Tall Oil Production Process and Characterization

By

Thomas Daniel Aro

Supervisor: Pedram Fatehi, PhD, P.Eng.

Thesis

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I've learned that sometimes it's enough to let it call the shots, but other times you have to let it take absolute control. Praise be to the LC. Made 'er.

TFD.

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Abstract

Existing kraft pulp mills have seen the necessity to branch out from traditional pulp and paper products to alternative value-added products such as bioenergy and biomaterials as a result of increasing competition in the forest products industry and the need for divergence from fossil fuels. Consequently, by-products from kraft pulp mills, including tall oil from extractives and modified lignin from black liquor, have seen a rise in valorization recently.

In this study, tall oil soap was received from a kraft pulp mill and transformed via acidification to crude tall oil. The reaction conditions of water content, reaction pH, reaction time, along with the application of settling additives were varied in order to determine optimized conditions. Optimized conditions without the use of settling additives were 100 wt.% H_2O, pH of 2.5 – 3.0, reaction time of 20 min, and incorporated industrially accepted values of reaction temperature (90 – 100 °C) and settling time (2 h).

When employing settling additives, both anionic and cationic polymers were tested. The Infinity^{TM} PS 3040 Pulp Processing Aid was an anionic polymer with the charge density -4.73 mmol/g and a molecular weight of 7.00×10^4 g/mol. When employed at a dry basis dosage of 0.0185 wt.% (0.05 wt.% wet basis), it produced crude tall oil with a 57.1 wt.% yield and an acid number of 142 mg KOH/g oil, based on the initial amount of raw soap added. These were increased compared to crude tall oil produced with no additive with a yield of 52.9 wt.% and acid number of 137 mg KOH/g oil. The second settling additive was xylan-AETAS-APS, a cationic xylan copolymer with a charge density of 3.81 mmol/g and molecular weight of 1.26×10^5 g/mol. The yield of crude tall oil was optimized with a dry dosage of 0.01109 wt.% (0.03 wt.% wet dosage), at 53.7 wt.%. A maximum acid number of 138 mg KOH/g oil was achieved with a dry dosage of 0.00729 wt.% (0.02 wt.% wet). Finally, an H-lignin copolymer, DMC-HL10, with a cationic charge density of 3.47 mmol/g and a preliminary molecular weight of approximately 32,000 g/mol was employed. With a dry dosage of 0.0037 wt.% (0.01 wt.% wet), a crude tall oil yield of 53.1 wt.% and acid number of 136 mg KOH/g oil were produced. Ultimately, analysis of variance (ANOVA) and Statistical Package for the Social Sciences (SPSS) analysis determined that no statistical optimal conditions were present.

The waste lignin from the tall oil production process was also characterized by charge density, solubility, CHNS, and molecular weight analysis, in order to determine if sulfonation with sulfuric acid during tall oil production had occurred. It was found that the anionic charge density increased from approximately 0 with unmodified kraft lignin to 0.2 – 0.4 mmol/g depending on the production process of tall oil. There was an increase in solubility from approximately 0 g/L to over nearly 2 g/L and an increase in sulfur content from as low as 0.23 wt.% to a maximum of 2.1 wt.%. Molecular weight of tall oil lignin was found to be approximately 1,700 g/mol, i.e. lower than those of unmodified kraft lignin (up to 25,000 g/mol) and lignosulfonates (up to 150,000 g/mol). Thus, it can be inferred that sulfonated kraft lignin may be produced from waste tall oil lignin, but further studies must be conducted before determining potential implementation in industrial processes such as dispersion and flocculation.

1. Chapter 1: Introduction

1.1. Overview

Due to recent changes in the bio-economy with respect to divergence from fossil fuels and an increase in sustainability requirements, the pulp and paper industry has had to vastly diversify the scope of their end-products. In addition, a decreased demand for traditional pulp and paper products has further resulted in a shift from paper to other value-added products such as biofuels and by-products (Rodriguez-Chiang et al., 2017; Haddad et al., 2017). An increased range of end-products of pulp mills also increases the profitability of the mills, which allows for a competitive market with increased desire for research development (van Heiningen, 2006). This is observed significantly in kraft pulp mills.

Kraft pulp mills have recently attempted to expand into Integrated Forest Biorefineries (IFBRs), in which pulp from cellulose is not the main end-product (van Heiningen, 2006). Rather, IFBRs are similar to petroleum refineries in which several important products may be isolated (Bokhary et al., 2017). These include all facets of wood, such as cellulose, hemicellulose, lignin, and extractives (Bokhary et al., 2017; Yang and Jaakola, 2011). Extractives are a minor but important aspect of wood, and include tall oil as a main constituent.

Tall oil, produced in its crude form (crude tall oil) has been exploited as a by-product of wood since the early 1900s (Panda, 2013). Crude tall oil is produced from the acidification of tall oil soap with sulfuric acid, which is formed during the kraft pulping process. Also present in the reaction mixture is residual black liquor and thus some lignin, as the separation of tall oil soap from black liquor is not completely efficient. Crude tall oil is brown, viscous, and ill-smelling, and has many uses in both its unrefined and refined forms as adhesives, detergents, drilling fluids, and asphalt additives, for example (Panda, 2013). Growth is expected to increase towards 2 million metric tons per year by 2018 (Baumassy, 2014). There are great variations in its composition, dependent on the geographic location of the wood, wood type, and storage time before pulping. Recent studies have been conducted showing that tall oil can be used as an intermediate to produce other value-added products, which should be exploited in order to increase the economic viability of existing kraft pulp mills as they transition into IFBRs (Marda, 2006; Lee et al., 2006; De Bruycker et al., 2014; Lappi and Alén, 2011). Optimizing the production process of tall oil as well as analyzing the composition and quality are important aspects of increasing this profitability.

Another aspect of IFBRs is the utilization of lignin. In the past, lignin was typically burned for fuel in the kraft recovery cycle; however, recently lignin has been used more for value-added products including flocculants and dispersants following isolation and chemical modification (Berlin and Balakshin, 2014). As mentioned above, lignin is present in the production of crude tall oil. It is typically recycled to the kraft recovery process for energy production (i.e. burning) following separation from the aqueous reaction waste portion of tall oil. Alternatively, it may be feasible to produce value-added chemicals from the waste lignin of the tall oil production process. Specifically, the waste lignin may be used in tandem with the waste sulfuric acid in solution to produce sulfonated lignin which may be further modified and characterized in order to determine a viable end-product. The sulfonated lignin may have applications such as flocculants or dispersants. Since lignin modification processes may be fully integrated into existing kraft pulping and tall oil processes, this may be highly beneficial to the economic value of existing processes.

In this MSc thesis, the optimization of the tall oil production process was analyzed. In addition, the characterization of the tall oil products for all reaction conditions was conducted. Waste lignin characteristics were determined for some of the reaction conditions in order to evaluate the potential feasibility of using the waste lignin for value-added products.

In Figure 1.1 below, a tree diagram is shown to simplify the results in Chapter three. This figure highlights the alternative routes of modification of kraft lignin and lignosulfonates, along with the connections between them and order in which they can be carried out.

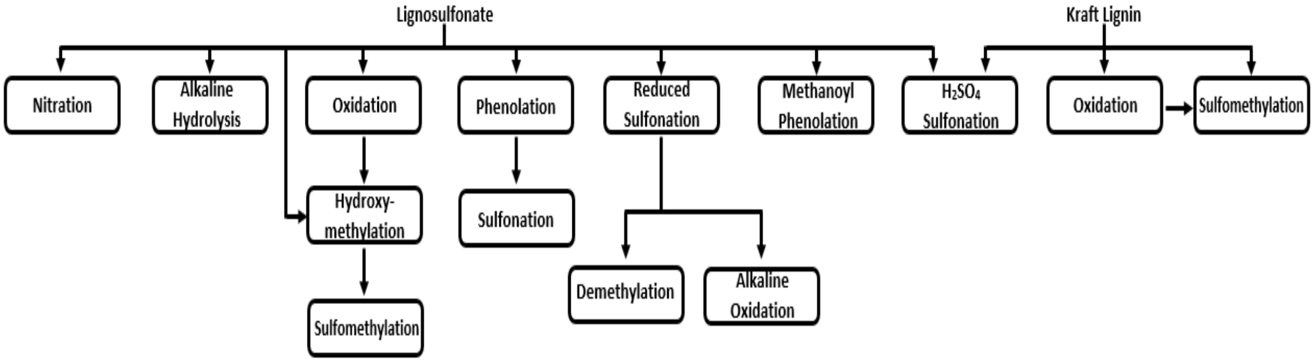

Figure 1.1. Tree diagram of modification procedures of lignosulfonates and kraft lignin.

In chapter one, a brief summary of the proceeding chapters contained in this thesis is provided. The objectives and novelty with respect to the topics in this thesis are also presented within this chapter.

In Chapter two, a detailed literature review is provided on the background, history, and advancements in the tall oil production process. This chapter covers the three main sections of the tall oil production process, including separation of tall oil soap from the kraft recovery process, the production of crude tall oil, and the fractionation of crude tall oil into refined portions. Advancements and alternatives to traditional methods in each of these sections are analyzed in detail. Detailed production schemes are developed and critically described, along with potential advantages and disadvantages for each method.

Chapter three is another detailed literature review which outlines the production and application of lignosulfonates and sulfonated lignin. Existing methods were analyzed, including current industrial production and isolation methods of lignosulfonates and sulfonated lignin. This chapter also outlines several alternative methods to sulfonate lignin from different pulping processes, along with methods to modify lignosulfonates from sulfite pulping and sulfonated lignin from other methods. Potential reaction schemes are highlighted for all proposed methods. The impact of the properties of the products from each of the production methods are analyzed with respect to potential industrial applications and future feasibility.

Chapter four outlines the research conducted to optimize the tall oil production process. Variables analyzed include: water content, reaction pH, reaction time, and settling additive type and dosage. The resulting yields, quality, and composition of each of the tall oil reaction conditions are reported and examined. Further analysis involves GC/MS of selected tall oil products to determine the relative and absolute amounts of specific fatty acid components. Also included is an analysis of the preparation method for tall oil GC/MS relative to industry to ensure accurate results. Finally, lignin from the tall oil production process is analyzed with respect to charge density, solubility, molecular weight, and CHNS to determine preliminary results for potential value-added products from the waste of the tall oil process.

Chapter five outlines the overall conclusions as well as recommendations for future work.

1.2. Objectives

The objectives in this thesis were to:

1. optimize the production of tall oil in terms of yield and characteristics with respect to water content, reaction pH, and reaction time;
2. determine the optimal type and dosage of settling aid using optimized reaction conditions in terms of crude tall oil yield and characteristics;
3. correlate the characteristics of produced crude tall oil with reaction conditions;
4. analyze and interpret the main acidic compounds present in selected crude tall oil samples using chromatographic methods, and;
5. analyze lignin samples from selected production methods for future application as value-added products.

1.3. Novelty of study

To the best of our knowledge, the following aspects have not been previously studied:

1. the correlation between reaction conditions and their impact on crude tall oil characteristics;
2. the impact of settling additive type and dosage on crude tall oil yield and characteristics,
3. the chromatographic analysis of tall oil products in regards to production method, and;
4. the characterization and utilization of waste lignin from crude tall oil product for value-added products.

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2. Literature Review – Tall oil production from black liquor: Challenges and opportunities[1]

2.1. 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.

Keywords: tall oil, extractives, biorefinery, separation, kraft process

2.2. 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 (Helm, 2000).

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[1] Aro T, Fatehi P, 2017a, Tall oil production from black liquor: Challenges and opportunities, Separation and Purification Technology, 175, 469-480

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 (Diesen, 2007). The conversion of kraft pulp mills to forest biorefineries was comprehensively discussed in the past (van Heiningen, 2006). 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 (Bessou et al., 2011; LigniMatch, 2010; IEA Bioenergy, 2007; Oveissi and Fatehi, 2015; Van der Drift and Boerrigter, 2006; Griffith et al., 2003; Kadla et al., 2002). 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 (Kouisni et al., 2012; Tomani, 2010). 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 chemicals (Fatehi et al., 2016; Huang, 2010; Kaylen et al., 2010; Cruz et al., 1999), or used as papermaking strength additive (Liu et al., 2010). It was also reported that lignin extracted and dissolved in the hydrolysis stage can be converted into biofuel, plastics, or carbon fibers (Yang et al., 2013; Axegard, 2008; Wang et al., 2015).

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 (Smook, 2002). They serve multiple functions in trees such as energy stores and as barriers to a biological attack (Stenius, 2011). In hardwoods, such as oak and willow, extractives account for roughly 1 – 8 wt.% of the wood (Stenius, 2011; Shackford, 2003). In softwoods, such as pine, extractives may contain up to 10 wt.% of wood (Shackford, 2003). These extractives include terpenes, fatty and rosin acids, sterols, and alkanes (Stenius, 2011); 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 (Sixta, 2006). 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 (Uloth, 1986; Grace, 1975). Studies also showed that the presence of tall oil soap in black liquor, particularly the rosin acid portion, increased the kraft mill effluent toxicity (Drew and Propst, 1981; Hutchins, 1979). 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 (Foran, 1992; Puustinen, 2015). 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 (Foran, 1992). 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 (Wansbrough, 2008). The commercialization of tall oil has grown to 1.6 million metric tons per year globally in 2006 (Marda, 2006). Currently, the United States, Scandinavian countries, Russia, and China are the leading producers of tall oil (Baumassy, 2014). Growth is expected to increase towards 2 million metric tons per year by 2018 (Baumassy, 2014).

Recent studies showed that tall oil could be converted to fuel at a much lower cost than did alternative biomaterials, such as vegetable oil (Marda, 2006; Lee et al., 2006). 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.

2.3. Tall oil compositions

Crude tall oil is characterized as a viscous and sticky dark brown liquid that is ill-smelling prior to refining (Marda, 2006). The refined tall oil is less brown and viscous but oily (Borglin, 1945). 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 (Wansbrough, 2008; Hampton, 1962). Figure 2.1 shows the chemical structures of some of these compounds. Unsaponified compounds are the fraction of lipids (fats) that do not form soaps in an alkaline solution and do not have any commercialized use in industry as of yet. The composition of the crude tall oil is subject to change with wood region and species, and other extraneous circumstances related to wood storage and pulping. The average yield of the crude tall oil varies in the range of 30 – 50 kg/ton of pulp (Sixta, 2006), which corresponds to a yield of 50 – 75% based on its original amount in wood (Shackford, 2003; Lappi and Alén, 2011; Fuenzalida et al., 2005).

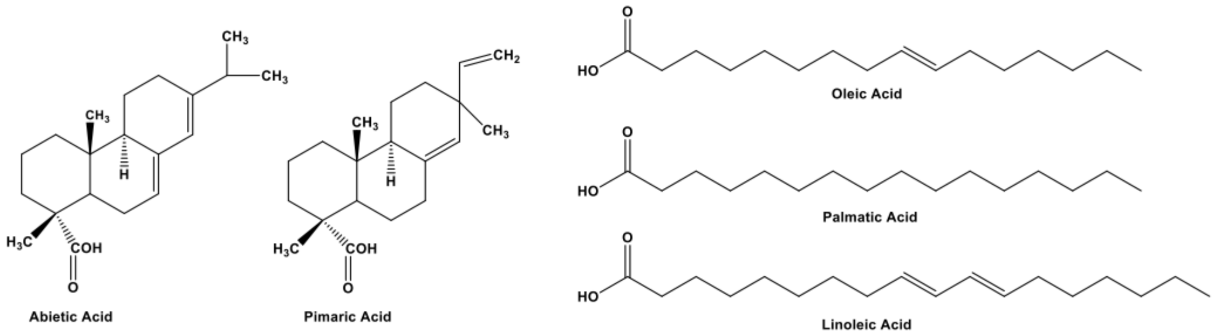

Figure 2.1. Chemical structure of tall oil compounds.

2.4. Current commercial tall oil production process

Figure 2.2 depicts a block flow diagram of the present process for the tall oil production that is integrated into the kraft pulping process. This process can be split into three sections including the tall oil soap isolation from black liquor, crude tall oil production from tall oil soap and tall oil purification and end use.

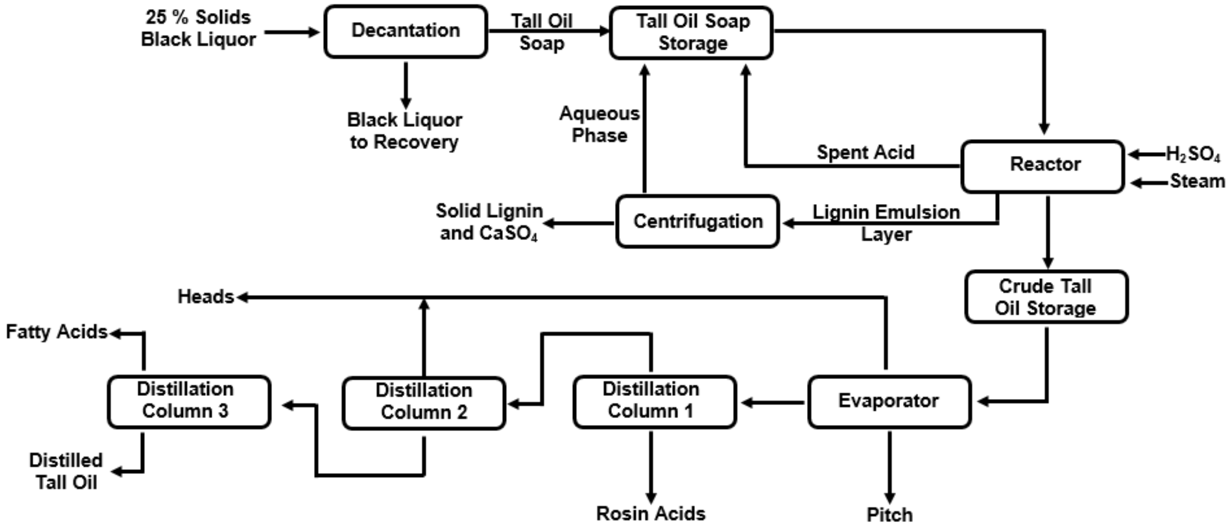

Figure 2.2. Commercial tall oil production process that is integrated into the kraft pulping process.

2.4.1. Isolation of tall oil soap from black liquor in the kraft pulping process

In the kraft pulping process, the highly alkaline nature of pulping results in the formation of various soluble sodium salts of fatty and rosin acids, lignin, and other woody constituents in black liquor (Panda, 2013). These salts are the main components of tall oil soap, which must be further processed. The black liquor produced from kraft pulping has typically 15 wt.% concentration (Kouisni et al., 2012). The tall oil soap constituents are soluble in black liquor at this concentration; as such, the soap remains in the black liquor solution when it is sent to the recovery process. However, tall oil soap has a lower density than black liquor; thus, it may be removed via settling and skimming (Figure 2.2) (Panda, 2013). When the black liquor's concentration becomes sufficiently high (i.e. to 25 wt.% solids), the soap becomes insoluble due to the common ion effect (Harding, 1968). However, a very high solid concentration or low temperature increases the viscosity of black liquor and hence decreases the removal efficiency of the soap. Therefore, the black liquor is concentrated to 20 – 30 wt.% solids in order to optimize the soap recovery from black liquor (Figure 2.2) (Foran, 1992; Wansbrough, 2008; Fuenzalida et al., 2005; Harding, 1968). The treated (i.e. decanted/skimmed) black liquor is sent to evaporators of the kraft recovery process, subsequently.

Once the soap is decanted (i.e. skimmed), it is collected and pumped to a central storage tank prior to the next stage treatment (Figure 2.2) (Foran, 1992). The collected tall oil soap has a water content of 30 – 50 wt.%. The soap is impure and contains lignin, mercaptans, and other partially soluble sodium salts, which will be handled in the purification process (Fuenzalida et al., 2005). However, in the current separation process, 20 – 40 % of tall oil soap presents in the black liquor remains soluble and is wasted (Harding, 1968). It was reported that the decanter had an efficiency of 60 – 90 % for separating the soap, which was significantly affected by the process parameters and wood species used in the pulping process (Foran, 1992; Lieberman and Ziegler, 1975).

2.4.2. Production of crude tall oil from tall oil soap

Once the tall oil soap is extracted via decantation/skimming (Figure 2.2), it must be transformed into crude tall oil. It must then be purified since there is residual black liquor present in the soap. The production of crude tall oil is mainly carried out by reacting the soap with a strong polar acid (usually 90 – 95 % sulfuric acid (Morris and Watkins, 1971)), which is known as acidulation

(Fuenzalida et al., 2005). The first step in the acidulation process involves the reaction of the tall oil soap with spent acid in the tall oil soap storage tank (Figure 2.2). Spent acid is the unreacted acid from the main reactor where the acidulation reaction occurs. This is conducted to initiate the acidulation reaction and reduce wastes. The soap/spent acid mixture is then sent from the storage tank to the main reactor (Wansbrough, 2008; Lawson and Amer, 1985). A batch process is commonly practiced in approximately 60% of all North American and European crude tall oil production plants (Panda, 2013). However, continuous processes are also available for the tall oil production (Noguiera, 1997; Thrush, 1965; Sullivan, 1958).

In a batch process, soap is heated to boiling with steam, and then acid is added. Typically, 200 – 300 kg of sulfuric acid is added per ton of crude tall oil (Canifru, 2013). In order to shorten the overall reaction time and to accelerate the reaction rate, the temperature should be maintained around 105 – 108 °C for 2 hours at pH 4 (Sellerholm et al., 2009). The resulting mixture is generally allowed to settle overnight in order to facilitate its separation (Wansbrough, 2008). The main reaction occurring in the production of tall oil from tall oil soap is shown in Scheme 2.1 (Wansbrough, 2008):

$$R - COO^{-}Na^{+} + H^{+} \rightarrow R - COOH + Na^{+} \tag{2.1}$$

This reaction converts the salt of fatty and rosin acids into their free carboxylic acid forms (Wansbrough, 2008; Fuenzalida et al., 2005). Following the overnight settling, three distinct layers form in the reactor. The crude tall oil is the lightest and, therefore, rises to the top of the reactor (Fuenzalida et al., 2005); this layer is fairly pure and may be removed with a variable position pump and sent for further processing (Oasmaa et al., 1997). The lignin and other ions in the mixture of the acidic tall oil will also undergo reactions with sulfuric acid. The acidulation of lignin produces insoluble lignin and lignin emulsion (Figure 2.2) (Fuenzalida et al., 2005). The lignin emulsion layer is separated by centrifugation to remove any insoluble lignin and $CaSO_4$ (a product of NaOH and H_2SO_4 reaction). Afterward, the insoluble lignin is sent to the recovery cycle of kraft process so that it can be used as an energy source. The separated oil/soap is returned to the reactor to reduce losses (Figure 2.2) (Wansbrough, 2008). The third layer, i.e. the aqueous phase, contains spent acid that can be returned to the soap storage tank to treat the tall oil soap (Wansbrough, 2008; Fuenzalida et al., 2005). The sulfide ions from black liquor also present in the mixture and will react with sulfuric acid to produce hydrogen sulfide (H_2S) gas. The H_2S gas is sent to a scrubber within the tall oil plant and neutralized with white liquor or caustic (sometimes integrated into the recovery process). Sodium sulfate (Na_2SO_4) is also formed during acidulation in the presence of black liquor.

In the continuous process, the tall oil soap is continuously diluted with water to reduce the viscosity of the mixture (Sullivan, 1958). The soap/water mixture is then reacted with dilute sulfuric acid with the ratio of 20/100 wt./wt. acid/tall oil (Sullivan, 1958). This mixture is fed to a centrifuge and then passed through a screener to release the H_2S and SO_2 gasses formed during the reaction and to remove any solids (Thrush, 1956). This process generates crude tall oil in the lighter phase with a yield of 95 – 98 % of the theoretical amount, and lignin and water content of 2 – 5 wt.% (Sullivan, 1958). The heavier phase contains water, acid, lignin, and other impurities. The crude tall oil could then be sent for further purification while the water and lignin mixture could be directed to the evaporators of the kraft process (Sullivan, 1958). Due to the residual black liquor present in tall oil soap, the efficiency of the crude tall oil production is low; and thus purifying the tall oil soap prior to acidulation could potentially increase the production efficiency and lower the tall oil production costs.

2.4.3. Purification of crude tall oil and its fractions' uses

Once the crude tall oil is separated, then it can either be commercialized as is or purified in order to produce viable end-use products (Figure 2.2) (Fuenzalida et al., 2005). As seen in Figure 2.2, the crude tall oil is distilled after production. The distillation process is performed based on the different volatilities of the components in the crude tall oil (Wansbrough, 2008). There are 3 continuous separation stages in the distillation process (Figure 2.2), from which 5 products are produced (Wansbrough, 2008). First, the crude tall oil is concentrated via evaporation, in which the volatile components and water are evaporated and collected. The overhead products are called heads. This step also generates a heavy part that is known as the pitch, which contains non-volatile components (Wansbrough, 2008). The primary product produced in the evaporation is then sent to the first distillation column (Figure 2.2). The rosin acids are separated in the first distillation column and produced in the bottom stream. The overhead stream from this column is sent to the second distillation column, in which any remaining volatile components are removed and combined with the volatile components collected via evaporation (Figure 2.2). The remaining mixture is sent to the final distillation column, which produces fatty acids in the overhead stream and distilled tall oil in the bottom stream. In one study, the distillation products of tall oil contained 10 wt.% volatile (light) products, 20 wt.% fatty acids, 5 wt.% distilled tall oil, 40 wt.% rosin acids, and 25 wt.% pitch (Wansbrough, 2008). The performance of distillation is strongly dependent on the specifications requested by the end users. Tall oil fatty acids have the largest market for end-uses compared to the other tall oil distillation products (Wansbrough, 2008; Panda, 2013). Tall oil fatty acids are produced at 90 – 98 % purity, which may deviate depending on actual end-use applications (Panda, 2013). The main uses for fatty acids include protective coatings and inks (30 %), chemical intermediates (30 %), soaps and detergents (15 %) and flotation (9 %) (Panda, 2013). Tall oil rosin acids are produced at approximately 90 – 95 % purity and are usually stabilized in alcohols to improve their solubility (Panda, 2013). The tall oil rosin acids may then be subjected to several reactions before being used as end products. These reactions can include hydrogenation and polymerization (Panda, 2013). The pitch can be used to produce sterols, such as phytosterols and phytostanols, rubber softeners, and as a component of drilling mud (Shahidi, 2006). Heads and pitch can also be used together to make asphalt fluid for road applications (Board, 2002). Heads may also be used as corrosion inhibitors and lubricants or as fuel (Rowe, 2012).

Alternatively, tall oil can be utilized in the industry without comprehensive fractionation. To do this, the crude tall oil is first dissolved in a naphtha solution with a one to one volumetric ratio and mixed with sulfuric acid (Panda, 2013; Fawkes and Gayer, 1942). This mixing is conducted to remove odour and colour-producing compounds, such as mercaptans, without substantially influencing the initial proportions of fatty and rosin acids present in the crude tall oil (Panda, 2013; Fawkes and Gayer, 1942). The temperature of this reaction and amount of sulfuric acid are all specified by the end users, desired colour, and viscosity requirements (Panda, 2013). The treated tall oil is rewashed with water and sodium hydroxide to neutralize any remaining sulfuric acid; it is finally stripped with steam in order to purify and later reuse naphtha. Due to the complex nature of crude tall oil and the complexity in naphtha purification and recycling, this is not usually the route taken for the use of tall oil (Panda, 2013).

2.5. Alternative processes

The following sections describe several alternative processes for each of the three sections of tall oil production mentioned previously. The processes are analyzed for their potential implementation into existing kraft pulping processes as well.

2.5.1. Alternatives to the extraction of tall oil soap from black liquor

2.5.1.1. Impact of polymer addition

Flocculation has been applied extensively in industry for isolating various components from different solutions and suspensions. In this respect, Lieberman and Ziegler (1975) reported that the presence of 100 g/L of polyoxypropylene-polyoxyethylene in black liquor at a temperature ranging 40-65 °C increased the tall oil soap recovery from 58 % to 70 %. In this process, the hydrophilic ends of the polymer bound with the hydrophilic ends of tall oil soap (hydrophilic/hydrophilic interaction), which increased the overall hydrophobicity of the polymer and thus promoted the separation of polymer/tall oil soap from the system (via floating to the top of the mixture) (Lieberman and Ziegler, 1975). The molecular weight of the polymer used for this purpose ranged from 1,000 to 16,000 g/mol, but a polymer with a higher molecular weight might further improve the recovery of tall oil soap (Lieberman and Ziegler, 1975). Alternatively, the addition of the polymer with dispersants or surfactants might be considered as an option (Lieberman and Ziegler, 1975).

Furthermore, the separation rate of tall oil soap, as well as the viscosity and purity of the soap would be increased by the polymer addition (Nopco, 2013). It was also reported that the polymer addition to black liquor increased the efficiency of downstream processes in black liquor recovery, as less tall oil soap was present in black liquor to adversely impact evaporators and recovery operations (Foran, 1992; Svarz et al., 2009). On the other hand, the polymer addition might decrease the efficiency of acidulation, and might interfere with the compositions of spent acid that was to be sent to the recovery section of the kraft mill operations (Lieberman and Ziegler, 1975).

2.5.1.2. Impact of insoluble neutral colloids

Figure 2.3 shows a process for producing tall oil soap via adding insoluble colloids, e.g. beta-sitosterol, to black liquor for the separation of tall oil. In this process, dilute black liquor is sent to a mixing tank in which beta-sitosterol is added prior to concentrating black liquor (Figure 2.3), which converts the soap from micelles to liquid crystal particles (Perttinen and Anttila, 2005).

These crystal particles agglomerate, which facilitates the soap separation (Perttinen and Anttila, 2005; Perttinen et al., 2005). The liquid crystal particles made of tall oil soap and beta-sitosterol rise to the top of the dilute black liquor and thus can be removed via skimming/decantation (Perttinen et al., 2005). The treated black liquor may then be concentrated to 25 wt.% solids via evaporation and sent for decantation as practiced in the traditional tall oil production process. The generated soap from this decantation would be skimmed and combined with the previously decanted tall oil soap (Figure 2.3). The treated black liquor is then returned to the kraft process. The tall oil soap would be used to produce crude tall oil and then purified (i.e. distilled) to produce fractionated tall oil components (as shown in Figure 2.2). In the distillation of tall oil produced in this process, beta-sitosterol remains with the pitch component (Figure 2.3). This pitch component may be subjected to further steam distillation to recover and/or produce more beta-sitosterol, as beta-sitosterol is a by-product of tall oil pitch (Holmbom and Erä, 1978; Cieselski and Hans, 1958).

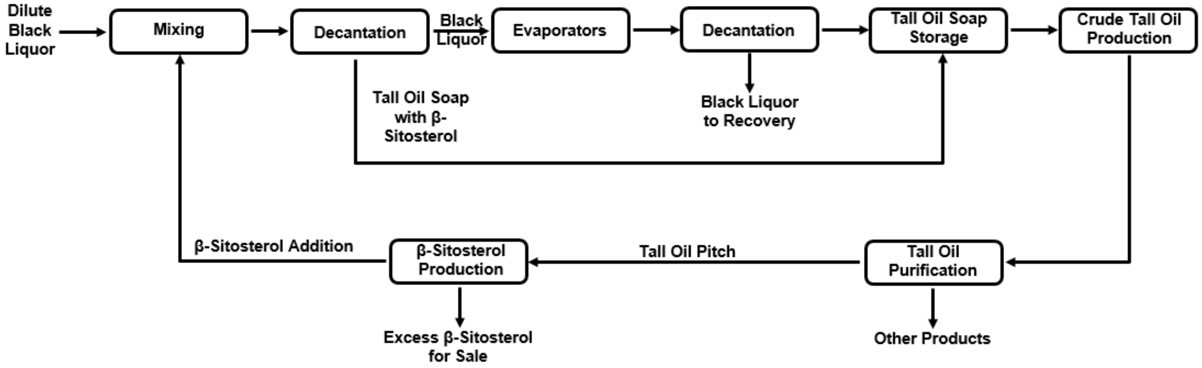

Figure 2.3. Flow diagram for a process that uses beta-sitosterol to treat black liquor for tall oil soap recovery.

Since beta-sitosterol is one product of the tall oil production process, its use in treating black liquor is well in harmony with tall oil production process and may not substantially increase the production cost of tall oil. Any excess beta-sitosterol of this process may be considered as a value-added product (Figure 2.3). It was stated that the use of 0.01 to 0.04 wt.% of beta-sitosterol increased the tall oil production yield by 10%, which improved the process stability and separation of tall oil soap from black liquor (wood species was unspecified) but decreased the need for sulfuric acid use in acidulation (Perttinen and Anttila, 2005; Perttinen et al., 2005; Perttinen and Vuorinen, 2012). It was also stated that the creation of crystals reduced the chance of foam generation in black liquor, which improved the quality of collected tall oil soap (Perttinen and Vuorinen, 2012). As such, the amount of wastes associated with the tall oil production process was reduced (Perttinen and Vuorinen, 2012). However, the use of beta-sitosterol would increase the overall complexity of the process, and reduce the overall beta-sitosterol production as a by-product of the process (since a part of this is recycled in the process).

2.5.1.3. Alkaline washing of tall oil soap

Figure 2.4 shows another alternative for improving the recovery of soap from black liquor. The spent acid generated in the acidulation process is mixed with sodium hydroxide solution to create alkaline solution at a pH of 10 – 13 (Morris and Watkins, 1971; Bowles et al., 2012). The spent acid is neutralized in order for the solution to contain Na_2SO_4, which increases the extraction of lignin in the salt form from tall oil soap (Morris and Watkins, 1971). This alkaline stream is mixed with tall oil soap in a washing tank an alkaline solution at 10 – 50 wt.% and temperature of 20 – 85 °C for 8 – 24 h (Morris and Watkins, 1971; Bowles et al., 2012). The tall oil soap may then be separated as the light phase by decantation or centrifugation (Figure 2.4).

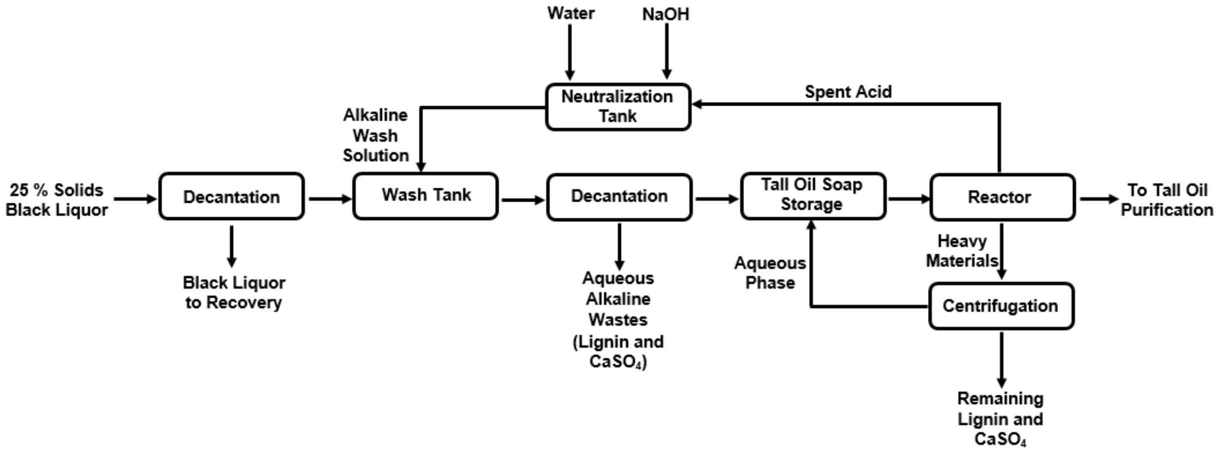

Figure 2.4. Process flow diagram of the alkaline washing of tall oil soap (Morris and Watkins, 1971).

An alkaline treatment (1/1 weight ratio of tall oil soap/alkaline solution) reduced the lignin content of the soap from 1.25 wt.% to 0.1 wt.% in one study (Morris and Watkins, 1971). The alkaline treatment removes lignin from tall oil soap, which can be separated following decantation as the heavier phase leading to purer tall oil soap (Morris and Watkins, 1971). The alkali solution has also been found to contain calcium ions, which form calcium sulfate during acidulation (Bowles et al., 2012). Additionally, calcium carbonate originating from black liquor but that comes with tall oil soap to acidulation may produce calcium sulfate (Bowles et al., 2012). The calcium sulfate may build up in the process with each subsequent recycle of spent acid causing process upsets if not removed (Bowles et al., 2012). Therefore, it is imperative that the tall oil soap is purified. The alkaline washing treatment of the soap will prevent the accumulation of calcium sulfate and lignin in the acidulation reactor, which will in turn increase the efficiency of acidulation. Another advantage of the alkaline washing process is the potential use of the centrifuged aqueous alkaline wastes (Figure 2.4) that contains lignin to produce lignin-based biofuel (Bowles et al., 2012).

However, the complete separation of the alkaline liquor from the tall oil soap is challenging in this process due to the viscous nature of the soap. Any remaining alkaline liquor in the soap will increase the consumption of sulfuric acid in the acidulation reactor, which has an adverse effect on the overall economy of the process (Kjellberg, 2006). Since the spent acid is being neutralized and used for alkaline washing, more sulfuric acid may be required in acidulation. This may decrease the economic benefits of the process.

