

Continuous tannin extraction by use of screw reactor

MARKKU KUOSA, ANTTI HEIKKINEN, TAPIO TIRRI, AND LASSE PULKKINEN

ABSTRACT: A pilot-size screw reactor (extraction unit) was used for tannin extraction of spruce. Yield of the same magnitude or better was obtained when comparing a screw reactor with batch reactors. A longer presoaking time in water seemed to be better than a short one for obtaining higher yield. A higher yield is obtained with lower dry-water ratio, which suggests that the internal diffusion in bark does not determine mass transfer as much as is the case without presoaking of bark. The higher dry-water ratio decreased the yield. The prior soaking of the bark also minimized the mechanical reactor feeding problems (clogging). The benefits of a screw reactor likely are that run time changes for different process conditions are flexible; it simplifies design and construction of an industrial unit for tannin production; and it saves space because of the need for fewer and smaller intermediate storage tanks.

Application: In this study, it is shown that presoaking has a crucial effect on yield in tannin extraction. This knowledge is important for further development of tannin extraction processes.

In recent years, research on tannin extraction from softwood bark (spruce) has become more active, because this tannin is rich in condensed flavonoid tannins and softwood bark is abundantly available from sawmills and pulp mills. There is very little tannin production in Europe [1,2]; however, the northern European wood processing industry makes an attractive base for tannin production and refinement [3-5]. Recovery of the chemical components of bark and better exploitation of those would enhance the economic value of biomass and would bring new opportunities for the forest industry sector.

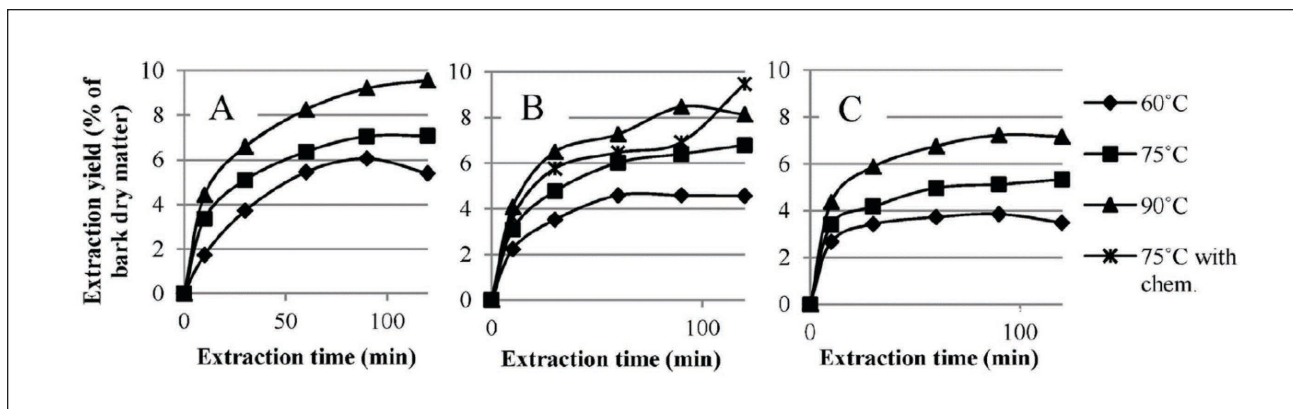
Hot water extraction is used for separation of tannin from the bark in wood species of the southern hemisphere. Tannin extracts obtained from oak, quebracho, and mimosa trees are utilized for leather manufacturing and treatment [6]. Tannins are also suitable for replacing phenol manufactured from nonrenewable natural resources. Phenol is used in resins for production of engineered products like medium-density fiberboard (MDF). Formulation of raw tannin has been studied for resin and glue applications [3,4].

There are a few patents for bark-based tannin production from the 1940s, 1950s, 1970s, and 1980s [7-11]. In newer patents [12-15], the whole process is presented as being continuous, but the extraction itself is more like a batch process, as seems to be the case in earlier patents (co-current or countercurrent batch) in which bark is recirculated back to the extraction phase a few or several times to increase the yield. The extract is typically separated from the bark by percolation or filter press, and after that, the extract is concentrated using an evaporator or by nanofiltration.

