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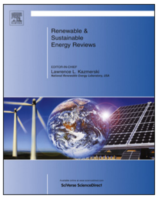

# Valorization of bark for chemicals and materials: A review

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ABSTRACT

The annual bark yield in Canada is as much as 17 million $m^3$. Currently, more than half of the bark is incinerated or landfilled and the remainder of the bark is mainly used as a cheap source of energy in saw/pulp mills. Both bark incineration and landfilling can lead to environmental problems. Due to the abundance of ash in bark and the lower sintering point of bark ash than that of wood ash, the combustion of bark can lead to fouling which would damage the combustors. Bark contains a large fraction of extractives and lignin (up to 50 wt% on a dry basis), which can be utilized as a renewable source of chemicals, particularly aromatic chemicals. The technical routes and technologies on the valorization of tree barks for chemicals and materials are reviewed in this paper. These include direct utilization of bark for wooden panels, and extraction for extractives (mainly tannin) and their the application in resins and foam materials, as well as conversion of bark via thermochemical technologies, mainly phenolysis, direct liquefaction in alcohols and pyrolysis. Finally, some challenges and perspectives on the production of chemicals and materials from bark are discussed.

**Contents**

## 1. Introduction

Currently, chemicals and energy are mainly derived from fossil fuels, which is challenged by the rapidly declined reserves and fluctuating prices of crude oil. Thus, research into alternative

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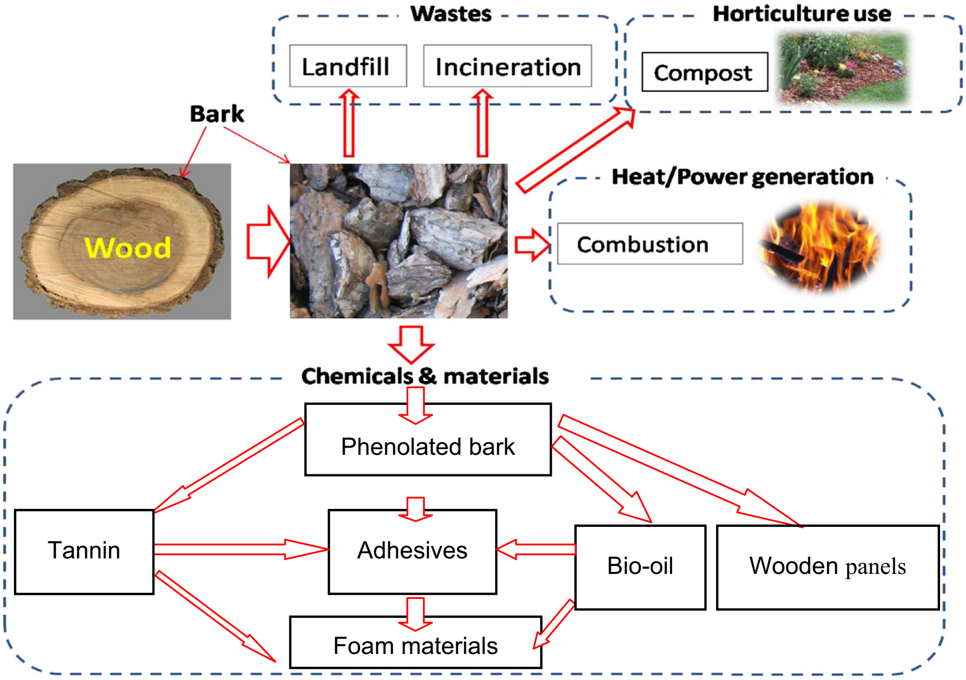

**Fig. 1.** Valorizations of tree barks.

sources for chemical and fuel production has attracted a great deal of attention. Biomass is mainly composed of cellulose, hemicellulose and lignin, as well as a small amount of extractives and ash. Through thermochemical and biochemical processes, biomass has the potential to provide value-added chemicals, such as reducing sugars, furfural, ethanol and other products. Bark, which is defined as all the tissues external to and surrounding the vascular cambium, comprises about 9–15% of a typical log by volume or 13–21% on a dry weight basis [1,2]. The annual bark yield in North America, mainly derived from pulp and wood industries, is estimated to be more than 50 million tons [3], among which around 17 million m$^3$ is produced in Canada [4]. Currently, bark is mainly used as an energy source by direct combustion in sawmills and pulp mills, or as compost for horticulture use. In the U.S., thermal energy production absorbs about 83% of softwood bark and 66–71% of hardwood bark, and the market share of bark for horticulture use is about 15% of softwood bark and 30% of hardwood bark [5]. In Canada, only a fraction of the bark is used for thermal energy production, and more than half of the bark is incinerated or landfilled as waste [4]. Compared with coal, bark's heating value is normally lower, 10 t of completely dry bark has a gross average heating value equivalent to that of 7 t of bituminous coal, but bark has negligible sulfur, which means bark combustion results in much less pollution to the environment [6]. Ash is the noncombustible part in bark and a high ash content tends to lower the heating values, while bark generally contains less volatile matters and a higher percentage of fixed carbon than wood [7], resulting in bark's higher caloric values than wood. It has been reported that the presence of resinous extractives in bark would contribute to increase in bark's heating values [8]. For example, Resch's research [9] showed that resin free bark pellets had higher heating values (HHV) of 17.2–22.8 MJ/kg while resinous bark had an HHV of 20.4–25.1 MJ/kg. Another advantage is that resinous bark pellets show better mechanical properties, so that the pellets are more durable [10].

However, bark's caloric value is still much lower than that of fossil fuel [11,12], and due to the abundance of ash in bark and the lower sintering point of bark ash than that of wood ash, bark combustion can lead to fouling which would damage the combustors. Thus, direct combustion of bark for energy recovery is not that economically advantageous. Studies have been conducted on various new applications of wood bark as pollutant absorbents [13–15], filler for phenolic resins when applied in plywood [16], metal ion or formaldehyde absorbers [12,17], and proanthocyanidin with antioxidant activity [18], etc. However, bark valorization is still challenging due to its heterogeneous structure, diverse chemical composition, low strength and dark color.

Bark is not either a favorable feedstock for the production of fermentable sugars due to the fact that it contains a higher content of lipophilic extractives, and aromatic compounds including tannin and lignin [19,20]. The presence of bark in the wood pretreatment processes necessary for sugar production decreases the recovery of sugars, furfural and 5-hydroxymethylfurfural in the pre-hydrolysate. Pre-hydrolysate resulting from the processing of bark-containing wood exhibits poorer fermentability into ethanol than that from the bark-free wood [21,22]. In contrast, the aromatic polyol structure components in bark favor its utilization in phenol formaldehyde (PF) resins and foam production. Valorizations of bark including utilization of bark in the production of chemicals and materials, e.g., wooden panels, tannin, resins and foams, bio-oils, etc., are summarized in Fig. 1.

Although barks have been widely used for medicine, dyes, spices, incense or phytotherapy, cork, animal bedding and absorption for pollutants, this review focuses on bark utilization for chemicals and materials, specifically for the production of wooden panels, tannin, resins and foams, as well as the thermochemical conversion of bark (via phenolysis, direct liquefaction, and pyrolysis), and the applications of bark thermochemical conversion products.

## 2. Chemical compositions of tree bark

Bark refers to all tissues external to and surrounding the vascular cambium. It can be divided into the inner bark and outer bark. Inner bark, the region of bark nearest to wood, is composed mainly of secondary phloem extending from the vascular cambium to the innermost or last-formed layer of periderm, and