2.5.2. Alternatives to the production of crude tall oil from tall oil soap

2.5.2.1. Direct electrolysis of tall oil soap

Crude tall oil can be produced from tall oil soap via the direct electrolysis of tall oil soap (Bowles et al., 2012; Huibers et al., 1992). This method involves a cathode chamber containing 0.5 – 2.5 M NaOH and an anode chamber containing anolyte, which is tall oil soap. The electrolysis is conducted at 50 – 80 °C, pH 10 – 12, and free of sodium ions (Huibers et al., 1992). A semi-permeable membrane is placed between the chambers. The cell potential of the electricity is 5 – 7 volts with a current density of 1 – 3 kA/m^3. The membrane is chosen based on its ability to allow for the permeation of sodium ions, but not hydroxide ions, and its inertness to tall oil soap and crude tall oil. Scheme 2.2 shows the electrolysis reaction of tall oil soap to crude tall oil (Huibers et al., 1992).

$$2R-COO^{-}Na^{+}+3H_2O \rightarrow 2R-COOH+2NaOH+\frac{1}{2}O_2+H_2 \qquad (2.2)$$

In this reaction, water is converted at the cathode to hydrogen gas and hydroxide ions. At the anode, sodium ions are liberated from the tall oil soap while crude tall oil is formed. The by-product of this chamber is oxygen gas. The sodium ions pass through the permeable membrane from the anode chamber to the cathode chamber and react with the hydroxide ions to form sodium hydroxide. The crude tall oil may then be separated from the analyte via distillation or centrifugation (Bowles et al., 2012).

Currently, sodium sulfate is produced in the acidulation process, and thus must be handled with the waste of kraft process. However, the direct electrolysis does not produce sodium sulfate. Another major advantage of this electrolysis is the production of sodium hydroxide. NaOH is used in the recovery section of kraft pulping and is considered a valued chemical in the kraft pulping process. A previous study showed that this process may be capable of recovering sodium hydroxide in the cathode chamber, and had a high efficiency of crude tall oil production (Huibers et al., 1992). The main disadvantages of electrolysis include the safety concerns associated with the manufacture of hydrogen and oxygen. The use of electricity will also introduce an extra cost to the process.

2.5.2.2. Use of carbon dioxide in acidulation

Alternatively, crude tall oil can be produced from tall oil soap with the help of carbon dioxide rather than sulfuric acid for acidulation. In this process, carbon dioxide and water are injected into the acidulation stage. Water is added at an approximate ratio of 0.9/1 wt./wt. of water/tall oil soap (Puustinen, 2015). Carbon dioxide is converted into carbonic acid, which reduces the pH of the solution and thus facilitates the reaction of tall oil soap. This process can be conducted in the temperature range of 20 and 30 °C and the pressure range of 50 and 100 atm. The use of carbon dioxide for this purpose will reduce the amount of acid required in the acidulation (Lawson and Amer, 1985). However, this process has a low yield as the production of carbonic acid is limited in the tall oil reactor. In other words, the pH of the soap mixture does not drop to an acceptable value, and sulfuric acid is still needed considerably (50 % of what is necessary for the traditional acidulation process) (Puustinen, 2015; Vardell and Wlliam, 1978).

To improve the reaction yield, a mixture of water-immiscible solvent (e.g. hexane) along with CO_2 was proposed for crude tall oil production (Vardell and William, 1978). Figure 2.5 shows a process based on the use of CO_2 and a solvent for crude tall oil production. In this process, a solvent (e.g. hexane) is first added with a weight ratio that is higher than 1/2 wt./wt. hexane/tall oil soap. Water is also used at 1/3 wt./wt. water/tall oil soap (Vardell and William, 1978). CO_2 is injected into the reactor to reduce the pH to 7 – 8 (Vardell and William, 1978). In one report, the reaction was conducted in the temperature range of 0 to 150 °C and 3 – 34 atm for 15 min, which generated crude tall oil with the yield of 55 – 60 % (based on the initial amount of soap) (Vardell and William, 1978). The solvent extracts the crude tall oil after tall oil production in the aqueous phase, which promotes the production of crude tall oil in the aqueous phase. In this method, the aqueous wastes are removed with settling and may be sent to the recovery cycle of the kraft process or wastewater of the mill (Vardell and William, 1978).

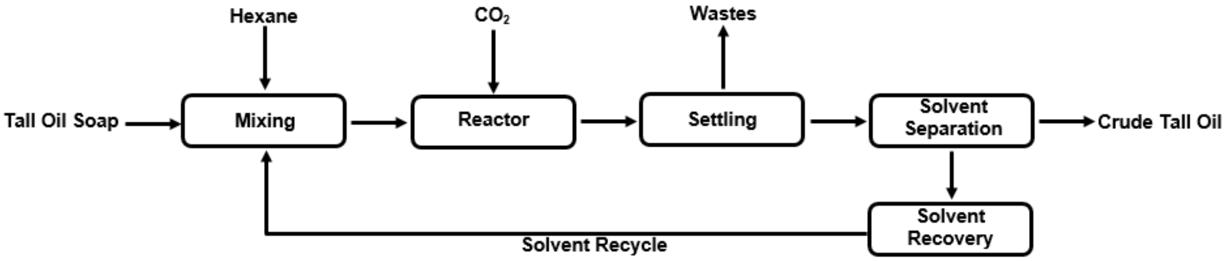

Figure 2.5. CO_2 Acidulation with solvent recovery.

However, solvents are expensive and often toxic, which would necessitate their recovery. This would increase the costs of the process and may introduce environmental concerns. Also, the use of a solvent is not well in harmony with the chemistry of kraft pulping process. In other words, solvent may adversely impact the kraft pulping chemistry if not well recovered from the system after use.

To improve the impact of CO_2 in acidulation, mixing CO_2 with the tall oil soap at supercritical conditions of 30 to 400 °C and pressures of 70 – 3400 atm was studied by Zosel (1969) as well as by Lawson and Amer (1985). Figure 2.6 shows a process for producing crude tall oil from tall oil soap under supercritical conditions. The tall oil soap is reacted and the extracted concurrently with CO_2 to produce crude tall oil with the yield of 68 % (Lawson and Amer, 1985; McHugh and Krukonis, 1994). After the reaction, the supercritical CO_2 and crude tall oil mixture may be separated via depressurizing, and CO_2 gas can be recycled (Lawson and Amer, 1985). This process is solvent free, has a high yield and is fast (quantitative values were not reported) (Taylor and King, 2001).

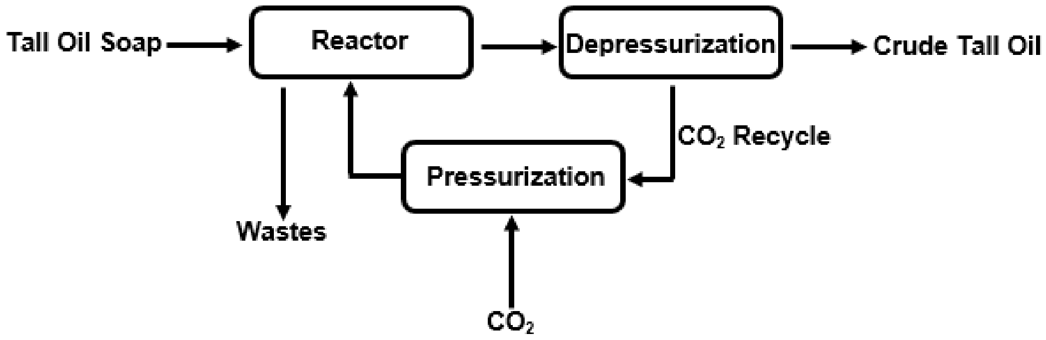

Figure 2.6. Supercritical acidulation of tall oil soap.

The major disadvantage of using supercritical CO_2 for tall oil production is its cost. Currently, CO_2 is obtained externally, and must further be pressurized and heated. The reactor that can handle supercritical conditions may also be expensive. However, CO_2 from the flue gas of the recovery boiler or lime kiln of the kraft process may ultimately be used for this purpose. Another disadvantage of using CO_2 is that the requirement of sulfuric acid in acidulation is not always completely negated. The acid requirement may only be decreased by 30 – 50 % in this case (Kjellberg, 2006).

2.5.2.3. Use of boron compounds in acidulation

In order to eliminate the use of sulfuric acid in acidulation, the use of boron compounds, specifically boron trifluoride or boric acid, was proposed in the past (Canifru, 2013). Sulfuric acid reported to increase sulfur emissions of the kraft process (Canifru, 2013). In the studies performed by Tate (1981), it was proposed that the addition of 20 – 24 wt.% boron trifluoride (or a complex thereof) in tall oil soap caused 51 – 53 % tall oil recovery in acidulation, whereas sulfuric acid has a typical yield of 50 – 75 % tall oil recovery (Shackford, 2003; Lappi and Alén, 2011; Fuenzalida et al., 2005), implying that boron compounds may replace sulfuric acid in the acidulation process. Boron trifluoride can be added to the tall oil soap, or directly to black liquor and the crude tall oil can then be separated from the system via centrifugation (Canifru, 2013).

However, the wastes produced in this process should be purified or recycled in order to decrease losses. Additionally, the cost of boron as boron trifluoride or boric acid is currently high; thus, using boron compounds without a recovery process would not be economical (Canifru, 2013).

2.5.2.4. Use of sodium sesquisulfate in acidulation

In the kraft pulping process, the pulp may be bleached with chlorine dioxide (ClO_2) in order to achieve an acceptable brightness for the final paper product. ClO_2 is generally produced on-site via reacting methanol, sodium sulfate, and sulfuric acid. The by-product of this reaction is sodium sesquisulfate ($Na_3H(SO_4)_2$), which is currently wasted or recycled within the ClO_2 plant to reduce chemical make-up (Canifru, 2013). Canifru (2013) proposed a process to replace completely sulfuric acid with sodium sesquisulfate in the acidulation. In this process, 35 – 45 wt. % sesquisulfate aqueous solution is made with a pH of 1.0 – 1.4 (Figure 2.7). In one set of experiments, the solution was reacted with tall oil soap at the weight ratio of 0.50 – 0.60 sodium sesquisulfate/tall oil soap and a temperature range of 90 – 150 °C for 5 – 20 min, which led to crude tall oil production with approximately 50 % yield (separated via centrifugation) (Canifru, 2013).

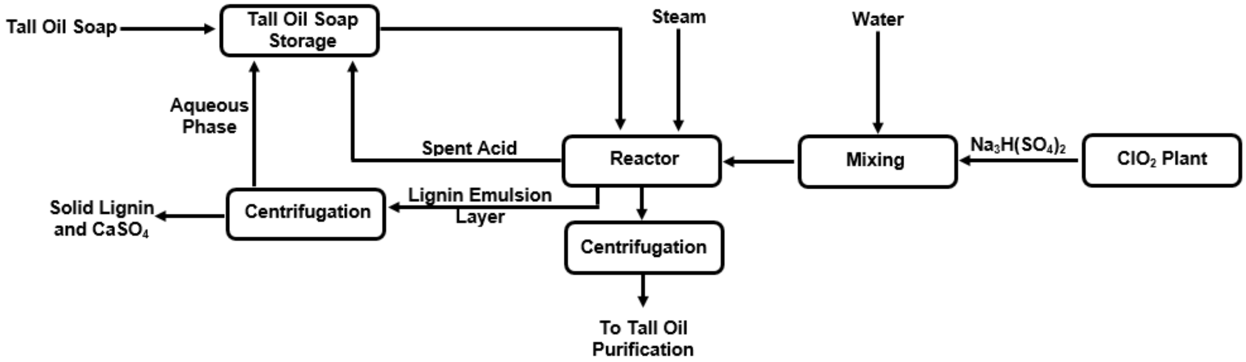

Figure 2.7. Integrated acidulation of tall oil soap with sodium sesquisulfate generated in chlorine dioxide plant.

The main advantages of this process are its potential integration into the current configuration of the kraft process and the decrease in consumption of H_2SO_4, which in turn decreased the operating costs and waste generation in the tall oil plant (Canifru, 2013).

Alternatively, sulfuric acid may be recovered from sodium sesquisulfate in the ClO_2 plant. Scheme 2.3 shows the reaction of sodium sesquisulfate and water to form sulfuric acid (AkzoNobel, 2015).

$$4\,Na_3H(SO_4)_2 + H_2O \rightarrow 2\,H_2SO_4 + 6\,Na_2SO_4 \qquad (2.3)$$

The product of this reaction can be filtered to produce pure sulfuric acid. In the current process practiced, sulfuric acid is returned to the chlorine dioxide reactor, but a part of this acid could be used in the acidulation if there is any surplus. Figure 2.8 shows a process for integrating ClO_2 production plant and tall oil production plant. In this process, a part of sulfuric acid that is produced by ClO_2 bleaching is sent to the acidulation reactor. The spent acid is then sent to the storage tank while lignin and other solid compounds are separated. The crude tall oil is separated and sent to the purification stage. As stated earlier, pure sulfuric acid use increases the sulfur emissions of the process (Canifru, 2013). To evaluate the feasibility of this process, the flexibility and capacities of ClO_2 generator and tall oil production plants should be investigated.

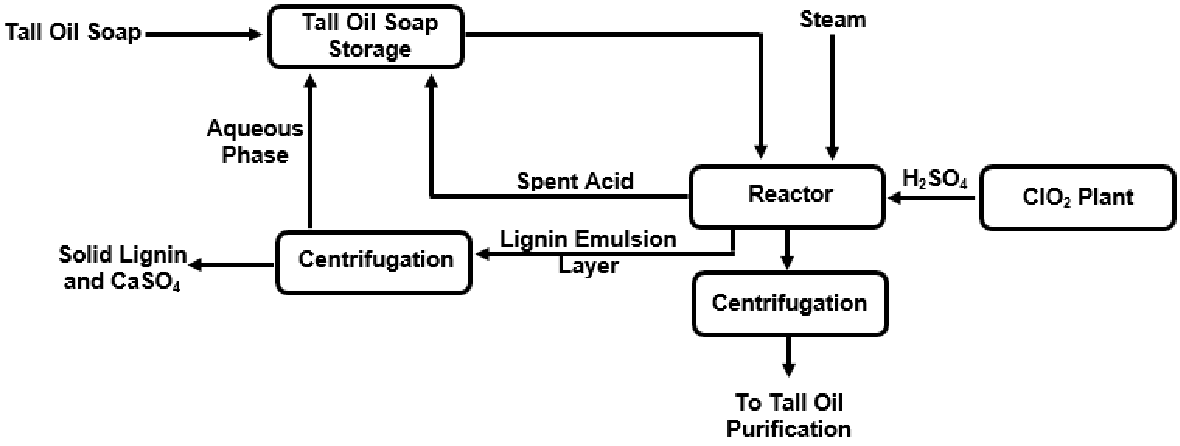

Figure 2.8. Acidulation of tall oil soap with H_2SO_4 from ClO_2 plant.

2.5.3. Alternatives to purification and fractionation of crude tall oil

2.5.3.1. Separation of fatty and rosin acids

Crude tall oil can be purified following different processes. Cleary et al. (1985) proposed a solvent-based method to refine fatty and rosin acids as well as tall oil (Figure 2.9). In this process, distilled tall oil is first combined with a hydrocarbon solvent, e.g. ethylacetate or aethylpropionate. The mixture is then sent to a packed column (usually containing silica-based materials), in which fatty acid is adsorbed on the adsorbent while rosin acid passes through the column. Then, rosin acid is recovered from the mixture via distillation, and the solvent is recycled. Once the rosin acids and the solvent have been eluted through the column, another solvent, e.g. iso-octane, toluene, or benzene, denoted as the diluent, can desorb the fatty acids from the column. Fatty acids may be recovered via distillation while the solvent may be recycled. In Figure 2.9, the black lines indicate the first part of the separation, in which the rosin acids are recovered; the second part, in which fatty acids are recovered, is denoted by the gray lines.

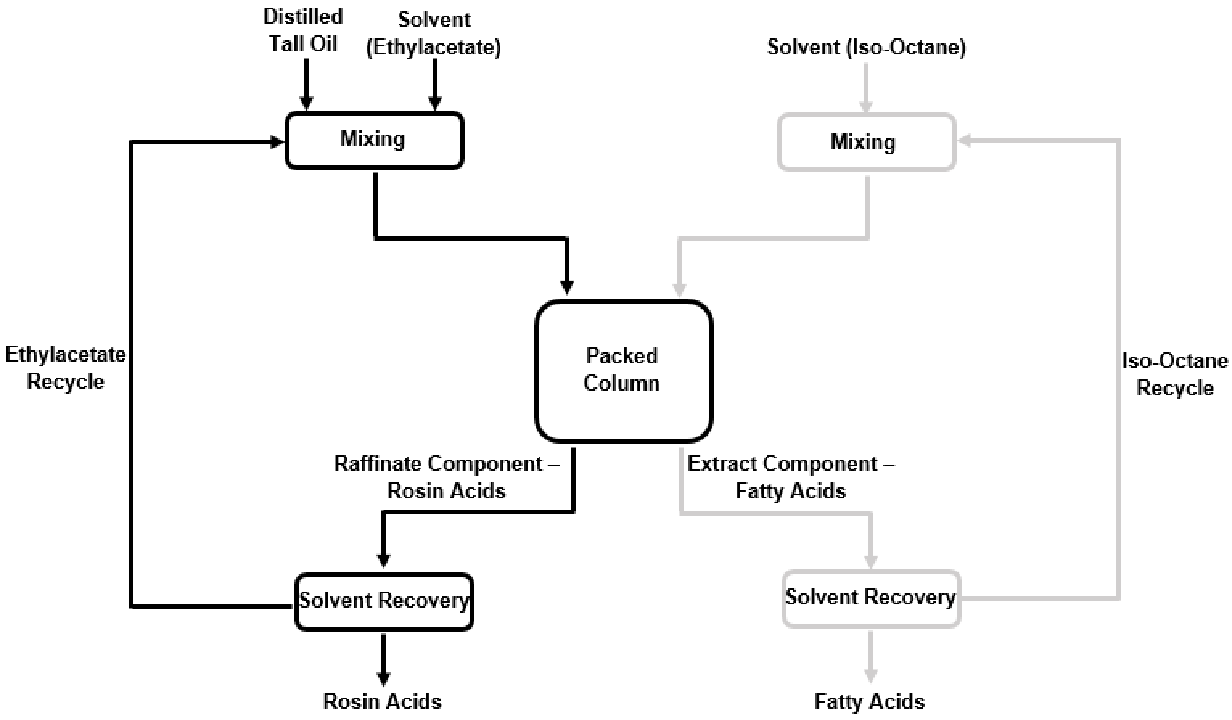

Figure 2.9. Purification of distilled tall oil.

In the experiments conducted by Cleary et al. (1985), the mixture entered the fractionation column at a temperature of 120 °C. First, the displacement fluid (i.e. ethylacetate) and distilled tall oil were charged to the column at a ratio of 80/20 wt./wt. ethylacetate/distilled tall oil (Cleary et al., 1985). The fatty acids in the distilled tall oil were retained, and the ethylacetate and rosin acids were eluted. Afterward, a pure solvent (i.e. diluent) was passed through the column to extract the fatty acids. In a similar study by Üstün (1996), the separation yields of 94% for each fatty and rosins acids were reported. The rosin acids may be used as soaps or paper sizing agents, and fatty acids can be used as plasticizers and surfactants (Panda, 2013; Cleary et al., 1985). A major disadvantage of this process is the use of solvents implying that the solvent recovery process is necessary and perhaps expensive (Johnson, 1991).

2.5.3.2. Production of biodiesel from crude tall oil

SunPine commissioned its first tall oil diesel plant in 2010, with a capacity to produce 100,000 m^3 of crude tall oil diesel per year (Back, 2016). In this process, crude tall oil is mixed with sulfuric acid and methanol (Back, 2016). Figure 2.10 shows the block flow diagram of this process. An esterification reaction occurs between acids of tall oil (mainly fatty acids) and methanol in an acidic medium producing the tall oil-based biodiesel (Back, 2016; White et al., 2011; Demirbas, 2008) (Scheme 2.4).

$$R - COOH + CH_3OH \xrightarrow{H^+} R - COOCH_3 + H_2O \tag{2.4}$$

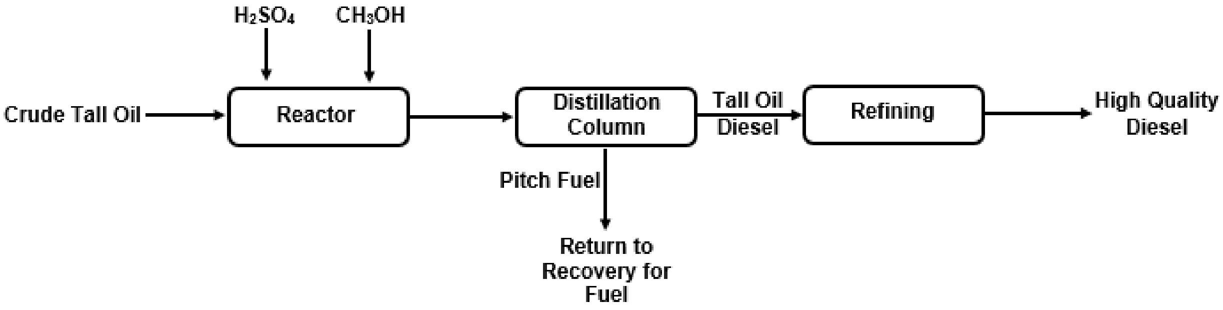

Figure 2.10. Integrated production of tall oil diesel.

The mixture is then sent to a distillation tower, where the components are distilled. The heavy part of this process, denoted as pitch fuel, is a wood-based fuel. This pitch fuel is different from the pitch component produced from the typical distillation of crude tall oil (Figure 2.2). The light part is considered as high-quality diesel fuel. In one set of experiments, tall oil diesel with an approximate yield of 65 – 70 %, and pitch fuel with the yield of 30 – 35 % were produced from the crude tall oil of pine, spruce and birch species (Back, 2016). In another study, 90% of the tall oil was converted to biodiesel when tall oil was treated with methanol under the conditions of 5/1 molar ratio of methanol/tall oil, 300 °C, 14 min reaction time and approximately 100 atm (White et al., 2011). Currently, pitch fuel is returned to the pulp mill to be used as fuel. It is intended that other valuable substances, including resin acids and sterols, be produced in this process in future (Back, 2016). The biodiesel production from tall oil can be performed if the tall oil production plant is sufficiently large to meet the economy of scale. For example, a mill in Sweden reported to require over 120,000 m^3 of crude tall oil per year to be able to produce biodiesel economically (Back, 2016).

2.5.3.3. Production of biodiesel from fatty acids of tall oil using methanol

Mkhize et al. (2015) outlined a process for producing biodiesel from crude tall oil using methanol in the presence of a heterogeneous catalyst. It was reported that the reaction of the fatty acid with methanol with the molar ratio of 10 with 3 wt.% tungsten zirconia catalyst at 250 °C for 4 h led to 70 % yield of biodiesel production (Mkhize et al., 2015). It was claimed that with a heterogeneous catalyst, the purification of the product and regeneration of the catalyst can be made easier compared with homogeneous catalysts, as homogeneous catalysts were not recoverable (Mkhize et al., 2015).

A major shortcoming of this process is that only the fatty acid portion of the crude tall oil participates in the reaction and forms biodiesel; as such, the other components of the crude tall oil are wasted (Lee et al., 2006; Mkhize et al., 2015). Additionally, the esterification reaction is significantly inhibited by water present in crude tall oil in the reaction (Lee et al., 2006), as water consumes the catalyst and reduces its efficiency (Kusdiana and Saka, 2004). As a result, water must be removed as produced, which would increase the complexity of the process. The other disadvantages associated with this process are the difficulties related to the regeneration of catalysts and long reaction time of the esterification process.

Alternatively, biodiesel can be produced from the fatty acid of crude tall oil via subcritical water hydrolysis followed by supercritical methanol treatment (Kusdiana and Saka, 2004b). However, Kusdiana and Saka (2004a,b) did not explicitly use tall oil fatty acids to produce biodiesel; their research still used similar fatty acids from rapeseed oil. Lee et al. (2006) proposed that this method may be viable for the fatty acids of tall oil. Figure 2.11 shows the block diagram of a process for producing biodiesel from crude tall oil (Lee et al., 2006).

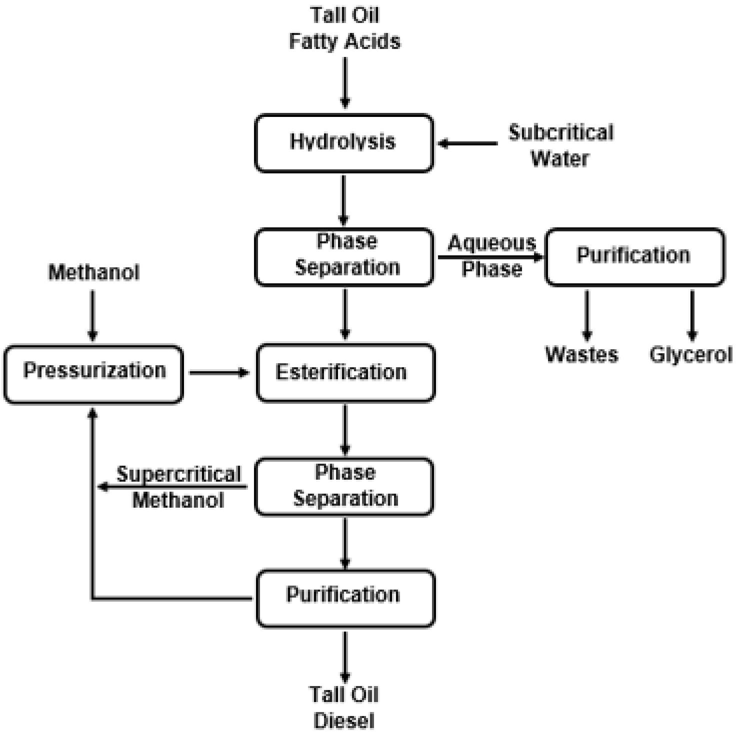

Figure 2.11. Production of biodiesel from tall oil with subcritical water and supercritical methanol stages (Lee et al., 2006).

In this process, fatty acids first undergo hydrolysis. The suggested conditions were treatment at a temperature of 270 °C and 10 MPa pressure for 20 min. The purpose of the hydrolysis reaction is to hydrolyze any triglycerides present in the feed to produce fatty acids (Hampton, 1962; Kusdiana and Saka, 2004b; Kusdiana and Saka, 2001a). The triglycerides also form glycerol via a side reaction, which must be subsequently separated. It must be noted that the hydrolysis reaction is reversible, and as such only runs to completion in a large excess of water at a 1/1 volumetric ratio of water/fatty acids (Kusdiana and Saka, 2004b). Once the hydrolysis reaction is completed, the resulting mixture is cooled and allowed to settle in order for phase separation to occur (Kusdiana and Saka, 2004b; Kusdiana and Saka, 2001a). The lower phase generated in this process is the water/glycerol which could be separated via distillation to recover glycerol to be sold as a value-added product (Kusdiana and Saka, 2004b). The resulting upper phase is the hydrolyzed product, which must then be sent to a distillation column to remove any remaining water. Alternatively, Minami and Saka (2006) proposed to evaporate water from the mixture first, then separate the glycerol and hydrolyzed phases via decantation.

Following the water separation, the hydrolyzed product is reacted with methanol under supercritical conditions. The reaction conditions were suggested to be methanol/fatty acid molar ratio of 42, 270 °C and 43 MPa and for 40 min, which yielded nearly 100 % methyl esters (biodiesel) (Kusdiana and Saka, 2004a). The mixture could then be evaporated at 90 °C for 20 min to recover methanol and the crude biodiesel could be further purified depending on its end use requirements (Kusdiana and Saka, 2001b).

There are many advantages of using this process over the other methods stated above: 1) the use of supercritical methanol negates the effect of water on the transesterification reaction (Kusdiana and Saka, 2004a); 2) the reaction requires a shorter time for completion, which implies that it needs a small reactor (i.e. a relatively small capital cost) (Lee et al., 2006); 3) a catalyst is not required in this process; and 4) glycerol is another value-added product of this process (Lee et al., 2006). The major disadvantage of this method is the use of solvents, which may make it challenging to be implemented in the kraft process.

2.5.3.4. Production of lignin by-products from acidulation of tall oil soap

As described previously, crude tall oil is currently produced via acidulation of tall oil soap with sulfuric acid. In this process, lignin salts precipitate from the solution and are now recycled to black liquor. Alternatively, the separated lignin could be used to produce other value-added by-products. Figure 2.12 shows a potential diagram of the use of lignin and spent acid from acidulation.

Huang (2014) reported a depolymerization process for kraft lignin using formic acid as an *in-situ* source of hydrogen. In the depolymerization reaction using formic acid, Huang reported a 77 wt.% of depolymerized lignin with an acid/lignin mass ratio of 0.7 and in the presence of an ethanol/water co-solvent at 50/50 vol. for 1 h at 300 °C and 2 MPa under a nitrogen atmosphere (Huang, 2014). The depolymerized kraft lignin may be used in the production of bio-based resins (Huang, 2014). Since sulfuric acid is readily available in the aqueous phase following acidulation that generates lignin precipitate, it may be advantageous to analyze the substitution of formic acid with sulfuric acid in the depolymerization reaction.

Alternatively, Li and Luo (2012) suggested that activated carbon could be produced from sulfuric acid-treated kraft lignin. The optimal conditions were determined to be 2 h reaction at 600 °C with 35 % sulfuric acid concentration under nitrogen environment (Li and Luo, 2012).

However, further research is needed to provide more relevant information in regard to the kraft lignin that is generated in the acidulation process (Colomba, 2015).

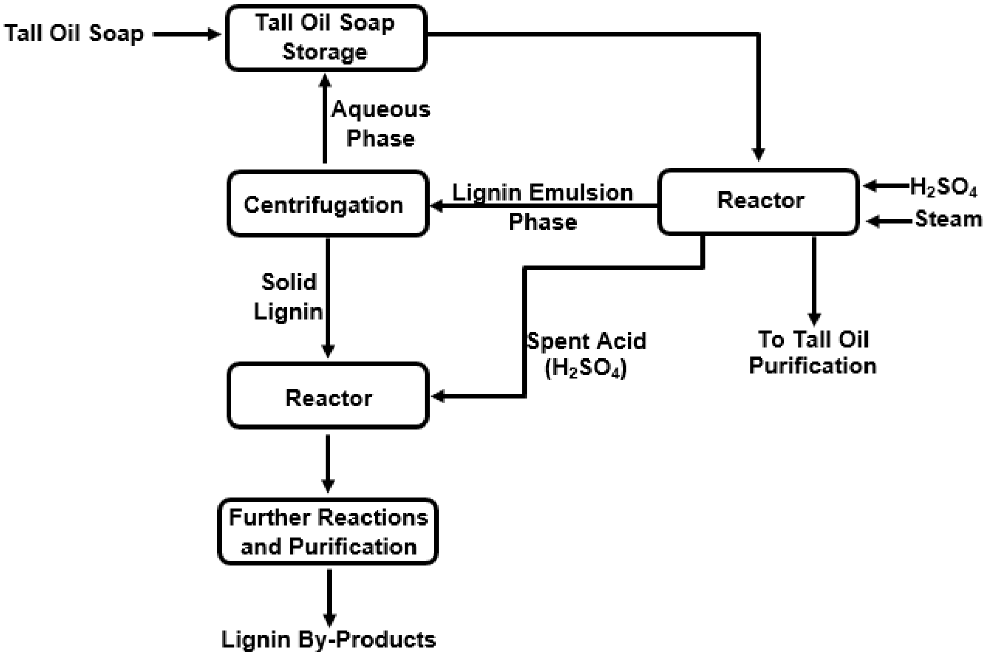

Figure 2.12. Potential lignin by-product production in the tall oil process.

2.6. Conclusions

This paper described several alternative methods proposed in the literature to separate, produce, and purify tall oil and tall oil derivatives from black liquor of the kraft pulping process. In addition, the perspective and challenges of each method were elaborated. For the separation of tall oil soap from black liquor, the use of neutral colloids to increase tall oil soap recovery seemed to be the most economically and technically feasible method. For the production of tall oil from its soap, the replacement of sulfuric acid with sodium sesquisulfate in acidulation seemed to be applicable in industry. This process is fully integrated into the kraft pulping process. The direct electrolysis method must handle gas production and increased costs due to electricity requirements. Also, CO_2 and boron acidulation are costly, and may not entirely negate the use of sulfuric acid for acidulation. Biodiesel production from tall oil may be implemented if the plant is sufficiently large to justify the economy of scale, but it will introduce some complexity to the tall oil production plant. The lignin-based value-added production process can also be implemented in the tall oil plant as it may be fully integrated into the tall oil production process. The other alternative methods, including the purification of distilled tall oil and the production of biodiesel from tall oil fatty acids, may be expensive presently.

2.7. Acknowledgement

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3. Literature Review – Production and application of lignosulfonates and sulfonated lignin[2]

3.1. Abstract

Lignin is the largest reservoir of aromatic compounds on earth and has great potential to be used in many industrial applications. In this review paper, alternative methods to produce lignosulfonates from spent sulfite pulping liquors and kraft lignin from black liquor of kraft pulping process are critically reviewed. Furthermore, options to increase the sulfonate contents of lignin based products are outlined and the industrial attractiveness of them is evaluated. This evaluation will include sulfonation and sulfomethylation of lignin. To increase the sulfomethylation efficiency of lignin, various scenarios including hydrolysis, oxidation, and hydroxymethylation were compared. In the present work, the application of sulfonated lignin based products is assessed and the impact of the properties of sulfonated lignin based products on the characteristics of their end-use application is critically evaluated. It was determined that sulfonated lignin based products have been used as dispersants in cement admixtures and dye solutions more than other applications, and their molecular weight and sulfonation degree were crucial in determining their efficiency. The use of lignin based sulfonated products in composites may benefit the hydrophilicity increase of some composites, but the sulfonated products may need to be desulfonated via alkaline and/or oxygen prior to their use in composites. To be used as a flocculant, sulfonated lignin based products may need to be crosslinked to increase their molecular weight. In this work, the challenges associated with the use of lignin based products in these applications are comprehensively discussed.

Keywords: kraft lignin, lignosulfonate, sulfonation, sulfomethylation, hydroxymethylation, desulfonation, composites, dispersants, flocculants

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[2] Aro T, Fatehi P, 2017b, Production and application of lignosulfonates and sulfonated lignin, ChemSusChem., 10(9), 1861-1877

3.2. Introduction

The world's most abundant renewable resource is biomass (wood and non-wood), of which the three main components are cellulose, hemicellulose, and lignin. In woody biomass, cellulose is the most abundant biopolymer, followed by lignin which accounts for 15 – 40 wt.% of wood (Inwood, 2014; Meister, 2002). Lignin is also the largest natural resource of aromatic compounds (Fatehi and Chen, 2016; Ragauskas et al., 2014). However, only 1 – 2 % of the 50 – 70 million tons of lignin produced annually is used for the production of value-added products, implying that it is an underutilized material (Inwood, 2014; Meister, 2002; Norgren and Edlund, 2014; Stewart, 2008). Today, lignin is primarily used for energy generation through combustion in pulping processes. As such, it is highly advantageous to identify lignin based value-added products and to develop processes for their production.

Integrated Forest Biorefineries (IFBRs) have been introduced as methods to increase the economic viability of the pulping industry (van Heiningen, 2006). This economic advantage can be achieved by utilizing the waste products of the pulping processes, such as lignin, in producing value-added products. Carbon fibre, polymer alloys, fillers, or dispersants could be regarded as lignin based value-added products (Gellerstedt et al., 2010; Holladay et al., 2007; van der Drift and Boerrigter, 2006; Azapagic, 2014; Doherty et al., 2011). To produce lignin based value-added products, lignin should be first separated from biomass, for which several methods can be employed. Kraft and sulfite pulping processes are known for their effective lignin separation from wood and hence are used worldwide. Kraft lignin is separated from wood with the help of NaOH and Na_2S (Vishtal and Kraslawski, 2011). Lignin from sulfite pulping processes is denoted as lignosulfonates, and is produced using sulfurous acid and/or a sulfite salt containing magnesium, calcium, sodium, or ammonium at varying pH levels (Meister, 2002; Fatehi and Ni, 2011a). Currently, lignosulfonates account for 90% of the total market of commercial lignin (Fatehi and Ni, 2011a; Suhr et al., 2015; Northey, 2002), and the total annual worldwide production of lignosulfonates is approximately 1.8 million tons (Stern and Schwarbauer, 2008).

However, lignosulfonates and kraft lignin have different properties as listed in Table 3.1. Lignosulfonates have generally more sulfur groups and thus a higher sulfonation degree than that of kraft lignin. Due to the presence of the sulfonated group, lignosulfonates are anionically charged and water soluble. The molecular weight of lignosulfonates can be similar to or larger than kraft lignin (Table 3.1).

Due to their unique properties, lignosulfonates have a wide range of uses, such as animal feed, pesticides, surfactants, additives in oil drilling, stabilizers in colloidal suspensions, and as plasticizers in concrete admixtures (Vishtal and Kraslawski, 2011; Fatehi and Ni, 2011a; Zhou et al., 2013; Ouyang et al., 2009; Madad et al., 2011; Joensson et al., 2012). However, the majority of pulp mills employ kraft technology for pulp production, and thus kraft lignin is more readily available for value-added production. In this regard, the sulfonation of kraft lignin to produce sulfonated kraft lignin has been practiced (Konduri and Fatehi, 2015; Ouyang et al., 2009).

The main objective of this work is to compare the production and modification of lignosulfonates from sulfite pulping processes and sulfonated kraft lignin from kraft pulping processes. This is the first study to evaluate different processes for the production of lignosulfonate and sulfonated kraft lignin and their potential applications.

Table 3.1. Properties of lignosulfonate and kraft lignin.

