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Essential oil composition of forest biomass stored under industrial conditions in Eastern Canada

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ABSTRACT

Changes to logging residues on storage, and their potential for essential oil extraction have not been thoroughly investigated. In this paper, storage effects are investigated using biomass harvested as part of a commercial harvest operation in New Brunswick, Canada. Effects were studied in the case of essential oils, and tests were conducted on piles either left uncovered, or covered with plastic or paper tarps. Variations in oils were measured over time at 0, 6 and 12 months and measured at varying depths throughout a pile. Oils were extracted through hydrodistillation and analyzed by GC-FID and GC–MS. The results demonstrate that after 12 months, essential oil yield decreases linearly and enriches in heavy terpenes with no significant impact from tarps. The deepest samples of a pile were also enriched in heavier terpenes. The results provide potential for profitable biorefinery operations of essential oil extraction from biomass.

1. Introduction

In recent years, there has been a rising interest in value-added forest products from underutilized biomass components available through the conventional forest harvest supply chain. In Canada there are two main contributing factors to this interest: a declining forestry sector which has resulted in high unemployment in rural areas, and an interest in renewable energy as a means for Canada to reduce its ecological footprint and help mitigate climate change. Thus, there is an interest in a multiple-use approach, where timber is targeted both as a feedstock for the manufacturing of conventional products (pulp and/or lumber) and in innovative uses such as energy production and essential oil extraction for flavour, fragrance and health purposes.

In a typical pulp chip supply chain in New Brunswick, a Canadian province with a high concentration of forestry operations, full trees are harvested and brought to a flail chipper. In the first stage of the flail chipper, bark and limbs are removed by flail drums and chains. These waste products (residues) are arranged into piles for use as hog fuel by the mill. The white wood proceeds through a chipper and is blown into trucks to supply the pulp mill directly. To ensure a steady supply of hog fuel, it is necessary to store the fuel through the winter season, however it is widely known that deterioration of the biomass occurs over storage, resulting in loss of mass, and chemical changes to the material.

Biomass residues or hog fuel may also be a valuable resource for natural chemicals. Extractives from the fuel, and essential oils in particular, can fetch high prices in the flavour and fragrance industries. These oils are comprised of hydrocarbon compounds naturally occurring in plant materials. The oils are of very low concentration in the plant and thus, when extracted at a large scale, can typically produce only small volumes. Despite this, the value of these oils is quite high. For example, cedar wood oil, sells for approximately 150 USD for 1 gallon (about 3.78 L) or about 13 USD per pound (Bulk Natural Oils, 2013; Texarome, 2013). The value depends on the quality of the essential oils, with therapeutic grade and organic essential oils fetching a higher price. The difference in quality is based on the process of extraction, where therapeutic grade oils are extracted solely by steam or hydrodistillation, while lesser grades utilize solvent extraction methods. The use of volatile oils in flavours and fragrances as well as in nutraceuticals, health foods and food additives are part of a growing industry (e.g. Boroski et al., 2012). As well, international development agencies in Canada and Australia have helped the underdeveloped nations of Bolivia and Papua New Guinea respectively, to develop part of this new industry in poor regions of their countries (Government of Canada, 2013; Australian Centre for International Agricultural Research, 2005). The Minnesota Department of Natural Resources

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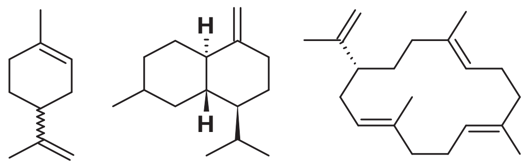

Scheme 1. Examples of a monoterpene (limonene, 10 carbons), sesquiterpene (cadinene, 15 carbons) and a diterpene (cembrene, 20 carbons) (Newman, 1972).

has also investigated economic opportunities for cedar oil production (Iddrisu,n.d.).

Essential oils are composed of a complex family of chemicals referred to as terpenes. These compounds are naturally produced by plants for a variety of reasons including defence against insect and pathogens and communication. Terpenes can be categorized by the number of carbons present in the molecular structure, for example, Scheme 1 shows a mono-, sesqui- and diterpene. Terpenes are all derived from the same biochemical precursor, isoprene, a 5-carbon molecule which is modified and combined to create different terpene structures (Zwenger and Basu, 2008). Depending on the species, there may be tens to hundreds of compounds present in an extracted essential oil mixture. Plant terpenoid composition is known to vary greatly according to local conditions, with the possibility that plants of the same species may differ greatly in essential oil compositions if located in slightly different climates or environments (Semiz et al., 2007).

