Sustainable Method for Recovery of Copper Naphthenate from Used Railroad Ties

A Thesis Presented for the
Master of Science
Degree
The University of Tennessee, Knoxville

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May 2018

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DEDICATION

I would like to dedicate this work to my mom, dad, brother, and fiancé for their continuous love and support during my graduate school process. Thank you all for your encouragement.

ACKNOWLEDGEMENTS

I would like to acknowledge my committee members, Dr. Nicole Labbé, Dr. Nour Abdoulmoumine, and Dr. Philip Ye for all of their help during the past two years. Thank you for sharing your time and knowledge with me. The innumerable amount of time dedicated to help me succeed, especially by my committee co-chairs Dr. Labbé and Dr. Abdoulmoumine, is very much appreciated.

Furthermore, I want to extend a great amount of gratitude to Dr. Pyoungchung Kim for acting as a mentor to me throughout my degree seeking process. His knowledge and devoted time were crucial to all aspects of my learning process. Thank you for constantly pushing me to think critically.

I also want to acknowledge Dr. Jeff Lloyd and Nisus Corporation of Rockford, TN for sharing their expertise in wood preservatives, as well as for providing the copper naphthenate and treated-wood samples I used in this research.

I want to recognize Dr. Stephen C. Chmely and Dr. Yagya N. Regmi for all of their input as co-authors of my first published peer-reviewed journal article. Dr. Chmely's chemistry expertise and Dr. Regmi's microscopy experience were crucial in this process and are very greatly appreciated.

Finally I would like to recognize my other group members, particularly Anna Kim, Choo Hamilton, and Dr. Warren Edmunds. Thank you for answering all of my questions, helping me with different laboratory techniques and equipment, as well as making me feel welcomed at the Center for Renewable Carbon (CRC) and at the University of Tennessee (UT).

ABSTRACT

Recovery of the wood preservative copper naphthenate (CN) from end-of-life railroad ties was investigated to promote the secondary use of this biomass as a fuel source and mitigate the negative impacts of landfilling and other alternative tie disposal methods. Thermal desorption of naphthenic acids from CN-treated ties preceded inorganic extraction with ethylenediaminetetraacetic acid (EDTA) and biodegradable chelating agents, 2,6-pyridine dicarboxylic acid (PDA) and 1-hydroxy ethylidene-1,1-disphosphonic acid (HEDP). Organic preservative components were recovered from thermal pretreatment at temperatures between 225 and 300 °C. This thermal desorption also mirrored torrefaction by increasing the ties' higher heating value and carbon content, in addition to lowering the moisture content within the biomass. These effects improved the biomass properties for use as a thermochemical conversion feedstock. Preservative component recovery was assessed at micro-, bench-, and pilot-scales, demonstrating scalability of the proposed process. Extraction efficiency of copper and other naturally present inorganics with PDA after thermal desorption was the most effective of those tested, further upgrading the properties of the biomass for pyrolysis. The ash content of the biomass was decreased by up to 64 % using PDA, and 100 % of copper was removed from both the raw sample and that desorbed at 225 °C specifically. Estimations of the bio-oil yields that would be generated from subsequent fast pyrolysis of the ties were completed based on a review of literature. The sample that has undergone both pretreatment steps is expected to generate the highest quantity of bio-oil from subsequent fast pyrolysis, as well as the highest quality.

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INTRODUCTION

Motivation

The use of copper naphthenate (CN) as a wood preservative is increasing due to its efficacy towards biological sources of degradation, as well as the reduced usage of preservatives like creosote that threaten human health. This rise in treated material has, in turn, led to a larger quantity of treated-wood waste that must be disposed of. The majority of this wood is typically reused as boiler fuel after it has been removed from railroads. Natural gas and other non-wood alternatives, however, are a less expensive boiler fuel alternative due to their low current cost. Recovering the preservative components from CN-treated waste will provide for its continued reuse while also improving the physical and chemical properties of the biomass for recycling as a bioenergy feedstock; thus ensuring the treated-wood waste disposal process is both economically and environmentally advantageous by offsetting costs associated with removal and creating a sustainable method for preservative reuse.

Research goal and objectives

This thesis aims to improve the commercial viability of used treated wooden railroad ties as a fuel source by developing a process to extract and recover copper naphthenate, thereby upgrading the ties as a pyrolysis feedstock for subsequent production of high quality bio-oil. Three research objectives met in addressing this main goal include to:

1. Demonstrate that the use of thermal desorption is an effective method for the removal and recovery of naphthenic acids from copper-naphthenate treated ties

using pyrolysis-gas chromatography/mass spectrometry and a bench scale fixed-bed reactor

2. Identify a biodegradable chelating agent for extraction of copper and other inorganics which have detrimental effects on the pyrolysis process from thermally desorbed copper-naphthenate treated ties
3. Demonstrate that optimal thermal desorption conditions for recovery of copper naphthenate and production of an upgraded thermochemical conversion feedstock using a continuous auger reactor produce bio-oil with high quality from subsequent fast pyrolysis

Copper naphthenate

Copper naphthenate (CN) is a wood preservative composed of copper ions and naphthenic acids with proven effectiveness against sources of biodegradation.[1] Copper ions have been recognized for their efficacy against algae, bacteria, fungus, mold, and insects.[2] Excess uptake of copper by these organisms leads to toxicity through enzymatic process disruption that causes cell death.[2] The majority of the naphthenic acids used in formulation of the preservative are carboxylic acids that can also be found in petroleum.[3]

CN is replacing previously common preservatives, like creosote and pentachlorophenol, because of its low mammalian toxicity and high retention.[2] It is an effective and green alternative for preventing the degradation of wooden products like utility poles, fence posts, and railroad ties.[2, 4] High-pressure treatment is used to impregnate wooden

railroad ties with this oil-borne preservative, specifically, before installation. Dilution of CN with No. 2 fuel oil improves the ability of the preservative to penetrate the wood's cell wall, thus ensuring better retention in the wood. This preservative is hydrophobic and insoluble in water due to the added carrier oil, which greatly improves its retention in wood and reduces leaching from treated ties into the surrounding environment.[5] Though most formulations used for wood treatment contain approximately 1% copper as metal in solution, the exact composition of CN varies between geographic source.[3] This variation is represented in the physical and chemical properties of the preservative. For example, the boiling point of CN fluctuates between 150 and 250 °C depending on the formulation.[6] The increased use of CN-treated wood is leading to the generation of more copper naphthenate treated wood waste. With further processing, this waste can serve as a readily available fuel source.[7-8]

Organic fraction removal

The cost for disposal of copper naphthenate-treated wood in landfills is approximately 22 to 60 USD/ton, while the average cost for discarding this biomass as boiler fuel is 15 to 25 USD/ton.[9-10] Recovery of the preservative from woody biomass would allow for its reuse and this recycling would both improve the sustainability of this process, as well as provide an economic benefit. Reusing the recovered preservative to treat new ties is also economically advantageous.

Thermal desorption, or thermal treatment of woody biomass within a torrefaction temperature range (200 and 300 °C) in the absence of oxygen, has been shown to

effectively recover oil-born preservatives from woody biomass waste.[8] Thermal desorption for removal of CN specifically has yet to be investigated. However, it has been shown to be an effective method for extracting creosote from railroad ties after their primary service life; recovering up to 79% of the preservative contained in used sleepers.[6] According to Kim and co-authors,[8] the largest removal of creosote achieved from used red oak (*Quercus rubra*) ties without complete decomposition of the wood matrix occurs between 275 and 300 °C using a fixed-bed reactor. This recovery method also results in wood with upgraded properties for thermochemical conversion processes, with effects similar to that of torrefaction pretreatment.[7-8]

Torrefaction of hardwoods has been reported to improve the energy density and storage stability, while lowering the specific grinding energy and average particle size of untreated biomass.[11] Volatilization of hydrogen and oxygen-rich compounds reduces the moisture content and, consequently, increases the percent carbon within the biomass.[11-13] These benefits together with a substantial rise in the higher heating value (HHV) improve the biomass' qualities for thermochemical conversion.[14]

Thermal desorption in this temperature range also affects the structural components of the lignocellulosic biomass; cellulose, hemicellulose, and lignin.[15-16] These chemical and structural changes are not studied as extensively as the physical changes that occur within the biomass, however. The decomposition of lignin is reported to occur between 275 and 500 °C, while cellulose and hemicellulose breakdown at lower temperatures (150 to 350 °C) and at a faster rate.[16-18] Hydroxyl dehydration and dissociation of side chains in hemicellulose occur at less severe torrefaction conditions, while

depolymerization occurs at higher temperatures.[15] Cellulose degrades as well, whereas structural changes within lignin occur as a result of bond linkage cleaving.[15-16]

Most inorganics do not volatilize within the torrefaction temperature range, however, so copper from the wood preservative, in addition to other naturally present inorganics, persist in the wood after thermal pretreatment. These inorganics can act as undesired catalysts during thermochemical conversion processes and result in generation of a lower bio-oil yield, as well as reactor degradation.[19-22] Therefore, a secondary method is needed for their extraction prior to use as a thermochemical conversion feedstock to further ensure that the disposal process is economically and environmentally advantageous**.**

Inorganic fraction removal

It has been shown that many inorganics present in biomass, and alkaline metals in particular, have an undesired catalytic effect on thermochemical conversion processes like pyrolysis; causing a decrease in bio-oil production.[19-22] They have also been shown to result in physical reactor degradation by accumulating on the reactor walls and conduits.[21] This leads to the need for more frequent upkeep and a more expensive process overall.

