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Review

Tall oil production from black liquor: Challenges and opportunities

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ABSTRACT

Tall oil is an important by-product of Kraft pulping processes. One possibility to improve the economic feasibility of Kraft pulp mills is to consider tall oil production from their wasted tall oil soaps. This review paper describes the current technology practiced to produce tall oil from the black liquor of Kraft pulping processes. Moreover, alternative processes to separate tall oil soap from black liquor, produce tall oil from the separated soap, purify tall oil, and to produce value-added products from tall oil are reviewed. The main perspectives and challenges associated with each process are comprehensively described. Currently, soap is separated from black liquor via decantation. To improve the efficiency of this separation, the application of neutral soluble colloids in dilute black liquor reported to be promising. Tall oil soap is converted to crude tall oil in the acidulation process via treating with sulfuric acid. However, the use of sulfuric acid forms calcium sulfate as a by-product of the process. The replacement of sulfuric acid with a sodium sesquisulfate solution is beneficial for decreasing the direct use of sulfuric acid in the tall oil production process. Crude tall oil can be used without purification as fuel. Its purification and subsequent reaction with methanol can lead to biodiesel production. However, this process may be complicated to implement in industry. The production of valuable lignin-based products from the tall oil production process may have benefits for the mills as these processes can be fully integrated into the Kraft pulping and tall oil production processes.

Contents

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1. Introduction

Since its inception in the late 19th century, Kraft technology has become a staple in current pulping processes across the world. The Kraft pulping process produces stronger pulp and is able to include chemical recovery to reduce costs, making it a superior option to most of other pulping methods [1].

However, the low price of Kraft pulp and increasingly tight competition from countries with low labour costs led Kraft pulp mills to seek diversity in products in order to improve their competitiveness [2]. The conversion of Kraft pulp mills to forest biorefineries was comprehensively discussed in the past [3]. In these processes, lignin-based chemicals (e.g. activated carbon, carbon fiber, and phenol), wood composites, sugar-based chemicals, polymers, ethanol and other liquid fuels can be produced [4–10]. Recently, the LignoBoost and LignoForce technologies have been employed to extract Kraft lignin from black liquor of Kraft pulping processes in order to produce alternative fuels or value-added lignin-based products [11,12]. In some mills, a hydrolysis stage is implemented prior to Kraft pulping in order to convert a paper-based Kraft process to a dissolving pulp-based (i.e. more value-added than paper-based) Kraft process. In addition, it was proposed that hemicelluloses extracted and dissolved in the hydrolysis liquor of hydrolysis-based Kraft process can be converted to xylitol, ethanol or chemical [13–16] or used as papermaking strength additive [17]. It was also reported that lignin extracted and dissolved in the hydrolysis stage can be converted into biofuel, plastics or carbon fibers [18–20].

The aforementioned processes are all based on hemicelluloses, lignin and cellulose uses of wood chips. However, wood contains extractives that are soluble in water or neutral organic solvents [21]. They serve multiple functions in trees such as energy stores and as barriers to a biological attack [22]. In hardwoods, such as oak and willow, extractives account for roughly 1–8 wt.% of the wood [22,23]. In softwoods, such as pine, extractives may contain up to 10 wt.% of wood [23]. These extractives include terpenes, fatty and rosin acids, sterols, and alkanes [22]; and are usually under-utilized parts of wood in pulping processes.

Tall oil is produced mainly from fatty and rosin acid extractives, which are non-volatile fractions [24]. The presence of tall oil soap in black liquor increases scaling in the evaporators of the Kraft process, and decreases the heat transfer in the evaporators and overall pulp production [25,26]. Studies also showed that the presence of tall oil soap in black liquor, particularly the rosin acid portion, increased the Kraft mill effluent toxicity [27,28]. Additionally, burning tall oil soap in the recovery boiler of the Kraft process increases sulfur emissions, decreases the boiler efficiency and boiler fouling rate, and causes control problems [29,30]. The load on recausticization in the Kraft recovery cycle is also increased in the presence of tall oil soap, which further reduces the efficiency of the Kraft process [29]. As such, tall oil is usually recovered from the recovery cycle of the Kraft pulping process to benefit the pulping process. Tall oil is one of the current commercially viable by-products of the Kraft pulping process [31]. The commercialization of tall oil has grown to 1.6 million metric tons per year globally in 2006 [32]. Currently, the United States, Scandinavian countries, Russia, and China are the leading producers of tall oil [33]. Growth is expected to increase towards 2 million metric tons per year by 2018 [33].

Recent studies showed that tall oil could be converted to fuel at a much lower cost than did alternative biomaterials, such as vegetable oil [32,34]. Due to the costs and environmental footprints associated with the use of fossil fuels, it is of great economic importance to produce fuels from other sources. From the abundance of extractives in wood, its large market, and the advantages associated with its removal from black liquor in the Kraft recovery process, the production of tall oil has significant benefits for the Kraft pulping process. As such, the implementation of tall oil production is well in harmony with converting traditional Kraft processes to more advanced and economically competitive processes and with reducing the environmental impact of fossil fuels. The main objectives of this work are to review the methods proposed for the production of tall oil from black liquor of Kraft pulping processes. The main novelty of this work is the critical analysis of the alternatives in the production of tall oil and of the challenges associated with the implementation of these options at industrial scales.

2. Tall oil compositions

Crude tall oil is characterized as viscous and sticky dark brown liquid that is ill-smelling prior to refining [32]. The refined tall oil is less brown and viscous but oily [35]. The typical chemical compositions of crude tall oil are 38–53 wt.% fatty acids, 38–53 wt.% rosin acids and 6.5–20 wt.% unsaponified (neutral) compounds [31,36]. Fig. 1 shows the chemical structures of these compounds. Unsaponified compounds are the fraction of lipids (fats) that do

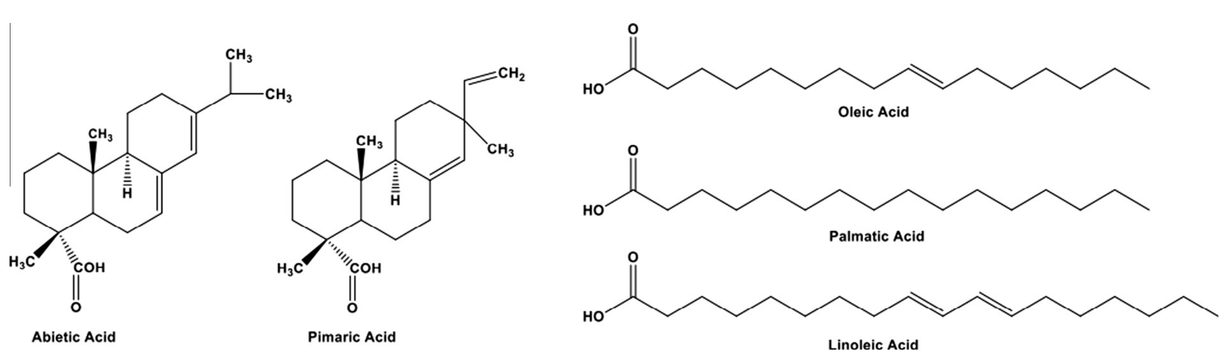

Fig. 1. Chemical structure of tall oil compounds.

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