Property	Lignosulfonates	Kraft Lignin	Reference
Sulfur amount, wt.%	3.5 – 8.0	1.0 – 3.0	Vishtal and Kraslawski, 2011
	5	1 – 2	Doherty et al., 2011
	4 – 8	1 – 1.5	Lebo, Jr. et al., 2007
	3 – 8	1 – 2	Stevanovich, 2016
	5.3 – 7.7	0.23	Oveissi and Fatehi, 2015
	3.56	-	Oveissi and Fatehi, 2014
Sulfonated content, mmol/g	1.25 – 2.5	0	Lebo, Jr. et al., 2007
	0.7 – 1.9	0	Oveissi and Fatehi,

			2015
	1.38	-	Ouyang et al., 2006
	1.68	-	Wu et al., 2012
	1.38	-	Yang et al., 2007
	2.34	-	Qiu et al., 2016
	-	0	Leitner et al., 2015
	-	0	Inwood, 2014
Water solubility, g/L	-	1.8	Kong et al., 2015
	10	0	Lebo, Jr. et al., 2007
	-	0	Konduri and Fatehi, 2015
Charge density, meq/g	-0.9	-	Oveissi and Fatehi, 2015
	-	0.01	Kong et al., 2015
	-	0	Inwood, 2014
Molecular weight, g/mol	1,000 – 150,000	1,500 – 25,000	Vishtal and Kraslawski, 2011
	20,000 – 50,000	2,000 – 3,000	Lebo, Jr. et al., 2007
	1,000 – 5,000	-	Yang et al., 2007
	2,400 – 140,000	-	McCarthy and Islam, 1999
	-	2,950 – 5,000	Pakkanen and Alén, 2012

3.3. Pathways to produce lignosulfonates and sulfonated lignin

There are two main commercial production methods for lignosulfonates and sulfonated lignin. The following sections outline these two methods.

3.3.1. Lignosulfonates from sulfite spent liquor

Lignosulfonates stem from the sulfite pulping processes, which are typically characterized by the pH of the processes and the bases used (Suhr et al., 2015). The typical pH of sulfite pulping process ranges from 1 to 5, with neutral sulfite semi-chemical pulping (NSSC) processes carrying out at pH 5 – 7 (Suhr et al., 2015; European Commission, 2001; Galkin and Samec 2016). The conditions of pulping processes impart different properties to lignosulfonates. The most commonly used bases are sodium and calcium, while magnesium or ammonium may also be employed (Suhr et al., 2015; Elumalai and Pan, 2011; Calvo-Flores et al., 2015). In the sulfite pulping process, the two main reactions occurring to solubilize lignin are sulfonation and hydrolysis (Elumalai and Pan, 2011). Figure 3.1 outlines these two reactions in typical sulfite pulping processes under acidic conditions (Matsushita, 2015; Goring, 1971). During this process, a loss of a hydroxyl group or cleavage of the α-ether linkage occurs to form a quinone methide intermediate with either phenolic or non-phenolic substrates via a benzylic cation (hydrolysis) (Matsushita, 2015). Next, sulfite ions present in solution add to this intermediate structure at the α-position to form benzyl sulfonic acid units (sulfonation), which contributes to increasing the solubility of the lignosulfonates (Elumalai and Pan, 2011; Calvo-Flores et al., 2015; Matsushita, 2015; Goring, 1971, Sixta, 1998; Sjöström, 1993; Hassi, 1985; Areskogh, 2011; Nedosvitii et al., 1994). Alternatively, a condensation reaction may occur between the benzlyic carbon of one molecule and the meta carbon (6th) position of the aromatic ring of another molecule, due to the presence of the benzylic cation; this may prevent the sulfonation reaction as it occurs at the α-position (Matsushita, 2015).

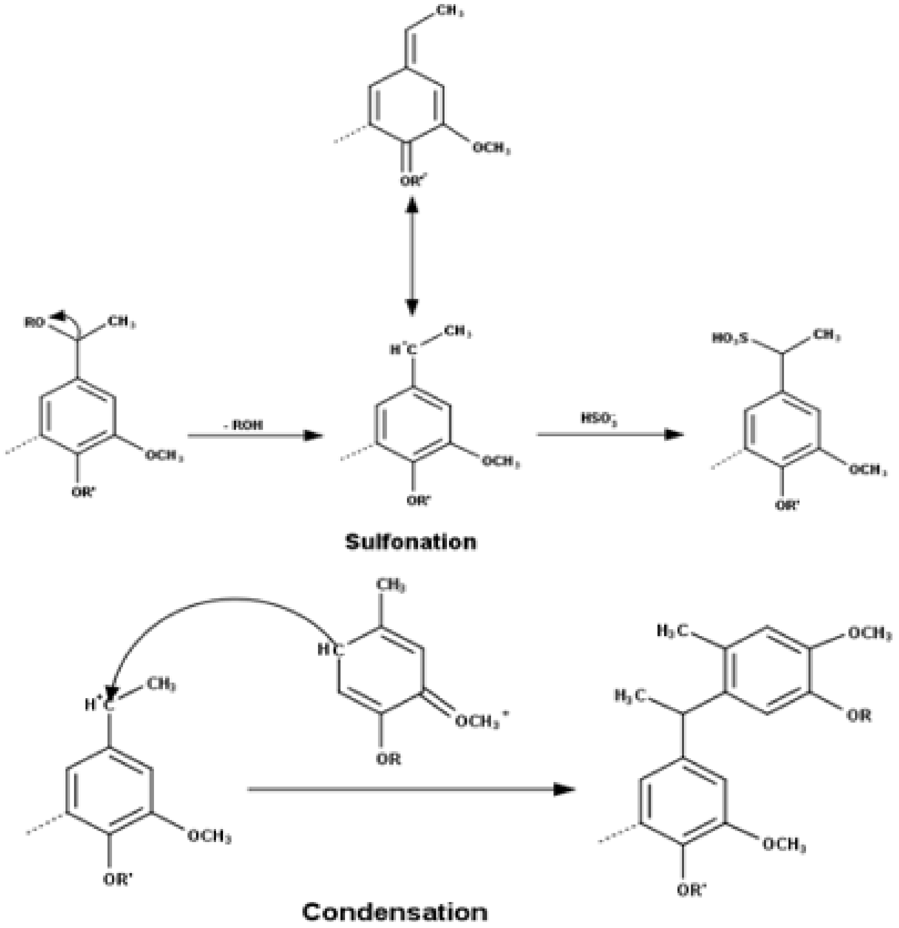

Figure 3.1. Reactions occurring during acidic sulfite pulping to produce lignosulfonates (Masushita, 2015).

Figure 3.2 outlines the sulfonation reaction occurring during neutral sulfite pulping to produce lignosulfonates (Matsushita, 2015; Goring, 1971). The difference between the mechanism of Figure 3.1 and Figure 3.2 is that, under neutral conditions (Figure 3.2), hydrolysis occurs with only phenolic-type intermediates, while sulfonation occurs due to the electron-withdrawing effect of the first sulfonic group addition (Matsushita, 2015). This sulfonic acid group on the α-position facilitates the addition of another sulfonic acid group at the β-position because of electron-withdrawing capabilities, resulting in the depolymerization reaction of the β-aryl ether bond (Matsushita, 2015).

It should be noted that the methoxy group shown on the aromatic ring structures in Figures 3.1 and 3.2 may be different depending on the sub unit of lignin. It is known that there are three main basic sub units of lignin: p-hydroxyphenylpropene (H) unit (no substituted carbon adjacent to para oxy-group), guaiacyl (G) unit (one substituted carbon adjacent to oxy-group), or syringyl (S) unit (both adjacent carbons to oxy-group substituted) (Wu et al., 2012; Ouyang et al., 2009; Galkin and Samec, 2016; Elumalai and Pan, 2011; Calvo-Flores et al., 2015; Matsushita, 2015; Goring, 1971). For simplicity, the G-unit is shown in Figures 3.1 and 3.2.

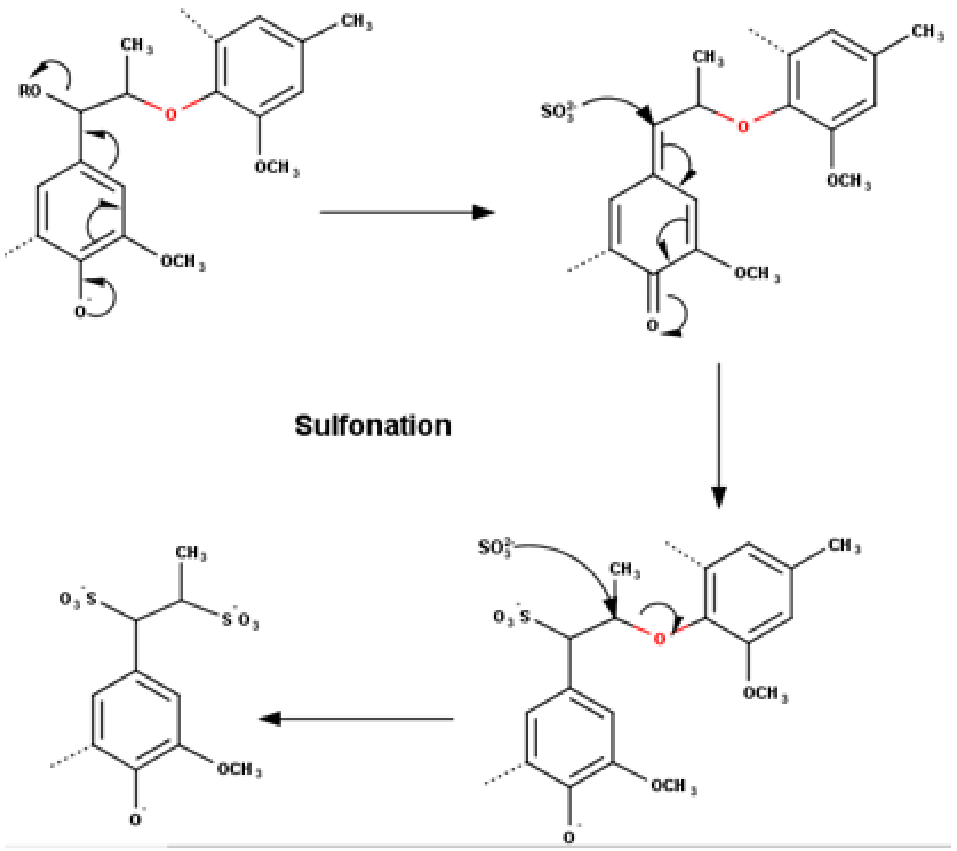

Figure 3.2. Reactions occurring during neutral sulfite pulping to produce lignosulfonates (Matsushita, 2015).

After sulfite pulping, lignosulfonates are removed from pulp via filtration and remain in the spent liquor of the pulping process. In addition to lignosulfonates, the spent liquor of the sulfite pulping process contains hemicelluloses and residual pulping chemicals (Restolho et al., 2009; Kuzmenko, 2010) wherein lignosulfonates account for 50 – 80 wt.% of the total solids in the mixture, hemicelluloses constitute up to 30 wt.% and inorganics represent roughly 10 wt.% (Suhr et al., 2015; Northey, 2002; Mänttäri and Nyström, 2009; Berry and Viswanathan, 2002; Brauns, 1967). Due to the wide range of conditions under which sulfite pulping can be conducted, and as a result lignosulfonates produced, lignosulfonate structures may vary considerably. However, a full lignosulfonate model structure has also been proposed by Matsushita (2015) and may be found elsewhere. Additional information on lignin and lignosulfonate structures and modification/biological engineering pathways for the purpose of biorefinery valorization has been covered extensively over recent years (Calvo-Flores et al., 2015; Rinaldi et al., 2016; Key and Bozell, 2016; Laurichesse and Avérous, 2014).

3.3.2. Separation of lignosulfonates from sulfite spent liquor

The spent liquor of the sulfite pulping process is dilute and contains other impurities; therefore, lignosulfonates should be separated from the spent liquor to have an increased commercial value. As lignosulfonates are water soluble products, they may not be precipitated by acidifying the spent liquor (Fatehi and Ni, 2011a).

Membrane filtration has been recognized as a commercial process for recovering lignosulfonates from spent sulfite liquors because lignosulfonates have a higher molecular weight than other components in the spent liquors, and the difference in the molecular weights allows for an effective separation (Fatehi and Chen, 2016; Vishtal and Kraslawski, 2011; Jönsson and Wallberg, 2007; Stoklosa and Hodge, 2014). Ultrafiltration has been commercially applied in a calcium bisulfite pulping process in Norway since 1981 (Mänttäri and Nyström, 2009; Bhattacharya et al., 2005; Borregaard Lignotech, 2008). In this process, the spent liquor is filtered through a polysulfone ultrafiltration membrane with a surface area of 1,120 m^2 and a molecular weight cut-off of 20,000 g/mol (Mänttäri and Nyström, 2009; Bhattacharya et al., 2005; Judd and Jefferson, 2003). A report on this system stated concentrating the spent liquor from 12 wt.% solids to 22 wt.% solids at a flow rate of 50 m^3/h (Fatehi and Chen, 2016; Bhattacharya et al., 2005). The retentate stream of this filtration contained up to 95 % pure lignosulfonates, while the permeate mainly contained hemicelluloses (Kuzmenko, 2010; Mänttäri and Nyström, 2009; Bhattacharya et al., 2005). Lifespan is a crucial characteristic of membranes. With daily cleaning/maintenance, the lifespan of these membranes was claimed to be 12 – 15 months (Mänttäri and Nyström, 2009; Bhattacharya et al., 2005). Cellulose acetate (at the temperature range of 50 – 60 °C) or Microdyn-Nadir UP010 membranes may also be used in this process (Fatehi and Chen, 2016; Kuzmenko, 2010).

However, there are drawbacks for using ultrafiltration to recover the lignosulfonates from the sulfite spent liquors. Despite worldwide use, ultrafiltration is not the most economical method for the separation of lignosulfonates, though it is the best of the current available commercial processes (Bhattacharya et al., 2005). Pressure-driven membrane filtration operations are susceptible to membrane fouling and concentration polarization, which cause a decline in flux across the membrane and inhibit production capacity (Bhattacharya et al., 2005). By implementing different sized membranes to recover lignosulfonates, a more precise, efficient, and pure separation could be achieved. Additionally, membrane separation method may not be selective to lignosulfonates due to a molecular weight overlap with hemicelluloses in solutions, which hinders the separation (Fatehi and Chen, 2016).

An alternative commercial method for recovering lignosulfonates is Howard method (Stoklosa and Hodge, 2014). Figure 3.3 shows Howard method that may be employed in sulfite pulping processes using calcium as the base. In this process, lime (calcium oxide) is added to the spent liquor initially to precipitate calcium sulfite at pH 8.5, which could be filtered and removed (Stoklosa and Hodge, 2014; Lo, 1970). The filtered calcium sulfite may then be subjected to a pH change and further purified to regenerate cooking chemicals (Howard, 1931). The addition of lime to the system in the following step, shown as the second precipitation stage in Figure 3.3, leads to the production of calcium lignosulfonates, which are solid at a pH greater than 12 (Howard, 1934). As such, calcium lignosulfonates may be washed and filtered (Howard, 1934). The recovery of lignosulfonate using Howard method can be as high as 90 – 95 % (Araújo, 2008; Hippale, 2015).

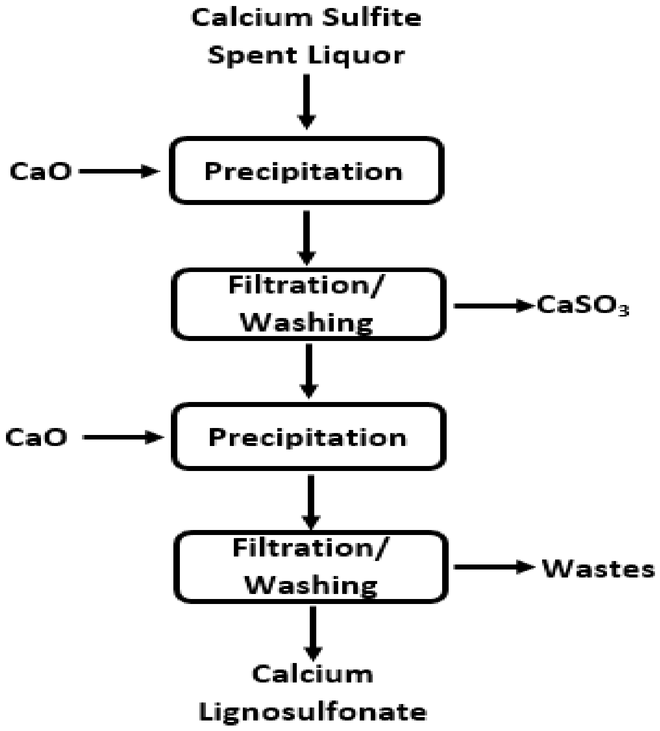

Figure 3.3. Howard method to separate calcium lignosulfonates from calcium sulfite spent liquor.

Other methods for separating lignosulfonates from spent sulfite liquor have been outlined by Fatehi and Ni (2011a), Fatehi and Chen (2016), and Lebo, Jr. et al. (2007). These include amine extraction, electrolysis, ion-exchange resin, Pekilo process (fermentation and ultrafiltration), and reverse osmosis. In amine extraction method, lignosulfonates are converted to water-insoluble lignosulfonic acid-amine adducts, which are then subjected to liquid-liquid extraction (Fatehi and Ni, 2011a; Fatehi and Chen, 2016). Electrolysis involves the desalination and demineralization of magnesium sulfite spent liquor under conditions of 125 mA/cm^2 at 60 °C for 3 h to produce lignosulfonates (Fatehi and Chen, 2016; Ringena et al., 2005). Ion-exchange resin separation may use sandstone or limestone as an adsorbent for lignosulfonates (Fatehi and Chen, 2016). Alternatively, ethanol can be used to precipitate lignosulfonates, which can be recovered through filtration and distillation (Fatehi and Chen, 2016). Ethanol may also be recovered and reused in the precipitation stage (Fatehi and Chen, 2016). Pekilo process was introduced to ferment hemicelluloses of the spent liquor with *Paecilomyces varioti*. The treated spent liquor could then be subjected to ultrafiltration to produce > 90 % of pure lignosulfonates (Fatehi and Ni, 2011a).

Reverse osmosis could also be employed to concentrate spent sulfite liquors (Ringena et al., 2005). However, these methods have not yet been commercialized, typically due to their high operating costs stemming from solvent usage and purification of products (Stevanovich, 2016).

3.3.3. Sulfonated lignin from kraft black liquor

The sulfite pulping process has many environmental issues, and thus only a small portion of market pulp (less than 10 %, roughly 7 million tons) is produced via the sulfite pulping process (Kuzmenko, 2010; Robinson et al., 1986; Lora, 2011). In contrast, kraft process is widely practiced to produce market pulp with better quality (Kuzmenko, 2010). As such, sulfonated lignin based products from kraft lignin can be produced. To produce sulfonated kraft lignin, unmodified kraft lignin should be initially separated from black liquor of the kraft pulping process. In the past, MeadWestvaco Corporation was the largest commercial producer of kraft lignin, but Domtar Corporation started kraft lignin production with a large capacity from black liquor in NC, USA in 2014 (Compere et al., 2005; Zakzeski et al., 2010). LignoBoost technology is practiced at Domtar and produces roughly 25,000 tons of lignin per year (Domtar, 2013). In this method, the addition of carbon dioxide to black liquor reduces its pH from 13 to 9 – 9.5 (Fatehi and Chen, 2016; Dilling, 1985a, 1991). The acidification of black liquor converts the ionic phenolic hydroxide groups present in the lignin molecule to their free forms, which causes the precipitation of kraft lignin (Dilling, 1985a, 1988, 1991). Alternatively, LignoForce technology has been applied in West Fraser Company in Alberta, Canada, to produce kraft lignin from black liquor. In this method, black liquor is oxidized with air or oxygen prior to acidification with both carbon dioxide and sulfuric acid (Kouisni et al., 2012). The extracted kraft lignin may be purified by washing and filtering. The LignoForce system allows for increased filtration rates, decreased acid usage, and a lower ash content of the extracted kraft lignin compared to LignoBoost-extracted lignin (Kouisni et al., 2012).

Once purified kraft lignin has been obtained, it can be sulfomethylated to produce sulfonated lignin, as conducted by MeadWestvaco Corporation (Meister, 2002). In this process, kraft lignin is reacted with sodium sulfite or sodium bisulfite and an aldehyde (i.e. formaldehyde) (Fatehi and Chen, 2016; Dilling, 1985a; Kamoun et al., 2003). Sulfomethylation can be carried out at 0.1 – 1.0 weight ratio of sulfite/lignin and 0.01 – 1.0 weight ratio formaldehyde/lignin at 100 – 160

°C and pH 9 or greater for 4 h (Adler and Mauritz, 1954). The preferred weight ratio of sulfite to formaldehyde is 1.3/0.8; an increased amount of sulfite decreases the molecular weight of the generated sulfonated lignin (Dilling, 1985b). Furthermore, the sulfonation (or sulfomethylation) reaction introduces sulfonic acid groups to the aromatic ring of the lignin structure, which is different from lignosulfonates originating from the sulfite pulping process where sulfonic acid groups are located on the aliphatic chain (Figure 3.1, 3.2) (Berlin and Balakshin, 2014). The sulfonated lignin from the kraft process is typically sold in calcium or sodium salt form and is less expensive than some lignosulfonates from sulfite pulping (Berry and Viswanathan, 2002).

As described, the lignin isolated from kraft process must be sulfonated in a second processing step to produce sulfonated kraft lignin. Thus, more challenges must be overcome to produce the desired end-use sulfonated products. On the other hand, sulfonated kraft lignin with a high purity and different degrees of sulfonation can be produced from kraft lignin, which are the main advantages of sulfonated kraft lignin over lignosulfonates with less purity and a sulfonated degree.

3.4. Alternative methods for producing lignosulfonates and sulfonated lignin

To produce lignosulfonates/sulfonated lignins with different degrees of sulfonation, molecular weights, and functional groups, alternative methods were proposed to widen the end use application of the products. These methods allow for various advantages over traditional production of lignosulfonates and sulfonated kraft lignin as previously described. The following sections explain these alternative methods.

3.4.1. Sulfuric acid treatment

Sulfuric acid treatment is one of the least complex alternative techniques to alter lignin and lignosulfonates (Compere et al., 2005). It is carried out in order to increase the sulfonation degree of the lignosulfonate or kraft lignin, which increases the solubility and charge density of the product.

Figure 3.4 outlines the process for sulfuric acid treatment of lignosulfonates. In this process, lignosulfonates were reacted at 1/4 weight ratio with concentrated sulfuric acid at 20 °C (Dilling, 1991). The mixture was neutralized with calcium oxide to precipitate calcium sulfate and filtered to produce soluble calcium lignosulfonates in the filtrate. The product could be dried. Alternatively, sodium carbonate could be added to form sodium lignosulfonates prior to drying (Dilling, 1991).

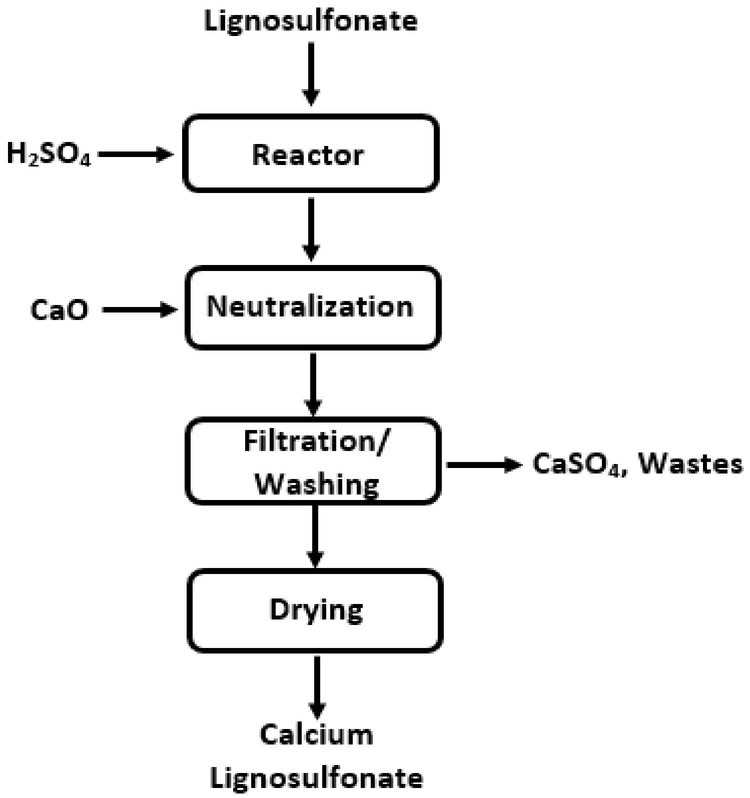

Figure 3.4. Sulfuric acid treatment of lignosulfonate.

The lignosulfonates produced via this method are soluble in a broad pH range; whereas commercial lignosulfonates have limited solubility at low pH levels (Dilling, 1991). The improved solubility is due to an increased amount of bound sulfonic acid groups on the structure of the lignosulfonates, and it was reported that this treatment could increase the sulfonate group of lignosulfonates to 4.1 mmol/g (Dilling, 1991).

Kraft lignin could also be modified using sulfuric acid. A similar process to Figure 3.4 may be used, but neutralization can be practiced with sodium carbonate rather than calcium oxide to precipitate the sodium salt of the sulfonated lignin (Dilling, 1991). This process reported to increase the sulfonate group of lignin by 2.5 mol/mol (Dilling, 1991). However, the product purification can be difficult due to the fact that the sulfonated lignin is water soluble. Membrane filtration may be required to serve for this purpose, but it may incur high operating costs and probably low production yields.

3.4.2. Nitration

To alter the surface properties of lignosulfonates for increased surface charge density, modification of the functional groups had been conducted. Figure 3.5 shows a process for producing nitro-lignosulfonates. Lignosulfonates from a calcium based sulfite liquor were nitrated and purified through several stages. In this process, concentrated nitric acid was added to spent sulfite liquor at 0.08/1 volumetric ratio, then reacted for 15 min, and then extracted at 1/1 wt./wt. with Amberlite LA-2 (an extraction solvent) in hexane (Sarkkinen, 1984). Nitro-lignosulfonates were extracted into the organic phase, which was isolated and further processed (Sarkkinen, 1984). Calcium oxide and water were added to the extracted organic phase to extract nitro-lignosulfonates, in which nitrites were moved into the aqueous phase. The excess calcium hydroxide formed from the reaction of calcium oxide and water could be removed by filtration.

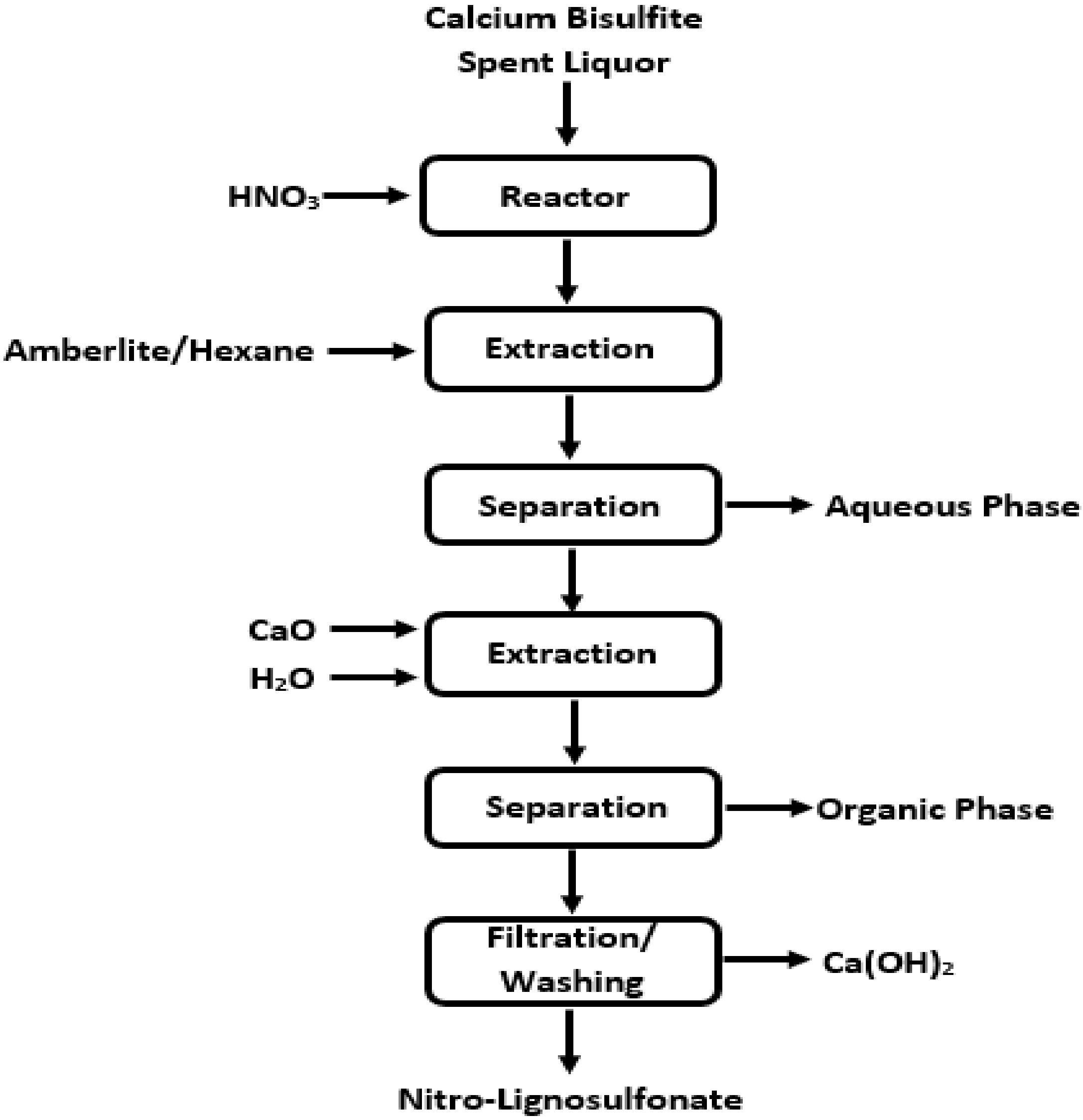

Figure 3.5. Production of nitro-lignosulfonates.

This process reported an increase in the nitrogen content of lignosulfonates from 0.1 wt.% to 0.58 wt.% following nitration (Almås et al., 2014; Jablonský et al., 2015; Ház, 2013). Due to the use of solvents, a recovery process is required to decrease the associated operating costs. However, this process may be difficult to implement in sulfite pulping if the recovery of the solvents is not efficient.

3.4.3. Alkaline hydrolysis of lignosulfonates

As lignin has a highly-condensed structure, its original reactivity is low and increasing its reactivity may be considered prior to its further use. Alkaline hydrolysis has been proposed to increase the reactivity of lignosulfonates (El Mansouri et al., 2006). Figure 3.6 depicts the alkaline hydrolysis and purification of lignosulfonates. In this process, lignosulfonates were reacted at 1/10 weight ratio with 2 % NaOH at 170 °C and pH 12 for 90 min (El Mansouri et al., 2006). The product may be recovered by drying following a pH adjustment as required.

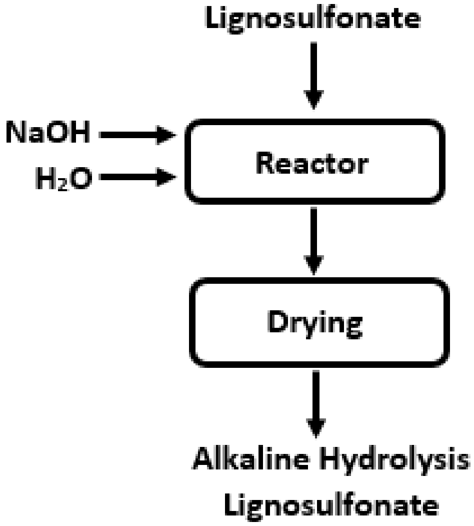

Figure 3.6. Alkaline hydrolysis of lignosulfonates.

In this process, the molecular weight of the product decreased from approximately 8,500 to 4,600 g/mol, while the number of reactive sites increased by 55 % (El Mansouri et al., 2006). The reactive sites were formed by the production of unimpeded hydroxyl groups during the hydrolysis of the lignosulfonate, which are more apt to react with other chemicals such as formaldehyde. This process can be easily implemented into the existing pulping processes as NaOH is readily available; however, the increased temperature of the reaction may be disadvantageous.

3.4.4. Hydroxypropyl sulfonation

Increasing the molecular weight of lignin whilst maintaining adequate sulfonation is important for some applications such as dispersants for dye solutions. Consequently, hydroxypropyl sulfonation of lignin had been proposed. Figure 3.7 illustrates a process for hydroxypropyl sulfonation of alkali lignin to produce a sulfonated product. As shown, sulfonation and crosslinking were carried out to produce sulfonated lignin. In one study, alkali lignin was mixed with sodium 3-chloro-2-hydroxy-propanesulfonate (0.35/1 weight ratio to lignin) for 2 h at 90 °C and pH 9.5 (Qin et al., 2015). Epichlorohydrin was added subsequently and the reaction was carried out for 1 h to crosslink the sulfonated lignin to different extents. The product may be dried prior to use.

It was found that the molecular weight of the hydroxypropyl sulfonated alkali lignin increased from roughly 9,000 to 15,000 g/mol as epichlorohydrin concentration increased from 12 to 36 g/L (Qin et al., 2015). The sulfonated product contained a similar sulfonate content, 2.1 mmol/g, to lignosulfonates (Qin et al., 2015).

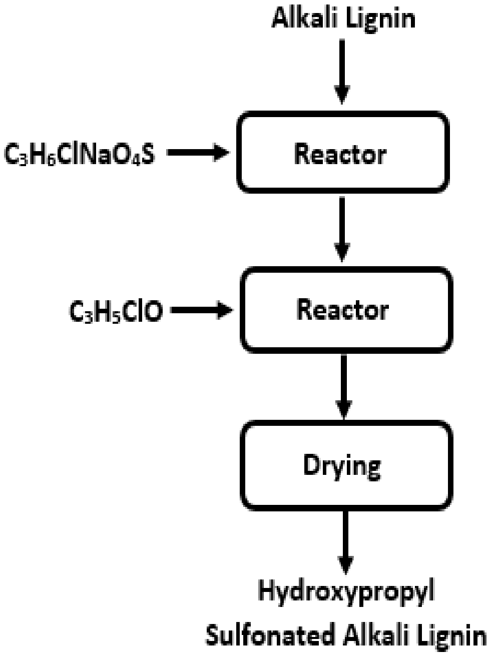

Figure 3.7. Hydroxypropyl sulfonated alkali lignin.

3.4.5. Hydroxymethylation

Another method of increasing the reactivity of the lignosulfonates, especially towards the incorporation into phenol-formaldehyde resins, is hydroxymethylation (Alonso et al., 2001). The hydroxymethylation of lignosulfonates also increases thermal stability by increasing their functional groups (Chen et al., 2014). Figure 3.8 presents a process for hydroxymethylating lignosulfonates. In this method, lignosulfonates are mixed with NaOH and formaldehyde. In one study, hydroxymethylation was carried out by dissolving lignosulfonates at 0.8/1 weight ratio of NaOH/lignosulfonates and reacting lignosulfonates with formaldehyde at 1/1 weight ratio for 5 h at 45 °C (Alonso et al., 2001). The product could be purified by drying or membrane filtration. Another study found that the optimal conditions of hydroxymethylation were 0.22/1 weight ratio of formaldehyde to lignosulfonates at pH 11 and 65 °C (Zhou, 2015).

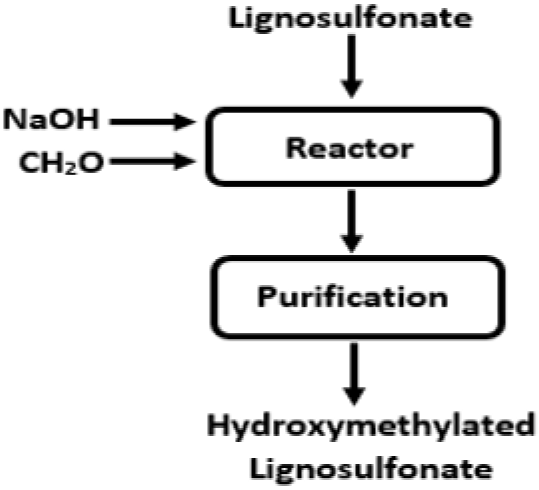

Figure 3.8. Hydroxymethylated lignosulfonate production.

It was found that the total hydroxyl group content of lignosulfonate was increased, the carboxyl content remained approximately constant, and the intrinsic viscosity increased from 5.29 to 5.60 mL/g; however, the phenolic hydroxyl content decreased from 0.98 to 0.64 mmol/g in another study (Zhou, 2015).

3.4.6. Methanolylphenol-lignosulfonate esters

To increase the usage of lignosulfonates as dispersants for dye applications, they should be more thermally resistant. In the past, lignosulfonates have been employed to function as dye dispersants, but they were not thermally stable. To improve the thermal stability, the modification of lignosulfonates with methanolylphenol (monohydroxyl benzyl alcohol) was proposed. This modification is similar to that shown in Figure 3.8. In the past, this reaction was conducted with 50 wt.% lignosulfonates in an aqueous solution at pH 10 with 0.5 mmol/g of 1-methanolylphenol/lignosulfonates for 5 h at 100 °C (Meister, 2002). The product of this reaction could be spray dried (Lin, 1985). Esterified lignosulfonates were found to have increased thermal stability and dispersion efficiency compared to unmodified lignosulfonates (Meister, 2002). This was because the ester bond provided by the phenol group increased the molecular weight of the lignosulfonate and hence improved its thermal stability.