After application of CN, copper specifically exists on the surface of the impregnated wood as Cu^{2+} ions.[23-24] The application of CN also causes the surface of the wood to become hydrophobic, and may reduce the conversion of Cu^{2+} to Cu^{+} or Cu_2O and limit the movement of copper within the wood structure.[25] Therefore, the thermal desorption

of CN-impregnated wood prior to metal removal may affect the copper present on the surface of the ties, in addition to its ease of extraction.[26]

Extraction of inorganics with chelating agents provides a method of removal that is cost-effective, has high efficiency, and does not cause a high amount of degradation to the biomass matrix. One of the most commonly used chelating agents for extracting copper is ethylenediaminetetraacetic acid (EDTA).[27] EDTA is shown effective at removing heavy metals from preservative-treated wood specifically, but is not biodegradable and thus persists in the environment.[29-30] Biodegradable chelating agents like 1-hydroxy ethylidene-1,1-diphosphonic acid (HEDP) and 2,6-pyridine dicarboxylic acid (PDA) are readily biodegradable, and therefore, are better suited for mitigating the undesired effects of inorganics within a thermochemical conversion feedstock.[27, 31-32] An additional advantage of PDA over other chelating agents is its ability to easily and quickly separate with copper and other inorganics after extraction under alkaline conditions; thus allowing for its reuse.[32-33] The ease of precipitating out copper with an increase in pH is advantageous for the possible recovery and reuse of the CN preservative for treating new ties.

Pyrolysis

Woody biomass serves as a renewable fuel source for thermochemical conversion processes, like pyrolysis. Pyrolysis of lignocellulosic biomass produces biochar, bio-oil, and non-condensable gases. Fast pyrolysis specifically combines moderate temperatures with rapid heating rates and short residence times to maximize the

quantity of bio-oil that is produced.[34] Slow pyrolysis, in comparison, favors the generation of solid char because a slower heating rate and longer residence time allows for more secondary reactions to occur.[35] The quantity and quality of these products vary with the conversion process operating parameters, in addition to the feedstock's physical and chemical properties.[36-37]

Among the physical properties that influence pyrolysis product quality, particle size and water content of the biomass are some of the most significant.[37] The suggested optimal particle size varies, however, based on differences in conversion technology, feedstock type, and desired product distribution. The pyrolysis of a feedstock with a smaller average particle size ensures optimal heat and mass transfer during heating, thus increasing the liquid yield.[38] Particles < 2 mm in size are recommended for fast pyrolysis using a fluidized bed specifically.[37-38] The moisture content of a feedstock also greatly influences the products generated and their composition. Moisture within biomass can make long-term storage difficult and transportation expensive, in addition to impacting the product quality and process efficiency.[39] Higher initial feedstock water content generates a lower-quality bio-oil that is less chemically stable and more corrosive.[38, 40-41]

The chemical properties of a feedstock also greatly influence pyrolysis products. High ash and lignin content both lower the quantity of bio-oil generated and increase char and gas formation.[38] Physical degradation of the reactor can also occur during pyrolysis of a feedstock with high ash content, further impairing the thermochemical conversion process.[42] However, lignocellulosic biomass with larger cellulose and hemicellulose

fractions have been reported to produce higher bio-oil yields with low water content and larger organic fractions, especially those with high cellulose content.[36,38]

Pyrolysis of preservative-free railroad ties offers a method for production of a bio-oil with upgraded properties than that of an untreated wood feedstock. Removal of the preservative also prevents contamination of the generated bio-oil with petroleum-based components that could cause problems like clogging and deposit formation.[43] We hypothesized that thermal pretreatment combined with inorganic extraction will both extract CN from the ties and produce high-quality end products. This recycling process will keep a significant amount of wood waste out of landfills and allow for possible reuse of the preservative components for treatment of new products, while generating a renewable fuel source.

CHAPTER I
LITERATURE REVIEW

Copper naphthenate

Copper naphthenate (CN) is a wood preservative known for its effectiveness at extending the service life of wooden products, like railroad ties, utility poles, and pilings. The average service life span of wood treated with CN ranges from 38 to 43 years.[44] Field studies by Duncan[45] investigate the effectiveness of copper naphthenate to sources of biodegradation. Her findings supported the efficacy of CN, comparing it to that of pentachlorophenol and creosote, against fungi and other wood-degrading organisms.

More recently, Barnes et al. published a conference paper[25] detailing their study that looked at the influence of pre- and post-treatment steaming on CN and its retention in treated wood poles. Samples were analyzed after 12 years of field exposure, and the formation of cuprous oxide was found to occur on the surface of the wood with all treatment conditions. The conversion of cupric to cuprous copper was also demonstrated, with conversion rates ranging from 9 to 32 % after long-term ground contact. However, no significant degradation occurred after the 12 years in any of the treated pole samples; thus further supporting CN efficacy detailed in the earlier literature. The study utilized hydrothermal pretreatment of the treated wood to increase preservative retention, but the effect of this method on the wood itself was not thoroughly investigated.

Though American Wood Protection Association (AWPA) standards dictate copper concentration and other aspects of CN formulations, to ensure consistency Zyskowski and Kamdem[44, 46] looked into several novel methods for quantifying the concentration of

this preservative in treated wood. Both UV-vis spectrophotometry and FTIR spectroscopy were tested. Solutions of the extracted preservative with hexane, toluene, diesel, and water were prepared to solubilize the CN prior to analysis. Their studies concluded that both techniques were effective methods for CN quantification within a range of 4 to 80 ppm. They also reported that a UV-vis peak at 680 nm and a FTIR band at approximately 1600 cm^{-1} both correspond to a copper-carboxylate interaction. Oil-borne preservative formulations, however, could not be quantified using this method because it was not possible to distinguish the carrier oil from the added solvent.

Organic fraction removal

Torrefaction is a common pretreatment method employed to improve the properties of lignocellulosic biomass for subsequent use as a thermochemical conversion fuel source; increasing the higher heating value and carbon content of the biomass, as well as reducing the moisture content and average particle size.[47-49] This method involves the thermal treatment of biomass in the absence of oxygen at a temperature between 200 and 300 °C.

Chen at al.[47] compared this method to traditional drying pretreatment. In their study, cotton stalk was dried at 110 °C for 6 hours and then torrefied in a tubular furnace at 220, 250, and 280 °C. Both the dried and the dried/torrefied samples were then pyrolyzed in a fixed-bed reactor at 500 °C under constant nitrogen flow. Torrefied stalks were found to have improved gridability and were more hydrophobic than the dried samples. Also, the oxygen content was reduced significantly, while the carbon content

and heating value increased. The amount of bio-oil produced, however, decreased as biochar production increased with a rise in torrefaction temperature. The chemical composition of the char was unchanged, but that of the bio-oil and non-condensable gasses varied. The results of this study highlighted one of the main undesired effects of torrefaction pretreatment, an increase in ash content of the biomass and consequently a reduction in the quality of the conversion products.

Optimization of torrefaction parameters is extensively studied in literature, but optimal parameters varied among feedstock types. For example, Chen et al.[48] studied the effect of torrefaction on the pyrolysis of pine. Pine wood particles were pyrolyzed at 520 °C after torrefaction at 225, 250, 275, or 300 °C for 15, 25, or 35 minutes in a tubular furnace. Only treatment at 275 and 300 °C affected the products from pyrolysis of the wood, improving the bio-oil quality by decreasing its acid content. A larger amount of gas and char were produced at higher temperatures. Additionally, biomass weight loss increased significantly from torrefaction at these two higher temperatures, while little change was experienced at 225 and 250 °C.

However, Zheng et al.[50] looked at the use of hydrothermal treatment (wet torrefaction) at reaction temperatures of 160, 170, 180, and 190 °C for 5 min to improve the properties of eucalyptus wood for pyrolysis. Treatment was conducted under a constant flow of nitrogen in a high-pressure batch reactor. Similar effects to that of Chen et al.[48] were recorded using these parameters; including improvement of both the higher heating value and the thermal stability. Additionally, this study used the feedstock to generate bio-oil with improved properties than that generated from the untreated

biomass. Because optimal parameters are not universal to all feedstocks, there is a need for further study of biomass resources that have yet to be investigated.

Gucho et al.[17] concluded that torrefaction temperature has much more of an effect on the properties of the torrefied biomass than the retention time at these temperatures do by studying the effect torrefaction parameters on beech wood and *miscanthus* (*sinensis*). This was the first study to compare the effects on woody biomass to that on grass. Temperatures between 240 and 300 °C, as well as retention times from 15 to 150 minutes, were examined. When optimized, they reported that the torrefied biomass had properties comparable to coal.