Traditionally, the industrial extraction of tannin is carried out with water [16]. According to [14], the operative conditions of the extractor are preferably as follows:

$T=90^{\circ}\text{C}$ – 110°C ; $\text{pH}=4$ – 6 ; $P=(0\text{--}1\text{ bar})$ $0\text{--}1$ – $10\text{--}1\text{ MPa}$; and duration of the extraction cycle is $3\text{--}4\text{ h}$. According to [15], the result of an excessively intense heat treatment (at about 110°C – 120°C for several hours) is that the chemical and physical characteristics of the wood bark may degrade because the long and intense heat treatment degrades the cellulose into hemicellulose and sugars. Hydrolytic degradation of hemicellulose may take place as early as at 100°C [17]. This degrades the further usability of the bark as a raw material [17-19]. Heat treatment at elevated temperatures to improve the extraction of tannin may also degrade the tannins contained in the wood bark, giving rise to tannic products of lower quality. According to several publications [17,20], a satisfactory extraction is carried out by a treatment for a duration of 2 h at a temperature of 70°C – 80°C , which is not harmful to either the woody material or the tannic substances it contains. Increasing the extraction temperature has been identified as the most effective factor for gaining higher yields in the water extraction of softwood bark [19-25], as seen in **Fig 1**.

In the literature, tannin extractions have generally been performed using liquid:bark ratios between 5:1 and 12:1, with better extraction yields at the lowest values [20,23,24,26,27]. Kempainen et al. [20] performed extraction of Norway spruce bark at 20:1, 10:1, and 7:1 with different extraction times and temperatures. For an extraction time of up to 15 min, higher yields at the lower liquid:bark ratios were observed, in agreement with the other studies; however, for longer extraction times (up to 2 h), the highest extraction yields were observed for the highest liquid:bark ratio. Fine milling to achieve an average particle size below 0.5 mm resulted in a noteworthy increase in the extraction yields, most likely due to the diffusion limiting factors of the



1. Extraction yield of tannin from winter bark at bench scale with varying solids contents (A: 5%, B: 10%, C: 15%) and temperatures without extraction chemicals [20].

extractives through the bark tissue, like agglomeration [24]. Bianchi et al. [21] studied the characterization of condensed tannins and carbohydrates in hot water bark extracts of European softwood species. Their total extraction yield of softwood barks ranged from 26.9 to 120.2 g/kg of dry bark, corresponding to pine and silver fir, respectively. Similar yields have been reported for hot water extractions of European softwood bark [20,28-30]. In these studies, consistent differences in yield were observed not only among different bark species, but also within the same species. Temperature had a major effect on the overall extraction yield. Selective extraction of only tannins or water-extractable carbohydrates was not possible. The extraction was scaled up to pilot scale, and an extract was produced with a promising 50% tannin content [20].

CONTINUOUS EXTRACTION APPARATUS

The laboratory-size extraction apparatuses for tannin extraction are Soxhlet-type devices [31] or batch-type reactors with mixers. Pilot-size extraction reactors are usually of batch type equipped with liquid circulation. In patents [12-15], the whole process is presented as continuous, but the extraction itself is more like a batch process (co-current or countercurrent batch) in which bark is recirculated back to the extraction phase a few or several times to increase the yield.

In this study, a pilot-size screw reactor (extraction unit) was used for tannin extraction of spruce. In the batch reactors, bark is packed in bags made of small-gauge net. This screw reactor was originally designed for mechanical pulp treatment and operates in a continuous co-current mode. The screw causes concentration gradients, which may intensify mass transfer. The benefits of a screw reactor are that it simplifies the design and construction of an industrial unit for tannin production and saves space because of the need for fewer and smaller intermediate storage tanks. A longer residence time increases the yield by some amount; however, in a screw reactor, the mixing rate decreases when the residence time increases. A solution could be periodically rotating the screw in the opposite direction. In

the manufacture of bark particles, the particle size is of great importance, as it affects treatability.

No reactor design offering optimization of a tannin extraction reactor design is found in the literature. However, the internal diffusion of wood particles seems to be controlling the extraction rate [32,33]. Capparucci et al. [34] studied the effect of solvent flow rate on the yield of extractable tannins from chestnut tree wood.