Alternatively, lignosulfonates were reported to be firstly hydroxymethylated as depicted in Figure 3.8, then reacted at 1.9 mmol/g with monohydroxyl benzyl alcohol/lignosulfonates for 5 h at 100 °C, which led to 0.05 – 4.0 mmol/g of hydroxybenzyl alcohol/lignosulfonates in the product (Lin, 1985). Hydroxymethylation pretreatment was found to produce product that had more uniformity in dispersing dye particles (Lin, 1985). Comparing the hydroxymethylated and non-hydroxymethylated esterified products, the heat stability was increased 6 times following the hydroxymethylation, while the viscosity of both were similar (22.4-26.4 cP) (Lin, 1985).

3.4.7. Oxidation

Another method for increasing the reactivity of lignosulfonates is oxidation. Oxidation with hydrogen peroxide is an environmentally friendly process that has been widely used in the pulping industry (Yuan et al., 2014; Hu et al., 2011). The process of oxidation is similar to that shown in Figure 3.8; however, hydrogen peroxide was used as a reactant instead of formaldehyde. In one study, 50 wt.% lignosulfonates was reacted at 0.3/1 weight ratio of H_2O_2/lignosulfonates for 0.5 h at 60 °C and pH 10 (Yuan et al., 2014). Nevertheless, oxidation with H_2O_2 can extensively degrade the lignosulfonate structure rather than reacting with the reactive sites, which may introduce difficulties into the practical application of this process (Hu et al., 2011). In another study, nitric acid was employed for oxidation of lignosulfonates. In this process, lignosulfonates were reacted at 0.5/1 weight ratio of HNO_3/lignosulfonate at 35 °C for 2 h. The product can be neutralized if necessary and recovered via filtration (Detroit, 1995). The product reported to have a 10-fold increase in dispersing dyes (Detroit, 1995).

3.4.8. Sulfomethylation

In the past, sulfomethylation had been used to raise the sulfonation degree of different types of lignin, resulting in higher solubility and charge density of lignin (Pizzi, 1994). Figure 3.9 shows a process for sulfomethylation and subsequent crosslinking of kraft lignin. In this process, kraft lignin was reacted at 0.80/1 weight ratio of sodium sulfite/lignin and 0.12/1 weight ratio of formaldehyde/lignin for 2 h at 140 °C to produce sulfomethylated lignin (Dilling, 1985a). Formaldehyde was subsequently added at a 0.6/1 molar ratio of formaldehyde/lignin and further reacted for 5 h at 100 °C and pH 7 (Dilling, 1985a). The product may be purified by filtration. It was found that the anionic charge density increased from 0 to -1.6 meq/g, the molecular weight increased from about 22,700 to 53,400 g/mol, and the sulfonate group content increased from 0.03 to 1.48 mmol/g (Konduri and Fatehi, 2015). Alternatively, sulfomethylated kraft lignin was proposed to be produced at a ratio of 1/0.9 mol/mol lignin/sodium hydroxymethyl sulfonate at 100 °C for 3 h without crosslinking (Konduri and Fatehi, 2015). The benefit of reacting with sodium hydroxymethyl sulfonate is to avoid two reaction stages, and to develop a simple process for producing sulfonated lignin; but in this case, the molecular weight of product would be low compared to the two-step process. However, the sulfomethylation may form condensed lignin structures, which hinder the reactivity of the product by having reactive sites blocked by the resulting complex structures (He and Fatehi, 2015).

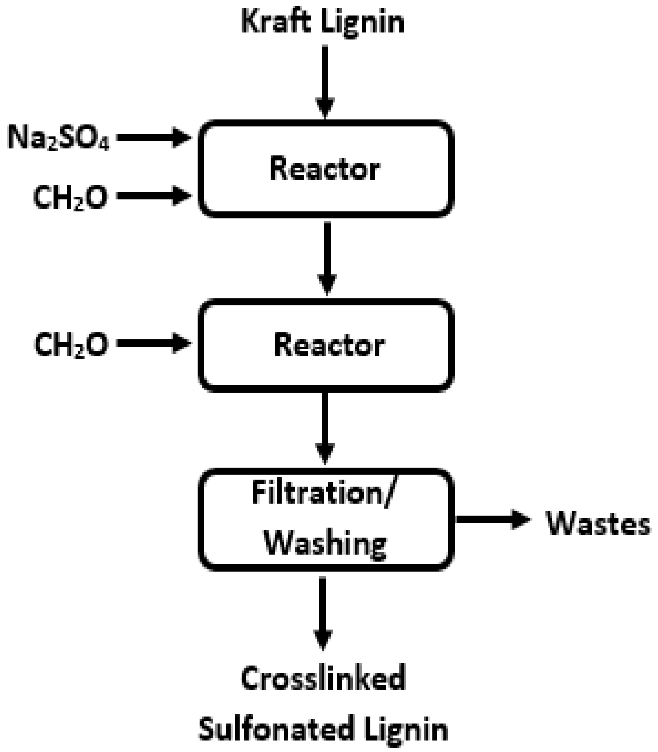

Figure 3.9. Sulfomethylation and crosslinking of kraft lignin.

Other technical lignins were also subjected to sulfomethylation (Madzhidova et al., 1998). In a process similar to Figure 3.9, dioxane lignin, nitrolignin, and hydrolysis lignin, among others were reported to be used under the conditions of 0.5/1 wt./vol. of lignin/CH_2O and 1/1 weight ratio of lignin/Na_2SO_3 at pH 8 and 95 °C for 3 h (Madzhidova et al., 1998). The product could be subjected to purification as required. As a result, the solubility of all of the technical lignins was reported to increase by up to 89 % (Madzhidova et al., 1998). However, the more condensed lignin (demethylated lignin, chlorolignin) had reported to behave poorly in the sulfomethylation reaction. A decrease in the amount of hydroxyl and carbonyl groups in the sulfomethylated products was also observed (Madzhidova et al., 1998).

3.4.9. Oxidation, hydroxymethylation, and sulfomethylation

The aforementioned methods may be combined to increase the reactivity of lignin. Figure 3.10 presents a process for the oxidation and sulfomethylation of lignosulfonates. In this scenario, oxidation was conducted on an alkaline sulfite pulping spent liquor (sodium base, pH 11 – 13) with peroxyacetic acid (PAA) at 30 wt.% for 2 h at 80 °C with 0.5 wt.% $FeSO_4$ as a catalyst (Hocking, 1998; Yu et al., 2013). Sulfomethylation was then carried out with 20 wt.% CH_2O and 30 wt.% Na_2SO_3 for 3 h at 95 °C. The resulting solution could be spray dried to yield a final product.

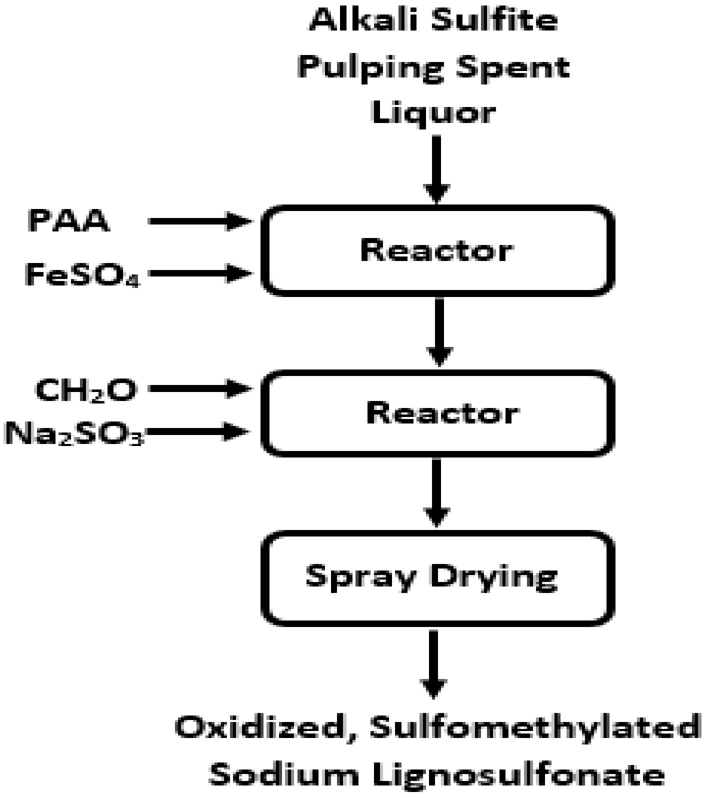

Figure 3.10. Oxidized and sulfomethylated sodium lignosulfonates.

Oxidation and sulfomethylation of lignosulfonates increased product's molecular weight from about 2,400 to 24,000 g/mol and sulfonation degree from 0.65 mmol/g to 1.45 mmol/g (Yu et al., 2013). Kraft lignin could also be used as a starting material for oxidation and sulfomethylation to yield a product (He and Fatehi, 2015). This process is similar to that described in Figure 3.10, but the oxidation can be carried out with nitric acid and sodium metabisulfite for sulfomethylation. In one study, kraft lignin was oxidized with nitric acid at 20 wt.% for 1 h at 100 °C, and subsequently sulfomethylated at molar ratios of 1/1 with formaldehyde and 0.5/1 with sodium metabisulfite at 100 °C for 3 h (He and Fatehi, 2015). The resulting product may be produced with ultrafiltration.

The molecular weight of the oxidized and sulfomethylated kraft lignin product (18,299 g/mol) was higher than that of kraft lignin (16,770 g/mol) (He and Fatehi, 2015). The sulfonation degree was approximately 2 meq/g, which was slightly higher than that of commercial lignosulfonic acid sodium salt (1.7 meq/g) and sodium lignosulfonates (1.6 meq/g) (He and Fatehi, 2015). However, the two-stage reaction may be more complex to be implemented in industry (He and Fatehi, 2015).

Alkali lignin had also been used as a starting material in a similar process; wherein oxidation and hydroxymethylation of alkali lignin prior to sulfomethylation were conducted. In one study, wheat straw alkali lignin was first oxidized with H_2O_2 (0.2/1 weight ratio H_2O_2/lignin) for 1 h at 85 °C with $FeSO_4$ catalyst (0.01/1 weight ratio $FeSO_4$/lignin) (Ouyang et al., 2009). Hydroxymethylation was carried out at 1/0.4 weight ratio of lignin/formaldehyde for 2 h at 75 °C and pH 9.5. Sulfonation occurred at 0.35/1 weight ratio of Na_2SO_3/lignin at 85 °C for 3 h (Ouyang et al., 2009). The molecular weight of the oxidized and hydroxymethylated sulfonated alkali lignin was reported to increase from 2,700 to 9,700 g/mol, while its sulfonate group content increased to 1.5 meq/g (Ouyang et al., 2009). Alternatively, oxidation and hydroxymethylation of alkali lignin were carried out individually prior to sulfomethylation (Ouyang et al., 2009). The results indicated that this method produced lignin with a lower solubility and sulfonation degree (Ouyang et al., 2009). In this process, the use of H_2O_2 for oxidation may not be selective and could cause undesired degradation/condensation reactions. As such, better results may be observed with the use of PAA or HNO_3 as reactants for oxidation.

Another technical lignin, hydrolysis lignin, could be used as a starting material for oxidation, hydroxymethylation and sulfonation processes. This lignin is produced as the by-product of cellulosic ethanol industry (Fatehi and Ni, 2011b). Hydrolysis lignin has a highly condensed structure with limited reactivity for value-added applications (Matsushita and Yasuda, 2005; Yasuda and Asano, 2000). To increase the reactivity of hydrolysis lignin and reduce the formation of condensed structures, oxidation and hydroxymethylation may be performed prior to sulfomethylation.

In the past, hydrolysis lignin was oxidized at 1/5 vol./wt. of H_2O_2/lignin at 50 °C for 1 h at pH 5 following the procedure outlined in Figure 3.10 (Wu et al., 2012). Hydroxymethylation was conducted with 0.75/5 vol./wt. of formaldehyde/lignin for 1 h at pH 9 and 75 °C.

Sulfomethylation was conducted via sodium sulfite treatment at 1/1 weight ratio of sodium sulfite/lignin at 90 °C for 5 h, which led to a product with a sulfonic acid group content of 1.29 mmol/g (Wu et al., 2012).

3.4.10. Phenolation and sulfonation

Phenolation of lignin and lignosulfonates had also been proposed to increase their reactivity. The process for phenolation of lignosulfonates is similar to that shown in Figure 3.8, but phenol was used as the reagent and oxalic acid as the catalyst in this process. In the past, phenolation of lignosulfonates was performed by reacting lignosulfonates with phenol at 120 °C for 160 min (Alonso et al., 2005). An advantage of phenolation is that the product is soluble in phenol, thus further purification of the product may not be required prior to use in phenol-formaldehyde (PF) resin production (Allan et al., 1989; Engelmann and Ganster, 2016). Nevertheless, high costs are associated with the implementation of the phenolation of lignosulfonates, though it is still a popular method of modification (Pérez et al., 2007; Hemmilä et al., 2013).

Figure 3.11 outlines a process in which phenolation was also carried out on hydrolysis lignin. In one study, phenolation occurred under the conditions of 0.15/1 weight ratio of lignin/phenol in 72 % sulfuric acid at 60 °C for 6 h (Yasuda et al., 1999). Phenolation in the presence of sulfuric acid does not appreciably change the molecular weight of lignin; this is advantageous because the only significant change in the product is the increased reactivity due to rise in the phenolic hydroxyl groups (Yasuda et al., 1999). The addition of one phenol group per lignin monomer was achieved through this phenolation route. Several methods of sulfonation were carried out on phenolated hydrolysis lignin, as shown in Processes A – D of Figure 3.11.

In Process A of Figure 3.11, phenolated hydrolysis lignin was hydroxymethylated with formaldehyde and purified, then sulfonated with a neutral sulfite solution. In one study, hydroxymethylation was performed similar to the previous methods (Matsushita and Yasuda, 2005). The product, hydroxymethylated phenolated hydrolysis lignin, was precipitated with HCl and then sulfonated at 0.1/1 vol./wt. of neutral sulfite solution/lignin at pH 8 and 150 °C for 2 h. The product can be purified with membrane filtration. The product of Process A had a sulfur content of 11.4 wt.% and a molecular weight of 15,600 g/mol (Matsushita and Yasuda, 2005).

With increased hydroxymethylation, sulfonation would increase due to more reactive sites participating in the sulfonation reaction.

Process B of Figure 3.11 outlines another method of sulfomethylating phenolated hydrolysis lignin. In this process, the sulfomethylation was conducted with 1.2/1 weight ratio of sodium hydroxymethyl sulfonate/lignin for 2 h at 100 °C under alkaline conditions (Matsushita and Yasuda, 2005). Sodium hydroxymethyl sulfonate was used instead of sodium sulfite (Konduri and Fatehi, 2015). The product was determined to have a lower sulfur content of 4.3 wt.% and higher molecular weight of 11,300 g/mol than those of commercial lignosulfonates (6.3 wt.% and 5,800 g/mol) (Matsushita and Yasuda, 2005).

Process C in Figure 3.11 shows the arylsulfonation of phenolated hydrolysis lignin. In this scenario, lignin was reacted with chlorosulfonic acid in the presence of chloroform or tetrachloroethane, and the product was purified with membrane (Matsushita and Yasuda, 2005). In this process, phenolated lignin was treated at 0.875/1 weight ratio of chlorosulfonic acid/lignin in chloroform (0.005 vol./wt. to lignin) for 1 h at 25 °C at pH 2 (Matsushita and Yasuda, 2005). It was reported that an increase in the reaction temperature from 0 to 25 °C during arylsulfonation of phenolated hydrolysis lignin resulted in an increase in sulfonation (9.0 to 9.5 wt.%) and molecular weight (approximately 9,500 to 22,000 g/mol) (Matsushita and Yasuda, 2005; Yasuda et al., 1999). When tetrachloroethane was used as an alternative solvent in this process, the sulfur content was increased to 14 wt.% (Matsushita and Yasuda, 2005; Yasuda et al., 1999).

In Process D of Figure 3.11, formaldehyde treatment of phenolated hydrolysis lignin prior to sulfonation is outlined. In this process, lignin was first reacted with formaldehyde to form resinified hydrolysis lignin and subsequently sulfonated with chlorosulfonic acid in the presence of tetrachloroethane. One study reported phenolated lignin was reacted at 1/0.005 vol./wt. ratio with formaldehyde for 2 h at 180 °C under alkaline conditions (Yasuda and Asano, 2000). The resinified phenolated lignin was filtered prior to dissolution in tetrachloroethane (at 0.02 vol./wt. to lignin) then reacted with chlorosulfonic acid (2.5 weight ratio to lignin) for 3 h at 100 °C in NaOH (Yasuda and Asano, 2000). The product could be filtered and dried to purify. The product‘s sulfur content was found to be 10.2 wt.% with a sulfonation degree of 1.37 groups/C_9 unit and a surface charge density of 3.2 meq/g (Yasuda and Asano, 2000). Sulfonation without resinification pretreatment yielded lower values of sulfur content, sulfonation degree, and surface charge density of 7.8 wt.%, 0.60, and 2.3 meq/g, respectively (Yasuda and Asano, 2000). As such, resinification pretreatment allowed for improved properties compared to unsulfonated sample, and thus the sulfonated products was proposed for use as ion-exchange resins (Yasuda and Asano, 2000).

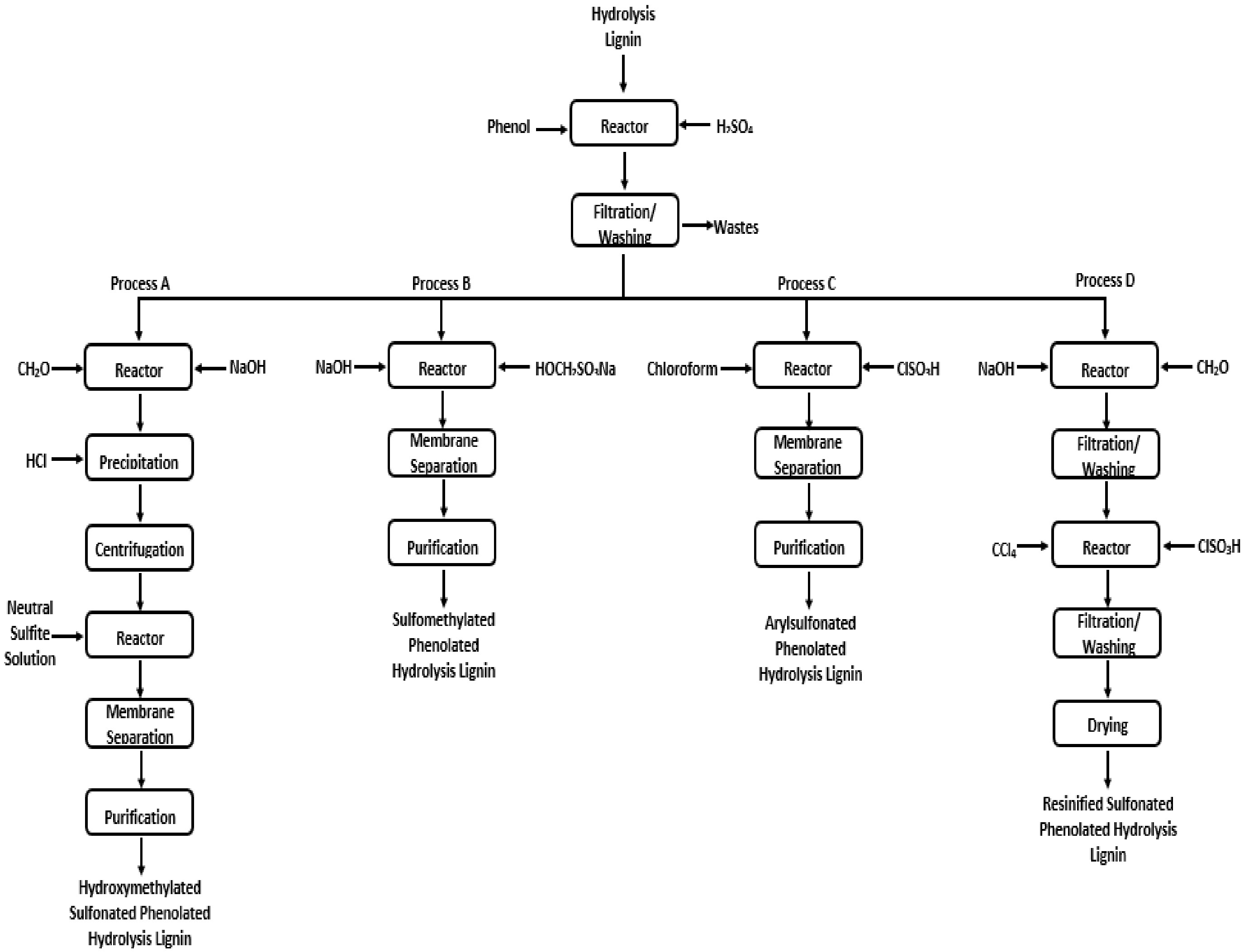

Figure 3.11. Sulfonation of hydrolysis lignin following phenolation.

3.4.11. Reduced-sulfur lignosulfonates and derivatives

The insolubility of lignosulfonates in water is crucial for use in some applications. Reducing the sulfur content of lignosulfonates was studied as a method for solubility reduction of lignosulfonates in the past (Doherty et al., 2011; Jencks and Regenstein, 2010). This allowed lignosulfonates to be considered for use in synthetic resin or storage batteries (Harmon, 1945). Figure 3.12 outlines a method to reduce the sulfur content of lignosulfonates. In process A, sulfur was removed from calcium lignosulfonates by reaction with sodium hydroxide and then the product was purified. This reaction was performed at 2/1 weight ratio of lignosulfonate/NaOH at 175 °C for 0.5 h (Orsino and Harmon, 1945; Salvesen et al., 1949; Salvesen and Harmon, 1950). In a subsequent stage, CO_2 was injected into the solution at 65 °C to precipitate calcium carbonate at pH 10.8, which may be removed by filtration (Harmon, 1945). The reduced-sodium lignosulfonates may be precipitated using H_2SO_4 at pH 3 – 4 and also recovered via filtration (Harmon, 1945; Orsino and Harmon, 1945). In this process, the sulfur content of the lignosulfonates was reduced from 7.0 wt.% to 3.5 wt.% (Harmon, 1945).

Process B in Figure 3.12 shows the demethylation of the reduced-sulfur lignosulfonates. Instead of precipitating lignosulfonates with acid as shown in Process A, a second addition of NaOH was conducted to remove a methyl group and increase the reactivity of the product. Subsequently, the product could be dried for use (Salvesen and Harmon, 1950).

The demethylation converts the guaiacol compounds of the lignosulfonates to catechols (ortho-diphenols), resulting in a product that is soluble only at a pH of 10.5 or greater, and is highly oxygen absorbent (Salvesen and Harmon, 1950). A disadvantage of this process is the oxygen-adsorbent nature of the product which makes its storage challenging and dangerous. An increased flammability is observed when adsorbed oxygen increases in the product, which could create heat to the point of ignition in storage (Salvesen and Harmon, 1950). In order to prevent heating, acidification of the product with CO_2 may be performed, which provides an opportunity for safer storage. In addition, the high pressure and temperature reaction may increase the costs of the operation and equipment.

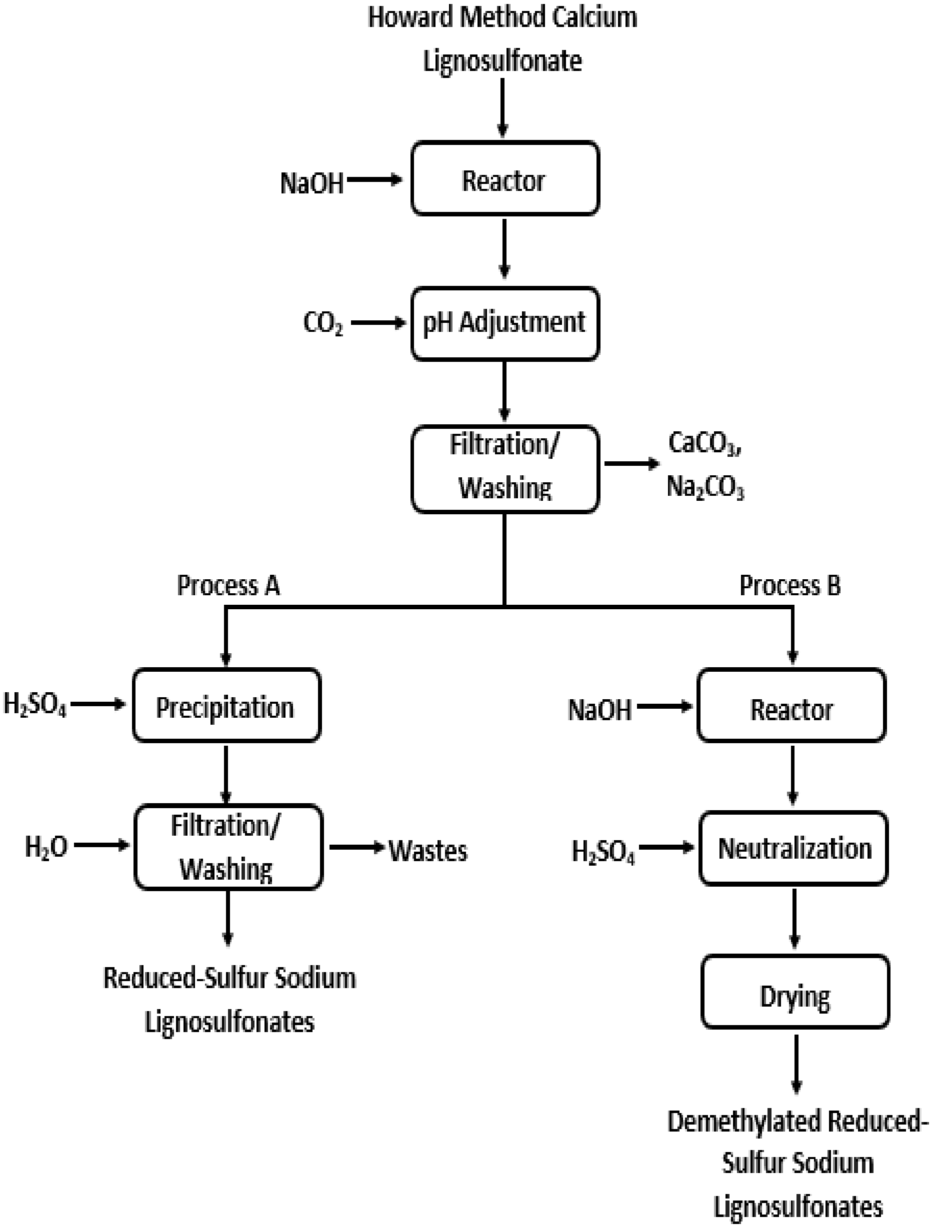

Figure 3.12. Reduced-sulfur and demethylated reduced-sulfur lignosulfonate production.

To produce low molecular weight lignosulfonates for use as dispersants, the alkaline oxidation of reduced-sulfur lignosulfonates was proposed in Figure 3.13 (Salvesen et al., 1949). In one study, calcium lignosulfonates were oxidized under alkaline conditions to reduce sulfur content. Oxidation was carried out at 0.25 – 0.4/1 weight ratio of oxygen/lignin at 160 – 175 °C for 1 h at pH 10.5 – 11.0. The precipitated calcium carbonate may be removed via filtration. The precipitation of lignosulfonates was conducted with H_2SO_4 at pH 3 – 4 and 80 – 90 °C, and the product may be washed and filtered (Salvesen et al, 1949). The product of this process differs from the reduced-sulfur lignosulfonates described in Process A in Figure 3.12 due to a decreased viscosity (Salvesen et al., 1949).

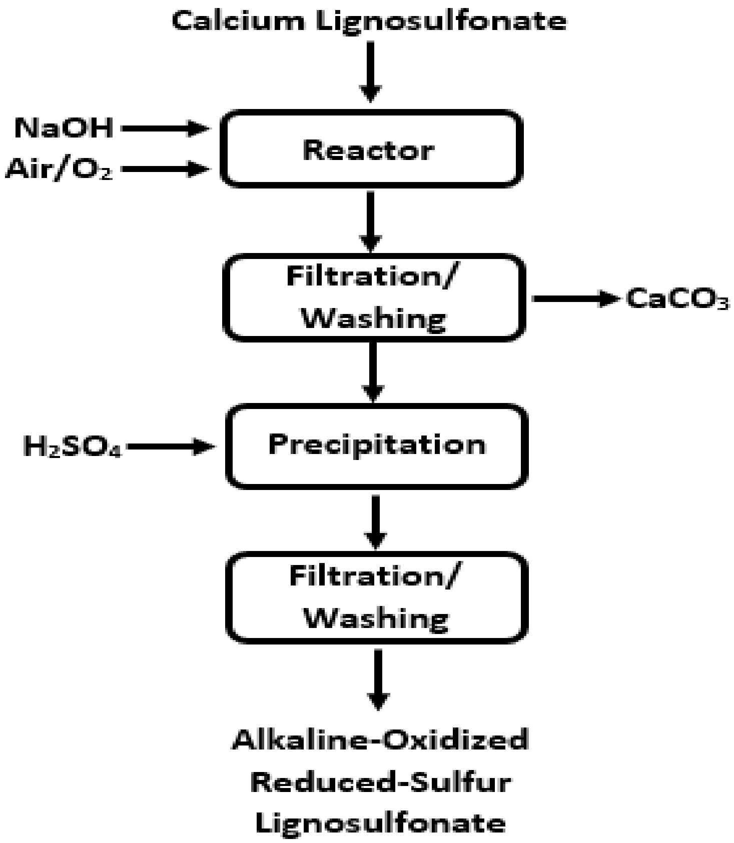

Figure 3.13. Alkaline-oxidized reduced-sulfur lignosulfonate production.

The alkaline oxidation would provide an opportunity to produce lignosulfonate with a lower sulfur content and molecular weight. However, the requirements of oxidation could raise the operation costs. Multiple washing and filtration stages would result in increased losses as well as excessive wastes which would have to be handled by the waste treatment facility. Thus, the costs of the production would be increased as well.

3.5. Impact of properties on application

Several commercial applications have been proposed based on the properties of lignosulfonates and sulfonated lignin. The following sections analyze the impact of the properties of lignosulfonates and sulfonated lignin on their end-use applications.

3.5.1. Dispersant and concrete additive

Dispersants and concrete additives (plasticizers) account for the widest use of lignosulfonates and sulfonated lignin. This is due to their appropriate molecular weight (10,000 – 50,000 g/mol), and anionic charge density (0.1 – 0.9 meq/g) stemming from the presence of functional groups (Meister, 2002; Vishtal and Kraslawski, 2011; Nedosvitii et al., 1994; Berlin and Balakshin, 2014; Šutý et al., 2013; Oveissi et al., 2016). Studies have also noted low toxicity of lignosulfonates in marinelife, which further increases potential for their safe use (Neff et al., 1981; Carr et al., 1982).

When ammonium is used as a base in sulfite pulping, produced lignosulfonates have usually a larger molecular weight than when either sodium or calcium are employed. This higher molecular weight was claimed to be related to the increased severity and rate of ammonium-based sulfite pulping, resulting in condensation reactions which would increase lignosulfonate molecular weight (Nedosvitii et al., 1994; Biermann, 1996). Sodium lignosulfonates typically have a lower apparent viscosity than calcium lignosulfonates, which is attributed to sodium having a stronger electrokinetic repulsive force than calcium increasing repulsion and thus reducing viscosity (Madad et al., 2011).

In one study, increasing the molecular weight of the lignosulfonates via oxidation and sulfomethylation enhanced their plasticizing abilities in concrete from 161 mm (unmodified) to 185 mm at a dosage of 0.3 wt.% lignosulfonates (Yu et al., 2013). Another study stated that the fluidity of the oxidized and sulfomethylated product was comparable to that of commercial naphthalene sulfonate (Ouyang et al., 2006; Šutý et al., 2013; Perche et al., 2003; Yang et al., 2008; Matsushita et al., 2007). Increasing the molecular weight of kraft lignin by oxidation and sulfomethylation increased the adsorption of the modified kraft lignin on cement particles to 6 mg/g lignin dosage (Madzhidova et al., 1998). This also increased the fluidity of the cement paste to 200 mm. In this case, the fluidity of unmodified kraft lignin was 70 mm and that of lignosulfonic acid was 190 mm at the same dosage applied (Madzhidova et al., 1998).

Increased viscosity is indicative of increased molecular weight. Increasing the molecular weight of the kraft lignin via sulfomethylation with sodium sulfite and crosslinking with formaldehyde increased the viscosity of the product (3700 cP compared to 1680 cP without crosslinking) to a level that allowed for effective use as a dye dispersant (Dilling, 1985a). The thermal stability of lignosulfonates was also an important factor to be used as a dye dispersant (Dilling, 1985a). An increase in molecular weight from approximately 2,000 to 14,000 g/mol by the hydyroxypropyl sulfonation of alkali lignin resulted in its improved heat stability, dispersibility of dye, and dye adsorption (Qin et al., 2015).

It was claimed that the hydrophobicity of lignosulfonates played an important role in their dispersing performance. In one study on calcium lignosulfonates, it was found that when lignosulfonates were fractionated based on molecular weight, the higher the molecular weight of the fraction, the lower the charge density and hydrophilicity of the fraction (Yang et al., 2008). As a result, the increased hydrophobicity allowed for an increased surface activity and decreased surface tension (surface tensions of 41.5 mN/m for the largest fraction and 66 mN/m for the smallest fraction) (Northey, 2002).

The nitration of lignosulfonates also seemed to impact the plasticizing capabilities of concrete admixtures. In one study, nitration to approximately 0.6 wt.% allowed for less water to be added to concrete mixtures (45 L water/m^3 concrete less), while the strength properties of the concrete were maintained at 25 mN (Sarkkinen, 1984). Increased nitrogen levels are also associated with corrosion prevention when applied as a concrete plasticizer (Sarkkinen, 1984).

The sulfur content of lignin based products appears to significantly impact their dispersion performance. In one report, reducing the sulfur content of lignosulfonates aided in increasing dispersion abilities by increasing hydrophobicity. This is because lower amounts of sulfonate groups result in less hindrance of hydrophobic adsorption between the hydrocarbon backbone of lignin and the material to which it adsorbs. Maintaining sulfur levels at 3.5 wt.% still allows for adequate solubility, whilst zeta potential is also increased by enhanced adsorption (Winowiski et al., 2003). An increase in sulfur content from 0.65 mmol/g to 1.45 mmol/g from oxidation and sulfomethylation of lignosulfonates contributed to improving plasticizing ability, as well as increased fluidity from 161 mm to 185 mm (Yu et al., 2013). An increase in sulfonation degree through the same modification of kraft lignin to 2.04 meq/g increased the charge density to 4.6

meq/g, which allowed for increased fluidity of cement paste compared to commercial lignosulfonates and lignosulfonic acid (He and Fatehi, 2015). Therefore, it may be concluded that the sulfur content of sulfonated lignin is essential for its solubility and dispersion, but at a high sulfur content or high molecular weight, the dispersion of lignosulfonate may be hindered.

An increase in the molecular weight, phenolic hydroxyl content, and sulfonation as a result of modifying lignosulfonates with hydroxybenzyl alcohol allowed for better dye dispersion capabilities. The adsorption of lignosulfonates onto dye was increased due to increased molecular weight and hydroxyl content, while the sulfonate groups caused stabilization via strong repulsive charges (Lin, 1983).

Increasing both the molecular weight and sulfonation degree of alkali lignin through oxidation and hydroxymethylation pretreatment before sulfonation decreased the surface tension (47.4 mN/m), and increased magnitude of zeta potential (-30 mV), adsorption (8.5 mg/g cement), and dispersibility (216 mm) over commercial lignosulfonates (48 mN/m, -26 mV, 5.9 mg/g cement, 210 mm, respectively) (Ouyang et al., 2009).

By increasing the available functional groups via oxidation, the dispersing capabilities of lignosulfonates were increased dramatically. As mud dispersants, the oxidized lignosulfonates outperformed commercial products by at least 90 % based on gel point determination (Detroit, 1995). For gypsum dispersion, dispersion efficiency was improved by 50 % following oxidation of lignosulfonates (Sears and Byrd, 1992). Increasing the thermal stability of lignosulfonates as a dispersant for drilling mud through hydroxymethylation allowed for values similar to commercial additive ferric chromium lignin sulfonate (Chen et al., 2014).

3.5.2. Lead-acid storage batteries

The lead-acid battery, commonly used in automobiles, is one of the world's most widely used rechargeable power sources, and can also act as a backup power supply (Matsushita et al., 2007). A lead-acid battery consists of cells containing lead as the anode and lead coated with lead oxide as the cathode, along with some other metals used for doping (Berera, 2006). Both the anode and cathode are contained in sulfuric acid; as electrical energy is generated by the battery, sulfuric acid is reduced to water. In order to regenerate sulfuric acid, an external power source must be used to recharge the battery. Since the anode and cathode plates are oxidized over time, corrosion occurs that decreases the size of the plates, reduces the capacity of the battery, and eventually the battery life (PowerThru, 2014). Additives known as expanders are used for maintaining the performance of the battery through numerous charge and discharge cycles (Calvo-Flores et al., 2015).

In order to expand the size of the plates, and thereby the battery capacity and lifespan, the use of organic materials have been studied (Orsino and Harmon, 1945). Organic matters such as lignocellulosic materials are inert and aid in preventing the corrosion of active materials used in recharging the battery (Orsino and Harmon, 1945). In this respect, lignosulfonates can be used, but high solubility has hindered their potential application in batteries. The acid-insolubility of lignosulfonates may be increased by reducing the sulfur content of the lignosulfonates, which may widen its application in the batteries (Harmon, 1945). By adding the reduced-sulfur lignosulfonates at 0.1 – 0.2 wt.% of the lead compound to a battery, foaming was reduced during battery use, which allowed for more efficient battery usage and less degradation due to reduced acidic foam formation (Orsino and Harmon, 1945). It was claimed that the application of lignosulfonates in batteries improved their life span to years, while batteries with no lignosulfonates claimed to work for days due to the corrosion of the lead plates (Lebo, Jr. et al., 2007).