Similarly, Kim et al. reported that thermal pretreatment of woody biomass could result in a feedstock with properties comparable to that of coal.[8] This article investigated a thermal desorption for removal of creosote from used railroad ties. Over 95 % of the wood preservative was recovered from the ties, in addition to the upgrading of the wood's properties for use as a fuel source, using thermal treatment within the torrefaction temperature range. This study also identified end-of-life railroad ties as an abundant renewable fuel source. However, the scope of Kim et al.'s study did not extend beyond creosote. Other wood preservatives, such as CN, are becoming more popular for treating railroad ties and other similar products because creosote is a probable carcinogen. These alternative preservatives often make use of copper ions in their compositions because of their known efficacy towards fungi and other sources of biodegradation.[2] For example, use of chromated copper arsenate (CCA) became very prevalent beginning in the 1950's because its formulation utilized not only copper to

prevent degradation of wood, but also chromium and arsenic to aid in copper retention and provide protection against copper-tolerant organisms.[2] The toxicity of this preservative has severely restricted its use in recent years, however. CN has a lower metal content than these other copper-containing preservatives and is more resistant to leaching.[2] The inorganics within these preservatives cannot be removed with thermal desorption because they do not volatilize within the torrefaction temperature range. Therefore, a secondary method must be employed to remove the inorganic fraction of CN, which is novel to this project.

Inorganic fraction removal

The inorganics in CN interact primarily with the lignin and cellulose fractions of the wood cell structures during treatment.[51] Copper in particular, as well as other naturally present inorganics within the railroad ties, have been shown to have negative effects on the pyrolysis process. For example, Rutkowski's study[22] showed the undesired effect of both copper and aluminum catalysts on pyrolysis of cellulose. Conversion without these added metals produced the highest yield of bio-oil due to a lesser breakdown of cellulose. Bio-oil production decreased as more catalyst was introduced into the system (at constant reaction temperture), while dehydration reactions increased.

Cheng and Wu[52] reported on the effect of inorganics on pyrolysis of lignin specifically. Bamboo was extracted with acetone and then enzymatic acidolysis was used to recover lignin from the biomass in their study. Increasing amounts of copper oxide (CuO) were added to the biopolymer prior to its fast pyrolysis in a tubular furnace at 700 °C for four

minutes. An increase in the liquid yield occurred from fast pyrolysis of the lignin with the addition of copper oxide up to about 5 wt.%. However, the amount of bio-oil produced began to quickly decrease with increasing amounts of this compound beyond that concentration. The authors suggested that the amount of liquid generated increased because the added CuO caused higher amounts of hydrogen to volatilize; but an explanation for the subsequent decrease was not provided. The same trend was seen with the quantity of solid char produced as well. However, the char's C/H ratio first decreased with an initial addition of CuO and then maximized with the addition of 5.14 wt.%, prior to increasing again with higher additive CuO (between 10.15 and 14.92 wt.%). This suggested that the range of additive concentrations is too small or that the variation may be due to another cause.

To address the resulting increase in ash from thermal pretreatment, as well as to remove inorganics with undesired effects on the pyrolysis process, extraction with chelating agents has been widely investigated. These compounds offer an alternative to traditional solvent extraction because of their high efficiency and their generally limited effect on the structure of the biomass. A study by Edmunds et al.[21] supported this use of chelating agents over solvents for inorganic extraction from switchgrass. Extractions were performed using a microwave system, and reaction times were varied (5, 10, 15, and 20 min). EDTA proved the most effective at removing all inorganics, while also preventing extreme degradation of the biomass. Approximately 90 % of the total ash were removed using microwave-assisted extraction with EDTA for 20 minutes. Though the reaction time for these experiments is short, which would be beneficial for applying

this process to a larger industrial scale, the microwave system creates an added energy requirement to the process, compared to that of a traditional batch extraction method.

Removal of Cr, Cu, and As using traditional batch extractions from CCA-treated wood with EDTA, nitrilotriacetic acid (NTA), and ethylenediamine-N,N'-disuccinic acid (EDDS) was investigated by Chang et al.[28] They compared extraction efficiencies between chelating agents, as well as among varying reaction temperatures (25, 50, 75, 100 °C), and solution pH (3, 4 5, 6). Higher temperatures were shown to increase efficiency of removing all three metals with each chelating agents, with copper being the easiest to extract in all cases. EDTA was most effective at removing copper, with little change in efficacy between 70 and 100 °C.

Though EDTA has traditionally been one of the most popular chelating agents used for inorganic removal, it has been shown to have negative effects when persisting in the environment because it does not readily degrade.[27, 53] Because of this, possible alternatives to EDTA are actively being researched. For example, Martins et al.[53] investigated several different chelating agents to test their biodegradability. To be considered readily biodegradable, a chemical must pass criteria set out by the Organization for Economic Co-operation and Development (OECD) that measures degradation within a 28-day period based on dissolved organic content measurements.[54] PDA was shown to be the only agent tested that was biodegradable. Biodegradation of PDA began after 24 hours and occurred rapidly, with over 60 % degradation after 2.5 days. Therefore, this chelating agent was shown to meet the OECD criteria for classification as a ready biodegradable substance. Simulations using

MINEQL+ software were also included in this study to examine their ability to complex with metal ions when no other ions are present, as well as when all are present, and there is an excess of Ca. Simulations demonstrated that 100 % of the copper complexed with PDA at all solution pH between 2 and 13. One hundred percent of cadmium, cobalt, iron, manganese, nickel, lead, and zinc also complexed with PDA over a broad pH range; with these ranges narrowing during testing with excess Ca in the system.

Because of its ready biodegradability and ease of complexing with a wide variety of inorganics within natural systems, studies comparing the performance of PDA with a number of 'traditional' chelating agents, like EDTA, for different applications have been recorded. Finding the best parameters for these extractions has also been investigated. For example, Pinto et al.[55] conducted a study that compared PDA with a second biodegradable chelating agent methylglycinediacetic acid (MGDA), as well as EDTA, for removal of transition metals and calcium from paper prior to bleaching. Computer simulations were used to determine the optimal pH range for extraction, and then metals were removed experimentally. PDA removed manganese and calcium efficiently but did not remove magnesium; while MGDA removed manganese well but was not as efficient as EDTA at removing calcium. Initial copper concentrations were very low and thus, not included in the extraction results.

Similarly, Macauley and Hong[32] studied lead removal from spiked soils; comparing the effectiveness of PDA against that of EDTA. PDA was shown to be effective across a large range of pH with an efficiency of over 80 %, which is comparable to that of EDTA.

The extracted lead was precipitated easily from the PDA by increasing the pH of the solution to approximately 10, allowing for complete recovery of the chelating agent and thus making it more favorable than EDTA.

During that same time, Hong and Chen[31] also published a study demonstrating the cadmium extraction efficiency of PDA from spiked soils. The same recovery of extracted metals through increasing the solution pH was recorded; identifying this trend in release of nickel, copper, lead, zinc, as well as cadmium.

Fast pyrolysis

Pyrolysis is the thermal decomposition of lignocellulosic biomass in an oxygen-free environment that generates three main products: liquid bio-oil, solid char, and non-condensable gases. Fast pyrolysis in particular utilizes shorter residence times and more rapid heating and cooling to generate a larger quantity of bio-oil than slow pyrolysis.[56] Wood preservative formulations often include heavy metals and other hazardous elements that persist in the biomass after service. Without extraction of these added inorganics prior to conversion, pyrolysis as a method of preservative-treated wood disposal results in inorganic-rich biochar that cannot be discarded in landfills due to the possibility of leaching into the environment.[51] However, minimizing the breakdown of the wood structural components, i.e. cellulose, hemicellulose, and lignin, from feedstock pretreatment is crucial for maximizing pyrolysis product yield. The quantities of each of these structural components vary between biomass types, which in turn have been shown to have an effect on the pyrolysis process.

Stefanidis et al.[36] investigated the effects of cellulose, hemicellulose, and lignin isolated from whole biomass on subsequent pyrolysis in a thermo-gravimetric analyzer and fixed bed reactor at 500 °C. Both the quantity and quality of the bio-oil generated were studied. Analysis of the products from these experiments revealed that pyrolysis of cellulose produced a large yield of bio-oil, while that of lignin generated a high amount of solid ash and that of xylan resulted in high gas and moderate amounts of bio-oil. The composition of the bio-oils generated also varied from one another. Bio-oil from pyrolysis of cellulose gave a product with high amounts of anhydrosugars, but pyrolysis of xylan resulted in bio-oil with larger water, phenol, and ketone contents. Finally, conversion of lignin resulted in phenolic-rich bio-oil. The interactions of these components with one another have also been shown to have an effect on pyrolysis. For example, Wang et al.[57] demonstrated that the interaction between hemicellulose and lignin promoted phenol formation but inhibited that of hydrocarbons. Additionally, the cellulose-hemicellulose interaction lessened levoglucosan production while encouraging the formation of products like furfural and acetic acid during pyrolysis of mixed biomass.

Water content of the biomass feedstock also plays a role in pyrolysis product quality and distribution. Dobele et al.[58] studied the changes that occurred within conversion products generated from hardwood samples after being dried prior to subsequent pyrolysis. They found that drying of the wood before pyrolysis between about 200 °C and 275 °C resulted in a decrease in the quantity of bio-oil produced, but its acid content was lower. A maximum bio-oil yield of over 60 % was produced with drying at 200 °C before pyrolysis at 550 °C. An improvement of the product's properties was also

reported at these conditions. These improvements include a decrease in the generated bio-oil's water and acid content, as well as an increase in its calorific value.