MATERIALS AND METHODS

Analysis of tannin content

Tannin content of the extract was analyzed using Mettler Toledo UV5 UV-Vis spectrophotometer for absorbance at 280 nm as described by Antoine et al. [35]. Highly purified quebracho heartwood extract was used for the calibration (Fintan QS, Silvateam S.p.A.; San Michele Mondovi, Italy). Water content of bark was measured by drying it in a heating chamber for 24 h at 105°C; after that, the sample was left to cool to 20°C for 60 min in a desiccator containing dehydrating silica gel before measuring the sample weight. The amount of bark needed for each extraction run was calculated based on the water content of bark, which was measured for the bark batch used. The electric conductance of tap water used in the experimental runs was in the range of 0.03–0.04 mS/m. The error of the calculated yield can be estimated to be in the range of $\pm 0.5\%$.

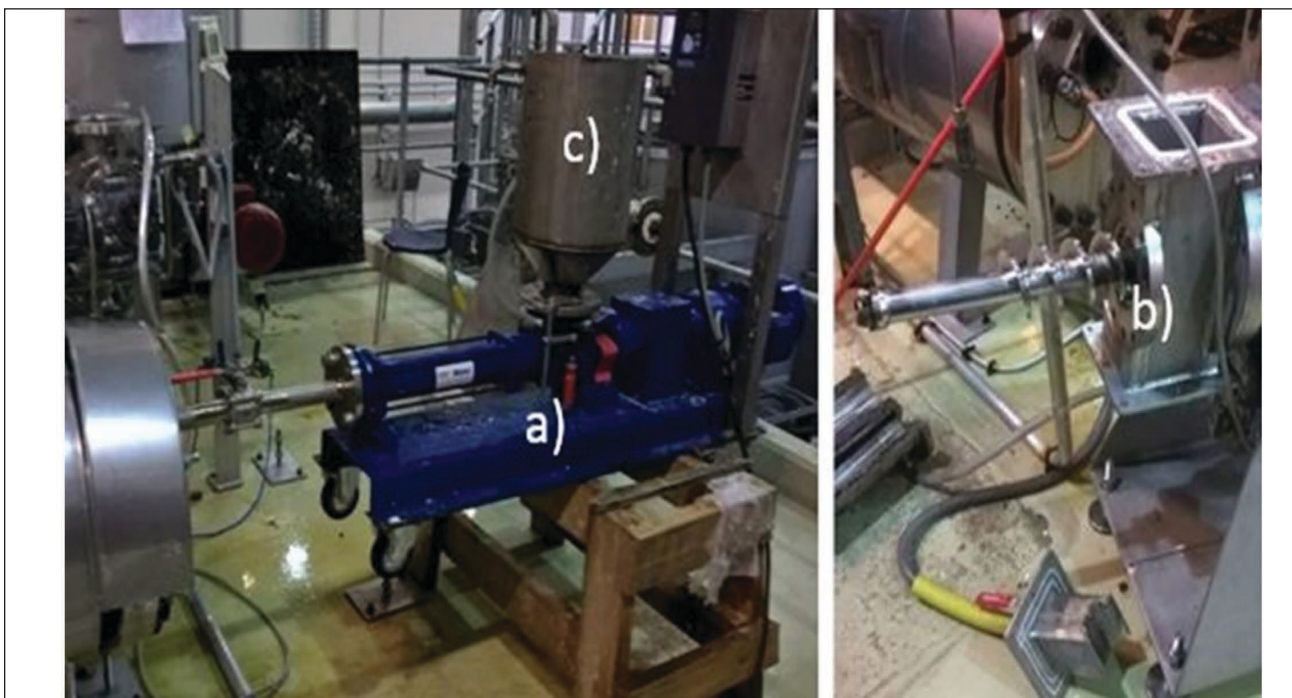
Screw reactor

The tannin extraction runs were carried out in pilot-size continuous screw reactor, as shown in **Fig. 2**. The length of the reactor vessel is approximately 2.2 m, and the inner diameter is 0.34 m.

The runs were carried out using two different feed modes: (a) eccentric screw pump, and (b) plug screw pump (**Fig. 3**). Several reactor feeding options were tested before the preliminary extraction runs. As a result of testing, atmospheric pressure was chosen for ease of running the adequate amount of liquid (water) through the reactor. The supplementary water was necessary for achieving the prop-



2. Pilot-size continuous screw reactor. Length of the reactor vessel is approximately 2.2 m, and the inner diameter is 0.34 m.



3. a) Eccentric screw pump, b) dismantled plug screw pump, and c) funnel-type vessel.

