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A case study for integrated forest biorefinery: Recovery of manool from evaporator condensate of a kraft pulp mill

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In memoriam of Professor Huiren Hu (1947–2016), who devoted his life to his students at the Pulp and Paper program of the Tianjin University of Science and Technology, Tianjin, China.

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ABSTRACT

The integrated forest biorefinery concept teaches the opportunity in producing value-added products from the pulp and paper manufacturing processes, in addition to the traditional pulp and paper products. Manool is a plant extractive that is available in many wood species, in particular, softwood, and can find high value applications, such as in the perfumery industry. The evaporator condensate from the kraft black liquor recovery process contains manool and can be a potential source for this valuable product. In this paper, the recovery of manool from the evaporator condensate that was further concentrated in a reverse osmoses (RO) process (known as the RO concentrate) in a kraft mill in Eastern Canada, was investigated. The results showed the manool content in the RO concentrate is in the range of 300–1500 mg/L for samples collected. A novel process was developed in recovering manool from the RO concentrate, which consists of (1) adsorption of manool (together with other organics) into absorbent, such as talc, (2) desorption from the adsorbent and (3) further upgrading of manool. About 90% of the manool from the RO concentrate can be adsorbed onto the talc under the optimal conditions. The adsorbed manool on talc can be subsequently regenerated by extraction using ethanol or dichloromethane, resulting in the crude manool product. The purity of this crude manool product was about 25%, which was further purified to 86% based on the chromatographic separation technology.

1. Introduction

(+)-Manool (Fig. 1) is a readily available natural diterpene from trees and plant materials. In the literature, there are many studies reported in extracting manool from these raw materials. Merz and Ritchie [1] reported a process of producing manool from Dacrydium biforme. A number of studies have used *Salvia officinalis* L. as the raw materials for extracting manool. For example, Bernotienė et al. [2] extracted manool (14.4–20.9% based on oil) from air dried plant of *S. officinalis* L. by hydro-distillation. The essential oil from *S. officinalis* L. contains various amount of manool [3,4]. Velickovi et al. [5] also studied the ethanol extracts from the flower, leaf and stem of *S. officinalis* L. Manool was the richest component of all identified compounds (0.12–0.39% on raw material) in the chemical composition of the extracts obtained [5]. Manool is a critical component of essential oil, a natural product that has a growing worldwide market [6]. Couladis et al. [7] determined the content and composition of essential oil in the leaves and flowers of 11 populations of *S. officinalis* L. (nine populations in Montenegro and two populations in Serbia), and the results showed that: (1) the yield of oils was generally higher in the leaves than the flowers; (2) the dominant sesquiterpenes were: α-humulene (7.70%), viridiflorol (13.19%) and manool (7.67%), which were based on the total extractives; and (3) in the flowers, percentages of sesquiterpenes, particularly manool (13.48 ± 3.56%) were significantly higher than that in the leaves.

Manool was also extracted from *Mentha spicata* ssp. *insularis*, and *Salvia desoleana* by supercritical extraction using carbon dioxide [8,9], which was very selective for manool. Aleksovski and Sovova [10] also extracted the dry leaves of *S. officinalis* L. using carbon dioxide-based supercritical extraction technology.

In the kraft process, multiple evaporators are used to concentrate the weak black liquor to high solid black liquor, and a waste

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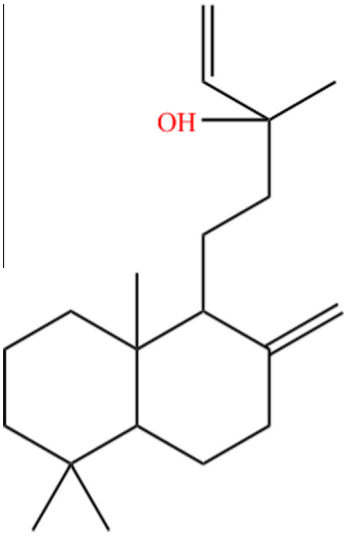

Fig. 1. Structure of manool.

stream, called the "condensate", was produced from the process. In many mills, the condensate is being treated in the effluent treatment plant to decrease its environment load. An alternative process is to use the reverse osmosis (RO) membrane technology to concentrate the condensate, which can then be sent to the recovery boiler for burning [11].

The RO concentrate contains many organics, and sulfur containing compounds (e.g., methyl mercaptan) [12]. A patent application was made on extracting organic compounds, such as manool, geranyl linalool ethyl guaiacol, eugenol, veratraldehyde, terpenes, cholesterol, from the RO concentrate [12]. The methods used were liquid-liquid extraction, and solid-liquid extraction. It is noted that such extraction methods would need significant amount of solvent since the RO concentrate is still a very dilute waste stream.