The parameters used for pyrolysis of woody biomass also greatly affect the distribution and composition of the products generated. Akhtar and Amin[38] supported that temperature was the operating parameter that most influenced the product yields during fast pyrolysis, with maximum bio-oil yield occurring between 500 and 550 °C. Similarly, the amount of bio-oil produced from fast pyrolysis of creosote-treat wood ties in a fluidized bed reactor was highest at 458 °C[59], while the largest quantity generated from pistachio shells occurred at 500 °C.[34] These moderate temperatures, when combined with rapid heating rates and short residence times, are reported to maximize bio-oil production.[34]

CHAPTER II
ENVIRONMENTALLY FRIENDLY PROCESS FOR RECOVERY OF WOOD PRESERVATIVE FROM USED COPPER NAPHTHENATE-TREATED RAILROAD TIES

A version of this chapter was originally published by Holly L. Haber, Pyoungchung Kim, Stephen C. Chmely, Jeff Lloyd, Yagya N. Regmi, Nourredine Abdoulmoumine and Nicole Labbé. I has been reprinted with permission from “Environmentally Friendly Process for Recovery of Wood Preservative from Used Copper-Naphthenate Treated Railroad Ties” in American Chemical Society’s *Sustainable Chemistry and Engineering*, 2017, DOI: 10.1021/acssuschemeng.7b02760. Copyright 2017 American Chemical Society.

Holly Haber collected the data presented in this journal article, wrote the journal article, as well as participated in the editing process. Dr. Kim assisted in data collection, analysis, and interpretation. Dr. Steven C. Chmely was involved in data interpretation and editing of the article. Dr. Regmi collected SEM micrographs used in the publication and also participated in editing of the final manuscript. Dr. Jeff Lloyd contributed to the revision process and provided subject matter expertise. Dr. Nicole Labbé and Dr. Nourredine Abdoulmoumine prepared the study’s experimental design and contributed heavily in data analysis. Dr. Labbé and Dr. Abdoulmoumine also were heavily involved in revising the publication. All authors prior to publication by Sustainable Chemistry and Engineering approved the final document.

Abstract

Removal of copper naphthenate (CN) from used wooden railroad ties was investigated to improve the commercial viability of this biomass as a fuel source and avoid alternative disposal methods, like landfilling. Bench-scale thermal desorption of organic preservative components from CN-impregnated ties was followed by extraction of the copper fraction with ethylenediaminetetraacetic acid (EDTA), 1-hydroxy ethylidene-1,1-diphosphonic acid (HEDP), or 2,6-pyridine dicarboxylic acid (PDA). Naphthenic acid (NA) and carrier oil was recovered at desorption temperatures between 225 and 300 °C and could potentially be recycled to treat new ties. The thermal treatment also mimicked torrefaction, improving the biomass properties for use as a thermochemical conversion feedstock. Chelation with PDA, a biodegradable chelating agent, after desorption had the highest extraction efficiency of copper and other naturally present inorganics; extracting 100 % of the copper from both the raw and 225 °C-treated samples. Optimized desorbed material showed a 64 % decrease in ash content when extracted with PDA; however, extraction efficiency decreased as desorption temperature increased, indicating that thermal treatment caused the inorganics to be less extractable. We concluded that the optimum desorption conditions were between 250 and 275 °C for 45 min followed by extraction with PDA when considering both NA removal and inorganic extraction efficiency.

Introduction

Copper naphthenate (CN) is an oil-borne preservative composed of naphthenic acids (NA) and salts of copper ions effective against fungi, bacteria, and molds.[1] Approximately 267 million cubic feet of lumber are treated with oil-borne preservatives, including CN and pentachlorophenol (both diluted in carrier oil), per year.[60] High-pressure treatment is used to apply CN into wooden railroad ties before field installation to slow biodeterioration. This treatment results in a retention of 0.06 pcf as copper in the wood and an assay zone of one inch from the edge of the tie.[61] After being removed from railroads, the majority of preservative-treated railroad ties become a fuel source in large industrial boilers permitted for burning biomass. Changes to boiler emissions regulations, like those dictated in the EPA's Non Hazardous Secondary Materials Rule for example,[62] combined with the low current price of natural gas has resulted in a larger amount of ties being discarded in landfills as an alternative. The use of fossil fuels and other non-wood alternatives has also increased in response, further contributing to the release of greenhouse gasses already augmented by the decomposition of CN-treated ties in landfills.[63]

Thermal desorption has been shown to be an effective treatment method for recovering the preservative creosote from used railroad ties.[8] Advantages of thermal desorption over the use of an organic solvent include a lower cost, no preservative dilution, and upgrading of the quality of the ties for further thermochemical conversion processes with improved properties similar to those of torrefied biomass.[11-13] Torrefaction, typically carried out between 200 and 300 °C, causes a substantial rise in the calorific value and

carbon content of woody biomass in particular.[14] The combined reduction in moisture and volatilization of oxygen and hydrogen-rich compounds during torrefaction results in a feedstock with a higher energy density, lower specific grinding energy, better storage stability, and smaller average particle size than untreated biomass; all of which are beneficial for thermochemical conversion processes.[64]

Although thermal treatment is an effective method for recovery of the organic fraction of wood preservatives, CN contains an additional inorganic fraction not found in creosote that remains in the biomass after desorption. Many inorganics, such as alkali and alkaline earth metals in particular, have been reported to possess undesired catalytic effects on thermochemical conversion processes like pyrolysis.[19-21] The presence of copper and these other metals leads to a decrease in yield and intensification of physical and chemical issues like slagging, clogging, and degradation of reactor walls from corrosion and deactivation of catalysts.[21] Chelating agents are often used as an extraction method for the removal of inorganics from biomass, including those that have these detrimental effects. One of the most common of these chelating agents is ethylenediaminetetraacetic acid (EDTA), which has shown high efficiency in heavy metal removal from preservative-treated wood.[28, 53, 65] This chelating agent, however, is not biodegradable and is hazardous to the environment,[28-29] causing its use to be restricted or banned for various applications in European countries.[66] Alternatives to EDTA, such as 1-hydroxy ethylidene-1,1-diphosphonic acid (HEDP) and 2,6-pyridine dicarboxylic acid (PDA), are gaining popularity for inorganic removal because of their comparable extraction efficiency to traditional chelating agents, as well as their

biodegradability.[32] HEDP belongs to the organophosphate group of chelating agents while PDA is a naturally occurring compound in bacterial spores.[27] HEDP chelates with copper in a 1:1 ratio like EDTA;[67] whereas PDA contains three possible coordination sites with metal ions and typically chelates in a 2:1 (chelator: metal) ratio.[32]

However, the thermal treatment of CN-impregnated wood may have an effect on the copper and naturally present inorganics found in the ties, in addition to the ease of their extraction with these chelating agents.[25, 68] For example, a study by Barnes et al.[25] found that steam treatment of CN-treated wood poles led to the formation of inert Cu_2O. Heat treatment in the presence of moisture can also cause the surface of the wood to become hydrophobic, which reduces the wood's uptake of water and limits the movement of these inorganics within the wood structure.[25, 64, 69-70] A higher hydrophobicity would also restrict water diffusion across the wood cell wall.

In this study we investigate the recovery of CN components from used railroad ties with thermal treatment between 200 and 300 °C and RT from 30 to 60 min followed by extraction with 1% solutions of EDTA, HEDP, and PDA. We propose that this process will improve the commercial viability of using spent ties as fuel if they can be recycled to capture the value of the copper naphthenate and oil and consequently be used to produce a high-quality feedstock for thermochemical processes like pyrolysis.

Experimental Section

Material

Copper naphthenate impregnated railroad ties composed of several different hardwood species including oak, hickory and gum, were provided pre-chipped by Nisus Corporation (Rockford, TN) in large 55 gallon plastic drums. Six whole ties were run through a commercial chipper and then a sub-sample was further processed using a knife mill to produce the material that was ultimately provided. The volume received was equal to that of approximately two ties, but contained mixed material from the original six. This was done to ensure the sample was representative with regard to both typical retention and commercial species mix. The chips were then ground using a Wiley Mill to less than 2-mm size prior to all analysis and stored in an airtight container.

Characterization of the used tie material

Proximate analysis of the untreated ties (as received) sample included determination of moisture content, ash content, and the percent volatile matter of the CN-treated railroad ties using American Society for Testing and Materials (ASTM) standard method D1762: Standard Test Method for Chemical Analysis of Wood Charcoal. To summarize, porcelain crucibles were heated in a furnace and then placed in a desiccator until completely cooled. Approximately 1 g of the ground ties was then added to each crucible and placed into an oven at 105 °C overnight to remove water. Samples were then cooled in a desiccator and weighed gravimetrically to determine moisture content.

These same crucibles were then covered with a lid and placed into a furnace at 950 °C for 10 min each. They were again cooled and weighed to determine volatile matter. Finally, the uncovered crucibles were placed in a furnace at 575 °C overnight, cooled and weighed to calculate ash content of the samples. All experiments were performed in triplicate.