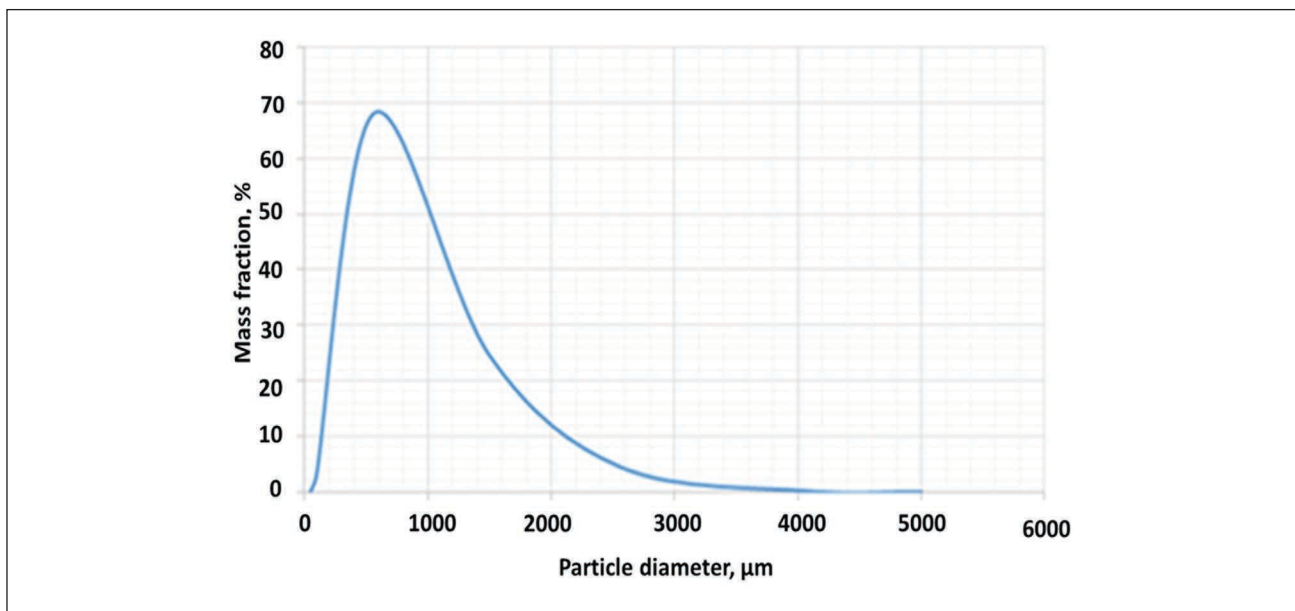
er bark/liquid ratio when the plug screw pump was used. According to the test runs, this pump allows 25% dry bark/liquid ratio at the minimum. The supplemental water was let into the reactor via separate pipeline next to the plug screw pump. When the eccentric screw pump was used, the bark-water suspension was fed using a funnel type ves-

sel (Fig. 3c). Air was fed below the screw axis. The air flow prevented the clogging of the bark at the feed point.

The preliminary extraction tests showed that both of the tested feeding modes, eccentric screw pump (a) and plug screw pump (b), can be used when suitable dry-water ratios are applied.



4. Three fractions obtained by use of the vibrating slope screen.



5. Particle size deviation of screened bark fraction 1 used for the experimental runs.

For successful reactor (Fig. 3) feeding, a dry-water ratio of 4% at the maximum (eccentric screw pump) or dry-water ratio of 25% at the minimum (plug screw pump) are needed (Fig. 2). The suspension dry-water ratio was adjusted using additional water feed at the feed end of the reactor.

Bark properties

Crushed pulp mill spruce bark received during May and June of 2018 from the Metsä Fibre Rauma mill in Finland was used in the experiments. The experimental extraction runs were carried out between six and eight months after

that. The crushed bark was stored in dry conditions in unheated storage.