In following the integrated forest biorefinery to produce other value-added products (in addition to pulp or paper) from the conventional pulp and paper manufacturing process [13,14], we recently undertook a project in recovering manool from RO condensate from an Eastern Canadian kraft mill. In light of the very diluted nature of the feedstock, the reported methods of extracting manool, such as liquid-liquid extraction, would need significant amount of solvent, the novelty of our approach in the present study was to recover manool by following the adsorption concept that was reported in the literature for removing inhibitors from the prehydrolysis liquor (PHL) and for recovering valuable chemicals (e.g., acetic acid, furfural) from a very diluted stream [15–17]. Different adsorbents, including activated carbon, lime mud, calcium carbonate, were studied for the dissolved lignocelluloses in the PHL [18–20]. In the present study, Talc, or activated carbon, will be used as the absorbents, for manool from RO concentrate. It should be noted that Talc has already been used to adsorb organic impurities, such as pitch, in the pulp and paper manufacturing processes.

The main objective of this project was to recover manool from the evaporator condensate by: (1) adsorption/concentration of manool present using an adsorbent, such as Talc; (2) desorption from the adsorbent and further upgrading of manool.

2. Experimental

2.1. Materials

The condensate samples were from a kraft mill in Eastern Canada, which has a Reverse Osmosis (RO) process to concentrate the evaporator condensate. The samples received were from the outlet of the RO.

The activated carbon used was from Carbon Resources, OXPURE™ 325W ULTRAPLUS, while the talc sample was purchased from Sigma Aldrich. Ethanol, dichloromethane (DCM), ethyl acetate, acetone, petroleum ether, were purchased from Fisher Scientific.

2.2. Methods

2.2.1. Adsorption treatment using activated carbon or Talc

The RO condensate sample (with 506 mg/L manool concentration) was treated with activated carbon or Talc as the adsorbent under the conditions of RO condensate to adsorbent ratio of 5–40 mL/g of adsorbent, 25–180 min, room temperature in a laboratory shake mixer that was set at a shaking speed of 200 rpm. Subsequently, the slurry was filtered using a 0.45 μm microfiltration membrane. The adsorbent, together with the adsorbed organics, were then collected, and pressed to about 25% solid content.

2.2.2. De-sorption experiments

The RO condensate sample (with 506 mg/L manool concentration) was used, and the adsorption was carried out by using Talc as the adsorbent under the conditions of RO condensate to adsorbent ratio of 30 mL/g of adsorbent, 25 min, room temperature in a laboratory shake mixer operated at a shaking speed of 200 rpm. The Talc, together with the adsorbed organics, was then obtained by vacuum filtration as described above.

The thus obtained talc samples, which had the adsorbed organics, were then subjected to desorption experiments by using ethanol, or dichloromethane (DCM) or ethyl acetate. Beakers containing about 20 g pressed organics-loaded Talc and 50 mL solvent, were placed in an ultrasonic bath for 10 min. Subsequently, the mixture was vacuum filtered and 0.45 μm microfiltration membrane. The filtrate was then collected, and concentrated in a rotavapor, which is denoted as the "crude manool" product.

2.2.3. Chromatographic separation for further purification/upgrading of crude manool

A silica gel-packed column was used and the eluents used were as follows: mixture of acetone and petroleum ether (PE) at a volume ratio of 1:25; mixture of ethyl acetate and PE (1–33 ratio), PE, PE/DCM (volume ratio of 7/3), and PE/DCM (volume ratio of 1/1).

2.2.4. Manool analysis

A ^{1}H NMR method was followed for the quantitative determination of manool, which was based on the vinylic proton characteristic peaks at 4.55 and 4.85 ppm of manool. All ^{1}H NMR spectra were recorded at 298 K in deuterated chloroform using a Varian/Agilent INOVA 300 NMR spectrometer at a frequency of 299.8 MHz. The results from the ^{1}H NMR method were compared to those from a GC-MS method [12], and a good agreement between these two methods was found.

3. Results and discussion

3.1. Proposed process to recover manool from kraft black liquor condensate

The manool concentration in the RO concentrate is low (a few hundred to a few thousand ppm), as will be shown in Table 1, therefore it is not economic to use typical technologies, such as distillation to recover manool. Even with liquid/liquid extraction technique, a large quantity of solvent will have to be used. In this project, our proposed strategy is to follow the adsorption concept