The diversity of structures in the terpene family of compounds is staggering. Thousands of compounds exist which differ in bond location, polarity, chirality, and configuration, with minor differences in the chemical structure creating significant differences in the perceived scent or flavour. As well, with such different structural forms comes differing physical characteristics especially in regards to boiling and melting points with large, polar terpenoids volatilizing at a much slower pace than small, non-polar terpenoids (Zwenger and Basu, 2008). The slight structural and physical differences between terpenoids are the features which are used for separation of mixtures of terpene compounds, through chromatographic techniques.

The majority of literature on changes to wood extractives on storage focuses on strategies for enhancing extractive losses, most specifically triglycerides, which are responsible for problematic pitch deposits in the pulp and paper processes. An excellent review of these biotechnological approaches can be found in Gutierrez et al. (2001). Extractives are readily lost on storage and it is appropriate to examine the impact of storage on yield losses and compositional changes. Losses are important not only for economic reasons but also health and safety reasons.

In the pulp industry (especially those using the sulphite and thermo-mechanical (TMP) processes), the benefits to wood storage, either as logs or chips, is the decrease that occurs in the extractive content. This is especially true for a reduction in the non-polar fraction of the extractives, which translates into reduced pitch problems in the mill. However, in the Kraft pulping process, the recovery of volatile terpenes and lipids as a crude tall oil is an important economic by-product of the process and loss of terpenes from the wood has a direct negative impact on the mill. Studies on losses in production of turpentine and tall oil have shown an 80% loss in 40 days for turpentine and a more gradual loss of tall oil of 85% over 90 days (Quillan, 1994). In a paper by Springer (1978) two earlier studies are referenced which show over 80% loss of turpentine production after a 1-month storage period. Generally, about 25–75% of all wood extractives are lost during outside storage (Assarson et al., 1970).

The terpene component of biomass, which is in higher concentration in a tree's foliage, will readily vaporize at moderately warm temperatures, hence the familiar aroma of conifer foliage. Colder temperatures in the winter inhibit evaporation and hence they accumulate in colder seasons. Granstrom (2010) found that there was a 90% loss of terpenes (original content was 0.1 g/1 kg odw) from freshly sawn Scots pine sawdust in just 10 days. Rupar and Sanati (2005) found that the rate of terpene loss increased from the spring to a maximum in the fall, over 200 days in stored piles of bark and wood, and forest residue chips from spruce and pine. The air emissions they measured contained monoterpenes, sesquiterpenes, with very slight amounts of diterpenes.

The biomass literature reveals examinations of extractive losses largely for health purposes or as indicators of degradation, rather than as valuable products and as such, little work was found regarding the impact of storage of forest residues for production of essential oils. Examination of herbal storage, however, reveals storage negatively impacts quality and quantity of oil produced. In order to preserve the yield and quality of essential oils, distillation immediately following harvest is necessary. Ram et al. (1989) studied loss of volatiles and quality of remaining volatiles after storage of rose-scented Geranium, *Pelargonium* sp. They reported decline in quantity and change in composition of volatiles after 1 day in storage. In addition, there is adequate evidence that tall oil and turpentine products derived from the resinous materials in coniferous species are rapidly deteriorated under relatively brief storage conditions.

This study aims to explore the potential of essential oil extraction from forest biomass harvested following a commercial forestry operation with extended storage. In particular, this study examines the effect of three storage treatments on essential oil quantity and quality, including varying the tarp coverage material of the biomass piles, variation in time of storage (with concomitant seasonal variations), and variation of sampling depth within the piles.

2. Materials and methods

2.1. Sample description

The commercial harvest for this study took place in mixed forest stands in southern New Brunswick, Canada in September of 2009. In the harvesting scenario, commercial stems were harvested with a feller-buncher and skidded (grapple) to a pile next to a flail-chipper equipped with top and bottom flail drums and chains. The delimber/debarker residues, consisting of branches and bark, were collected and stored in piles on well-drained landings. Three piles were set up to measure the effects of a particular tarp covering on essential oil content. The first treatment was left uncovered (referred to as 'Uncovered'), the second was covered with a paper tarp produced by Walki Group Oy (2013) (referred to as 'Paper') and the third was covered by a plastic tarp produced by InterWrap (InterWrap, 2013) (referred to as 'Plastic'). The paper tarp was composed of two layers of wet strength paper, a layer of polypropylene netting, and a final thin polyethylene layer. The plastic tarp was composed of recyclable polypropylene and consisted of a three layer structure.

Once piled, initial biomass samples from the surface of the piles were immediately collected, indiscriminate of species and size ('Control' sample, taken at $t = 0$). Remaining piles were subsequently sampled after 6 ($t = 6$) and 12 ($t = 12$), months of storage. At the 6 and 12-month mark, biomass was collected from a depth of approximately 1 m into the pile. In addition, variations in essential oil within a pile was analyzed in order to gain an understanding of within-pile variation by sampling an uncovered pile at 12 months at three depths: 1 m, 2.5 m, and 3.5 m. The full set of treatments are outlined in Table 1.