The bark was divided into three fractions using a vibrating slope screen of mesh size 6 mm. The average particle size of bark used was 0.7 mm (fraction 1; **Fig. 4** and **Fig. 5**). The particle size deviation of fraction 1 was measured using a vibrating sieve. The dry sieving was accomplished with a laboratory Retsch AS200 (Retsch; Haan, Germany) oscillating sieve. The diameter of the sieves was 20 cm. The sieving time was 10 min at nominal amplitude 50. The extraction runs with fractions 2 and 3 were too difficult

Screw Type	Soaking Time, H	Temperature, °C	Feeding Mode	Suspension Flow Rate, L/h	Nominal Residence Time, min	Dry-Water Ratio, %	Yield Extract, %	Yield, Phenolic Compounds (tannin)
Standard screw	1	80	Eccentric screw pump	25.8	20	4	2.79	2,1
Standard screw	1	85	Plug screw pump	57	20	13	2.9	2.5
Mixing screw	1	110	Eccentric screw pump	164	50	3	4.5	2.7
Mixing screw	24	110	Eccentric screw pump	168	50	3	7	3.7
Mixing screw (modified)	Dry feed	110	Plug screw pump	184	50	2.3	2.9	1.8
Mixing screw (modified)	48	110	Eccentric screw pump	203	50	3	12,5	9,7
Mixing screw (modified)	96	110	Eccentric screw pump	203	50	3	17.0	11.8
Mixing screw (modified)	48	110	Eccentric screw pump	102	100	3	22.5	13.7
Mixing screw (modified)	96	110	Eccentric screw pump	102	100	3	14.0	11.6
Standard screw	48	110	Plug screw pump	102	50	16	2.5	1.5
Standard screw	48	110	Plug screw pump	160	50	8	3.8	2.3

1. Results of the experimental runs carried out with the continuous crew reactor.

to carry out because of wood sticks that caused clogging at the reactor feed. The water content of bark batches used for the experimental runs was, on average, 25%.

Reactor operation parameters

Before each run, the reactor was filled with water to half of the reactor height and heated to running temperature. During each run, the suspension level was kept constant at half of the reactor height, and temperature was adjusted with steam. The temperatures of the experiments were 80°C, 85°C, and 110°C. The nominal residence times were 20, 50, and 100 min. The nominal residence time is adjustable by rotation rate of the screw and is based on test runs carried out by the manufacturer of the reactor. The bark was soaked before each run at 20°C. The soaking times were 1, 24, 48, and 96 h. At the feed point of bark, the used suspension dry-water ratios were 3%, 4%, 13%, 26%, and 75%. In the case of the plug screw pump, the additional water was fed at the feed end of the reactor to adjust the bark-water ratio to the desired value (**Table I**).

Screw types

Because the reactor was in daily industrial use, slightly different types of screws were used for practical reasons. The major portion of the runs was carried out with a modified

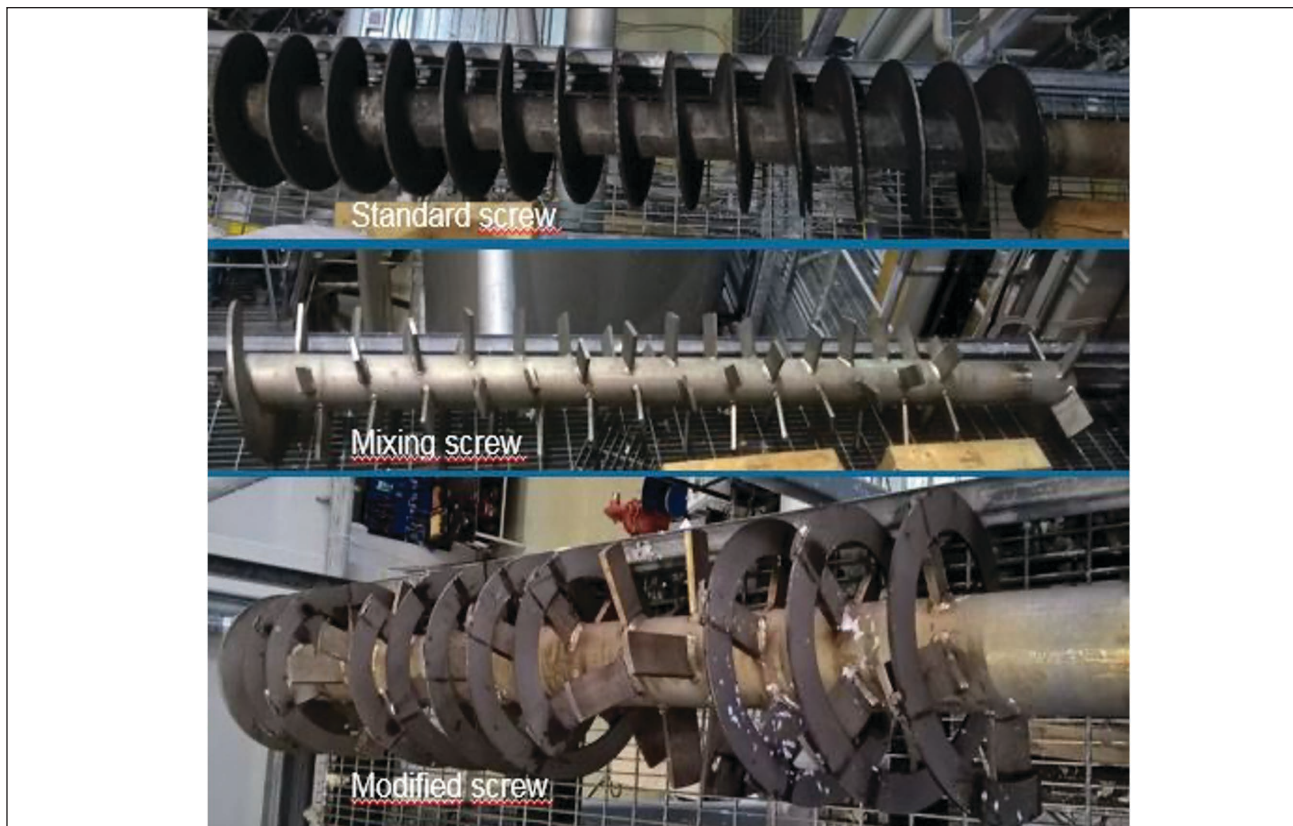
mixing-type screw or standard screw. A couple of runs were performed with a mixing-type screw. The screws used in the continuous screw reactor are shown in **Fig. 6**.

