998). "Stability and deposition tendency of colloidal wood resin," *Nord. Pulp. Paper Res.* 13(1), 64-67. DOI: 10.3183/npprj-1998-13-01-p064-067

Sundberg, A., Strand, A., Vähäsalo, L., and Holmbom, B. (2009). "Phase distribution of resin and fatty acids in colloidal wood pitch emulsions at different pH-levels," *J. Disper. Sci. Technol.* 30(6), 912-919. DOI: 10.1080/01932690802646249

Sundberg, K., Thornton, J., Ekman, R., and Holmbom, B. (1994). "Interactions between simple electrolytes and dissolved and colloidal substances in mechanical pulp," *Nord. Pulp. Paper Res.* 9(2), 125-128. DOI: 10.3183/npprj-1994-09-02-p125-128

Wågberg, L., and Ödberg, L. (1991). "The action of cationic polyelectrolytes used for the fixation of dissolved and colloidal substances," *Nord. Pulp. Paper Res.* 6(3), 127-135. DOI: 10.3183/npprj-1991-06-03-p127-135

Wang, S., Lu, A., and Zhang, L. (2016). "Recent advances in regenerated cellulose materials," *Prog. Polym. Sci.* 53, 169-206. DOI: 10.1016/j.progpolymsci.2015.07.003

Wang, L. K., Shammas, N. K., Selke, W. A., and Aulenbach, D. B. (2010). *Flotation Technology*, Humana Press, Totowa, New Jersey, United States. DOI: 10.1007/978-1-60327-133-2

Willför, S., Pranovich, A., Tamminen, T., Puls, J., Laine, C., Suurnäkki, A., Saake, B., Uotila, K., Simolin, H., Hemming, J., *et al.* (2009). "Carbohydrate analysis of plant materials with uronic acid-containing polysaccharides–A comparison between different hydrolysis and subsequent chromatographic analytical techniques," *Ind. Crop. Prod.* 29(2–3), 571-580. DOI: 10.1016/j.indcrop.2008.11.003

Zasadowski, D., Hedenström, E., Edlund, H., and Norgren, M. (2012). "Use of a Voith flotation cell for removal of lipophilic extractives and Mn ions from spruce thermomechanical pulping process waters," *BioResources* 7(3), 2784-2798. DOI: 10.15376/biores.7.3.2784-2798

Zasadowski, D., Strand, A., Sundberg, A., Edlund, H., and Norgren, M. (2014a). "Selective purification of bleached spruce TMP process water by induced air flotation (IAF)," *Holzforschung* 68(2), 157-165. DOI: 10.1515/hf-2013-0045

Zasadowski, D., Yang, J., Edlund, H., and Norgren, M. (2014b). "Antisolvent precipitation of water-soluble hemicelluloses from TMP process water," *Carbohyd. Polym.* 113, 411-9. DOI: 10.1016/j.carbpol.2014.07.033

Zinkel, D. F., Lathrop, M. B., and Zank, L. C. (1968). "Preparation and gas chromatography of the trimethylsilyl derivatives of resin acids and the corresponding alcohols," *J. Chromatogr. Sci.* 6(3), 158-160. DOI: 10.1093/chromsci/6.3.158

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