3.5.3. Flocculant

Flocculants are widely used to decrease the settling time of solutions/suspensions and/or to increase the amount of the settled materials. Effective flocculants require good adsorption onto particles through both surface charge and molecular weight. Lignosulfonates and sulfonated lignin have long been exploited as flocculants (Oveissi and Fatehi, 2015; Ludwig, 1974). One study employed lignosulfonates to flocculate sulfur slurry used in copper heap leaching at a dosage of 0.2 wt.% and improved its density from 40 to 67 % (Bouffard et al., 2009). The lignosulfonates used in this application did not interfere with other aspects of copper leaching.

However, unmodified lignosulfonates and sulfonated lignin are often insufficiently effective to be commercially viable flocculants, and as such should be used along with other flocculants (Ludwig, 1974; Rachor and Ludwig, 1975). In one study, lignosulfonates were also applied to various food processing wastewater streams at dosages of 20 – 40 ppm in combination with xanthan gum and carrageenan (Miller, 1996). Increasing lignosulfonates dosage provided clearer effluent, however flocs size was adversely affected. Including xanthan gum at 8 ppm increased floc size and allowed for 85 % removal of BOD, 67 % removal of NH_3, and 91 % removal of suspended solids (Miller, 1996). Preparing an amphoteric flocculant copolymer of 50 wt.% acrylamide, 25 wt.% lignosulfonates, and 25 wt.% chitosan resulted in dye removals of 50 – 100 % at a dosage of 300 mg/L for various dyes (He et al., 2015). These values were comparable with those of commercial flocculants with increased environmental advantages as lignosulfonate was used.

Lignosulfonates and sulfonated lignin have been found to be effective flocculants when their molecular weight was increased via crosslinking (Ludwig, 1974; Liu et al., 2011). In one study, lignosulfonates were modified using polyethylene glycol and tosyl chloride, and the products were tested in a 4 wt.% clay suspension containing 1000 ppm NaCl (Ludwig, 1974). This modification resulted in settling times of 80 – 136 s, whereas the settling time for unmodified lignosulfonates was 570 s (Ludwig, 1974). Another study increased the molecular weight of the lignosulfonates by crosslinking with formaldehyde and dimethylamine in alkaline conditions, followed by mesyl disulfonate ester (Rachor and Ludwig, 1975). The product was used as a flocculant in a clay water slurry, when it decreased the settling time to 50 s at a 10 ppm dosage compared to 600 s settling time when no additive was used (Rachor and Ludwig, 1975).

3.5.4. Metal adsorbent

Metal adsorbents or complexing agents are materials that have the ability to bind with metals to form metal complexes. The carboxylate and sulfonate groups of lignosulfonates can act as potential complexation aids for metals (Abu-Dalo et al., 2013). This occurs through cation exchange mechanisms, in which the salt (e.g. sodium salt) of the functional group of lignosulfonates exchanges irreversibly with the metal contaminants in solutions (e.g. Co^{2+} or Hg^{2+}) (Abu-Dalo et al., 2013; Demirbas, 2007).

The increased sulfonation of the lignosulfonates can allow for better metal complexation, as sulfonate groups have a higher affinity for adsorbing metals (Abu-Dalo et al., 2013). Lignosulfonates were used as corrosion inhibitors for iron in a potable water distribution system

(Abu-Dalo et al., 2013). The complexation efficiencies of lignosulfonates at 100 g/L dosage were 95 % with iron and copper and 70 % with zinc (Villén et al., 2007).

Increasing hydroxyl groups of lignosulfonates through hydroxymethylation allowed for an increased complexation ability of 23.3 % with Zn, 18.9 % with Mg, and 24.9 % with Cu (Zhou, 2015). It was summarized that the main contributor of lignosulfonates complexing ability was derived from hydroxyl groups (Zhou, 2015).

3.5.5. Dust suppressant

Lignosulfonates have also been used as dust suppressants (Calvo-Flores et al., 2015). Lignosulfonates were sprayed onto dirt roads and became viscous as water evaporated during drying; this trapped the dust and prevented particulate air pollution (Calvo-Flores et al., 2015). Lignosulfonates are better alternatives than other types of dust prevention chemicals (i.e. calcium chloride) as they are more efficient – they provide a better road surface coverage and decreased maintenance requirements through improved surface drainage (Brown and Elton, 1994). Lignosulfonates are also non-toxic, non-corrosive, and biodegradable, reducing the potential environmental impact compared to synthetic alternatives (Calvo-Flores et al., 2015). However, a major disadvantage of lignosulfonates usage in this area is their water solubility. In this case, lignosulfonates may leach from the surface of the road during heavy rainfalls (Brown and Elton, 1994).

3.5.6. Antioxidant and pharmacological effects

Antioxidants are materials that prevent the oxidation reaction of oxygen-containing reactive free radicals (Dizhbite et al., 2004). They are important in health/cosmetic applications to prevent the destruction of healthy cells in the human body, and material science applications to prevent the degradation of the materials used as (for example) composites. Lignin and lignosulfonates have been examined for their antioxidant abilities in both cases, due to the phenolate and carboxylate groups, which impart antioxidant effects (McCarthy and Islam, 1999; Madad et al., 2011; Jablonský et al., 2015; Vinardell et al., 2008; Vasile et al., 2013). The syringyl units of the lignosulfonates (methoxyl group ortho to phenolic hydroxyl group) aid in enhancing antioxidant effects (Madad et al., 2011; Vasile et al., 2013). This is due to an increased chelating property of the phenolic hydroxyl group and radical-scavenging capability (Zhou et al., 2006).

One study showed that lignosulfonates completely inhibit hemolysis of human blood induced by AAPH (2,2'-azobis(2-aminidopropane), a radical initiator) at a concentration of approximately 200 µg/mL in blood (Vinardell et al., 2008). Another study reported the partial inhibition of DPPH (2,2-diphenyl-1-picrylhydrazyl) with an increase in lignosulfonates grafted copolymer (Dizhbite et al., 2004; Shogren and Biswas, 2013). The phenolic content increased from 0 to 0.97 wt.% due to the incorporation of the lignosulfonates, causing an increase in DPPH inhibition from 0 to 31 % (Shogren and Biswas, 2013). Additionally, lignosulfonates were found to be non-irritant to eyes and skin; thus, they have potential to be used in cosmetic products (Vinardell et al., 2008). The lignin incorporated in the polypropylene blends increased the antioxidant abilities of the composite from an oxidation induction period of 7.18 min to 11.12 min, indicating the prevention of the oxidation reaction (Vasile et al., 2013).

In addition to antioxidant capabilities, studies have shown that lignosulfonates have antiviral properties, most likely stemming from their polyanionic characteristics as well as molecular structure (Suzuki et al., 1989a,b; Vocac and Alphin, 1968). Lignosulfonates have anticoagulant, anti-ulcerogenic, and anti-tumor activities when used *in vivo* to Sarcoma 180 tumor cells (Suzuki et al., 1989b). Lignosulfonates have been shown to activate macrophages, which results in the growth in murine (rat) bone marrow cells at a minimum concentration of 10 µg/mL of lignosulfonates in the culture medium of murine peritoneal resident macrophages, which is comparable to typical macrophage activators (Suzuki et al., 1989b). Consequently, lignosulfonates may be used as a part of immunochemotherapy drugs for some diseases (Suzuki et al., 1989b). In particular, lignosulfonates dosed at 50 µg/mL resulted in the complete inhibition of cell death caused by HIV, HIV-specific antigen production, along with syncytia formation, possibly due to the prevention of the CD-4 receptor and HIV interaction (Suzuki et al., 1989a,b; Vocac, 1968). This means that lignosulfonates could be used to develop anti-HIV drugs to stimulate the immune system (Suzuki et al., 1989a,b). Another study showed vaginal contraceptive potential for lignosulfonic acid, a derivative of lignosulfonates (Tollner et al., 2002). At a dosage of 1.5 mg/mL, lignosulfonic acid was found to block fertilization in macaque oocytes. This interesting property along with its antiviral potential properties may allow for lignosulfonic acid/lignosulfonate containing materials to act as both contraceptives and antimicrobials (Tollner et al., 2002).

3.5.7. Composites

Lignosulfonates and sulfonated lignin may be incorporated into different composites in order to increase biodegradability and replace expensive synthetic materials. Lignosulfonates may be added to polyesters (i.e. polybutylene succinate) in order to enhance the hydrophilicity of the composites (Calvo-Flores et al., 2015; Agafitei et al., 1999; Lin et al., 2010). It was found that an increase from 0 to 4.5 wt.% of epoxy-modified lignosulfonates in a polyethylene terephthalate composite increased the melting point of the composites from 256 °C to 265 °C (Agafitei et al., 1999). In this system, the volume resistivity of the polymer blend with lignin (a measure of the insulating ability) increased three magnitudes from 10^{13} to 10^{16} $\Omega\cdot$cm, the surface resistivity, another measure of insulating ability, increased three magnitudes (from 10^{11} to 10^{14} Ω), and its dielectric constant, indicative of electrical storage potential, increased from 2.92 to 4.42 (Agafitei et al., 1999).

Lignosulfonates have also been integrated into PF resin products due to their phenolic group content and large molecular weights. These properties allow for increased gelation rates, which indicate how quickly resin begins to harden (Doherty et al., 2011; Calvo-Flores et al., 2015; Alonso et al., 2005). The increased gelation rates may raise the speed of the production and minimize the costs associated with resin formation. Lignosulfonates incorporation may replace 40 – 70 % of PF resin (Doherty et al., 2011; Lewis and Lantzy, 1989).

Ammonium lignosulfonates are better suited for use in PF resins than lignosulfonates produced with other bases (Alonso et al., 2004). Ammonium lignosulfonates had an increased amount of both phenolic hydroxyl groups and available aromatic protons, which increased lignosulfonates' reactivity with formaldehyde (Alonso et al., 2004; Alonso et al., 2006). Moreover, PF resins formed with ammonium lignosulfonates have improved properties than calcium, sodium or magnesium due to increased solubility (Engelmann and Ganster, 2016; Pérez et al., 2007; Alonso et al., 2004; Panda, 2005). Lignosulfonates from softwood are more suitable than hardwood lignosulfonates for phenol-formaldehyde resins due to increased aromatic reactive sites (Alonso et al., 2006). The reactivity of nitrogen within the structure of ammonium lignosulfonates, if present as a primary or secondary amine, has increased the reactivity with formaldehyde for forming PF resins (Allan et al., 1989).

On the other hand, lignosulfonates confer water sensitivity to composites as water-soluble sulfonate groups present in lignosulfonate structure (Allan et al., 1989). In addition, the molecular weight of lignosulfonates and sulfonated lignin is larger than phenol, which can reduce the compatibility of lignosulfonates and sulfonated lignin in composites (Allan et al., 1989). To increase the reactivity of the lignosulfonates towards phenol for incorporation into PF resin, hydroxymethylation was proposed. It was found that the number of hydroxymethyl groups increased (number unspecified), which increased the potential reactive sites (Alonso et al., 2004). Furthermore, the reactivity of the lignosulfonates was increased from 0.32 mol/100 g lignin to 0.51 mol/100 g lignin through alkaline hydrolysis (El Mansouri et al., 2006). By increasing the phenol content in lignosulfonates through direct phenolation, and incorporating into PF resin foams, the compression modulus of the foams increased from 0.25 to 2.18 MPa over conventional foams (Hu et al., 2012).

The applications of lignosulfonates in polyolefin were also investigated. At 5 wt.% lignosulfonates, the tensile strength of the polyolefins (70 wt.% polypropylene and 30 wt.% polyethylene) increased 20 % and its elongation at break increased 25 % (Cazacu et al., 2004). The lignosulfonates incorporated into poly(N-ethylaniline)/lignosulfonate composites at 2.5 wt.% increased the solubility of the composite and allowed for better electrical conductivity (He et al., 2012). However, poor adhesion between lignosulfonates and other polymers had been noted due to the heterogeneity of lignosulfonates in composites (Notley and Norgren, 2009).

The incorporation of the oxidized lignosulfonates as a binder in green composites was reported in the past (Yuan et al., 2014). The oxidized lignosulfonates may be combined with polyethylenimine to form a binder for medium density fibreboard composites, which allowed for a binder usage of 20 wt.% yielding acceptable moduli of rupture and elasticity (35.7 MPa and 4696 MPa, respectively), tensile strength (24.3 %), and internal bonding strength (1.23 MPa) (Yuan et al., 2014).

3.5.8. Ion-exchange resin

Ion-exchange resins are high surface area active materials on an inert base which allow for the exchange of similarly charged ions (Luáces, 1949; Alchin, 2008). As lignin and lignosulfonates have metal complexing capabilities, research has been done to increase their use for ion-exchange (Alchin, 2008).

In order to produce sulfonated lignin with an ion-exchange capacity similar to commercial ion-exchange resins, phenolation followed by resinification and sulfonation of hydrolysis lignin was performed (Yasuda and Asano, 2000). The ion-exchange capacity was 3.2 meq/g for the lignin produced by this method; whereas commercial phenol-type and sulfonated lignin resins had a charge density ranging 2 – 3 meq/g (Yasuda and Asano, 2000). The capacity of styrene type cation-exchange resins produced under the same conditions varied between 4 – 5 meq/g, which implied that sulfonated lignin had inferior properties to styrene type ion-exchange resins (Yasuda and Asano, 2000). Another study investigated the condensation polymerization of lignosulfonates with glucose, which resulted in an ion-exchange capacity of 4.1 mmol/g and a specific surface area of 13 – 20 m^2/g, and the product could be used effectively to remove Cr^{3+}, Cu^{2+}, Ni^{2+}, Pb^{2+}, and Cd^{2+} (Liang et al., 2013). The cationic exchange capacity of the lignosulfonates may be applied to sensor applications, despite its pH sensitivity (Notley and Norgren, 2009).

3.6. Summary

This paper provided a review on the pathways to produce lignosulfonates and sulfonated lignin. Among methods proposed for separating lignosulfonate from spent pulping liquor, ultrafiltration seems to be industrially applicable. Kraft lignin may be extracted via the LignoBoost or LignoForce technology from black liquor. Among the methods proposed to increase the sulfonation degree of lignin, sulfonation using sodium sulfite was relatively easy to implement, but sulfomethylation was more industrially attractive as it increased the sulfonate degree and molecular weight of lignin to some degree. To improve the sulfomethylation efficiency of lignin, various pretreatment methods were proposed, but alkaline oxidation was reported to be very effective in activating lignin for sulfomethylation reaction. Alkaline pretreatment with or without oxygen was also reported as a method to desulfonate lignosulfonate. Sulfonated lignin based products have been extensively used as dispersants in cement admixtures and dye solutions. It was reported that the molecular weight and sulfonate group had significant effects on the efficiency of lignosulfonate as a dispersant. Although kraft lignin was not a suitable dispersant because of its low solubility in water, a high degree of sulfonation was not recommended for dispersant production for cement admixtures. For battery use, lignosulfonates with a low degree of solubility were recommended, which could be achieved via desulfonating lignosulfonates. For flocculant application, sulfonated products with a large molecular weight were recommended, which could be achieved via crosslinking lignin of lignosulfonates via phenolation or hydroxymethylation, for instance. Sulfonated lignin based products could also be used as dust suppressants, but their main barrier was their water solubility. In composite applications, the compatibility and hydrophilicity of sulfonated lignin based products were reported to be important. In polystyrene composties, lignin based sulfonated products improved their hydrophilicity, while in PF resin, they were hydroxymethylated initially so that they would not hamper the hydrophobicity of resin when applied. Sulfonated lignin based products have also been proposed to be used as ion exchange resins and antioxidants but more research needs to be examined for these new applications.

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4. Tall oil and lignin characterization and process optimization

4.1. Abstract

In this work, the process for tall oil production was optimized, which was carried out by varying reaction time, reaction pH, water content, and settling additive. The yields and properties of the end products were systematically investigated. Tall oil products were analyzed for acid number and composition. Gas chromatography/mass spectrometry was also used to analyze the tall oil products. The lignin isolated in tall oil process was also analyzed for its charge density, solubility, elemental components and molecular weight analysis. It was found that a reaction pH in the range of 2.5 – 3.0, 100 wt.% water addition (based on raw soap reacted), a reaction time of 20 min, temperature of 90 – 100 °C, and 2 h settling time yielded products with the maximum yield of 52.9 wt.% and acid number of 137 mg KOH/g oil. With respect to settling additives, the anionic Infinity^{TM} brand additive at a dosage of 0.0185 wt.% (dry basis) resulted in the largest crude tall oil yield and acid number of 57.1 wt.% and 142 mg KOH/g oil, respectively. Cationic xylan-[2-(methacryloyloxy)ethyl] trimethylammonium methyl sulfate-ammonium persulfate (xylan-AETAS-APS) at a dosage of 0.0073 wt.% (dry) resulted in its largest acid number (138 mg KOH/g oil) and a dosage of 0.0111 wt.% (dry) resulted in the largest crude tall oil yield (53.7 wt.%). The cationic enzymatic hydrolysis lignin-[2-(methacryloyloxy)ethyl] trimethylammonium chloride additive (DMC-HL10) at a dry dosage of 0.0037 wt.% had a yield of 53.1 wt.% and an acid number of 136 mg KOH/g oil. However, following ANOVA and SPSS analysis, none of these conditions could be determined as statistically significant, and as such none of these conditions could be considered optimized from a statistics point of view. Lignin from the tall oil production process was found to have an anionic charge density of 0.2 – 0.4 mmol/g and a solubility of approximately 0.7 – 2.0 g/L, both of which were higher than those of unmodified kraft lignin, but less than those of lignosulfonates. The molecular weight of lignin sample was 1,700 g/mol, which was smaller than those of kraft lignin and lignosulfonates. These results indicate that lignin of tall oil process may have an application as a value-added product if further modified.

4.2. Introduction

In wood, the main constituents are cellulose, lignin, hemicellulose and extractives (Sjöström, 1993). Extractives can be classified into several groups, including aliphatic and acyclic compounds, gums (polysaccharides), phenolic compounds and others (i.e. sugars, amino acids) (Stenius, 2000). Extractives are typically present in small amounts in wood (less than 10 % by weight); however, they should be removed from fibrous materials in order to improve the quality of paper they would make (Imamura, 1989; Sjöström, 1993).

Tall oil is produced as a by-product of the extractives in wood following kraft pulping process, and is most abundant in pine wood (Panda, 2013). In the kraft pulping process, the fatty and rosin acids, which compose part of the extractives in wood, react with the highly alkaline cooking liquor to form soluble sodium salts (Panda, 2013; Foran, 1992). These salts comprise tall oil soap, along with some neutral compounds, and naturally separate from black liquor in the kraft recovery process (Foran, 1992). Tall oil soap may be separated from black liquor by skimming, and should be removed from the kraft recovery process in order to improve the efficiency of kraft pulping (Foran, 1992; Gossage, 1976). Once removed from black liquor, tall oil soap is reacted with concentrated sulfuric acid to form crude tall oil, which is brown, viscous, and poor-smelling, comprised mainly of fatty and rosin acids, and is in solution with lignin, spent sulfuric acid, and other residual organic compounds (Marda, 2006; Fuenzalida et al., 2005). The crude tall oil is removed from the reaction mixture and sent for further processing, but lignin is returned to the kraft recovery process for energy production, and the spent acid is reused in the pulping process (Wansbrough, 2008; Fuenzalida et al., 2005).

In the past, crude tall oil has been refined in order to produce more pure fatty acids, rosin acids, and other fractions (Fuenzalida et al., 2005; Panda, 2013). However, recent advancements in tall oil use have been proposed in order to increase the economic viability of existing kraft pulping processes. This has been conducted in conjunction with converting the tall oil processes into integrated forest biorefineries (IFBRs), in which traditional pulp and paper products are not the primary products (van Heiningen, 2006). Lee et al. (2006) reviewed the production of biodiesel from tall oil. The desire is not only for increasing profitability of pulp mills, but a divergence from traditional fossil fuels. Marda (2006) also examined the production of biodiesel from crude tall oil without refinement. Work has also been carried out on the conversion of tall oil fatty acids to biofuels using catalysts (Rozmyslowicz et al., 2010). The refined portion tall oil fatty acid has also been used in asphalt mixtures in several cases (Moriyasu et al., 2017; Shin et al., 2017), and oxidized tall oil production has been in growing use (Phun et al., 2017). Lignin has been studied heavily for use in different applications. Unmodified lignin and lignin from the tall oil production process has traditionally been used as a source of fuel in kraft pulping processes; however, it is advantageous to modify kraft lignin to produce value-added products with various uses to increase economics of kraft pulp mills. Dispersants and flocculants from kraft lignin have been a topic recently. He and Fatehi (2015) prepared a dispersant from sulfomethylated kraft lignin. Dye dispersants have also been produced from sulfomethylated kraft lignin, and sulfonated lignin is used widely by the cement industry (Meister, 2002). The ability of kraft lignin to act as a dispersant or flocculant is dependent on its modification process; sulfonation and sulfomethylation are both widely employed to accomplish the task (Berlin and Balakshin, 2014).

Considering the advancements in tall oil and lignin usage, the tall oil production process can be revisited.

In this chapter, the optimization of crude tall oil production was conducted, along with the characterization of tall oil and the waste lignin present in this process. The optimization was carried out using several parameters of the tall oil acidulation procedure, including reaction water content, pH, and reaction time. Different settling additives, which aid in increasing the yield of tall oil, quality of tall oil and decreasing settling time, were also studied. Tall oil characterization was also carried out for all tall oil products. Lignin characterization was conducted on selected products from different tall oil production conditions in order to determine the potential of producing value-added products from lignin. Molecular weight, elemental, charge density and solubility analyses were carried out on the selected lignin samples.

4.3. Experimental

4.3.1. Raw materials

In this work, tall oil soap was provided by a company located in northern Ontario. Infinity^{TM} PS3040 Pulp Processing Aid was also supplied by the same company. Concentrated sulfuric acid (95 – 98 wt.%) and isopropanol (2-propanol) were purchased from Fischer company. Ethanol and toluene were purchased from ACP Chemical company. Methanol was purchased from Caledon Laboratories. Heptadecanoic acid (≥98 %), 97 % oleic acid, 99 % linolenic acid, 99 % linoleic acid, N,N-dimethylformamide dimethylacetal (DMF-DMA), diethyl ether (ethyl ether), phenolphthalein, sodium sulfate, and potassium hydrogen phthalate (KHP) were all purchased from Sigma-Aldrich and used as received. Polydiallyldimethylammonium chloride (pDADMAC) from Sigma-Aldrich and potassium polyvinyl sulfate (PVSK) from Wake Pure Chemical Industries Ltd., Japan were diluted to approximately 0.005 M prior to use. Hydranal®-Composite 5 and Methanol Dry for use with Karl-Fischer titrations were supplied by Metrohm. Potassium hydroxide (KOH) was purchased from VWR company. Cellulose acetate dialysis membrane (molecular weight cutoff of 1000 g/mol) was obtained from Spectrum Laboratories Inc., USA.

4.3.2. Production and neutralization of crude tall oil and lignin

Crude tall oil was produced from tall oil soap by its reaction with sulfuric acid diluted in water. Water and settling additive (as required) were added to a 500 mL Erlenmeyer flask with constant stirring and heating. Concentrated sulfuric acid was added directly to the water according to industrial practice and the desired parameters (Resolute Forest Products, 2016; PCTM Standard 6, 1996). Once the desired temperature was reached, 100 g tall oil soap was added to the flask and allowed to react for a certain time at 90 – 100 °C, then transferred to a 250 or 500 mL separatory funnel and allowed to settle in a 105 °C oven for 2 h. Following settling, crude tall oil was decanted and washed with water to pH 5 – 7, then analyzed appropriately. The middle lignin emulsion layer was separated and dialyzed at pH 7 while changing water every 4 h for the first 12 h and then once a day for 2 days for purification. The purified lignin solution was then vacuum filtered and dried in a 105 °C oven to obtain a solid product. The dried lignin was then washed with ethanol and vacuum filtered again in order to remove remaining tall oil, then dried in the oven. The investigated parameters for tall oil production were water content (25 – 175 wt.% of soap addition), pH of solution (2.0 – 6.0), reaction time (10 – 40 min), additive type (Infinity^{TM} PS3040 Pulp Processing Aid, Xylan-AETAS-AP10, and DMC-HL10), and additive dosage (0.01 – 0.05 wt.% [wet basis] of soap).

4.3.3. Acid number of tall oil

The acid number of the washed crude tall oil was determined according to PCTM Standard 1 (1996) and ASTM Standard D465 (2015). First, 0.5 N KOH in methanol solution was made by dissolving 33 g of KOH in methanol and diluting to 1 L with methanol. This solution was standardized weekly using potassium hydrogen phthalate (KHP) by dissolving approximately 1 g of KHP in 24 mL of water and 16 mL of isopropanol. Exactly 1.0212 g of KHP in solution will be neutralized by 10.0 mL of 0.5 N KOH solution (ASTM Standard D465-15, 2015). The actual normality of the solution could be determined using the exact weight of the KHP for standardization. Neutralization was determined using potentiometric titration. A 905 Titrando unit from Metrohm associated with a 10 mL 800 Dosino dosing unit, a combined liquid-liquid pH glass electrode, and Tiamo 2.0 software were employed for titration. To test crude tall oil with the standardized solution, 0.6 – 1.0 g of tall oil was weighed to the nearest 0.001 g in a glass beaker and dissolved in 5 mL toluene and 15 mL isopropanol. The tall oil solution was titrated with 0.5 N KOH solution to the inflection point, which indicated the endpoint of the reaction. This value was used to calculate the acid number of tall oil using Equation 4.1. The acid number characterization was carried out in triplicate for each sample to ensure accurate values.

$$AN = \frac{V \times N \times 56.1}{m_{sample}} \tag{4.1}$$

where:

AN = acid number; the amount of KOH required to neutralize 1 g of oil, mg KOH/g oil

V = volume of 0.5 N KOH solution at inflection point, mL

N = actual normality of alkali solution, N

m_{sample} = sample weight, g

4.3.4. Rosin acid content of tall oil

Rosin acid content was measured using potentiometric titration with the same 0.5 N KOH solution as described in Section 4.3.3, and according to standard testing methods (PCTM Standard 17, 1996). In this method, fatty acids are esterified by methanol in the presence of sulfuric acid, then rosin acid content is determined by titration following the neutralization of sulfuric acid catalyst (PCTM Standard 17, 1996). 2 g oil was measured to the nearest 0.001 g into a 250 mL flat-bottomed boiling flask with a stir bar. 30 mL methanol was added to dissolve the tall oil followed by 2.0 mL methyl sulfuric acid solution (20 wt.% sulfuric acid in methanol). The solution was refluxed for 30 min and cooled to room temperature. Potentiometric titration was conducted as previously described and the volume of KOH between the first and second inflection points was recorded. Equation 4.2 was used to calculate the amount of rosin acids in tall oil, reported to the nearest 0.1 %, again conducted in triplicate.

$$RA = \frac{(V_2 - V_1) \times N \times 30.24}{m_{sample}} \tag{4.2}$$

where:

RA = rosin acid content, wt.%

V_2 = volume of KOH solution at second inflection point, mL

V_1 = volume of KOH solution at first inflection point, mL

30.24 = equivalent weight of abeitic acid, a typical rosin acid / 10

4.3.5. Unsaponifiables content of tall oil

Unsaponifiables in tall oil were measured following standard testing methods, using 0.5 N KOH and potentiometric titration with the equipment explained previously (PCTM Standard 19, 1996). 2 g tall oil, measured to the nearest 0.001 g, was added to a 250 mL flat-bottomed boiling flask. Approximately, 6 mL of 2 N KOH solution (132 g KOH in 150 mL H_2O, diluted to 1 L with ethanol) was added to the flask (PCTM Standard 19, 1996). The solution was refluxed for 90 min and allowed to cool to room temperature. 50 mL water was then added to the flask and transferred to a 250 mL separatory funnel. The flask was rinsed with 15 mL of ethyl ether and transferred to the funnel. The separatory funnel was shaken well and allowed to settle; the lower aqueous layer was decanted into a second separatory funnel and extracted with another batch of fresh 15 mL ethyl ether. The aqueous layer from the second extraction was decanted into the original flask and the top ether layer was combined with the first ether layer in the first separatory funnel. The aqueous solution was transferred to the empty separatory funnel and extracted for a third time with 15 mL ethyl ether. The aqueous layer was transferred to the original flask and the third ether wash was combined with the previous volumes. A final ether extraction was conducted with 15 mL ether. The aqueous layer was then discarded and the ether layers combined. The combined ether layers were washed with 30 mL water portions until the aqueous layer was neutral (colourless) to phenolphthalein solution (1 % in ethanol) (PCTM Standard 19, 1996). The washed ether solution was then transferred to a tared beaker (measured to the nearest 0.001 g) and allowed to evaporate in a water bath. The separatory funnel was washed with 15 mL of ether and transferred to the beaker and allowed to evaporate. Once evaporated, 2 mL of acetone was added to the beaker to obtain a clean and dry residue, and then the beaker was placed in a 105 °C oven until no water remained. After cooling to room temperature in a desiccator, the beaker was weighed to the nearest 0.001 g. The remaining solution was then dissolved in 5 mL toluene and 20 mL isopropanol, and 5 drops of phenolphthalein solution was added. The solution was then titrated to a coulometric endpoint using 0.5 N KOH solution. The amount of unsaponifiables was calculated using Equation 4.3, and reported to the nearest 0.1 %. This test was carried out in triplicate.

$$UNS = \frac{m_{dry} - (A \times N \times 30.24)}{m_{sample}} \times 100 \tag{4.3}$$

where:

UNS = unsaponifiables content, wt.%

m_{dry} = mass of dry solution, g

A = volume of 0.5 N KOH solution at coulometric endpoint, mL

4.3.6. Moisture content of tall oil

Moisture content was measured with the 870 Karl Fischer (KF) Titrino plus unit and 801 stirrer from Metrohm, using the KFT Ipol method. First, the titration vessel was filled with approximately 50 mL of Hydranal® Methanol Dry solution as a titration medium. The titrant, Hydranal® Composite 5, was prepared against Hydranal® Water Standard 10, where 10.0 mg = 1 wt.% H_2O. Once the exact titre of the Composite 5 was determined (in triplicate), tall oil could be tested. Tall oil was tested by injecting a known volume of tall oil, measured to the nearest 0.0001 g (ASTM Standard D803-15, 2015; PCTM Standard 4C, 1996). Inputting the weight of sample produced an exact measurement of moisture content, to 0.01 %, using the software of the instrument.

4.3.7. Fatty acid content of tall oil

Following the above characterization techniques, the fatty acid content could be determined using a mass balance, as shown in Equation 4.4. This equation is valid when the fatty acid content is greater than or equal to 5 wt.%, as is the case with tall oil (PCTM Standard 20, 1996).

$$FA = 100 - RA - UNS - MC \tag{4.4}$$

where:

FA = fatty acid content reported to nearest 0.1 %, wt.%

MC = moisture content, wt.%

4.3.8. Gas chromatography/mass spectrometry of tall oil

In order to determine the individual acid and neutral species present in tall oil samples, gas chromatography/mass spectrometry (GC/MS) was performed. To prepare the tall oil samples for analysis, 0.050 g of tall oil, 0.015 g of heptadecanoic acid, and 0.5 mL of methanol were added to an anhydrous vial and reacted with 1 mL of N,N-dimethylformamide dimethyl acetal (DMF-DMA) at 60 °C for 30 min to derivatize the tall oil components (McGuire and Powis, 1998; ASTM Standard D5974-15, 2015). 0.5 – 1.0 µL of the derivatized sample was injected into the GC/MS unit and analyzed following filtration with 0.22 µm pore size syringe filters. The GC/MS equipment used was a Shimadzu QP-2010S unit with LabSolutions GCMSsolution software. The GC column was SHRXI-5MS (30 m length, 0.25 mm ID, 0.25 µm df), made of fused silica. High purity helium carrier gas (Praxair, Thunder Bay, ON, Canada) was used with an average linear velocity of 38.0 cm/s (Nogueira et al., 1995). The injection temperature was 300 °C and the split ratio was 100:1. The ion source temperature was 220 °C and the interface temperature of the GC-MS was 280 °C. The GC oven temperature was programmed as an initial hold at 150 °C for 5 min, then a 5 °C/min increase to 260 °C and a hold at 260 °C for 20 min (McGuire and Powis, 1998; ASTM Standard D5974-15, 2015; Nogueira et al., 1995). Peak identifications were made by Wiley Registry^{TM} of Mass Spectral Data 8th Edition. It must be noted that the compounds analyzed were in their methyl ester forms following derivatization and thus were identified as such. There were two methods used to analyze the results of the GC/MS.

The first method is based on the relative response factor (RRF) of the main individual compounds within the tall oil samples (ASTM Standard D5974-15, 2015). The RRF method involves the use of an internal standard, which is an acid present in the tall oil samples in small amounts and may be used as a basis to determine absolute values of acidic compounds. Margaric (heptadecanoic) acid or myristic (tetradecanoic) acid are typically used for internal standards (ASTM Standard D5974-15, 2015; McGuire and Powis, 1998). As mentioned above, margaric acid was used as the internal standard. In order to determine an RRF, a calibration curve was produced using samples with milligram quantities of margaric acid (~15 mg), as well as linoleic (*cis*-9, *cis*-12-Octadecadienoic) acid and oleic (*cis*-9-Octadecenoic) acid in varying amounts (0, 5, 10, 15, 20, 25 mg). The RRF values for both linoleic and oleic acid were calculated for each solution using their areas as reported from the spectra, with Equations 4.5, 4.6, and 4.7 (ASTM Standard D5974-15, 2015).

$$RRF_i = \frac{W_i A_{IS}}{A_i W_{IS}} \tag{4.5}$$

$$W_i = m_i P \tag{4.6}$$

$$W_{IS} = m_{IS} P \tag{4.7}$$

where:

RRF_i = relative response factor of individual compound

W_i = weight of individual compound in methyl ester form, g

A_{IS}= peak area of individual compound

A_i = peak area of internal standard

W_{IS} = weight of internal standard, g

m_i = mass of individual compound, g

m_{IS} = mass of internal standard, g

P = purity of individual compound, unitless

Averaging the values of the RRF for each individual acid compound for each calibration curve solution allowed for a conversion from relative values of area generated by the GC/MS analysis to absolute percentages for the compounds using Equation 4.8. This calculation was carried out following the testing of crude tall oil samples.

$$AC_i = \frac{A_i RRF_i W_{IS}}{A_{IS} W_S} \times 100 \tag{4.8}$$

where:

AC_i = individual acid compound absolute percentage in crude tall oil sample, %

W_S = crude tall oil sample weight, g

Thus, a back calculation yields the mass of either linoleic or oleic acid in the crude tall oil samples as shown in Equation 4.9.

$$W_{AO} = AC_i \times W_S \tag{4.9}$$

where:

W_{AO} = weight of acid compound in oil sample, g

The second method is also calculated using a calibration curve, albeit in a different manner. Following the GC/MS analysis of each of the standard solutions, the area of each individual acid compound is plotted against the mass of the acid compound in the calibration samples. A linear trendline through the origin allowed for the production of an equation which correlates the acid compound area to the mass in solution. The equation for linoleic acid is shown in Equation 4.10 and oleic acid in Equation 4.11.

$$Area = 6{,}937{,}587{,}132W_l \tag{4.10}$$

$$Area = 9{,}139{,}411{,}271W_o \tag{4.11}$$

where:

W_l = weight of linoleic acid in standard, g

W_o= weight of oleic acid in standard, g

The GC/MS analysis of the tall oil samples produced a value of area for both acid compounds, which is then used to determine the actual weight of the acid compound in the crude tall oil sample by rearranging Equations 4.10 and 4.11 to solve for W, the weight of each of the acid compounds in the oil sample, as shown in Equations 4.12 and 4.13.

$$W_{ls} = \frac{Area_{ls}}{6{,}937{,}587{,}132} \tag{4.12}$$

$$W_{os} = \frac{Area_{os}}{9{,}139{,}411{,}271} \tag{4.13}$$

where:

W_{ls} = weight of linoleic acid in crude tall oil sample, g

$Area_{ls}$ = area of linoleic acid in crude tall oil sample

W_{os} = weight of oleic acid in crude tall oil sample, g

$Area_{os}$ = area of oleic acid in crude tall oil sample

The results of these two methods may be compared using the percent difference method, Equation 4.14 or 4.15, depending on the acid compound analyzed.

$$PD = \left|\frac{(W_{AO}-W_{Is})}{W_{AO}} \times 100\right| \tag{4.14}$$

$$PD = \left|\frac{(W_{AO}-W_{Os})}{W_{Ao}} \times 100\right| \tag{4.15}$$

where:

PD = percent difference between method 1 and method 2, %

4.3.9. Solubility of lignin

Following purification as outlined in above, lignin solubility was measured by weighing 0.1 g of lignin and suspending in 10 mL of deionized water in a water bath shaker at 150 rpm and 30 °C overnight (Konduri and Fatehi, 2015). The samples were vacuum filtered and the cake was dried in a 105 °C oven overnight. The solubility could be determined using Equation 4.16.

$$S = \frac{m_d}{m_i} \times 100 \tag{4.16}$$

where:

S = water solubility, wt.%

m_d = mass of dissolved lignin, g

m_i = initial mass of lignin, g

4.3.10. Charge density analysis

To measure the charge density, the samples were first dried overnight in a 105 °C oven to remove moisture. 0.1 g of sample, measured to the nearest 0.0001 g, was suspended in 10 mL water using a water bath shaker at 150 rpm and 30 °C overnight (Konduri and Fatehi, 2015). The samples were vacuum filtered and the supernatants and precipitates were collected, and their charge density was analyzed separately. For the soluble portion, 1 mL of the supernatant was injected into the BTTG Mütek^{TM} PCD-04 particle charge detector cell (Germany) and Mütek^{TM}

PCD T-3 titrator (Germany), bulked to 10 mL of total solution with distilled water, and titrated against 0.005 M pDADMAC standard solution using Equation 4.17. To test the insoluble portions of samples, first back-titrations were performed in triplicate using a separate pDADMAC solution (i.e. not the standard solution and at approximately 0.05 M) as the control sample against PVSK and recorded. 0.05 g insoluble portion (precipitate), measured to the nearest 0.0001 g, was suspended in 50 mL of pDADMAC solution. The charge density of the insoluble portions were carried out against PVSK as the titrant using Equation 4.18. The total charge density of the sample was determined using Equation 4.19.

$$CD = \frac{C_{pDADMAC}V_{pDADMAC}}{V_S C_S} \times 1000 \tag{4.17}$$

$$CD_{INS} = \frac{(V_{Control} - V_{PVSK})C_{PVSK}V'_{pDADMAC}}{V_{INS}m_{INS}} \tag{4.18}$$

$$CD_{Total} = CD \times S + CD_{INS}(1 - S) \tag{4.19}$$

where:

CD = charge density of soluble portion, mmol/g

$C_{pDADMAC}$ = concentration of standard pDADMAC, mol/L

$V_{pDADMAC}$ = consumed volume of standard pDADMAC solution, mL

V_S = volume of soluble sample solution added to PCD cell, mL

C_S = concentration of soluble sample, g/L

CD_{INS} = charge density of insoluble portion, mmol/g

$V_{Control}$ = volume of PVSK consumed by control sample, mL

V_{PVSK} = volume of PVSK consumed by insoluble sample, mL

C_{PVSK} = concentration of standard PVSK solution, mol/L

$V'_{pDADMAC}$ = volume of pDADMAC back titration solution to make insoluble portion suspended, mL

V_{INS} = volume of insoluble sample solution added to PCD cell, mL

m_{INS} = mass of dried insoluble sample added to PDADMAC for back titration, g

CD_{Total} = total charge density of sample, mmol/g

S = solubility of sample, unitless

4.3.11. Molecular weight analysis

The weight average molecular weight of lignin was determined by gel permeation chromatography (GPC) analysis (GPC Max VE 2001 separation module and a Viscotek TDA 305, Malverin). Lignin solution was created at 2 – 3 g/L in 0.1 M $NaNO_3$ and stirred overnight, then filtered with a 13 mm diameter nylon filter (pore size 0.2 µm) prior to analysis. 0.1 M $NaNO_3$ solution was used as eluent with a flow rate of 0.7 mL/min. The columns utilized were PolyAnalytic PAA206 and PAA203, operated at 35 °C. The standard for GPC calibration was polyethylene oxide (Konduri and Fatehi, 2015, 2017b).