However, no measurable difference in the yield was obtained between the screw types used during this research, and the focus remained on the effects of residence time, bark/liquid ratio, and presoaking. The effects of different mixers will be studied in the future.

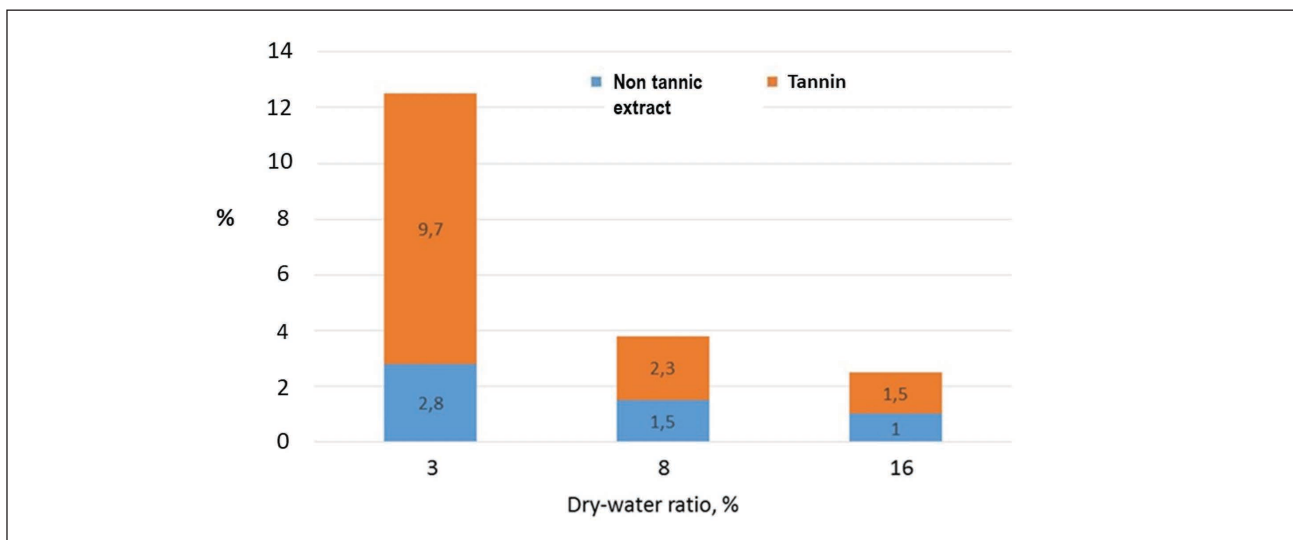
RESULTS AND DISCUSSION

The tannin content of the extract was analyzed using the UV-Vis spectrophotometer for absorbance at 280 nm. The results of the experimental runs are shown in **Table I**.