Removal of oil and naphthenic acids by thermal desorption

Pyrolysis-gas Chromatography/Mass Spectrometry (Py-GC/MS) was used to monitor the desorption of preservative components under different temperatures and residence times from the CN-treated railroad material. The method was adapted from that used by Kim et al. to desorb creosote in used ties.[8] This screening was done using a Frontier EGA/Py-3030 D micro-pyrolyzer and autosampler connected to a PerkinElmer Clarus 680 Gas Chromatography and Clarus SQ Mass Spectrometer. Approximately 300 $\pm$ 30 µg of the raw sample were put into each sample pan that was placed into an autosampler, which then fed into the pyrolysis furnace. The pyrolysis furnace was maintained at 200, 225, 250, 275, or 300 °C for 10, 20, or 30 min. When each residence time ended, helium (1 mL/min) carried the resulting vapor into the GC-injection port (270 °C) at a split ratio of 80:1. Once there, the following GC temperature program was started: begin at 50 °C for 4-min holding time, increase to 280 °C at 5 °C/min, and then hold for 5 min at 280 °C. An Elite 1701 MS capillary column was used for vapor separation prior to MS analysis. MS analysis was conducted with a source temperature

of 270 °C and electron ionization of 70 eV. The results were then compared with the NIST library for identification. Triplicates were collected for each Py-GC/MS experiment. After testing with Py-GC/MS, thermal desorption of oil and NA with a bench-scale fixed bed reactor was tested to determine the scalability of this process (Figure S1). Desorption of the organic fraction of the CN from the railroad ties was tested at 225, 250, 275, and 300 °C for 30, 45, and 60-min residence time under constant nitrogen flow of 2 L/min. Longer retention times (RT) than with the Py-GC/MS were used to address the slower heat transfer through the tubular furnace of the fixed-bed reactor. Additionally, only the highest four temperatures were investigated with this reactor because very little desorbed preservative was observed at 200 °C by PyGC/MS. The fixed-bed reactor consisting of a tubular furnace was fitted with four condensers to collect the desorb preservative. Approximately 30 g of CN-treated wood (as provided) was placed inside of the furnace at each time-temperature combination. Nitrogen gas carried the volatilized compounds from the sample to the condensers where they were then collected using 250 mL of acetone solvent. All four condensers were filled with liquid nitrogen during the full duration of each run to condense the vapor.

Analysis of recovered naphthenic acids and carrier oil

The liquid fraction from the walls of the condensers after desorption at each condition was recovered after the complete removal of the acetone using a rotary evaporator. Each recovered liquid was combined with approximately 1.7 µL of cyclopentylacetic acid and 1300 µl of toluene to form solutions. A 1 µL aliquot of each solution was then

directly injected into the GC/MS for identification and quantification of the recovered preservative components desorbed from the ties. A PerkinElmer Clarus 680 Gas Chromatograph coupled with a Clarus SQ Mass Spectrometer was used for this analysis at a split ratio of 50:1 with the GC-injection port maintained at 270 °C. The GC temperature program started at 50 °C, was held at that temperature for 4 min, then increased to 280 °C at 5 °C/min, and finally held for 10 min at 280 °C. An Elite 1701 MS capillary column was again used for volatilized vapor separation prior to analysis using MS and comparison with the NIST library. MS analysis was conducted with a source temperature of 270 °C and electron ionization of 70 eV. Triplicates were collected for each GC/MS experiment.

Analysis of thermally treated solid fraction

The particle size distribution of each sample after being thermally treated was determined using a set of sieves with multiple particle sizes (2.83 mm, 2.38 mm, 2 mm, 0.4 mm, < 4 mm) and a mechanical shaker. The portion of sample remaining in each sieve after shaking for five min at 500 rpm was determined gravimetrically and compared to that of the untreated sample. Proximate analysis of the solid wood samples after thermal desorption was also conducted using the same methods employed to characterize the untreated sample in section 2.2, and ultimate analysis using a 2400 Series II CHN Analyzer (PerkinElmer) was conducted to measure the percentage of carbon, hydrogen, oxygen, and nitrogen within the thermally desorbed samples. Additionally, scanning electron microscope images were collected on a Zeiss

Dual Beam FIB/SEM instrument. The samples were deposited on double sided carbon tape and coated with gold prior to characterization

Extraction of inorganics with chelating agents

Copper and other biomass inorganics that negatively affect pyrolysis were extracted from the thermally desorbed ties using a 1 % solution of EDTA (pH 5.5), HEDP (CAS 2809-21-4) (pH 1.5), or PDA (CAS 499-83-2) (pH 4). The thermally desorbed ties were also extracted with deionized water as a control. The pH of chelating agents affects their extraction efficiency, so this parameter was adjusted to values shown to have high extraction efficiency of copper in the literature. [31, 68, 71] Ammonium hydroxide was used for pH adjustment of the solutions, so as not to introduce any new inorganics into the systems. A traditional batch extraction method was used where the reaction temperature was held constant at 75 °C during each three-hour extraction with constant stirring at 150 rpm. A solution: liquid ratio of 15:1 was used for each test.[18, 19] After each extraction, the solid was separated from the liquid using a Whatman no.2 filter. The liquid was then centrifuged for 20 min at 1000 rpm to further remove any small solid particles from the liquid samples.

Inductively coupled plasma-optical emission spectrometry (ICP-OES) (Perkin Elmer Optima 7300 Dual View, Shelton, CT) was conducted after chelation to determine the inorganic composition of the liquid extracted from the ties. Reagent grade nitric acid (67-70 %) (1 mL) was added to 15 mL of each liquid sample for acidification of the solutions, which were then passed through 0.2 µL filters and analyzed using ICP-OES analysis to

determine the composition of inorganics leached from each sample. The determined phosphorous concentration extracted from each sample chelated with HEDP was corrected based on the molecular weight of the chelating agent.

Results and Discussion

Removal of oil and naphthenic acids by thermal desorption

Copper naphthenate is composed of NA, copper ions, and carrier oil.[46] Because the inorganic fraction of the preservative does not volatilize at the selected temperature range, only the oil and NA (organic fraction) can be removed by thermal desorption. Pyrolysis-gas Chromatography/Mass Spectrometry (Py-GC/MS) was used to monitor the desorption of these NA, as well as the carrier oil, from the used railroad ties at 200, 225, 250, 275, or 300 °C for varied residence times to determine the optimal thermal desorption conditions. Several hundred different compounds that vary based on the source make up naphthenic acid; so quantifying the amount of this component contained within the ties using Py-GC/MS is difficult. Instead of clearly defined CN peaks, the presence of the NA results in a bump shape along the baseline of the pyrograms (Figure S1.2).[3] The area decreases as the preservative is removed from the wood ties. The tall clearly-defined peaks that appear from a RT of about 30 to 50 min can be identified as tetradecane, nonadecane, and other solvent compounds.

Figure 1 shows thermal desorption of the ground ties using Py-GC/MS at a constant temperature (275 °C) with the RT varying from 10 to 30 min, while Figure 1.2 depicts a change in desorption temperature at a constant time. Little variation in the pyrograms

occurred with an increase in RT. However, a slight decrease in the NA area with an increase in temperature supports that more preservative component is desorbed at higher temperatures (Figure 1.2). Higher temperatures also result in the detection of larger carbon dioxide, acetic acid, furfural, and other phenolic compound peaks (Figure 1.1), which indicates the partial decomposition of the wood matrix. Peaks present at approximately 30.7 and 32.7 min RT increase in height at higher temperatures, due to an increase in phenolic compounds from the breakdown of lignin; thus further demonstrating this decomposition.[8] This loss in carbon negatively affects the wood's yield as a potential thermochemical conversion feedstock by resulting in a smaller amount of upgraded feedstock produced, as well as increases the ash content (%) of that feedstock. Therefore, there is a trade-off between the highest removal of preservative at these higher temperatures and the degradation of the wood matrix.

Thermal desorption of NA on a larger scale using a fixed bed reactor was then conducted to assess the scalability of the process and validate the trends seen by Py-GC/MS. It was also possible to monitor mass loss at this scale (Table 1.1). Mass loss with the lowest treatment severity (desorption at 225 °C for 30 min) is 17.2 % and reaches 54.7 % at the highest. A larger mass loss is expected with a greater decomposition of the wood matrix. In all cases, there is a significant increase between the 30 and 45-min RT trials, but a much smaller difference between the 45 and 60-min at each temperature (Table 1).