4.3.12. Elemental analysis

The elemental analysis of lignin was conducted using an Elementar Vario EL Cube Elemental analyzer by a combustion analysis method. Following isolation and purification as previously outlined, the samples were dried in a 105 °C oven overnight to remove any remaining moisture. Approximately 2 mg of sample was weighed in silver vessels and loaded into the integrated carousel of the elemental analyzer. The samples were transferred automatically into a combustion tube and subsequently burned at 1200 °C. The combustion gases were reduced and analyzed for carbon, hydrogen, nitrogen, and oxygen content of the samples, reported as a weight percentage (Konduri and Fatehi, 2015).

4.3.13. Analysis of variance

Analysis of variance (ANOVA) of the results was conducted using both Microsoft Excel Add-ins and IBM Statistical Package for the Social Sciences (SPSS), 64-bit edition. Analysis using Microsoft Excel was conducted using ANOVA: Single Factor for both crude tall oil yield and acid number for all variable conditions. All values for each production parameter were analyzed; that is, each trial result was considered in each analysis. Microsoft Excel ANOVA could then predict if a significant difference was present, based on the 95 % confidence interval ($\alpha = 0.05$); if the probability value (P-value) was less than this α, a significant difference was present between the results of the reaction conditions. However, it could not be used to determine a specific difference present in the results, only that a difference was present. As a result, SPSS was used for each set of oil yield and acid number results. These tests were conducted using the Univariate General Linear Model, because a single variable outcome was present. A Scheffe post-hoc test was used because the group sizes (i.e. number of trials run) were not equal. The outcomes of the SPSS testing allowed for the direct comparison between each of the variables to be considered. For example, in the case of varying reaction time, ANOVA in Excel could determine if a difference was present, and SPSS could individually compare 10 min reaction time to 20 min, 30 min, and 40 min, to determine if there was a statistical difference (based on α-values) between individual reaction variables.

4.4. Results and analysis

4.4.1. Water content

The first reaction parameter that was varied in the production of tall oil was the water content of the reaction, with values of 25, 50, 75, 100, 150, and 175 wt.% of tall oil soap added. The other conditions of the reaction were based on industrial values (Resolute Forest Products, 2016; PCTM Standard 6, 1996, Finer and Timonen, 2017), using 100 g of tall oil soap, a reaction pH of 3.0 – 3.5 (achieved using concentrated sulfuric acid), reaction (agitation) time of 30 min, no settling additive, 90 – 100 °C reaction temperature, and 2 h settling time. Figure 4.1 shows the results of the yields of the individual layers of the products, including crude tall oil, lignin, and spent acid, with respect to the initial amount of tall oil soap addition.

As expected, the recovery of spent acid increases as the water content is increased, since water is contained mainly within the spent acid. This is because tall oil moisture content (i.e. water content) remains roughly consistent at under 3 wt.% (Panda, 2013). The lignin yield decreases slightly from approximately 13 to 8 wt.% as the water content is increased, possibly due to decreased lignin precipitation. As pH increases, lignin becomes more hydrophilic, and thus stays in solution, mainly in the spent acid portion (Zhu, 2013). The crude tall oil yield remains fairly constant, around a value of 50 wt.%; however, there is a slight increase to a value of 54.7 wt.% at a 100 wt.% water content. This may have been due to both an increased efficiency of settling and separation of the layers. Meanwhile, a disproportionate increase in spent acid yield is also observed at a 100 wt.% water addition. Though this is observed, which does not follow overall trends (Figure 4.1), the values are fairly consistent throughout the trials for spent acid yield. In industrial production of tall oil, spent acid is simply recycled to reduce fresh acid consumption during acidulation (acidification) (Wansbrough, 2008). In order to decrease reactor volume and handling issues while maintaining efficient separation of crude tall oil, the overall volume, which is most effectively achieved by decreasing water addition, should be kept to a minimum. For this reason, the 100 wt.% water content will be used in further investigation, except for reaction pH and reaction/agitation time, as these were performed concurrently with water content optimization prior to determining final optimized conditions.

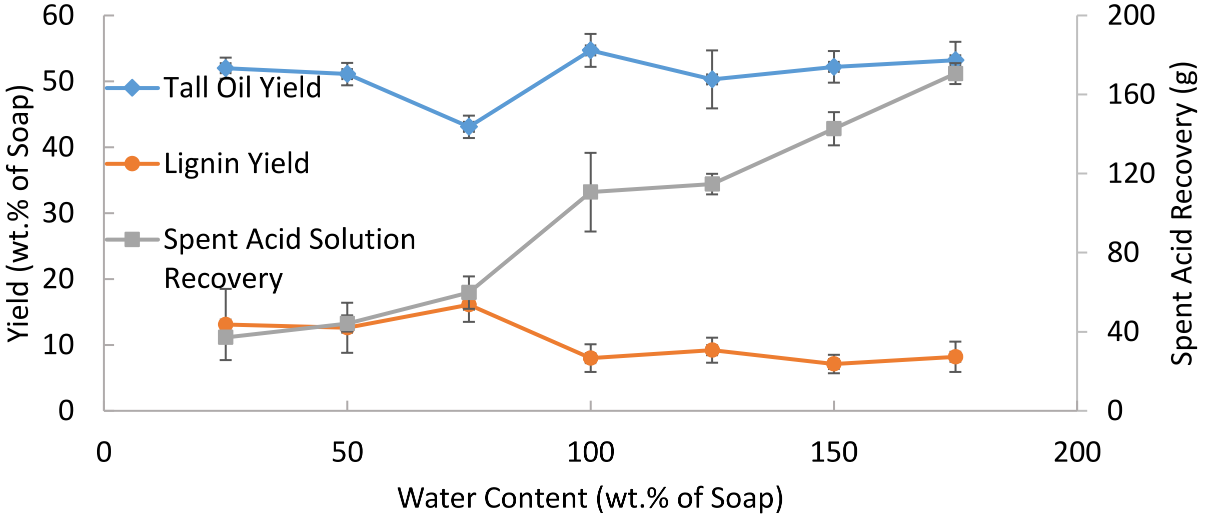

Figure 4.1. Yield of the layers of the crude tall oil optimization reaction varying water content at a temperature of 90 – 100 °C, pH of 3.0 – 3.5, reaction time of 30 min, and a settling time of 2 h.

Figure 4.2 presents the acid number of each of the crude tall oil samples produced while varying the water content of the reaction. It is important to note that the samples were washed with water to a neutral pH (5.5 – 7.0 [PCTM Standard 6, 1996]); therefore, Figure 4.2 accurately depicts the amount of acid contained in the sample. There is a slight peak at a 100 wt.% water to an acid number of 139 mg KOH/g oil, which marks the maximum value of acid number for these products. While the range is small, between approximately 133 and 139 mg KOH/g oil, there is a notable increase to consider this an optimized value. Typical global acid numbers of crude tall oil range from approximately 128 – 174 mg KOH/g oil (Panda, 2013; Hampton, 1962), and therefore the values obtained are within the range. The northern USA and Canadian values of acid number range from 125 – 135 mg KOH/g oil, so the quality of the present oil is higher than that of samples from similar locations (Foran, 1992; Fuenzalida et al., 2005). Thus, aside from concurrent optimization reactions (as previously stated), it is confirmed that 100 wt.% H_2O will be used in later experimentation, as it produces the best quality tall oil in terms of acid number as well as yield. This is increased over other industrial values of 30 wt.% H_2O and 75 wt.% H_2O (Resolute Forest Products, 2016; PCTM Standard 6, 1996).

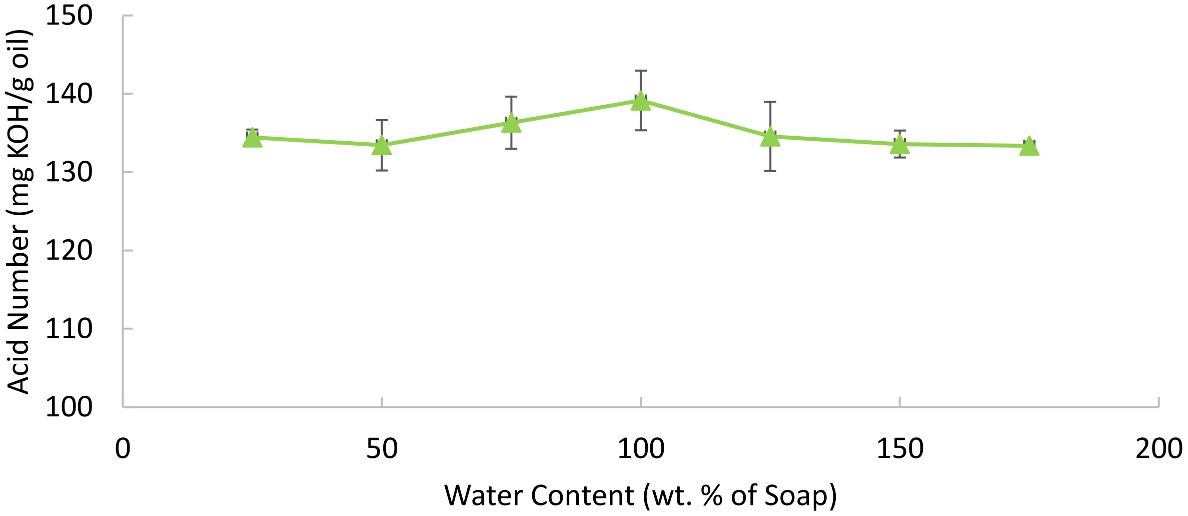

Figure 4.2. Acid number of crude tall oil samples produced by varying the water content of the reaction, with a temperature of 90 – 100 °C, pH of 3.0 – 3.5, reaction time of 30 min, and a settling time of 2 h.

In addition, the components of the tall oil products were determined. These included fatty acid content, rosin acid content, unsaponifiables, and moisture content. Figure 4.3 depicts these values while altering water content. It is shown that there are no appreciable changes in any of the values for these properties of the crude tall oil. As these properties typically depend on the type and source of wood, they are not expected to change dramatically as the water content is changed (Panda, 2013). However, there is a slight increase in unsaponifiable content at a 100 wt.% H_2O to 17.8 wt.%. Unsaponifiables are the undesired portions of tall oil, as they are not as valuable as the acids following further refinement. Interestingly, also at a 100 wt.% water addition, the acid number is at a maximum (Figure 4.2). It would be expected that the acid number and unsaponifiables would have an inversely proportional relationship – as unsaponifiables increase, acid content decreases, and as such acid number would decrease as well. However, this is not the case, as noted by Figures 4.2 and 4.3. Further analyzing Figures 4.2 and 4.3, it can be observed that the fatty acid content decreases slightly to 57.7 wt.% at 100 wt.% H_2O, while the rosin acid content increases to 23.3 wt.%. This may account for the direct proportionality observed between unsaponifiables and acid number. Finally, the moisture content of all of the samples is approximately 1.2 wt.%, with very slight deviations; this is typical of tall oils, as moisture contents range from 0.3 – 2.7 wt.% (Panda, 2013).

The values obtained for most constituents of the crude tall oil produced were on the higher end of the typical ranges found in literature. Fatty acids were in the range of approximately 57 – 60 wt.%, whereas literature values vary from 32 – 67 wt.%, largely dependent on the wood species and location (Lappi and Alén, 2011; Wansbrough, 2008; Hampton, 1962, Aro and Fatehi, 2017a, Panda, 2013). More specifically, tall oil from northern USA and Canada typically contains 50 – 60 wt.% fatty acids, which closely resembles the values for the tall oil tested presently (Foran, 1992). Rosin acids (22 – 24 wt.%) were actually outside of the lower range of global literature values for tall oil, typically in the range of 27 – 67 wt.% (Lappi and Alén, 2011; Wansbrough, 2008; Hampton, 1962, Aro and Fatehi, 2017a, Panda, 2013). Once again, typical northern USA and Canada tall oils vary slightly from global averages mentioned above (25 – 35 wt.%), though the presently tested samples are still not contained in this range from literature (Foran, 1992). However, as previously mentioned, tall oil composition ranges dramatically; the storage time of the wood prior to pulping may have also negatively impacted the rosin acid contents (Panda, 2013). Unsaponifiables (16 – 18 wt.%) were on the higher end of literature values, typically 7 – 20 wt.% worldwide and only up to 18 wt.% in North America (Lappi and Alén, 2011; Wansbrough, 2008; Hampton, 1962, Aro and Fatehi, 2017a, Panda, 2013; Koski, 2008; Foran 1992).

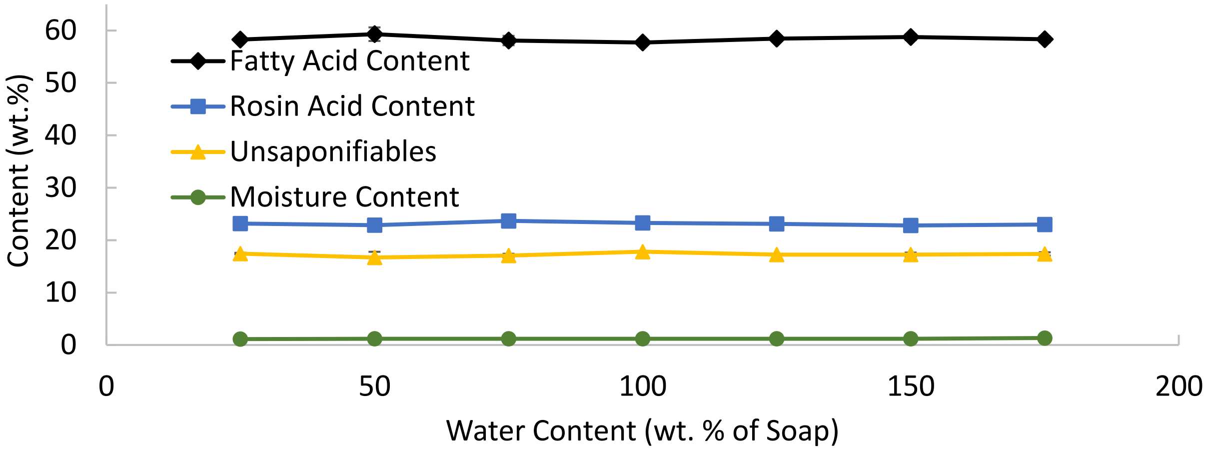

Figure 4.3. Fatty acid, rosin acid, unsaponifiable, and moisture content of crude tall oil with varying water contents, produced at a pH of 3.0 – 3.5, reaction time of 30 min, settling time of 2 h, and a temperature of 90 – 100 °C.

4.4.2. Reaction pH

The reaction pH was also varied in the production of tall oil. For these reactions, the other parameters included 100 g of soap, 50 wt.% water addition, 30 min of reaction time, and 2 h of settling time. Figure 4.4 shows the yields associated with varying the pH of the reaction; a 0.5 range of pH values is used for each level of acidification, as this is performed in industry (Resolute Forest Products, 2016; PCTM Standard 6, 1996).

The yield of crude tall oil increases overall from 49.8 wt.% at pH 5.5 – 6 to 56.1 wt.% at pH 2.0 – 2.5. Crude tall oil yield has been shown to decrease with lower amounts or concentrations of acid (Finer and Timonen, 2017). Analyzing the yields alone, the lowest pH range seems to give the highest crude tall oil yield. However, a greater amount of acid addition may decrease oil quality through polymerization, decarboxylation, and esterification; and therefore, other characteristics must be analyzed before selecting an optimal pH range (Resolute Forest Products, 2016; Wansbrough, 2008). The spent acid recovery is generally consistent around 52 g while varying the reaction pH, with a slight decrease in the range of pH 4.5 – 5.0 to 50 g. The lignin yield varies substantially between 7 and 13 wt.% when the reaction pH changes. It would be expected that the lignin yield would increase with an increase in reaction pH due to increased lignin precipitation nearer to neutral pH values, however, this trend was not observed overall (Zhu, 2013). One explanation for the variation in lignin yields with respect to pH ranges could be that sulfonation of lignin occurred, which would change the hydrophilicity and hence precipitation values of the lignin (Dilling, 1991; Aro and Fatehi, 2017b). This would cause a decrease in insoluble lignin at lower values of pH, increasing spent acid recovery and decreasing lignin yield as observed.

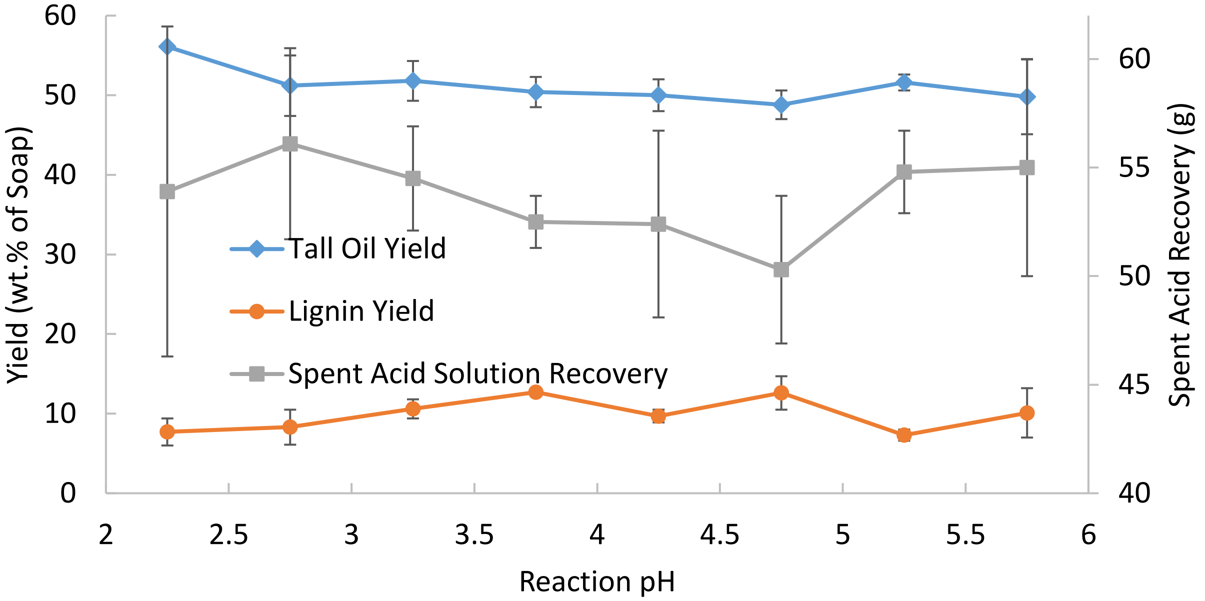

Figure 4.4. Yield of the layers of the crude tall oil optimization reaction varying reaction pH at a temperature of 90 – 100 °C, water content of 50 wt.%, reaction time of 30 min, and a settling time of 2 h.

Figure 4.5 shows the acid number of the washed crude tall oil samples when reaction pH was varied. Following the large increase in the acid number between pH 5.5 – 6.0 and pH 5.0 – 5.5, the values of the acid number are fairly consistent at the remaining pH ranges, between 134 and 137 mg KOH/g oil. The decrease in acid number at high pH values correlates to a decreased conversion of soap to oil and thus decreased quality (Finer and Timonen, 2017). Contrary to potential decarboxylation or esterification occurring with a decrease in pH, there was no significant decrease in the acid number of the samples, which would indicate side decomposition reactions occurring (Resolute Forest Products, 2016). The acid number of 2.0 – 2.5 pH range was 136 mg KOH/g oil, slightly below 2.5 – 3.0 pH range value of 137 mg KOH/g oil. Alongside this acid number and good yield of crude tall oil, it was decided that the pH range of 2.5 – 3.0 will be used for future experiments rather than pH 2.0 – 2.5. This pH range is also within typical values for industrial applications, and would decrease chemical costs due to lower sulfuric acid requirements (Resolute Forest Products, 2016; PCTM Standard 6, 1996). Increased pH ranges were not used as these would result in lower yields, incomplete reactions, and lower oil quality, which would negatively impact the economics of the process. Once again, the values of acid number for the present samples (134 – 137 mg KOH/g oil, excluding highest pH range values) were slightly above literature values of northern USA and Canadian tall oil acid numbers, ranging from 125 - 135 mg KOH/g oil (Foran, 1992; Fuenzalida et al., 2005).

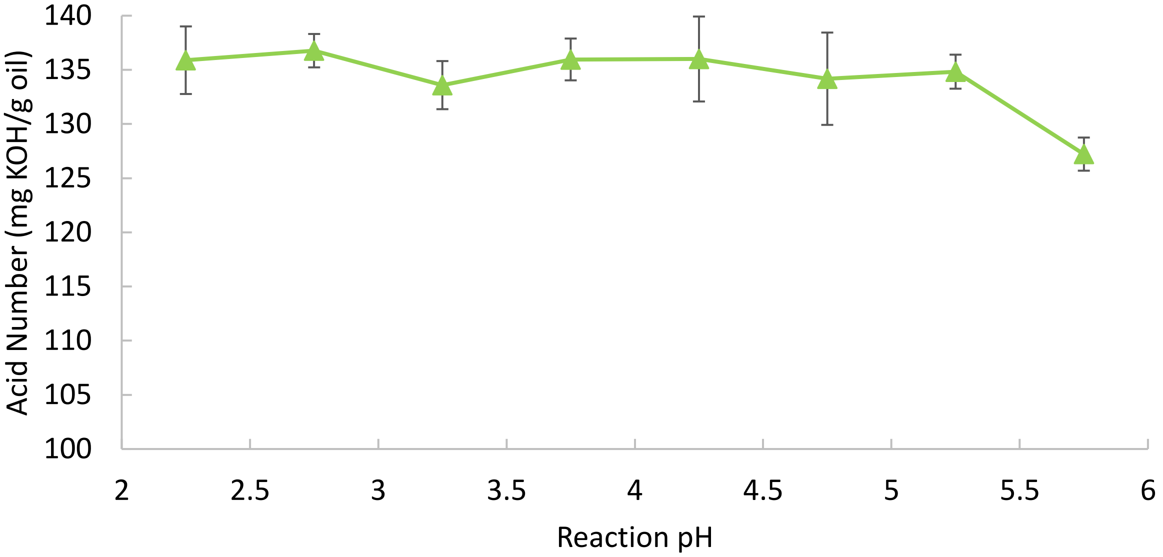

Figure 4.5. Acid number of crude tall oil samples produced by varying the pH of the reaction, with a temperature of 90 – 100 °C, water content of 50 wt.%, reaction time of 30 min, and a settling time of 2 h.

Once again, the rosin acid, fatty acid, unsaponifiables, and moisture content were also determined for the pH variant reactions and shown in Figure 4.6. The fatty acid values for all conditions range from approximately 58 to 60 wt.%, not showing a large deviation for any pH range. The lack of changes is also observed for rosin acids for the samples, ranging from 20.8 wt.% at pH 4.5 – 5.0 to 23.3 wt.% at pH 2.5 – 3.0. Again, the fatty acid content is within literature values previously stated, meanwhile the rosin acid values are below the typical values observed both globally and in northern USA and Canada (Foran, 1992; Lappi and Alén, 2011; Wansbrough, 2008; Hampton, 1962, Aro and Fatehi, 2017a, Panda, 2013). The unsaponifiables range from approximately 16 – 18 wt.% as expected. The moisture content of the samples was the greatest at higher pH values (2.27 wt.% at pH 5.5 – 6.0) and decreased to 1.17 wt.% at the chosen range of 2.5 – 3.0. This increase in moisture content at higher values of pH may have accounted for the yields of these samples being similar to lower pH samples; less soap reacted to form oil at a higher pH, though the yields were still similar throughout. In addition, unreacted soap may have been entrained in the oil layer with lower levels of acidulation due to fractionation issues, giving false values of yield (Resolute Forest Products, 2016).

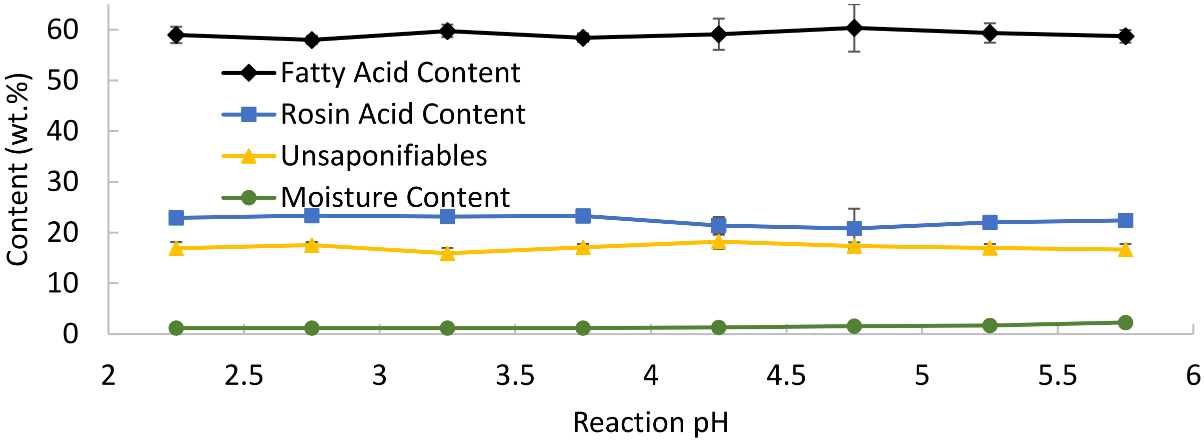

Figure 4.6. Fatty acid, rosin acid, unsaponifiable, and moisture content of crude tall oil with varying pH values, produced with 50 wt.% water, reaction time of 30 min, settling time of 2 h, and a temperature of 90 – 100 °C.

4.4.3. Reaction time

The next reaction parameter analyzed was reaction time. Reaction time began as soon as all reactants were added to the reaction vessel and ranged from 10 to 40 min in 10 min increments. Figure 4.7 outlines the resulting yields of varying reaction time, with 100 g tall oil soap, pH 2.0 – 2.5, 150 wt.% water, temperature of 90 – 100 °C, and settling time of 2 h. The lower pH range and increased water content were used in this case as it was done concurrently with the previously outlined tests, prior to completing optimization and characterization.

Figure 4.7 shows that the oil yield for the reaction time variation is fairly consistent, between roughly 54 and 57 wt.% of soap added. A slight increase occurred at 30 min reaction time, resulting in an oil yield of 57.1 wt.%. The spent acid recovery decreased from approximately 184 to 171 g, which was not an appreciable difference as it was less than 10 %. The lignin yield varied between 9 and 12.5 wt.%, following an overall increasing trend from 10 to 40 min reaction time. It would be expected that as reaction time increases, the lignin in solution would have more time to react with the sulfuric acid, thus increasing the sulfonation of the lignin and increasing its solubility at lower values of pH, hence decreasing its yield (Aro and Fatehi, 2017b). However, this was not the case, as yield increased with reaction time. Ultimately, this information alone was not enough to decide on a reaction time that produced the optimized results.

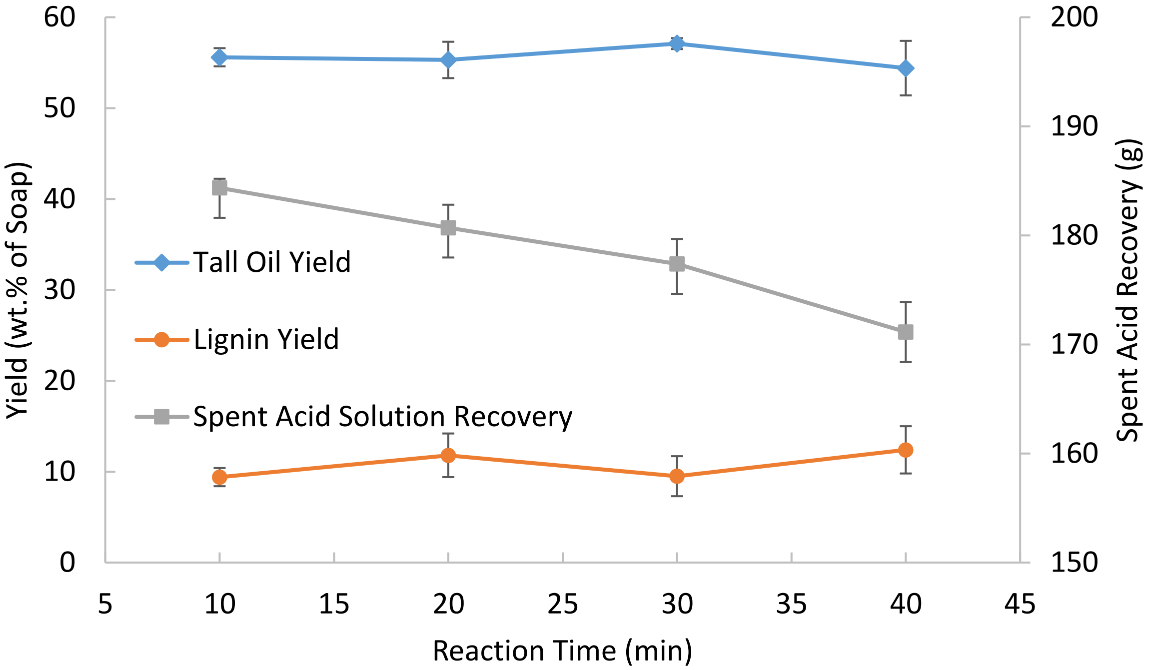

Figure 4.7. Yield of the layers of the crude tall oil optimization reaction varying reaction time at a temperature of 90 – 100 °C, pH of 2.0 – 2.5, water content of 150 wt.%, and a settling time of 2 h.

Acid number was also analyzed for the optimization of reaction time and the results are shown in Figure 4.8. As can be seen, there is not a large variance in acid number, from 133 to 137 mg KOH/g oil. The maximum value occurred at 20 min reaction time. Therefore, the selected optimized time was 20 min to be used alongside previously determined optimized conditions. The values for acid number for these conditions were on the upper end of the range for northern USA and Canadian values, which typically range from 125 – 135 mg KOH/ g oil (Foran, 1992). In addition to the yield and acid number information, selecting a decreased reaction time aids in economic value of the production process. This draws on heuristic design information for sizing reactors, where reaction (residence) time is first chosen and has direct impacts on reactor size and cost (Silla, 2003). Decreasing reaction time also allows for increased numbers of reactions to be carried out by reducing overall batch time.

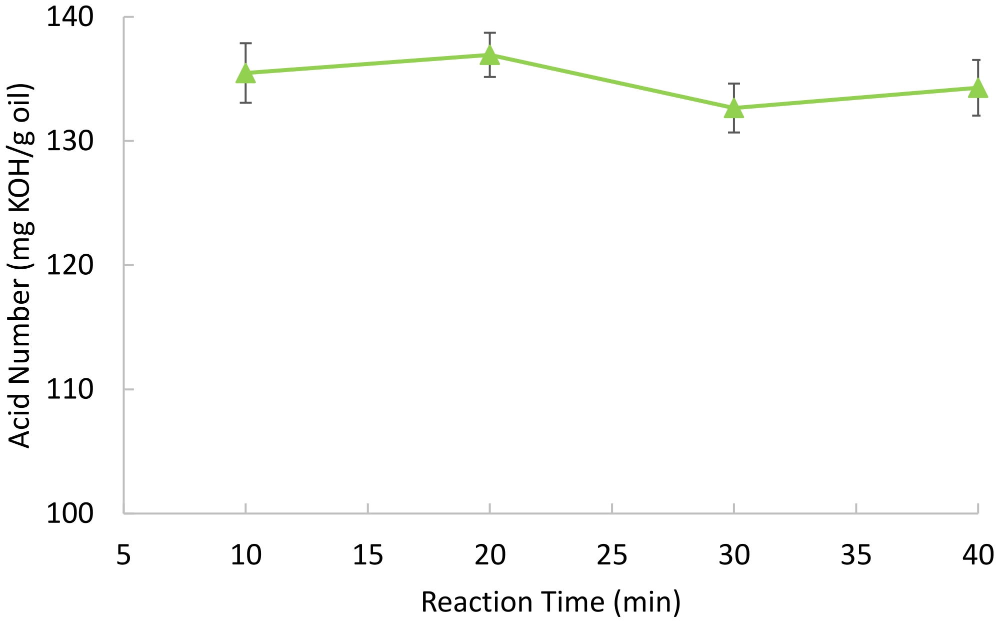

Figure 4.8. Acid number of the crude tall oil optimization reaction varying reaction time at a temperature of 90 – 100 °C, pH of 2.0 – 2.5, water content of 150 wt.%, and a settling time of 2 h.

Figure 4.9 provides the values of fatty acid, rosin acid, unsaponifiables, and moisture content of the crude tall oil products resulting from varying the reaction time. There was little to no deviation in these values regardless of reaction time. The fatty acid content ranged from 54.8 to 55.9 wt.%, the rosin acid increased from 23.4 to 24.5 wt.%, and the unsaponifiables slightly changed from 19.2 to 19.6 wt.%. The moisture content was nearly unchanged; a maximum value at 40 min was 1.22 wt.% and a minimum value at 1.16 wt.% was obtained for both 10 and 20 min reaction times. However, the slight increase in moisture content within the tall oil samples overall may account for part of the decreased spent acid yield observed in Figure 4.7; some of the water in solution may have been entrained into the oil. All of these values were similar to previous values; only the rosin acid content was outside the acceptable ranges, as observed in previous reactions (Lappi and Alén, 2011; Wansbrough, 2008; Hampton, 1962, Aro and Fatehi, 2017a, Panda, 2013; Koski, 2008; Foran, 1992).

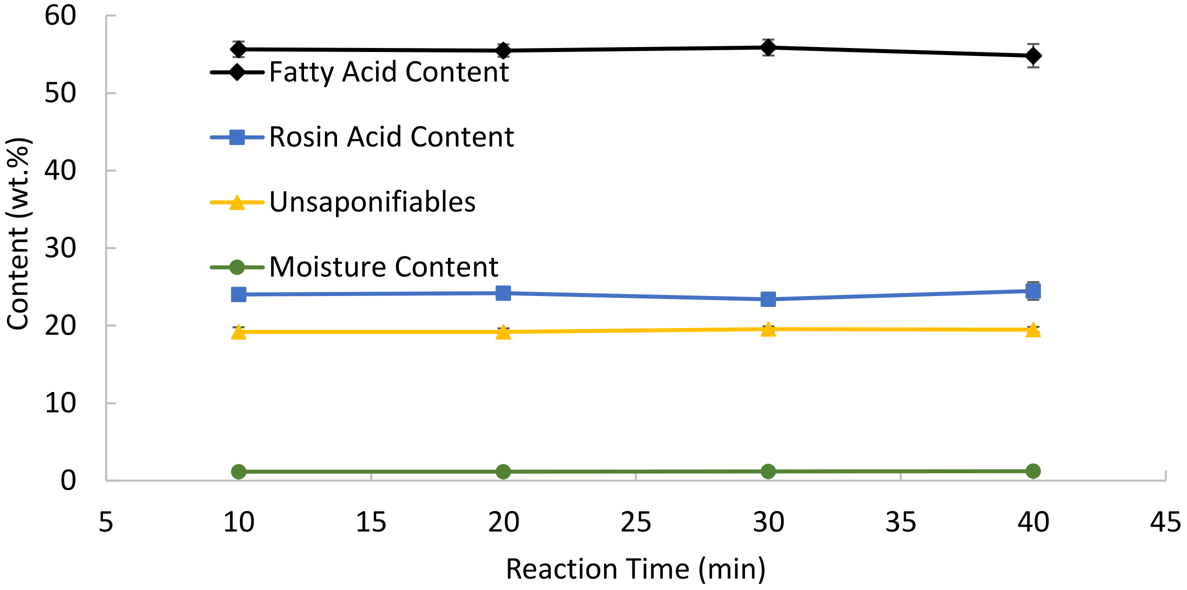

Figure 4.9. Fatty acid, rosin acid, unsaponifiables, and moisture content of the crude tall oil optimization reaction varying reaction time at a temperature of 90 – 100 °C, pH of 2.0 – 2.5, water content of 150 wt.%, and a settling time of 2 h.