Table I consists of nine columns. The first column is for the screw type that was in use. The second column shows the time the bark was soaked in water before each run. The soaking water was taken into consideration when calculating the total amount of water in the bark-water suspension. The sixth line of soaking time is “dry feed,” meaning that there was no soaking of bark before the experimental run. The third column is for feed mode that shows what kind of pump was in use. The suspension flow rate column informs the flow rate of the bark-water suspension through the screw reactor. The dry-water ratio is the mass-based



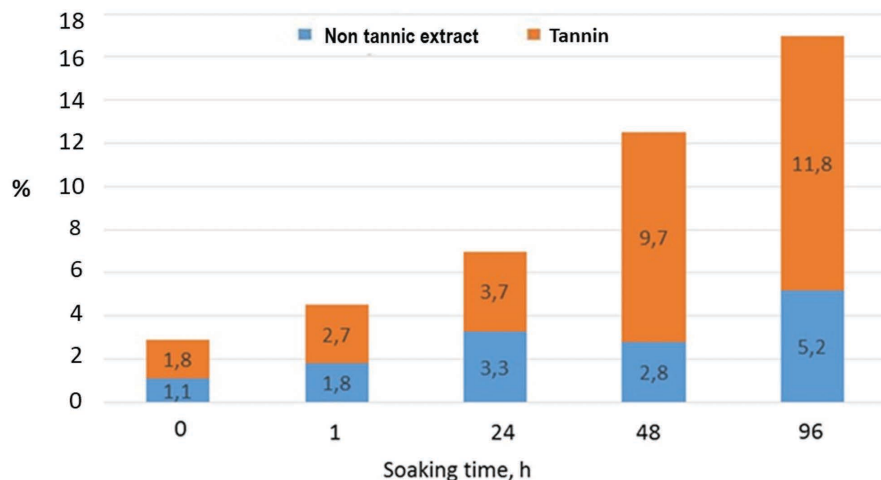
6. Screw types used in the continuous screw reactor during the experimental runs



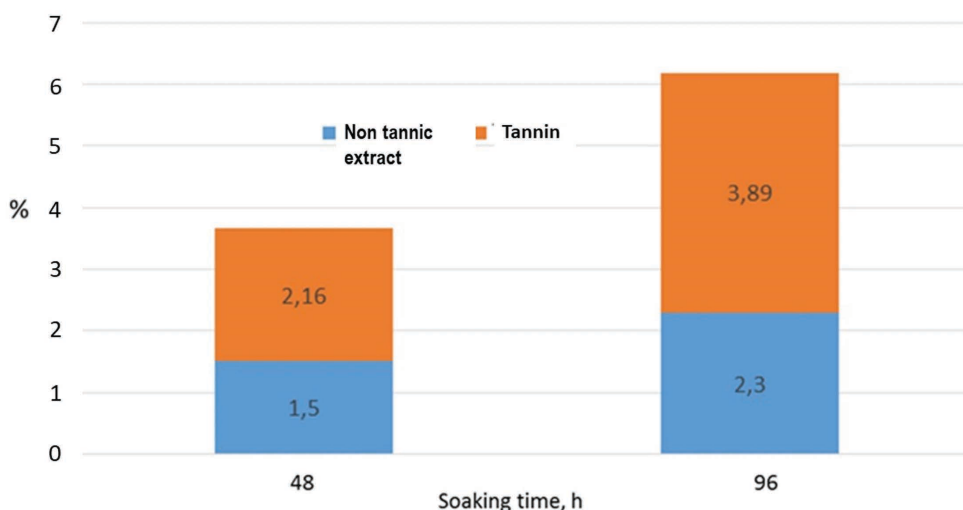
7. Yield percentages of extracts at different dry-water ratios. The presoaking time was 48 h. The nominal residence time was 50 min.

relationship of the dry bark and water of the suspension. In Table I and **Fig. 7**, it can be deduced that higher dry-water ratio produces higher yield. A longer presoaking time seemed to be better than a short one for obtaining higher yield (Table I, **Fig. 8**, and **Fig. 9**). The mechanism for obtaining higher yield probably takes place by opening the pore structure in the bark, which enhances mass transfer from the inner bark. During the 96 h of preliminary soak-

ing for the 10% bark-water suspension at 20°C, only 1.4% of extract from the dry weight was dissolved in soaking water, which shows that extraction during presoaking does not explain the higher yield. According to [13], improved results will be achieved if the milled bark and enriched wash liquor are slurried in the extraction tank at elevated temperatures for an aging period prior to initial separation in the filter. An aging period of between 10 min and 1 h,



8. Yield percentages of extracts with different presoaking times of bark. Extraction temperature was 110°C. The nominal residence time was 50 min. The dry-water ratio was 3%, except with dry feed, when the dry-water ratio was 2.3%.