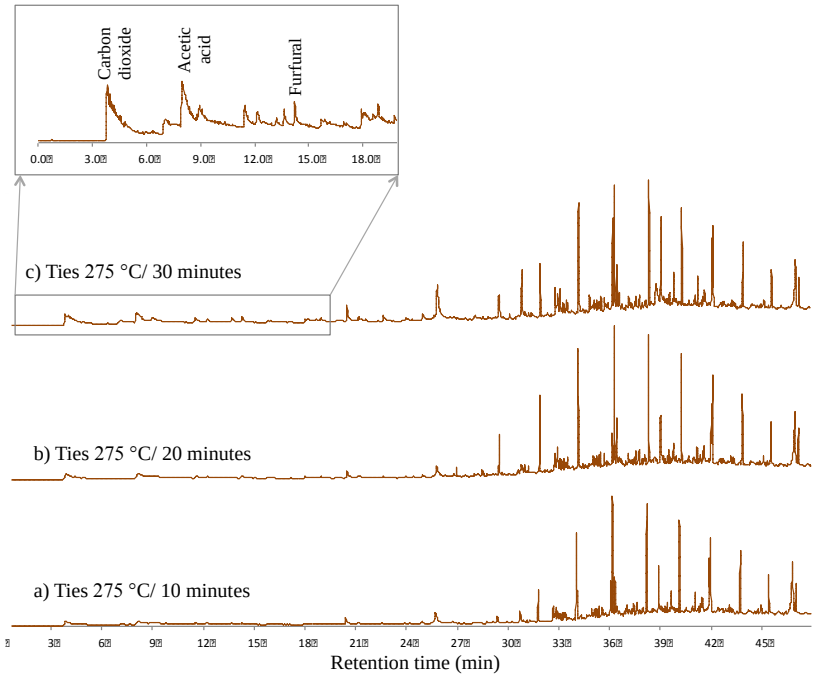


Figure 1.1. Thermal desorption of copper naphthenate-treated railroad ties by Pyrolysis-Gas Chromatography/Mass Spectrometry at 275 °C for (a) 10 min, (b) 20 min, and (c) 30 min.

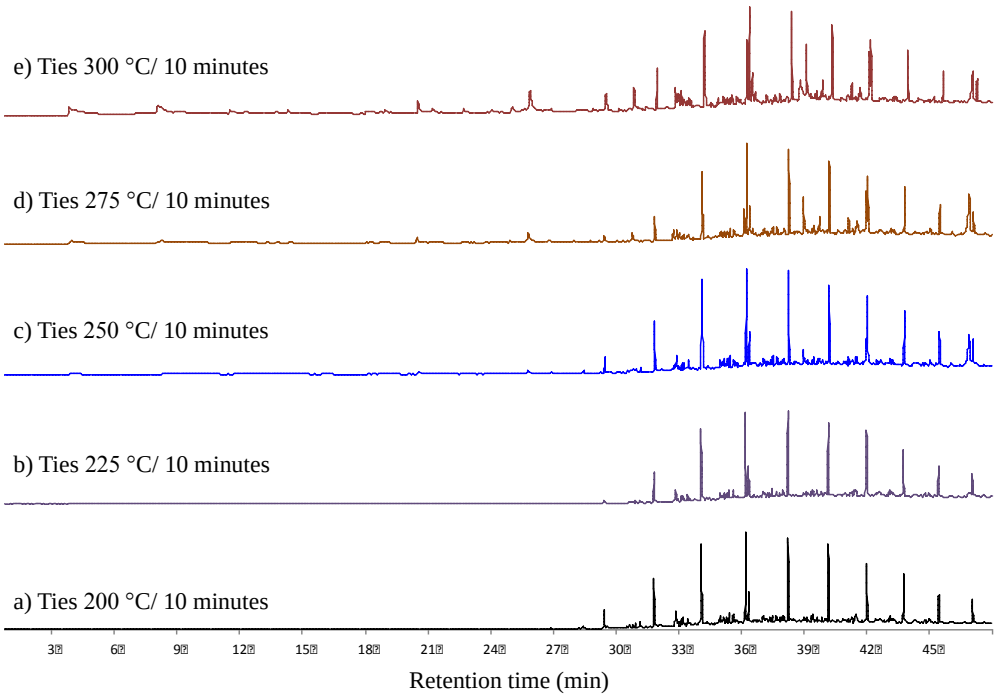


Figure 1.2. Thermal desorption of copper naphthenate-treated railroad ties by Pyrolysis-Gas Chromatography/Mass Spectrometry for 10 min at (a) 200 °C, (b) 225 °C, (c) 250 °C, (d) 275 °C, and (e) 300 °C.

For example, a difference in mass loss of about 4 % occurred at 275 °C when the residence time was lengthened from 30 to 45 min; however, a change of only about 1 % occurred when the residence time was increased from 45 to 60 min. Thus, for optimal NA desorption, a RT of 45 min should not be exceeded at any treatment temperature.

In addition to a higher removal of NA and carrier oil solvent from the ties, these mass losses can be attributed to the removal of moisture and the loss of carbon from the breakdown of the wood matrix, in particular hemicellulose.[64] Higher amounts of carbon dioxide and water are released at more severe torrefaction conditions. A greater decomposition of the wood constituents occurs as severity of thermal treatment conditions increase, as seen in the Py/GC-MS data in Figure 1. Thus, severity should be minimized when generating a feedstock for subsequent thermochemical conversion. The trends seen with thermal desorption using the bench-scale reactor mirror those observed by Py-GC/MS, which supports scalability of the desorption process.

Scanning electron microscopy (SEM) was used to verify that a higher breakdown of the wood structure occurred as bench-scale thermal desorption temperature rose. Intervessel pitting and scalariform perforations, typical of hardwoods, are visible in the vessels of the thermally desorbed samples in SEM images at 250 °C (Figure 1.3c) and 275 °C (Figure 1.3d).[72] Degradation of these tissues becomes larger and more prevalent as thermal desorption temperature increases, with almost complete morphological degradation occurring at 300 °C (Figure 1.3e). [17, 73] This decomposition can be attributed to the breakdown of biomass components like lignin (275- 500 °C), cellulose and hemicellulose (150 – 350 °C). [17-18]

Table 1.1: Mass loss of copper naphthenate-treated railroad ties from bench-scale thermal desorption under varying retention time and temperature

Desorption temperature (°C)	Desorption time (min)	Average mass loss[a] (%)
225	30	17.2 (0.3)
	45	20.4 (0.5)
	60	20.9 (1.9)
250	30	23.4 (0.2)
	45	27.3 (0.3)
	60	28.9 (0.6)
275	30	32.9 (0.5)
	45	37.4 (1.1)
	60	38.6 (0.4)
300	30	45.0 (0.4)
	45	49.2 (2.8)
	60	54.7 (1.2)

[a] Average (standard deviation) of triplicates

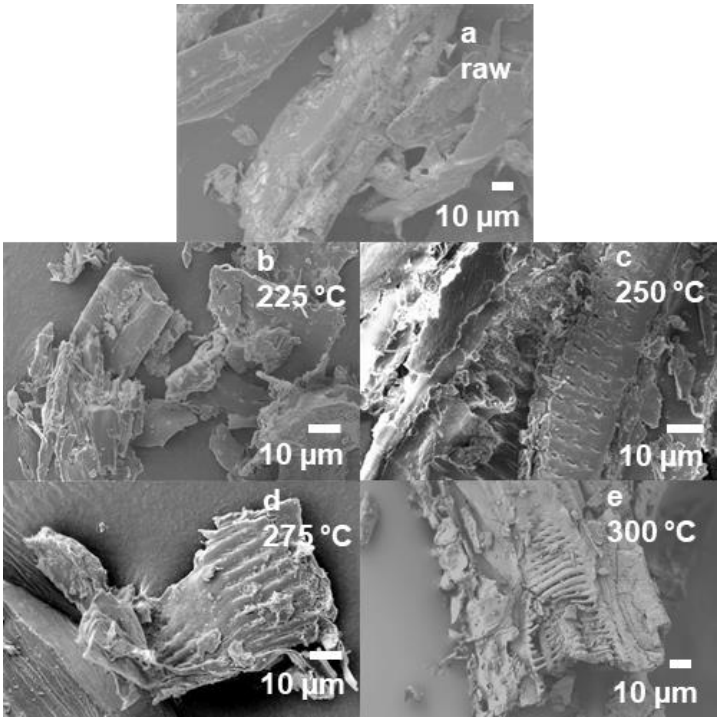


Figure 1.3. Scanning electron micrographs of wood ties thermally desorbed with a bench-scale fixed bed reactor for 45 min at (a) raw sample (no thermal treatment), (b) 225 °C, (c) 250 °C, (d) 275 °C, and (e) 300 °C.

Properties of recovered naphthenic acid and carrier oil

After each thermal desorption using the bench-scale reactor, the condensed liquid was recovered from the reactor using acetone. This liquid fraction was composed of two distinct phases, a water fraction and an organic fraction, which were separated and weighed for yield quantification (Table 1.2) prior to analysis. The amount recovered increases with thermal desorption time and temperature (Table 1.2). Approximately 0.11 g of total liquid was recovered with a 30-minute thermal treatment at 225 °C, while 0.28 g were removed using the most severe treatment conditions of 300 °C and 60 min. Because the organic fraction of the recovered liquid includes mainly preservative components and wood decomposition byproducts, this increase in yield suggests both a larger amount of naphthenic acid and carrier oil being desorbed, as well as a larger decomposition of the wood matrix.