4.4.4. Settling additives

Settling additives are used to increase the separation efficiency during settling following crude tall oil production, in order to aid decanting the tall oil. Additives are typically water-soluble and anionic, and can include naphthalene sulfonates or lignin derivatives for example (Hart, 1998; Sadler, 1957). However, kraft lignin is anionic (Oveissi and Fatehi, 2015). Cationic additives would be expected to neutralize the charge of lignin and result in hydrogen bonding, flocculation formation, and settling (Oveissi and Fatehi, 2015; Wang et al, 2016). Thus, some alternative cationic settling aids were analyzed. Additives are applied as a solution into the bulk reaction mixture; however, the dosage must be calculated on a dry basis. For example, in terms of the Infinity^{TM} additive, the solids concentration was determined to be 37.2 wt.%. The wet dosage of the settling additives was 0.01, 0.02, 0.03, 0.04, and 0.05 wt.% of soap added. On a dry basis, this equates to approximately 0.00372, 0.00744, 0.0112, 0.0149, and 0.0186 wt.% of soap (100 g soap addition). Table 4.1 outlines the properties of each of the settling additives employed in the following sections.

Table 4.1. Properties of tall oil settling additives.

Additive	**Concentration (wt.%)**	**Charge density (mmol/g)**	**Molecular weight (g/mol)**
Infinity^{TM} PS 3040 Pulp Processing Aid	37.2 ± 0.2	-4.73 ± 0.03	$7.00 \pm 0.25 \times 10^4$
Xylan-AETAS-APS	37.2	3.81	1.26×10^5
DMC-HL10	37.3	3.47	3.2×10^4

4.4.4.1. Infinity^{TM} PS 3040 pulp processing aids

The first settling additive studied was the Infinity^{TM} PS 3040 Pulp Processing Aid. Figure 4.10 provides the yields of the layers following the production of crude tall oil using the optimized conditions of 100 g soap, 100 wt.% water, pH 2.5 – 3.0, reaction time 20 min, and settling time 2 h. The Infinity^{TM} additive dosage was 0, 0.0043, 0.0077, 0.0115, 0.0152, and 0.0185 wt.% on a dry basis, corresponding to 0, 0.01, 0.02, 0.03, 0.04, and 0.05 wt.% (of tall oil soap) on a wet basis. It can be seen that as the dosage increases, the tall oil yield increases after an initial decrease compared to no additive. A similar trend is observed for the lignin yield; the lignin yield decreases overall following an increase compared to using no additive. The oil yield increases from roughly 47 to 57.1 wt.%, with a maximum value at 0.0185 wt.% dry dosage (approximately 0.05 wt.% wet basis); the oil yield with no additive was found to be 52.8 wt.%. The lignin yield decreases from 18.6 wt.% to 8.3 wt.% as dosage increases, compared to a yield of 11.8 wt.% without additive. The reason for this initial comparative increase may be that at lower concentrations, the charges introduced by the settling additive are insufficient to impact the charges present within the lignin layer, which inhibit the ability of settling (Oveissi et al., 2016). The spent acid recovery remains roughly constant around 127 g, similar to the value obtained without the settling additive, showing that the settling additive mainly supports the separation of oil from lignin. Literature has shown that the addition of as little as 0.0025 wt.% (dry basis) additive with a large molecular weight (greater than 1000 g/mol) and charge increased the settling efficiency of crude tall oil over 2 h from 12 % to 31 % (Patrick, Jr and Thomas, Jr, 1974). The lignin layer volume decreased from 20 to 5 % over the same time and same basis in the study, thus corroborating the results obtained with the Infinity^{TM} settling aid (Patrick, Jr and Thomas, Jr, 1974). It was stated that lignin was present in the crude tall oil layer at the interface between the layers, which explains why the lignin yield would decrease. As settling improves with the use of the Infinity^{TM} aid, the total amount of the lignin emulsion layer decreases due to a decreased amount of entrained oil (Patrick, Jr and Thomas, Jr, 1974). However, these studies were conducted with cationic samples; as such, cationic settling aids will be analyzed and compared to the anionic Infinity^{TM} aid in following sections. Furthermore, lignin produced from the kraft pulping process, as is the case in the tall oil samples, has an increased amount of phenolic hydroxyl groups as a result of the pulping process (He and Fatehi, 2015). Phenolic hydroxyl groups carry a negative charge, which may be intensified by the anionic settling aid (Paradies, 1995; Hart, 1998). As a result of the increased overall charge, improved separation between the lignin and tall oil is observed (Hart, 1998); however, cationic settling additives may impact settling of the lignin layer due to adsorption and flocculation more significantly. While in the case of the Infinity^{TM} additive, the highest dosage of additive produces the most oil, it may not be economical on a large scale or produce the highest quality oil; thus, further analysis must be done to determine the optimal value of dosage.

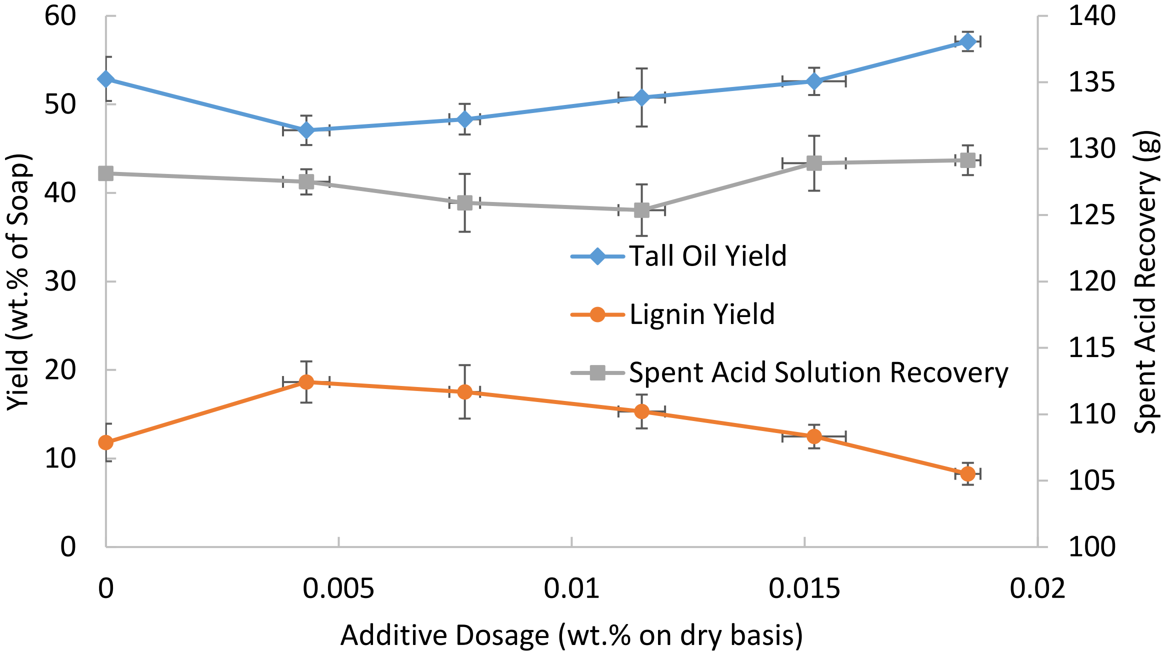

Figure 4.10. Yield of the layers of the crude tall oil optimization reaction varying the amount of settling additive InfinityTM PS 3040 Pulp Processing Aid at a temperature of 90 – 100 °C, pH of 2.5 – 3.0, water content of 100 wt.%, and a settling time of 2 h.

The acid number of the oil samples produced with settling additive usage were determined and presented in Figure 4.11. The acid numbers of the samples are fairly consistent, ranging from 137 – 142 mg KOH/g oil, increasing overall as the settling aid dosage increases. Once again, the acid number is the greatest with the highest dosage of settling additive using the Infinity-brand product. The acid numbers using this settling additive are slightly greater than those without the additives, displayed in previous sections as well as in the first data point of Figure 4.11 (137 mg KOH/g oil). The previously reported values of acid number during optimization trials are in the range of approximately 127 – 139 mg KOH/g oil, with no acid numbers above 140 mg KOH/g oil. The values for acid number using the Infinity^{TM} aid are also greater than literature values for northern USA and Canada crude tall oil (125 – 135 mg KOH/g oil) (Foran, 1992). It is apparent that employing a settling additive not only increases the yield of the oil produced by the reaction at optimum conditions of 0.0185 wt.% (dry basis) (Figure 4.10), but also increases the quality of the oil in terms of acid number (Figure 4.11). This was also observed by Patrick, Jr and Thomas, Jr (1974) when employing a settling additive in comparison to no additive. A possible reason for this increase in quality is that without the settling additive, lignin will entrain lower quality oil within the oil layer, “pitch,” thereby lowering the acid number and overall quality (Patrick, Jr and Thomas, Jr, 1974). With better separation of lignin, this phenomenon is not observed.

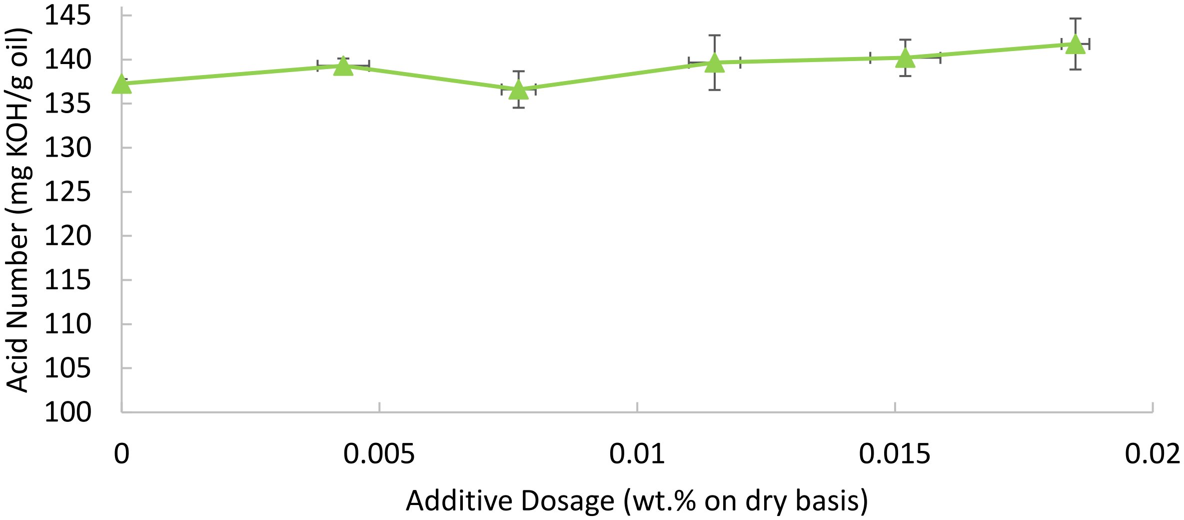

Figure 4.11. Acid number of the crude tall oil optimization reaction varying the amount of settling additive InfinityTM PS 3040 Pulp Processing Aid at a temperature of 90 – 100 °C, pH of 2.5 – 3.0, water content of 100 wt.%, and a settling time of 2 h.

Figure 4.12 outlines each of the constituents of the tall oil products involving the Infinity^{TM} settling additive. The fatty acid content of each of the samples is approximately 57 wt.%, with a maximum value of 57.6 wt.% at a dosage of 0.0152 wt.% (dry basis). Once again, this value is similar to the previous tests conducted on the oil samples produced, as well as the sample with no additive. The rosin acids range from 22.5 wt.% to a maximum of 23.9 wt.% at 0.0115 wt.% (dry basis) settling additive; without additive, the rosin acid content is slightly lower, at 22.7 wt.%. Interestingly, the unsaponifiables content at this dosage of 0.0115 wt.% (dry basis) is at the minimum for all tested samples; a value of 18.0 wt.%. As unsaponifiables content decreases, the undesirable portion of the oil also decreases, expecting an increase in oil quality. However, the acid number at this dosage is an average value. The values for fatty and rosin acid contents, as well as unsaponifiables, are similar to literature values, though the unsaponifiables (18 – 19 wt.%) are on the high end the observed range for northern USA and Canadian values of 12 – 18 wt.% and the rosin acids are slightly below the range of 25 – 35 wt.% (Lappi and Alén, 2011; Wansbrough, 2008; Hampton, 1962, Aro and Fatehi, 2017a, Panda, 2013; Koski, 2008; Foran, 1992). The moisture content of the samples is low once again, between 1.07 and 1.64 wt.%, with the maximum at 0.0115 wt.% (dry basis) settling additive dosage (0.03 wt.% wet basis). This may account for the median value of acid number (indicator of oil quality) discussed previously, as increased water content would result in decreased quality.

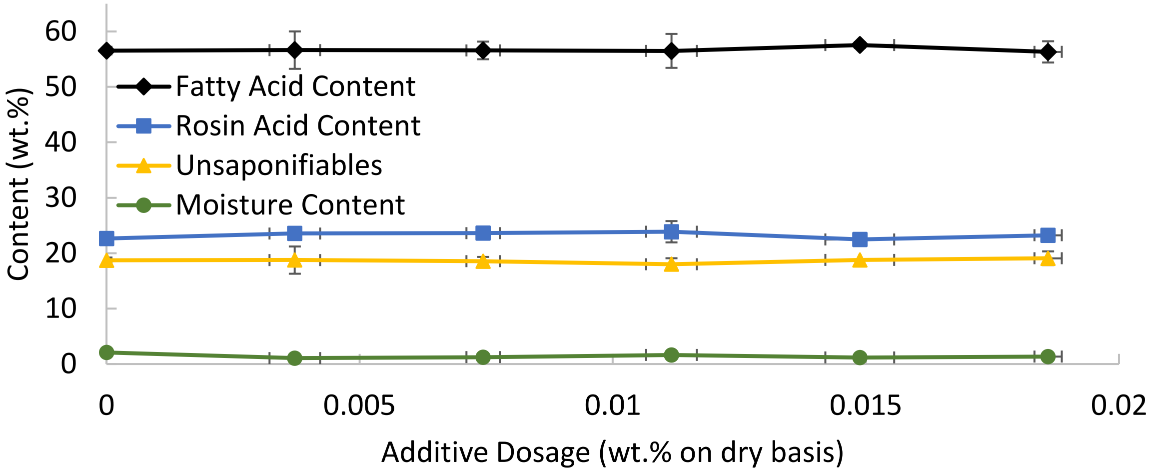

Figure 4.12. Fatty acid, rosin acid, unsaponifiables, and moisture content of the crude tall oil optimization reaction varying the amount of settling additive InfinityTM PS 3040 Pulp Processing Aid at a temperature of 90 – 100 °C, pH of 2.5 – 3.0, water content of 100 wt.%, and a settling time of 2 h.

4.4.4.2. Xylan-AETAS-APS

The next settling aid employed was a xylan copolymer with a cationic charge density of approximately 3.8 mmol/g and a molecular weight of approximately 126,000 g/mol, used to produce a solution with a concentration of 37.2 wt.%. Xylan is a natural polymer produced from the prehydrolysis liquor of the kraft-based dissolving pulp process and corn cobs, among other methods, and has been functionalized to produce copolymers in the past for use as flocculants (Wang et al., 2016; da Silva et al., 2012). Xylan is highly abundant and underused, which increases its desire for flocculation purposes (Konduri and Fatehi, 2017a). AETAS was used as the reagent, also known as [2-(methacryloyloxy)ethyl] trimethylammonium methylsulfate, with ammonium persulfate (APS) as the initiator. AETAS is a type of quaternary ammonium methacrylate (QAM) which has been found to inhibit the degradation, thereby increasing stability, of the molecules to which it has been bound while maintaining the high reactivity and solubility of the molecule (Fuller et al., 1980; Tezvergil-Mutluay et al., 2011). In this case, AETAS aided in increasing the stability of xylan under conditions such as increased temperature where it may otherwise degrade and become inactive. Figure 4.13 provides the yields of the layers following the production of crude tall oil using the optimized conditions of 100 g soap, 100 wt.% water, pH 2.5 – 3.0, reaction time of 20 min, and settling time of 2 h, with varying dosages of the xylan copolymer settling aid. Once again, the exact dosage of the xylan copolymer is 0, 0.0037, 0.0073, 0.0111, 0.0148, and 0.0186 wt.% on a dry basis. Using the 37.2 wt.% solution, these correspond to approximately 0, 0.01, 0.02, 0.03, 0.04, and 0.05 wt.%.

Figure 4.13 shows that the yield of crude tall oil varies from approximately 46 wt.% to 53.7 wt., with a maximum yield of crude tall oil at 0.01109 wt.% (dry basis), or approximately a 0.03 wt.% dosage on a wet basis. The maximum oil yield when employing the Infinity^{TM} settling additive was approximately 57 wt.%, however this occurred at a maximum dosage of 0.05 wt.% (wet basis). At the same dosage of 0.03 wt.% (wet basis), the xylan additive outperforms the Infinity^{TM} additive 53.7 wt.% to 50.8 wt.%; this is a similar dosage to that used in industry (Resolute Forest Products, 2016). Without additive, the oil yield was 52.9 wt.%, showing a slight improvement in settling efficiency when employing the xylan copolymer additive. The lignin yield is overall largely increased in comparison to the Infinity^{TM} brand aid (8 – 18 wt.%) as well as sample without additive (11.8 wt.%), varying from 16 – 21 wt.%. There is no apparent trend in the lignin yields within the additive-containing samples besides the overall increase compared to no additive. This may be as a result of an opposite charge density of the xylan copolymer in comparison to the Infinity^{TM} aid. As shown in Table 4.1, the charge density of the Infinity aid is approximately -4.7 mmol/g, whereas the xylan-AETAS-APS is approximately 3.8 mmol/g. Since kraft lignin has slightly anionic properties, and tall oil lignin is also shown to be anionic (see Section 4.6), it would be expected that the cationic xylan copolymer would have an increased impact on separation efficiency (He and Fatehi, 2015; Paradies, 1995; Patrick, Jr and Thomas, Jr; 1974). However, the yield of lignin using the xylan copolymer is larger than when employing the Infinity^{TM} aid, which is in conjunction with the report from Hart (1998) and not Patrick, Jr and Thomas, Jr (1974). Patrick, Jr and Thomas, Jr (1974) reported that a positive charge in particular decreased the lignin layer volume and increased crude tall oil settling; however, it is shown here that an anionic charge more strongly impacts tall oil settling. In addition, the large molecular weight of the xylan copolymer, 126,000 g/mol, compared to the Infinity^{TM} additive, 70,000 g/mol, may have resulted in dispersion properties rather than flocculant. There is a large influence between molecular weight, solution pH, dosage, and the presence of other constituents which may have ultimately led to reduced flocculating and settling abilities of the xylan on the solution (Konduri and Fatehi, 2017b). In addition, the molecular weight of a polymer may result in the flocculation of one particle size, whereas it will result in the dispersion of another particle size; this may have been the result in this case (Crowl, 1967). The combined application of xylan as both flocculants and dispersants may have negatively impacted settling results in this case (Konduri and Fatehi, 2017a,b).

The acid recovery ranges from roughly 116 – 125 g, with the minimum of 115.8 g occurring at a dry dosage of 0.01109 wt.% (0.03 wt.% wet basis). Thus, the maximum oil yield was observed at the same dosage as the minimum acid yield. This could indicate that the xylan copolymer aids in settling by increasing the amount of oil removed from the total solution, not by settling lignin from the oil layer (such as observed by the Infinity^{TM} aid). This is also observed when analyzing the trends of the additive-containing samples compared with trials which do not contain additive. There is an overall decrease in the acid recovery and increase in lignin yield when the xylan-copolymer additive is used. Elaborating from above, the conclusion from this observation is that the additive aids in the settling of the oil from the overall mixture; however, the settling efficiency of the acid and lignin is negatively impacted. That is, there is more acid entrained in the lignin emulsion layer, which would result in an increase in the yield of the lignin layer and a decrease in the acid recovery layer, as displayed in Figure 4.13. This may be due to the emulsifying effects of lignin. Studies have found that lignin, even unmodified kraft lignin, have emulsion stabilizing effects (Rojas et al., 2007). On the other hand, modified xylan copolymers have also shown to exhibit surface-active properties (Ebringerová et al., 2005). These combined constituents may act on both the acid and any entrained oil in the lignin emulsion layer as stabilizers until the molecular weight and charge of the xylan copolymer is able to overcome the stabilizing forces and increase settling of lignin/water.

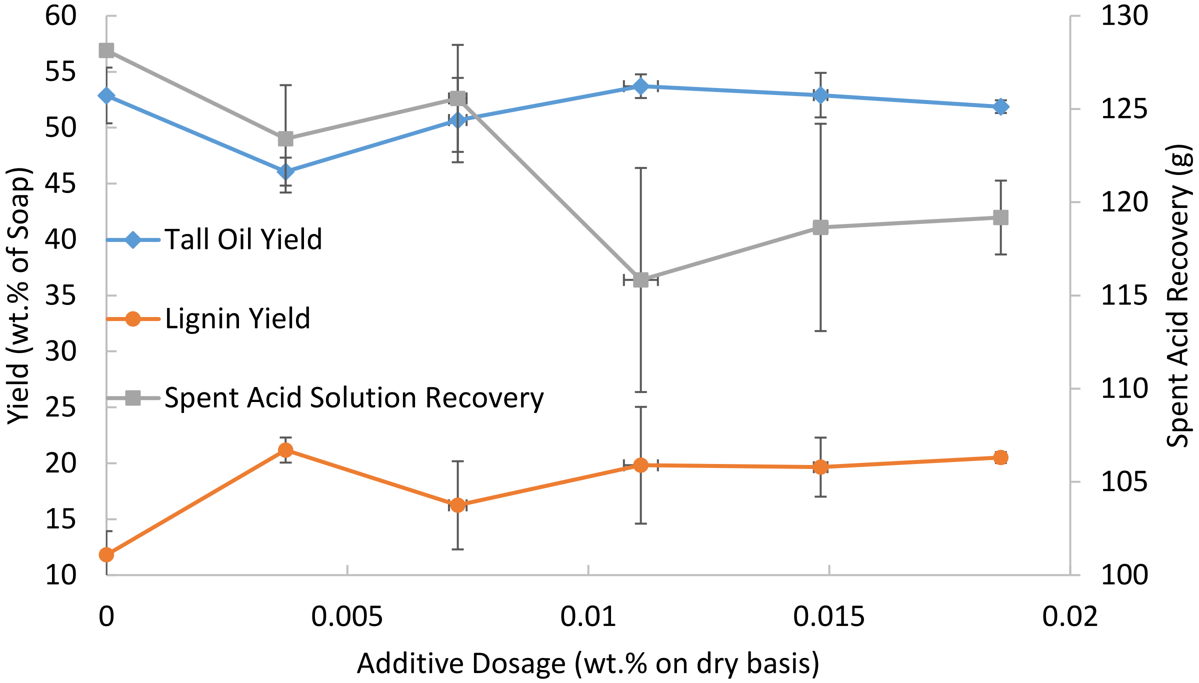

Figure 4.13. Yield of the layers of the crude tall oil optimization reaction varying the amount of settling additive Xylan-AETAS-APS at a temperature of 90 – 100 °C, pH of 2.5 – 3.0, water content of 100 wt.%, and a settling time of 2 h.

Figure 4.14 presents the acid numbers of the samples produced using the Xylan-AETAS-APS settling additive. The acid numbers for this aid are slightly lower than those using the Infinity^{TM} aid (139 – 141 mg KOH/g oil), ranging from 134 mg KOH/g oil at 0.01109 wt.% (0.03 wt.% wet) to 138 mg KOH/g oil at 0.00729 wt.% (0.02 wt.% wet). Thus, the additive dosage at which the oil yield is the greatest (0.03 wt.% wet) produces oil with the lowest quality in terms of acid number. In addition, the acid number of the sample without a settling aid (137 mg KOH/g oil) is slightly greater than the majority of the samples which do use the xylan settling aid. Overall, the acid numbers determined for these products are still slightly above average for northern USA and Canada crude tall oil values, typically 125 – 135 mg KOH/g oil (Foran, 1992).

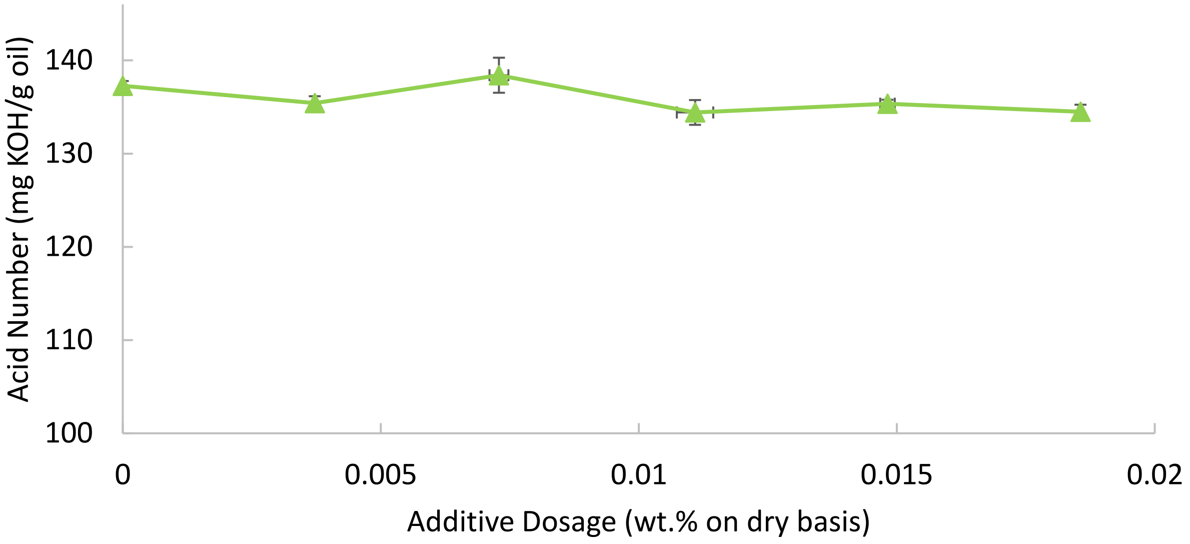

Figure 4.14. Acid number of the crude tall oil optimization reaction varying the amount of settling additive Xylan-AETAS-APS at a temperature of 90 – 100 °C, pH of 2.5 – 3.0, water content of 100 wt.%, and a settling time of 2 h.

The fatty acid, rosin acid, unsaponifiables, and moisture content of the samples produced with the xylan copolymer settling aid can be found in Figure 4.15. The fatty acid content varied slightly from 55.8 wt.% at 0.00372 wt.% dry (0.01 wt.% wet) to 57.5 wt.% at 0.01482 wt.% dry (0.04 wt.% wet). These values are within typical ranges for Canadian crude tall oil (Foran, 1992). The average fatty acid values for both the xylan copolymer (56.6 wt.%) and the Infinity™ additive (56.7 wt.%) were approximately the same. The rosin acid content of the samples using xylan setting additive, 22.0 – 22.8 wt.%, were significantly less than the literature values for Canadian crude tall oil of 25 – 35 wt.% (Foran, 1992). The average rosin acid content using the xylan copolymer was less than that using the Infinity™ additive by about 1 wt.%. This may have been due to phenolic substances within the xylan structure, which may have been more attracted to the aromatic carboxylic groups of rosin acids, causing interactions and the removal of a small amount of rosin acids from crude tall oil into the lignin emulsion layer (Wansbrough, 2008; Ebringerová and Hromádková, 1999). The unsaponifiables using xylan additive were slightly above range at 18.4 – 19.4 wt.%, and slightly higher than when Infinity™ settling additive was employed. This may have accounted for a decrease in acid number, as unsaponifiables do not contribute to oil quality. Finally, the moisture content for these samples was slightly higher than previous samples, potentially because of the xylan copolymer acting on the oil separation from the complete mixture, rather than oil from a specific component in the mixture. This may have contributed to the increased moisture contents in oil samples of 1.79 – 2.50 wt.%, which were also increased in comparison to the samples produced using the Infinity™ aid. Ultimately, it can be summarized that the use of the xylan-AETAS-APS copolymer for settling of tall oil results in decreased quality of oil; this can be attributed to a decrease in acid number (a major indicator of quality), as well as a decrease in rosin acid content and increase in unsaponifiables (neutral) content. The moisture content of the xylan-employing samples also increased slightly in comparison to the Infinity™ samples, which further follows the trend.

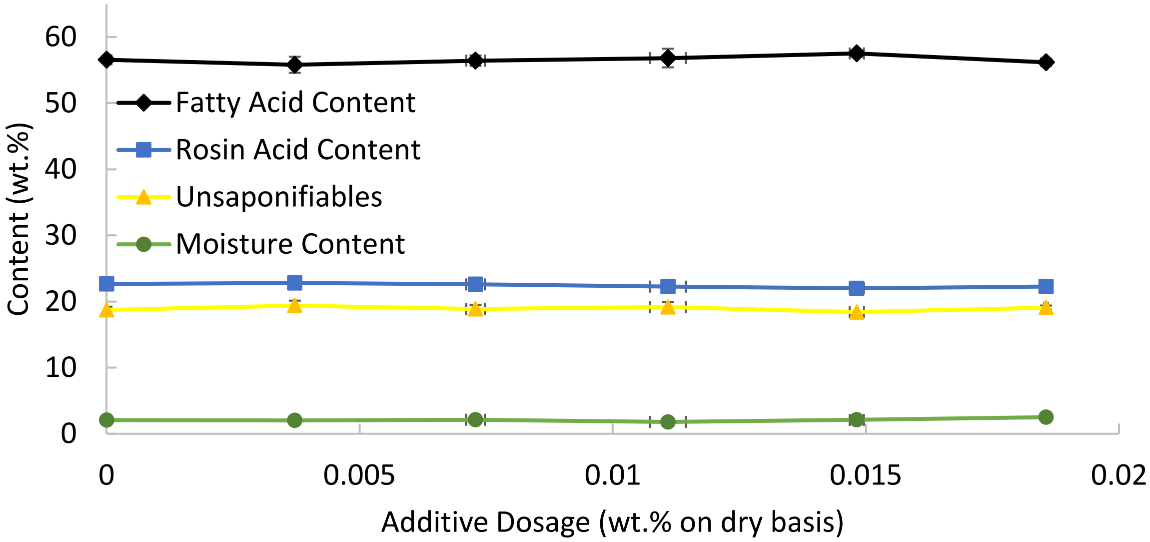

Figure 4.15. Fatty acid, rosin acid, unsaponifiables, and moisture content of the crude tall oil optimization reaction varying the amount of settling additive Xylan-AETAS-APS at a temperature of 90 – 100 °C, pH of 2.5 – 3.0, water content of 100 wt.%, and a settling time of 2 h.

4.4.4.3. DMC-HL10

The final settling aid employed for tall oil settling is DMC-HL10. This type of settling additive is an H-lignin-METAC copolymer. H-lignin is enzymatic hydrolysis lignin, which was provided by FPInnovations. Hydrolysis lignin has a condensed structure with limited reactivity and is produced as a by-product of the cellulosic ethanol industry (Mahmood et al., 2015; Matsushita and Yasuda, 2005; Yasuda and Asano, 2000). METAC stands for [2-(methacryloyloxy)ethyl] trimethylammonium chloride and is a quaternary ammonium methacrylate (QAM) with one ammonium group in the structure (Makino, 2002). METAC has been used to increase the flocculation efficiency of ineffective biopolymers, and as such was applied to lignin and used for the settling of crude tall oil in the past (Wang et al., 2016). The charge density of the H-lignin-METAC copolymer is approximately 3.5 mmol/g (Table 4.1), with a solubility of 70 %. Preliminary testing provided a molecular weight of approximately 32,000 g/mol. A solution of 37.3 wt.% was produced in order for addition to the crude tall oil production process. The dry dosages of the H-lignin-METAC copolymer are 0, 0.00368, 0.00739, 0.0112, 0.149, and 0.0186 wt.% (dry basis), which correspond to 0 to 0.05 wt.% inclusive on a wet basis.

Figure 4.16 shows the yields of crude tall oil and lignin emulsion layers, as well as the recovery of spent acid when employing the lignin-METAC copolymer as a settling additive. As can be seen, the oil yield is roughly consistent while varying doses, ranging from 51.0 wt.% at 0.0112 wt.% (dry dosage; 0.03 wt.% wet) to a maximum of 53.2 wt.% at 0.0149 wt.% (dry; 0.04 wt.% wet). Without additive, the yield of crude tall oil is 52.9 wt.%, which is increased in comparison to the averages when employing the lignin settling additive. On average, the yields using the DMC-HL10 additive (52.2 wt.%) are slightly larger than those using the xylan-AETAS-APS additive (51.1 wt.%) and Infinity^{TM} additive (51.2 wt.%). At the wet dosage of 0.03 wt.% as applied in industry, the xylan settling additive had the best yield (53.7 wt.%), and the Infinity^{TM} additive and lignin additive were similar at 50.8 wt.% and 51.0 wt.%, respectively. However, oil yield alone is not enough of an indicator to select an optimized dosage or additive type for crude tall oil settling. The lignin yield increases as H-lignin-METAC copolymer dose increases, from 11.8 wt.% without additive to 18.2 wt.% at the maximum dosage. This trend is similar to the one observed with the xylan copolymer and opposite to that of the Infinity^{TM} additive. Since the H-lignin-METAC copolymer is less cationic than the xylan copolymer (Table 4.1), more of the polymer may be required to overcome the anionic strength of the lignin in the emulsion layer; this amount may not have been sufficient at lower dosages to result in a decrease in the lignin emulsion layer yield (Oveissi et al., 2016). If the charge of the settling aid was not sufficient to overcome the total charge of the layer, more acid may have been entrained in the layer as well, resulting in a further increase in the yield of the lignin emulsion layer as observed. Once again, it can be seen that the yields of the cationic lignin copolymer are lower than the anionic Infinity^{TM} settling aid; this is in conjunction with the information reported by Hart (1998), that anionic settling additives are better for tall oil settling. The molecular weight of the lignin copolymer, obtained through preliminary results which require further testing, was approximately 32,000 g/mol. Typically, small to intermediate molecular weight polymers act as dispersants, whereas large molecular weight polymers act as flocculants; this is because the long polymer chains can more effectively bridge between particles in solution and aid in settling (Kissa, 1999). The Infinity^{TM} and xylan copolymers examined in previous sections had large molecular weights, whereas the lignin copolymer has a slightly smaller molecular weight. This may have resulted in an increase in dispersant properties, which may explain the decrease in efficiency of the lignin copolymer in terms of yield and quality in comparison to the other settling additives and without additive. The spent acid recovery when using the lignin additive ranges from approximately 120 to 125 g, decreased in comparison to the additive-free trial (128 g). As the lignin yield increases, the oil yield remains approximately constant, and the spent acid solution recovery decreases overall, it may be said that the H-lignin-METAC copolymer acts only to a small extent on the oil separation and more on the entrainment of spent acid into the lignin layer.

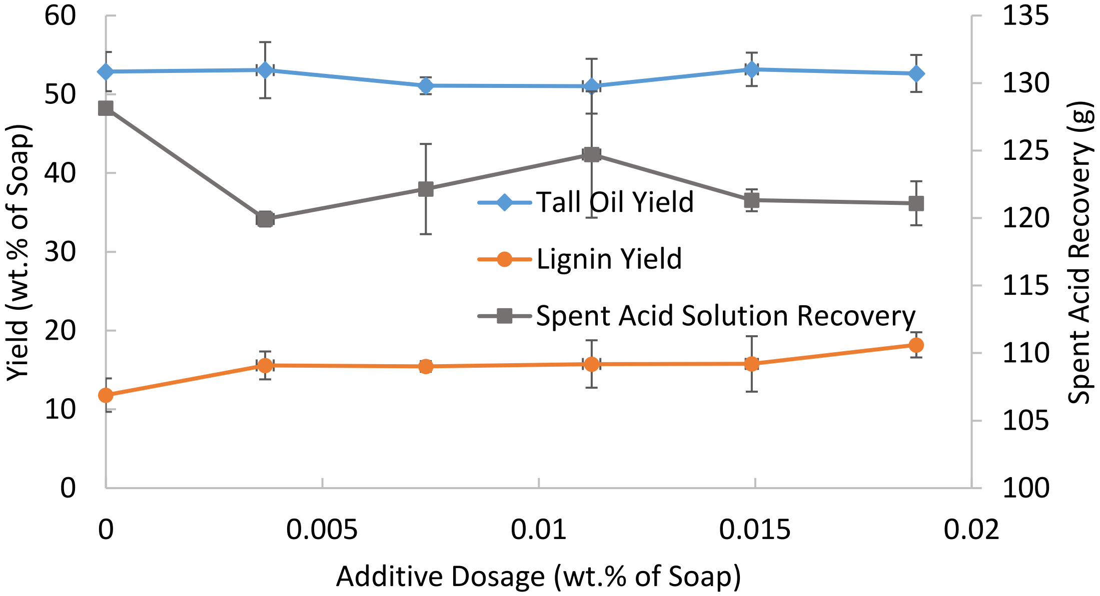

Figure 4.16. Yield of the layers of the crude tall oil optimization reaction varying the amount of settling additive DMC-HL10 at a temperature of 90 – 100 °C, pH of 2.5 – 3.0, water content of 100 wt.%, and a settling time of 2 h.