9. Yield percentages of extracts with different presoaking times for bark when plug screw pump was used. The dry-water ratio was 8%. Extraction temperature was 110°C. The nominal residence time was 50 min.

preferably between 15 and 45 min and most preferably between 20 and 40 min. has been found effective in increasing the rate of extraction of tannins in accordance with the invention. Steam pretreatment may have the same kind of effect on the yield of phenolic compounds [37]. A cold water extraction phase before hot water extraction may also have a similar effect on yield [38].

According to the data in Table I, the longer nominal residence time does not seem to be advantageous for higher yield. However, more data is needed to assure the effect on yield between the nominal residence times of 50 and 100 min.

Almost all soaking water bypasses the feed point when a plug screw pump is used. This bypassing is characteristic of when the plug is formed at the feed point. When a plug

screw pump is used for feeding, the positive effect of soaking may be somewhat reduced. This could stem from the fact that the bark is strongly compressed at the feed point of the pump. This hypothesis needs further experimental runs for assurance. However, better yield is obtained through longer soaking time with use of a plug screw pump as well (Fig. 9).

CONCLUSIONS

A longer presoaking time for bark seemed better than a short one for obtaining higher tannin yield. During the four days of preliminary soaking of a 10% bark-water suspension at 20°C, only 1.4% extract from the dry weight is dissolved in soaking water, showing that the extraction during presoaking has little effect on tannin yield. In fact, the feed

point-passed extract should be taken into consideration when calculating the final yield of extraction in the case of the plug screw pump. This would increase the presented yields somewhat. The preceding soaking of the bark also minimized the mechanical feeding problems that are caused by clogging. If a soaked suspension of about 3%–4% is used, a continuous feeding system with a storage tank would be easy to design because of good handling properties with a suspension at that dry/water ratio. A higher tannin yield is obtained with a lower dry/water ratio, suggesting that the internal diffusion in bark does not determine mass transfer as much as is the case without presoaking of bark. The use of a plug screw pump may take away some of the positive effects of presoaking. Because the reactor is in daily industrial use, slightly different types of screws were used for practical reasons. The effect of screw type has not been taken into consideration in this paper and is beyond the scope of the current study. **TJ**

ACKNOWLEDGEMENTS

This work was financed by Business Finland and partner companies. The authors are grateful to all participants involved in this study.

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ABOUT THIS PAPER

Cite this article as:

Kuosa, M., Heikkinen, A., Tirri, T., et al., *TAPPI J.* 20(2): 139(2021). <https://doi.org/10.32964/TJ20.2.139>

DOI: <https://doi.org/10.32964/TJ20.2.139>

ISSN: 0734-1415

Publisher: TAPPI Press

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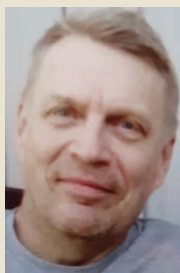
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ABOUT THE AUTHORS

We chose to study this topic because recycling of side streams in the wood processing industry is of high interest at South-Eastern Finland University of Applied Sciences (Xamk) and at Lappeenranta-Lahti University of Technology (LUT), and it is also connected to sustainability science. LUT and Xamk both have a long research history in the pulp and paper industry. These days, this research is more and more focused on the biorefinery field.

The most difficult aspects of this research were the feeding problems at the extraction reactor feed end, as we discuss in this paper. The runs were carried out using two different feed modes: (a) eccentric screw pump, and (b) plug screw pump. Several reactor feeding options were tested before the preliminary extraction runs.

It was interesting to discover the bark handling methods and usability of analytic methods we applied, and I was surprised about the ease of bark extraction. The most surprising finding was how much



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presoaking of bark affects the yield of tannin.

Biorefinery mills can benefit from the information in our research for development of new tannin extraction processes. The next step is to study how mixing affects tannin yield. It is also important to find a method for reactor feeding where bark particle size is not a limiting factor.

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