Table 1.2: Yield of organic liquid fraction from bench-scale thermal desorption of ties

Thermal desorption temperature (°C)	Retention time (min)	Weight of extracted organic phase (g)[a]
225	30	0.11
	45	0.11
	60	0.12
250	30	0.15
	45	0.19
	60	0.19
275	30	0.19
	45	0.21
	60	0.21
300	30	0.19
	45	0.19
	60	0.28

[a] per 30 g of raw biomass treated

Aliquots from the recovered organic fraction were combined in solution with toluene and cyclopentylacetic acid before being directly injected into a GC/MS for identification and quantification of the major components. The profile of the liquid phase is very similar to the profile obtained from the desorbed vapor by Py-GC/MS. The major peaks are identified as compounds derived from the carrier oil solvent that was used to help CN penetrate the wood ties' cell walls. The bump shape below the solvent peaks and above the baseline in each chromatogram is caused by the presence of NA (Figure S1.2).[3] In regards to the solvent peaks, no differences exist between the different desorption conditions; however, the total NA area is larger with an increase in temperature (Figure 1.4). Due to the lower boiling point of NA (130 - 240 °C) in comparison with the carrier oil solvent (280 - 340 °C), this component of the preservative would be expected to volatilize at the lower desorption temperatures; thus supporting the observation.[74-75] The amount of NA recovered at temperatures above 250 °C drastically rises from that at less severe conditions. However, very little difference exists between the 45 min desorption at 275 °C and 300 °C. This plateau suggests that NA removal is maximized between 250 and 275 °C.

Properties of solid residual thermally treated ties

The moisture content of the thermally desorbed railroad ties decreases with an increase in time as well as temperature (Table 1.3). Moisture content of the railroad ties prior to treatment is 9.6 %, which is reduced to 1.3 % after desorption at 300 °C for 60 min.

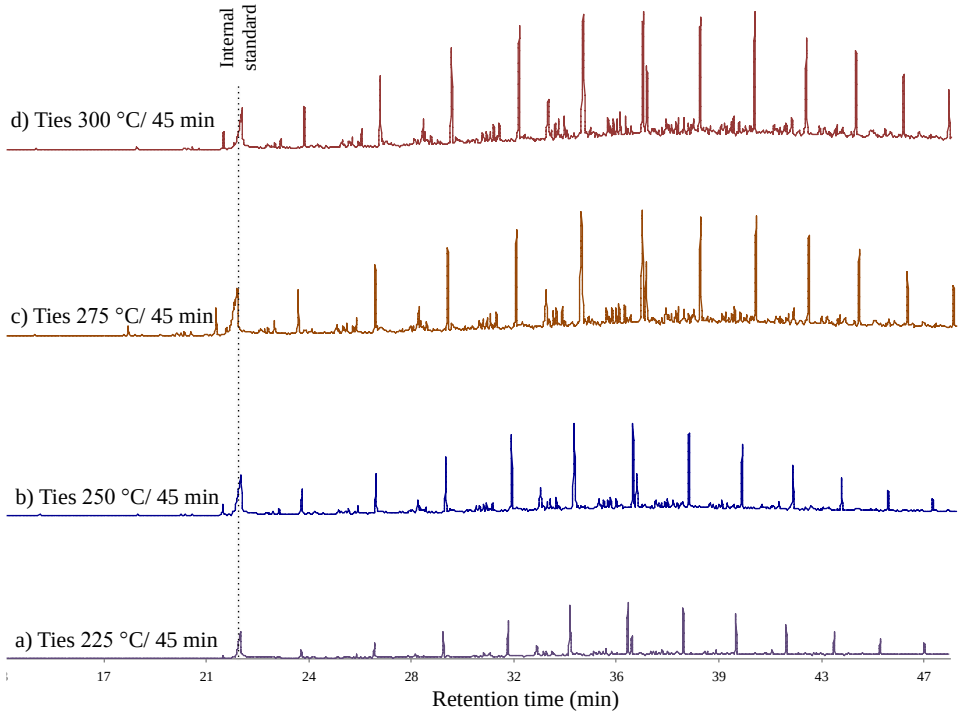


Figure 1.4. Gas Chromatography/Mass Spectrometry of recovered liquid organic phase from bench-scale thermal desorption of railroad ties for 45 min at (a) 225 °C, (b) 250 °C, (c) 275 °C, and (d) 300 °C.

Lower moisture content is beneficial for a pyrolysis feedstock by making the material easier to store and transport prior to conversion, in addition to producing a higher quality bio-oil.[64] Therefore, thermal treatment improves the wood quality for use as a pyrolysis feedstock. Removal of hydrogen and oxygen in the form of water and other compounds results in a higher amount of fixed carbon present in the ties as desorption temperature and time increase. The same trend can be seen with the change in carbon content which augments from 51.0 to 59.3 %, accompanying a decrease in hydrogen and oxygen from 6.7 to 5.2 % and 41.5 to 33.4 % respectively. The ash content is relatively low in all conditions, but slightly increases from 1.2 % in the starting material to 1.9 % at the highest desorption severity; thus further supporting conditions with lower severity for optimizing recovery of NA from the ties.

The percentage of smaller sized particles also increases as a result of this greater decomposition (Figure 1.5). The number of smaller particles present in all desorbed samples is larger than in the untreated sample. Approximately half of the particles in every desorbed sample are between a 0.4 and 2 mm particle size. Biomass particle size is often reduced as a result of torrefaction[76] due to the wood becoming more brittle and more easily ground; therefore, this trend is expected within our selected desorption temperature range.

Table 1.3: Proximate and ultimate analysis of used railroad ties thermally desorbed with a fixed bed reactor

Desorption Temperature (°C)	Desorption Time (min)	Moisture Content (%)	Ash Content (%)	Fixed Carbon (%)	% C	% H	% O*
Starting material	-	9.6 (0.3)	1.2 (0.1)	4.0	50.5 (0.2)	6.7 (0.3)	41.5 (0.3)
225	30	4.7 (0.1)	1.0 (0.1)	12.9	50.9 (0.2)	6.2 (0.1)	42.2 (0.3)
	45	4.0 (0.1)	1.0 (0.1)	13.4	51.0 (0.4)	5.8 (0.1)	42.9 (0.5)
	60	3.3 (0.1)	1.0 (0.1)	13.7	50.5 (0.2)	5.8 (0.2)	43.1 (0.2)
250	30	2.9 (0.1)	1.1 (0.1)	17.2	50.7 (0.1)	5.8 (0.1)	42.1 (0.2)
	45	2.8 (0.1)	1.2 (0.1)	18.1	52.0 (0.2)	5.9 (0.4)	41.0 (0.6)
	60	2.7 (0.4)	1.2 (0.4)	17.5	52.4 (0.3)	6.0 (0.1)	40.7 (0.4)
275	30	1.2 (0.3)	1.3 (0.2)	20.1	53.1 (0.3)	5.8 (0.1)	39.7 (0.4)
	45	1.0 (0.1)	1.4 (0.1)	22.5	54.2 (0.1)	5.7 (0.1)	38.6 (0.1)
	60	1.0 (0.4)	1.4 (0.2)	23.7	54.9 (0.1)	5.4 (0.1)	38.1 (0.2)
300	30	1.7 (0.2)	1.4 (0.2)	27.2	56.5 (0.1)	5.2 (0.3)	36.8 (0.3)
	45	1.2 (0.3)	1.6 (0.1)	31.7	57.3 (1.4)	5.2 (0.2)	35.8 (1.6)
	60	1.3 (0.7)	1.9 (0.3)	33.4	59.3 (0.4)	5.2 (0.1)	33.4 (0.5)

Mean (standard error)
* Percent oxygen calculated by difference

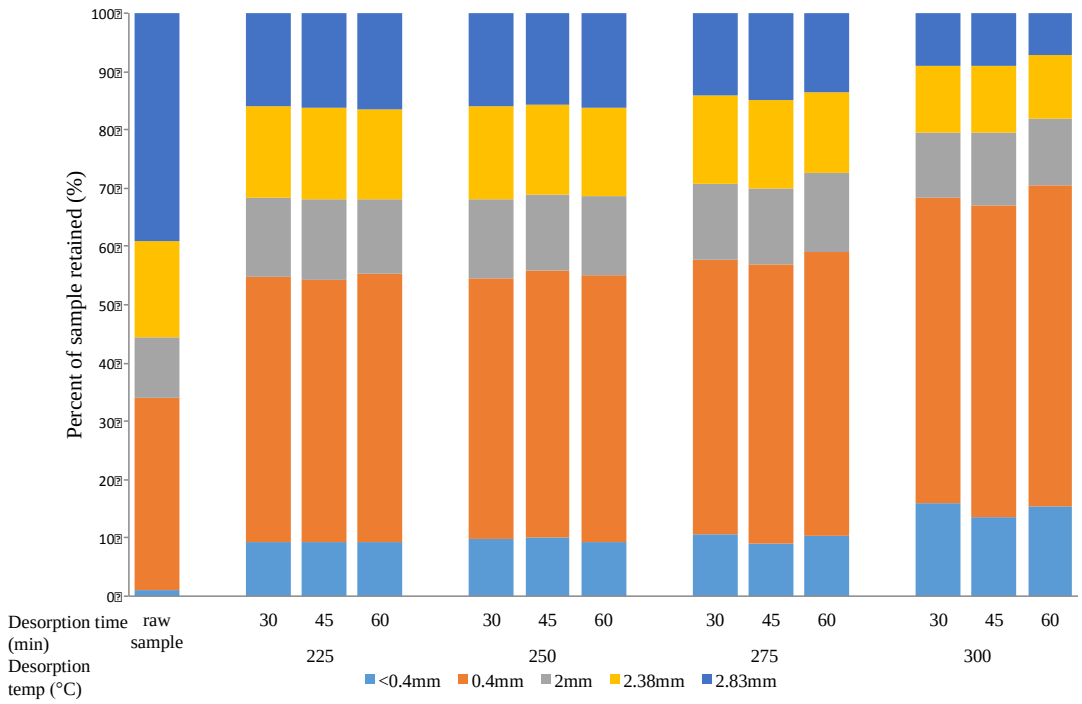


Figure 1.5. Particle size distribution of railroad ties after thermal treatment at varied temperatures and retention times.