Figure 4.17 outlines the acid number of the samples produced with the H-lignin-METAC copolymer as a settling additive. Without additive, the acid number is 137 mg KOH/g oil; with the use of the additive, the acid number ranges from 136 – 137 mg KOH/g oil. As such, there is no apparent impact on the quality of the crude tall oil with respect to acid number when the lignin copolymer is used. The acid number values with the lignin copolymer (136 mg KOH/g oil) are comparable to the samples produced using the xylan copolymer (136 mg KOH/g oil) and slightly below the Infinity^{TM} additive (139 mg KOH/g oil). These values are once again on the higher end of the range for northern USA and Canada crude tall oil values, typically 125 – 135 mg KOH/g oil (Foran, 1992).

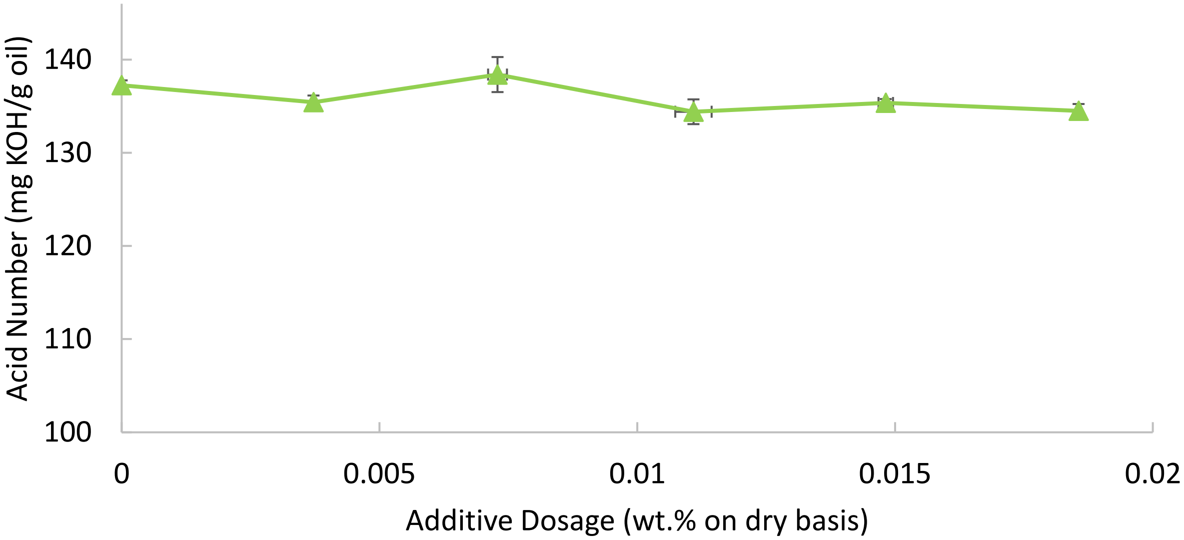

Figure 4.17. Acid number of the crude tall oil optimization reaction varying the amount of settling additive DMC-HL10 at a temperature of 90 – 100 °C, pH of 2.5 – 3.0, water content of 100 wt.%, and a settling time of 2 h.

Figure 4.18 outlines fatty acid, rosin acid, unsaponifiable, and moisture content of the samples produced with the H-lignin-METAC copolymer settling aid. The fatty acid content ranges from 55.8 to 58.4 wt.%, increasing with additive dosage. These values are slightly larger than both those for the Infinity^{TM} additive (56.7 wt.% average) and the xylan-AETAS-APS additive (56.6 wt.% average). The rosin acids range from 22.0 to 22.5 wt.%, similar to the xylan additive but once again decreased in comparison to the Infinity^{TM} additive; this may be as a result of the affinity of the cationic lignin copolymer to the rosin acid structures, resulting in some entrainment into the lignin emulsion layer. This is not observed in the yield or a decrease in acid number. The unsaponifiables content decreases from 19.1 wt.% to 17.3 wt.% with an increase in dosage; a decrease overall from the unsaponifiables content of 18.7 wt.% without additive usage. This overall decreasing trend was not observed for either of the other settling additives employed in this study. The decrease in both rosin acid and unsaponifiables contents may be as a result of H-lignin-METAC copolymer affinity for these types of substances in solution; this must be further examined. The moisture content of the samples produced using the lignin copolymer do not follow a trend (1.82 – 2.53 wt.%), and are similar to the moisture content values using the xylan copolymer. Once again, the fatty acid content resembles that of typical northern USA and Canadian tall oils (50 – 60 wt.%) (Foran, 1992). Rosin acids were slightly below typical values of 25 – 35 wt.%, and unsaponifiables are on the upper end of the maximum typically observed (18 wt.%) (Lappi and Alén, 2011; Wansbrough, 2008; Hampton, 1962, Aro and Fatehi, 2017a, Panda, 2013; Koski, 2008; Foran 1992).

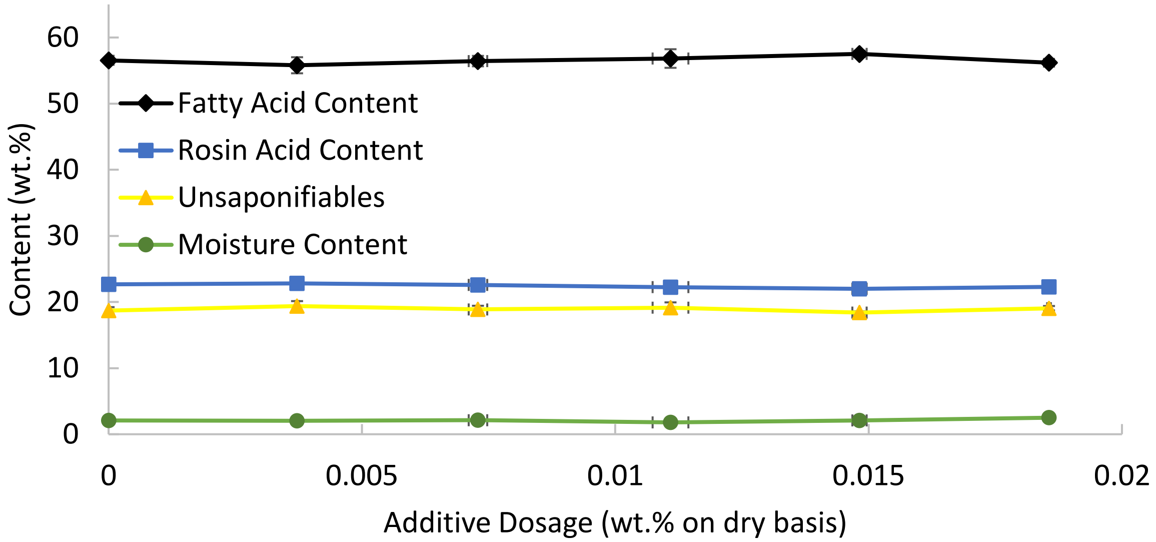

Figure 4.18. Fatty acid, rosin acid, unsaponifiables, and moisture content of the crude tall oil optimization reaction varying the amount of settling additive DMC-HL10 at a temperature of 90 – 100 °C, pH of 2.5 – 3.0, water content of 100 wt.%, and a settling time of 2 h.

4.5. Analysis of variance of tall oil results

Following the optimization of the tall oil production process, including water content, reaction pH, reaction time, and the usage of settling aids, analysis of variance (ANOVA) was conducted on the results obtained. ANOVA analysis was conducted in order to determine if there were statistical differences between the results obtained. The optimized conditions above were based upon trends in figures and potential industrial benefits, and ANOVA was conducted in order to determine their reliability.

ANOVA was conducted for the reaction water content, reaction pH, reaction time, and each of the settling additive dosages in terms of both oil yield and acid number. ANOVA was conducted in Excel in order to determine if there was a statistical difference overall, and Statistical Package for the Social Sciences (SPSS) was used to determine where that difference occurred. In the case of water content, it was found that the P-value following ANOVA analysis in Excel was 1.7×10^{-5}, much below the confidence interval of $\alpha = 0.05$. SPSS was used to determine where the statistical difference was located. Table 4.2 shows the results of the SPSS results.

Table 4.2. Analysis for statistical variation between crude tall oil samples produced when varying reaction water content. P-values between samples are shown in the table.

Reaction Condition	25 wt.% Water Content	50 wt.% Water Content	75 wt.% Water Content	100 wt.% Water Content	125 wt.% Water Content	150 wt.% Water Content	175 wt.% Water Content
25 wt.% Water Content	-	0.903	0.03	0.972	0.906	1.00	0.993
50 wt.% Water Content	0.903	-	0.038	0.325	1.00	0.818	0.505
75 wt.% Water Content	0.03	0.038	-	0	0.037	0.01	0.01
100 wt.% Water Content	0.972	0.325	0	-	0.331	0.982	1.00
125 wt.% Water Content	0.906	1.00	0.037	0.337	-	0.823	0.511
150 wt.% Water Content	1.00	0.818	0.001	0.982	0.823	-	0.997
175 wt.% Water Content	0.992	0.505	0.001	1.00	0.511	0.997	-

It was found that there was only a statistical difference between the values of oil yield for 75 wt.% water and the other values. This can be attributed to the average values of oil yield; for 75 wt.% water content, an average yield of approximately 43 wt.% was determined. Meanwhile, the other crude tall oil yields ranged from approximately 50 – 54 wt.%. As a result, a statistical difference was observed between the values of 75 wt.% water content but not between the other values. Consequently, it can be concluded that a change in water content does not appreciably change the crude tall oil yield. For acid number of the samples produced when varying water content, an overall P-value of 0.24 was obtained, greater than the 95 % confidence interval. As a result, it may be concluded that varying water content has no appreciable statistical impact on acid number of crude tall oil samples.

When varying reaction pH, a P-value of 0.15 was obtained following ANOVA analysis of the crude tall oil yield results. Thus, no appreciable statistical difference in yield was observed when altering the reaction pH. However, ANOVA analysis determined an overall P-value of 0.012, less than the $\alpha = 0.05$ threshold for the acid number results. SPSS showed that the appreciable difference occurred between the 5.5 – 6.0 pH range and the 2.5 – 3.0 pH range (P-value = 0.047). This means that there was a statistical difference specifically between the acid numbers when these reaction conditions were employed. Studying the average value of acid number for these ranges, a pH range of 2.5 – 3.0 yielded an acid number of 137 mg KOH/g oil whereas a pH range of 5.5 – 6.0 yielded 127 mg KOH/g oil. Unfortunately, there was not a statistical difference between any other sets of data, and it cannot be concluded that there was a statistical difference in acid number when varying pH range of the tall oil reaction.

In terms of reaction time, ANOVA analysis yielded an overall P-value of 0.40 for the crude tall oil yield and 0.17 for the acid number. Both of these values were above the 0.05 threshold and thus it may be concluded that there was no statistical difference in the crude tall oil yield or acid number of tall oil when varying the reaction time.

For the Infinity^{TM} settling aid, it was determined through ANOVA that there was a statistical difference in the yield values (P-value = 7.16×10^{-4}) but not for the acid number values (P-value = 0.98). When conducting SPSS analysis, it was found that there was a statistical difference between the yield values for 0.05 wt.% (wet) dosage and 0.01 wt.%, 0.02 wt.%, and 0.03 wt.% (wet) dosages. However, there was not a statistical difference between the 0.05 wt.% dosage and the optimized (no additive) crude tall oil yield or the 0.04 wt.% (wet) dosage. Thus, while there was a statistical difference in the yields between the maximum dosage and the lower dosages of Infinity^{TM} additive, an optimized value could not be deduced from SPSS or ANOVA analysis.

For the xylan-copolymer settling aid, there was a statistical difference determined through ANOVA analysis for both yield (P-value = 0.011) and acid number (P-value = 2.8×10^{-3}). Analysis through SPSS showed a statistical difference in the oil yields between the 0.01 wt.% (wet) dosage and both the 0.03 wt.% (wet) and 0.04 wt.% (wet) dosages (P-values = 0.027 and 0.051, respectively). This is because the oil yield was markedly lower at 0.01 wt.% (46 wt.%) compared to those at 0.03 wt.% (54 wt.%) and 0.04 wt.% (53 wt.%). Thus, no conclusion could be made to determine an optimized value for xylan additive dosage in terms of oil yield because no statistical difference was found. For acid number, there was a statistical difference determined between the 0.02 wt.% (wet) dosage and the 0.03 wt.% (wet) and 0.05 wt.% (wet) dosages, at P-values of 0.015 and 0.022, respectively. This was as a result of the acid number of the 0.02 wt.% (wet) dosage being 138 mg KOH/g oil while 0.03 wt.% and 0.05 wt.% (wet) were both approximately 134 mg KOH/g oil. As a result, the 0.02 wt.% (wet) dosage of xylan produced statistically superior values of acid number when compared to these other dosages. However, there was not a statistically significant difference in acid number otherwise, and as such no optimized value could be determined for the xylan-copolymer settling additive.

Finally, for the lignin-copolymer additive, ANOVA determined a P-value of 0.90 for crude tall oil yield and a P-value of 0.29 for acid number. As a result, no statistical significance was obtained and thus, no optimized condition could be concluded from the use of the lignin additive.

In conclusion, no optimized condition from the previous section could be statistically certified following the utilization of ANOVA and SPSS programs. As a result, none of the previous conditions could be considered fully optimized solely from a statistical outlook.

4.6. Tall oil GC/MS

Gas chromatography/mass spectrometry (GC/MS) analysis was also conducted on selected tall oil products. These tests were used to confirm the main components of crude tall oil samples produced via different reaction conditions. Following the method outlined in the experimental section, a complete profile of acid and neutral compounds can be produced, as observed in Figure 4.19 and Table 4.3 for the optimized crude tall oil reaction conditions without additive use.

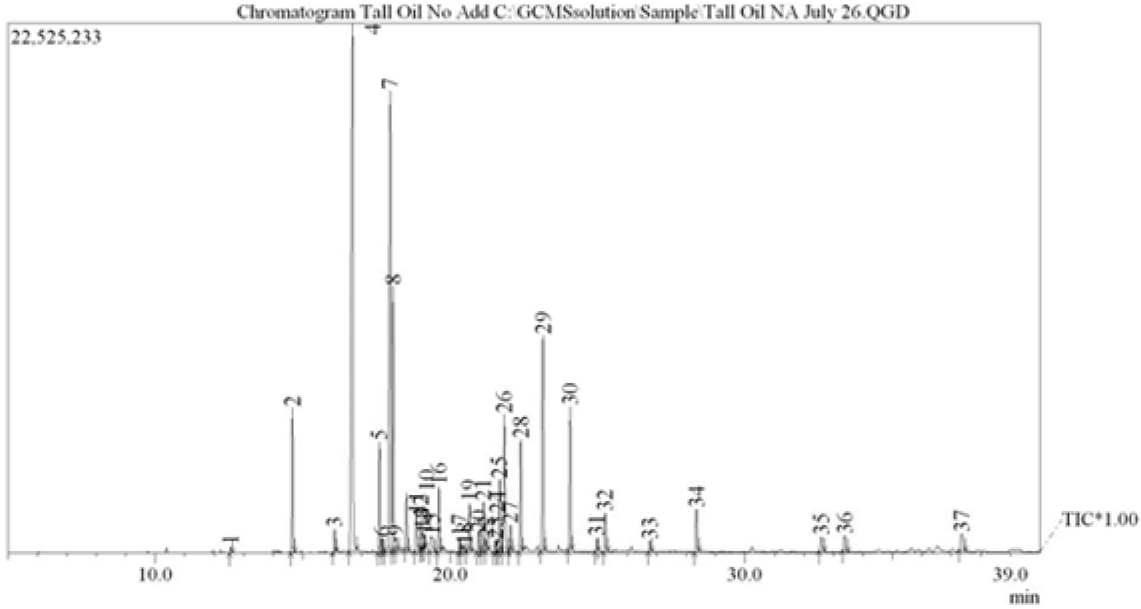

Figure 4.19. Chromatogram of an optimized crude tall oil sample produced using 20 min of reaction time, pH of 2.5 – 3.0, 100 wt.%, of water content, 2 h of settling, 90 – 100 °C, and no additive. The compounds are outlined in Table 4.2.

Table 4.3. Relative amounts of the main components of an optimized crude tall oil sample produced using 20 min of reaction time, pH of 2.5 – 3.0, 100 wt.%, of water content, 2 h of settling, 90 – 100 °C, and no additive.

Peak Number	Retention Time (min)	Area	Area (%)	Height	Height (%)
1	12.560	682206	0.17	272585	0.23
2	14.652	16080564	3.89	6154073	5.13
3	16.084	2384631	0.58	949678	0.79
4	16.690	102602029	24.82	22413686	18.68
5	17.607	12952102	3.13	4679681	3.90
6	17.702	1647722	0.40	586032	0.49
7	17.970	73913701	17.88	19575791	16.32
8	18.068	32649698	7.90	11246392	9.37

9	18.160	2181011	0.53	577968	0.48
10	18.523	6876536	1.66	2421595	2.02
11	18.855	5479993	1.33	1489189	1.24
12	19.008	3751318	0.91	1314137	1.10
13	19.065	2031257	0.49	757837	0.63
14	19.133	1414345	0.34	527220	0.44
15	19.392	4080461	0.99	634954	0.53
16	19.625	8118405	1.96	2760601	2.30
17	20.325	1529862	0.37	582057	0.49
18	20.483	1587910	0.38	253894	0.21
19	20.659	5835202	1.41	2049869	1.71
20	20.961	2188726	0.53	784170	0.65
21	21.130	5602649	1.36	2090893	1.74
22	21.229	1771714	0.43	478477	0.40
23	21.526	1444979	0.35	486513	0.41
24	21.607	1348781	0.33	458609	0.38
25	21.619	9034539	2.19	3054264	2.55
26	21.837	19763134	4.78	5824448	4.86
27	22.044	2993375	0.72	1124573	0.94
28	22.398	13960295	3.38	4738641	3.95
29	23.149	29386140	7.11	9150883	7.63
30	24.070	16631232	4.02	6103780	5.09

31	24.974	1494098	0.36	541929	0.45
32	25.261	4787032	1.16	1653534	1.38
33	26.773	1494098	0.30	460514	0.38
34	28.355	4787032	1.40	1812007	1.51
35	32.593	1222186	0.68	613171	0.51
36	33.384	2964249	0.72	641008	0.53
37	37.350	4399488	1.06	699008	0.58
TOTAL		4133798889	100.00	119963661	100.00

Using the WILEY-8 software for compound analysis did not yield completely accurate results due to the wide array of compounds present in unfractionated crude tall oil, and as such are not reported. The spectra of many components are very similar, and the software uses a similarity search which is not perfectly consistent throughout all sample testing. However, the main components such as margaric acid (internal standard), linoleic acid, and oleic acid can be accurately identified through the samples based on retention time and relative amounts; these were the most consistently abundant acid compounds in the GC/MS tests. In Figure 4.19 and Table 4.3, margaric acid is peak 4, linoleic acid is peak 7, and oleic acid is peak 8. Similarly, other crude tall oil samples were analyzed using GC/MS, with these peaks easily identifiable. High values of linoleic and oleic acid are consistent with typical tall oil fatty acid products (McGuire and Powis, 1998). Other fatty acids include palmitic (hexadecanoic) acid – peak 2 in Figure 4.19 and Table 4.3; linolenic (*cis*-9, *cis*-12, *cis*-15-Octadecatrienoic) acid – peak 21 in Figure 4.19 and Table 4.3; and some isomers of linoleic acid (McGuire and Powis, 1998; Duncan, 1989). Since fatty acids are so abundant in the crude tall oil samples analyzed (see previous analysis sections), it is expected that the fatty acid constituents would be most abundant in the GC/MS spectra. Fatty acids are also eluted through the column and detected before rosin acids, and are therefore easier to identify (Taylor and King, 2001). Rosin acids are much less abundant in the tall oil and eluted through the column later, which cause difficulties in analysis. Several peaks in Figure 4.19 and Table 4.3 are identified by the software as 1-

phenanthrenecarboxylic (levopimaric) acid (peaks 19, 20, 28 – 31), which may be caused by several reasons, most notably column type (Keirsey, 2015). There are several types of GC columns for analyzing different components, as a result of column polarity, functional groups, and capillary or packed column types (Keirsey, 2015; Holmbom et al., 1974). Isomers of rosin acids are similar and in decreased amounts in the crude tall oil samples, and have the same basic structure; decreased resolution due to column specifications increase difficulties in identifying each isomer (Coll et al., 2001). This may result in the several peaks simply identified as 1-phenanthrenecarboxylic (levopimaric) acid as mentioned. As only one column was available for analysis, these factors may have a large impact on the resolution of the analysis and identification of products. Future crude tall oil GC/MS testing may require a specific column for tall oil, or fractionation of crude tall oil into its purified portions. Ultimately, based on the increased amounts and resolution of the margaric acid internal standard, linoleic acid, and oleic acid, the two methods of absolute analysis may still be employed. Table 4.4 highlights the results of these analytical methods for various production methods of crude tall oil samples, along with the differences between the two.

Table 4.4. GC/MS results for several production methods of crude tall oil and the difference between the analysis methods.

Oil Sample Variable	Acid % (Method 1)		Acid Weight (Method 1, g)		Acid Weight (Method 2, g)		Weight Percent Difference (%)	
	Linoleic Acid	Oleic Acid	Linoleic Acid	Oleic Acid	Linoleic Acid	Oleic Acid	Linoleic Acid	Oleic Acid
0.04 wt.% DMC HL-10	0.189	0.0587	0.0105	0.00326	0.0114	0.00381	8.4	16.9
0.04 wt.% Xylan-AETAS-APS	0.179	0.0565	0.0965	0.00304	0.0995	0.00338	3.1	11.1
pH 2.5 – 3.0	0.159	0.0358	0.00904	0.00204	0.00638	0.00155	29.5	24.0
25 wt.% Water Content	0.179	0.0429	0.00923	0.00221	0.00676	0.00174	26.8	21.1
No Additive (pH 5.5 – 6.0)	0.186	0.0412	0.00982	0.00218	0.00638	0.00152	35.0	30.0
No Additive (Optimized)	0.185	0.0576	0.0106	0.00330	0.0107	0.00357	0.4	8.3

Table 4.4 shows the accuracy of the GC/MS analysis methods. Method 1 uses the average RRF values calculated from calibration curve standards to provide absolute values of linoleic and oleic acid weights. Method 2 uses the calibration curves for oleic and linoleic acids to correlate the observed area with the absolute weight of the acids in solution. It must be stated that the weight of the total crude tall oil sample used in the GC/MS analysis is roughly 0.05 g, hence the

small quantities of acids observed. The right column of Table 4.4 shows the difference between the two methods of these weights. Several crude tall oil solutions are analyzed in order to determine the accuracy; since the values of percent difference are relatively low given the small quantities of acids present in the crude tall oil samples, it can be stated that both methods provide accurate values of absolute weights of the two notable fatty acids in the samples.

The solutions presented in Table 4.4 were also used to determine the repeatability of the GC/MS solution preparation procedure. This was conducted be determining the average values of the peak area percentages of linoleic and oleic acid and comparing these averages with those from previous studies. This comparison was conducted in order to determine the accuracy of the DMF-DMA preparation procedure. The results are presented in Table 4.5. The literature investigation values were conducted on tall oil fatty acid solutions (i.e. crude tall oil following fractionation), and it was observed that the relative amounts of the fatty acid compounds were larger than those in the current study. The values of importance are the standard deviations of the relative acid amounts, which represent the accuracy of the preparation of the crude tall oil samples. Observing Table 4.5 shows that the standard deviation for the values of the current study are slightly larger than those determined previously; however, the values still allow for adequate analysis of the GC/MS results. It must also be noted that solutions produced under different conditions were used to analyze the derivatization accuracy in this study, whereas previous studies used tall oil fatty acid solutions produced under the same conditions for each measurement, in order to determine an average. This may have caused an increase in standard deviation observed in Table 4.5. In summary, due to the accuracy between the two methods of linoleic and oleic acid sample weight determination, along with the consistent preparation of samples for GC/MS analysis and similarity of the sample chromatograms to similar literature results, the GC/MS analysis is able to accurately depict at least the fatty acids present in crude tall oil samples, along with rosin acid constituents.

Table 4.5. Standard deviations of linoleic and oleic acid average peak area to ensure derivatization consistency.

Analyte	**Average peak area (%)**		
	Current Study (Crude Tall Oil)	**McGuire and Powis, 1998 (Tall Oil Fatty Acid)**	**ASTM Research Report D01-1101, 1996 (Tall Oil Fatty Acid)**
Linoleic Acid	20.42 ± 2.67	35.27 ± 0.71	35.20 ± 0.61
Oleic Acid	7.71 ± 0.47	46.52 ± 1.45	47.17 ± 1.82

4.7. Tall oil lignin characteristics

Lignin from select tall oil production methods was also analyzed in order to determine the initial feasibility of sulfuric acid sulfonation of lignin and the results are available in Table 4.6.

First, the total anionic charge density of the soluble and insoluble portions of lignin were approximately 0.2 – 0.4 mmol/g. Charge density is an important characteristic of both dispersants and flocculants for use in polyelectrolyte systems (Konduri and Fatehi, 2015). The lignin samples were produced using non-optimized conditions of the tall oil production process, and as such there is some variation between the charge density values. This is expected; as pH is increased or decreased during the tall oil production, or diluted depending on the amount of water addition, there will be less sulfuric acid available to react with the lignin in solution. This impacts the extent of reaction and results in a varied charge density value, since the charge density is largely related to the sulfonate groups (He and Fatehi, 2015). Comparing the values of tall oil lignin to those of unmodified kraft lignin in Table 3.1, there is a marked increase in anionic charge density. The values increase from roughly 0 meq/g in Table 3.1 to approximately 0.2 – 0.4 mmol/g. This is due to the slight sulfonation of the waste lignin in the tall oil production process as a result of sulfuric acid being present in the reaction mixture (Dilling, 1991). While there is an increase in charge density, these values are still lower from typical lignosulfonate charge density values of -0.9 meq/g (Table 3.1). As a result, further studies on the sulfonation of lignin with sulfuric acid should be conducted in order to reach a viable level of charge density for application of this lignin as a flocculant or dispersant.

The tall oil lignin had a higher solubility than kraft lignin (Table 3.1). Table 4.6 outlines the solubility of the sulfuric acid sulfonated tall oil lignin, which ranges from roughly 0.7 – 1.9 g/L. The average of these values (1.25 g/L) is increased over the average of unmodified kraft lignin (0.6 g/L) (Table 3.1). This indicates that there was an increase in sulfonation, as sulfonate groups convey solubility to lignin (Inwood, 2014).

CHNS analysis was also conducted for the lignin samples, shown in Table 4.6. Nitrogen content was not reported as it was 0 % for all samples. As can been seen, carbon and hydrogen contents are similar for all samples, however the sulfur content changes substantially. The sulfur content is lowest with the pH 5.5 – 6.0 sample and greatest with 100 wt.% water content (produced at a pH of 3.0 – 3.5). Once again, this is expected, as increased sulfonation with sulfuric acid occurs with increased pH (Dilling, 1991). This coincides with the solubility values obtained for the samples; the sample with the lowest solubility has the lowest sulfur content as well. Compared to Table 3.1, the sulfur contents of lignin are approximately the same. However, observing the pH 5.5 – 6.0 values, a low sulfur content correlates to a low solubility. As such, it can be inferred that the sulfur content and solubility of the unmodified lignin in the tall oil soap is low. Thus, an increase in both sulfonation and solubility were observed in comparison to kraft lignin.

Molecular weight analysis could only be carried out for the tall oil lignin sample produced at pH 5.5 – 6.0, due to difficulties with solubility and small amounts of sample produced following neutralization and washing. The molecular weight of this sample was determined to be approximately 1,700 g/mol using gel permeation chromatography (GPC). This value is lower than those found in Table 3.1 for unmodified kraft lignin, which range from 2,000 – 25,000 g/mol. This may indicate that degradation of the lignin structure occurred during the tall oil production reaction, possibly due to the increased temperature and high acidity as a result of increased amounts of sulfuric acid. Production of sulfonated lignin using sulfuric acid had been proposed to require a low temperature (< 40 °C), which may have resulted in the possible degradation (Dilling, 1991). The molecular weight of this sample was much lower than typical lignosulfonate values (Table 3.1), which range up to 150,000 g/mol. Since high molecular weight and charge density is an asset to lignin use as a flocculant and dispersant, further modification would be required for tall oil lignin to be used in this application (Oveissi and Fatehi, 2015; Yang et al., 2007).

Table 4.6. Tall oil lignin characteristics.

Tall Oil Lignin	**Charge Density (mmol/g)**	**Charge Density, Soluble (mmol/g)**	**Charge Density, Insoluble (mmol/g)**	**Solubility (g/L)**	**Carbon (%)**	**Hydrogen (%)**	**Sulfur (%)**	**Molecular Weight (g/mol)**
pH 4.0 – 4.5	-0.31 ± 0.06	-0.79 ± 0.00	-0.049 ± 0.062	1.14	65.8	6.3	1.7	-
pH 5.5 – 6.0	-0.38 ± 0.10	-1.46 ± 0.08	-	0.67	65.2	7.4	1.0	1,701
100 wt.% H_2O	-0.22 ± 0.03	0.45 ± 0.02	0.031 ± 0.010	1.94	68.2	8.0	2.1	-

4.8. Discussion and summary

Table 4.7 shows the optimized dosage for each of the settling additives in terms of both crude tall oil yield and acid number. This table shows that with the maximum applied dosage, the Infinity^{TM} aid results in the largest crude tall oil yield and largest acid number with respect to both other additives. The second lowest dosage for the xylan additive (0.02 wt.%, wet basis) resulted in the largest acid number for that additive; however, it was still decreased in comparison to the Infinity^{TM} additive. The third largest dosage of the xylan additive (0.03 wt.%, wet basis) resulted in the largest yield of crude tall oil; but it is still less than the Infinity^{TM} settling aid. Finally, the lignin additive required the lowest dosage (0.01 wt.%, wet basis) to result in a slight increase in oil yield in comparison with no settling additive, along with a comparable acid number. These values for the lignin additive were both less than the Infinity^{TM} results and a median value in comparison to the two xylan-copolymer optimized dosages.

As a result, comparing dosage, yield, and acid number values, the optimized conditions included 100 wt.% water addition, pH 2.5 – 3.0, reaction time 20 min, 90 – 100 °C temperature, 2 h settling time, and an additive dosage of 0.0185 wt.% (dry basis) of the Infinity^{TM} brand settling aid. Although tall oil lignin is anionic as previously shown, anionic polymers function better than the cationic polymers as settling additives analyzed in this study. This may be due to the anionic polymers intensifying the repulsive anionic charge of the lignin, which would result in improved separation from crude tall oil (Hart, 1998). This is contrary to other literature, showing that cationic polymers function better as settling aids (Patrick, Jr and Thomas, Jr, 1974), although there is an observed increase in settling ability of said cationic polymers when compared to no settling aid. The large molecular weight of the xylan copolymer used for settling may have ultimately resulted in dispersion, rather than flocculation effects, or a mixture of both. Xylan has been used for both applications, and as such, may have resulted in a dispersion of lignin layer, increasing the volume and hence yield (Konduri and Fatehi, 2017a,b). The lignin copolymer had a smaller molecular weight, which is typically a characteristic of dispersants; as a result, more dispersive, rather than flocculant, effects may have been observed (Kissa, 1999).

Table 4.7. Optimized dosages for each crude tall oil settling additive with respect to crude tall oil yield and acid number of crude tall oil samples.

Additive	**Dosage (wt.%), dry basis**	**Crude Tall Oil Yield (wt.%)**	**Acid Number (mg KOH/g oil)**
Infinity^{TM} PS 3040 Pulp Processing Aid	0.0185	57.1	142
Xylan-AETAS-APS	0.0073	50.7	138
	0.0111	53.7	134
DMC-HL10	0.0037	53.1	136

However, following ANOVA and SPSS analysis, though the figures show slight trends and local maxima, there was not a statistically appreciable difference when varying any of the reaction parameters or settling additive dosages. Further testing must be done in order to determine if there is an impact between the reaction conditions and settling additives, and both cationic and anionic aids should be examined.

The GC/MS results indicate that the components within tall oil are consistent and in line with literature. The samples were prepared consistently as well; thus, the GC/MS results may be considered reliable. The two main fatty acids in the tall oil samples were linoleic and oleic acid, accounting for approximately 0.16 – 0.19 wt.% of the tall oil samples. The percent differences between the testing methods were all under 35 %, which further indicates reliable data was obtained. Further research with more standard solutions containing other expected fatty and rosin acids, along with neutral fractions where possible, is recommended to be completed in order to provide more quantitative data for the specific acid components in the crude tall oil solutions. Alternatively, crude tall oil samples may be fractionated into the fatty and rosin acid fractions as in industry prior to GC/MS analysis, which may aid specifically in identifying rosin acid components.

The lignin analysis indicates that there was some sulfonation of tall oil lignin, as there was an increase in sulfur content and solubility in comparison to the starting material. The anionic charge density was greatest for the sample with the lowest solubility and sulfur content, which may have been due to residual crude tall oil present in the clean lignin samples. Regardless, there was an increase in the anionic charge density of all samples (0.2 – 0.4 mmol/g) compared to literature values of kraft lignin (approximately 0 mmol/g). The molecular weight of the tall oil lignin sample that was tested (1,701 g/mol) was smaller than both unmodified kraft lignin (up to 25,000 g/mol) and lignosulfonates (up to 150,000 g/mol), indicating that crosslinking or some other modification should have been conducted prior to tall oil lignin use as a dispersant or flocculant. It is recommended that further testing be performed on tall oil lignin produced via different methods in order to determine the viability of sulfonation of waste tall oil lignin using spent sulfuric acid in solution.

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5. Conclusions and Recommendations

5.1. Conclusions

In this study, crude tall oil was produced from tall oil soap under different conditions in order to determine optimized parameters in terms of both yield and quality. Lignin was also characterized from the waste of the tall oil production process.

Water content was found to be optimized at a median value of the range tested, which was increased over what is practiced in industry. This allowed for increased yield and quality, and also an improved ease of handling and separation. The reaction pH was similar to industrial conditions, and did not result in a decrease in quality of tall oil, as is suggested when increased acidulation of tall oil occurs. The reaction time for the tall oil production process was slightly lower than industrial times, which aids in decreasing batch times for reaction and settling. The fatty acid, rosin acid, unsaponifiables, and moisture content were all fairly consistent between different conditions, and were similar to those in the same geographical area, which is one of the main impact factors on tall oil composition.

Several tall oil settling additives were employed, each with their own merits. The Infinity^{TM} additive resulted in the largest yield and quality of tall oil; however, it is not a green product and readily available like the lignin and xylan settling additives. Also, the largest dosage of Infinity^{TM} additive resulted in the best conditions. On a large scale, this translates to an increased cost, which lowers profitability. Lower dosages of both the lignin and xylan settling additives produced similar values of yield and quality compared to the Infinity^{TM} additive, albeit slightly lower. Two of the middle dosages of the xylan copolymer additive resulted in good values of yield and quality, whereas the lowest dosage of the lignin copolymer additive resulted in comparative values of the same characteristics. On a large scale, a low dosage of settling additive would reduce the operational costs. In addition, lignin is readily available throughout the kraft pulping and recovery process, which would increase ease of access.

The waste lignin produced from the tall oil production process was found to be slightly sulfonated by the spent sulfuric acid used for acidulation. The impact of these findings indicate that with further analysis, value-added lignin may be produced from the tall oil production process for use as a dispersant or flocculant. The charge density, solubility, and sulfonation are improved in comparison with unmodified kraft lignin, which may increase waste tall oil lignin valorization in future processes. The molecular weight of the lignin tested was decreased in comparison to both kraft lignin and lignosulfonates, which would hinder end-use applications. Furthermore, the lignin analyzed from the tall oil production process had overall inferior characteristics in comparison with lignosulfonates, which are widely used in similar applications. As such, further sulfonation and molecular weight alteration of the lignin would be required in order to compete with current industrial products.

5.2. Recommendations

While settling additives were studied, along with their impact on tall oil qualities, future work may be conducted on other types of settling additives in order to determine a green, biodegradable, and effective solution. Further studies may improve the yields of tall oil, which in turn may impact the divergence from fossil fuels as tall oil is used for more green biofuels.

In addition, the impact of settling additives on the settling time and efficiency would be a good area of study. Increasing the settling efficiency to decrease time spent during settling would decrease batch production time for tall oil and thereby increase overall production. Specific analysis of the impact of settling additive on the settling time would be advantageous.

While some characterization of lignin products was done in this study, further analysis would allow for an accurate representation of the viability of producing value-added products such as flocculants and dispersants from the waste lignin of the tall oil production process. Future studies may examine further sulfonation and/or modification of lignin in addition to the sulfuric acid sulfonation, which occurs in the tall oil production process currently. This analysis may result in increased profitability as a result of a further transition of existing pulping processes, along with the tall oil process, into integrated forest biorefineries.