A reduction in particle size is also advantageous for the subsequent chelation process.[77-78] Typically, higher extraction efficiencies are achieved when extracting from smaller biomass particles than larger chunks due to an increase in specific wood surface area.[77-78] Larger surface area allows the metals to become more accessible to the chelating agents.[78]

Extraction of inorganics with chelating agents

Following thermal desorption, extraction of the inorganics within the thermally treated ties was tested using deionized water and 1 % solutions of three chelating agents: EDTA, HEDP, and PDA. Figure 6 demonstrates the composition of inorganics extracted from the thermally desorbed samples with the bench-scale reactor for 45 min at temperatures between 225 and 300 °C. Overall extraction efficiency of inorganics from the thermally desorbed ties is the highest with PDA, followed by HEDP, EDTA, and then water (Figure 1.6). Over 90 % of copper and other inorganics known for having detrimental effects on pyrolysis are extracted from the raw sample using all of the agents tested (Table S1.3). This supports the replacement of EDTA with the more environmentally friendly chelating agents, PDA and HEDP, for removal of copper and biomass inherent inorganics. Additionally, it is noteworthy to point out that both potassium and sodium are completely extracted from the ties using only water, which is consistent with what has been reported in the literature.[21] With all chelating agents, as well as with water, extraction efficiency significantly decreases with increasing thermal desorption severity. For example, 1.37 mmol/L of copper is extracted using PDA from

the non-desorbed sample, but only about 0.4 mmol/L is leached from the sample desorbed at 300 °C prior to extraction (Table S1.4). This demonstrates that as the thermal desorption temperature used for NA removal increases, inorganics become harder to remove from the ties. Percent removal of calcium decreases by 67.3, 56.7, 40.2, and 17.3 % with water, EDTA, PDA, and HEDP respectively from the untreated sample to the sample desorbed at 300 °C for 45 min (Table S1.3). This same trend is present for all inorganics quantified. Therefore, a tradeoff between NA recovery and inorganic removal must also be taken into consideration when determining optimal conditions for CN removal from the used railroad ties.

The cause of this decrease in extraction efficiency with increasing desorption temperature could be due to several possible reasons. It has been demonstrated that thermal treatment can lead to oxidation of the metals;[25, 44, 68] for example converting copper to copper oxide. These oxides are inert and insoluble, thus reducing the amount of inorganics able to be extracted from the ties.[68] While torrefaction decreases particle size and increases surface area, this treatment is also known to cause woody biomass to become more hydrophobic,[64, 69] which could be another cause of the reduction in extraction efficiency. A more hydrophobic wood structure would be much harder to penetrate by the chelating agents. Without access into the wood structure, fewer inorganics would be accessible and removed from the ties. Only those on the surface would be extracted.

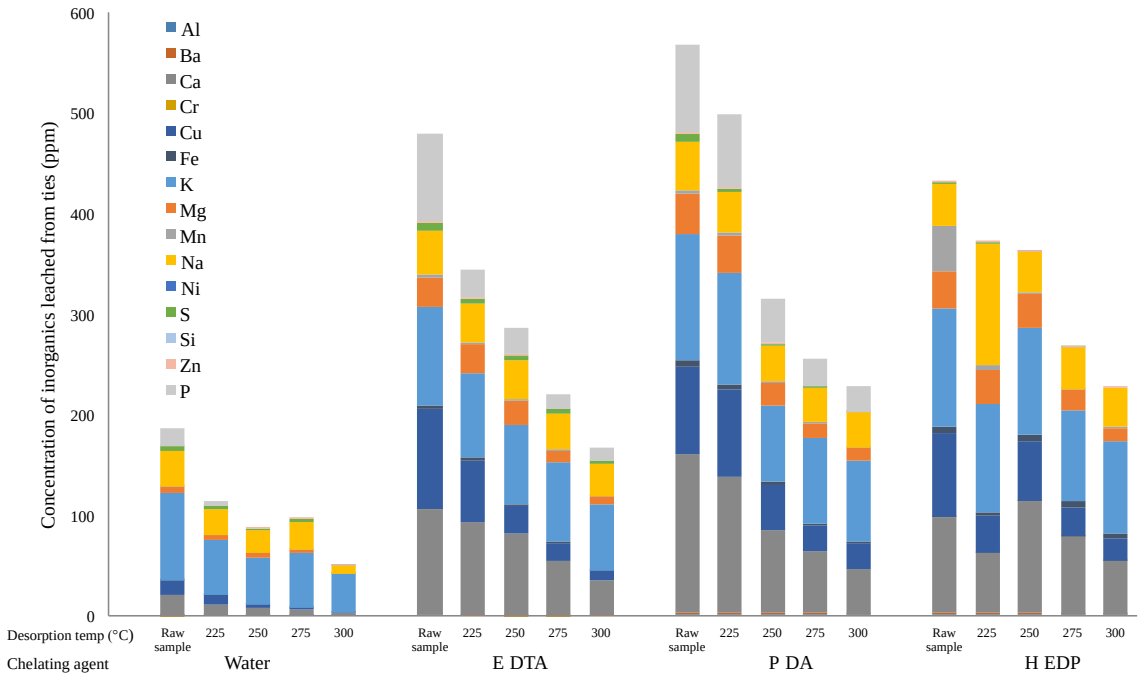


Figure 1.6. Inorganic composition of railroad ties extracted with EDTA, HEDP, PDA, or water after thermal desorption.

The ash content of the thermally treated ties steadily rises with an increase in thermal desorption temperature for all chelating agents tested, but drops significantly after chelation for all samples except those extracted with HEDP (Figure 1.7). Samples extracted using HEDP have significantly higher ash content than the others, which can be attributed to the introduction of additional phosphorous from the HEDP itself. The other chelating agents are composed of only carbon, hydrogen, oxygen, and nitrogen, while HEDP includes phosphorous. No washing of the wood was done after extraction to prevent additional water use that would increase cost and energy associated with implementing this process at an industrial scale; therefore, some of the HEDP and other chelating agents could remain in the solid fraction.

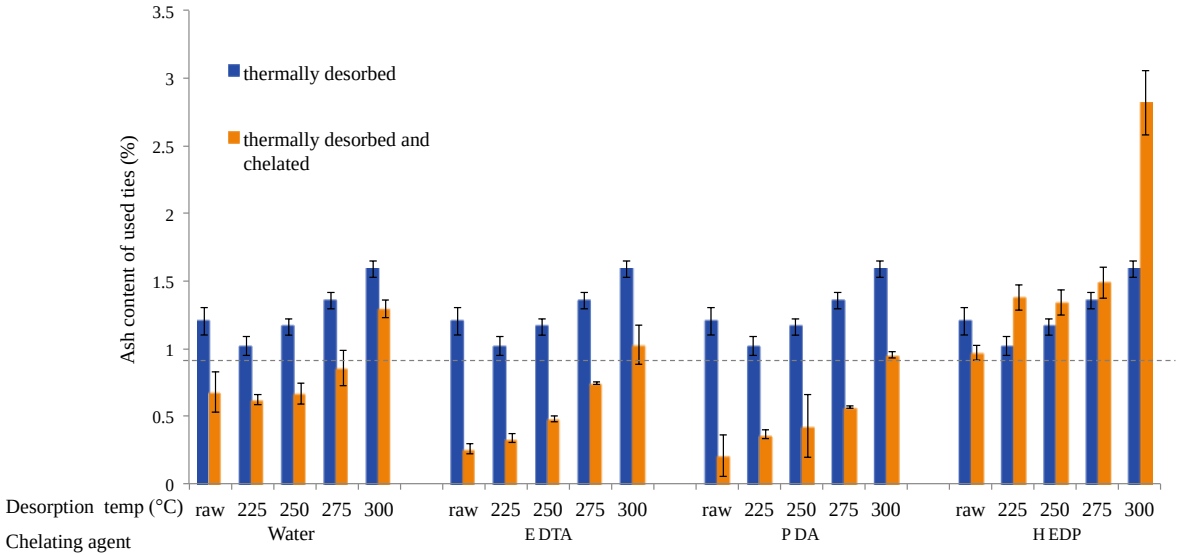


Figure 1.7. Effect of thermal desorption and chelation on ash content of copper naphthenate-treated ties.

For thermochemical conversion, an ash content below 0.9 % is desirable, with an even smaller content preferable.[79] The dashed line in Figure 1.7 represents this threshold. Thermal treatment of the ties between 250 °C and 275 °C followed by extraction with EDTA, PDA, or water result in biomass with an ash content lower than this desired limit; with PDA extracted samples having the lowest ash content of the three (0.4 to 0.6 %) (Figure 1.7).

Therefore, the conditions suggested for optimum preservative removal are a temperature between 250 and 275 °C and a residence time of 45 min, followed by inorganic extraction with the chelating agent PDA. This determination takes into consideration a trade-off between upgrading the ties for future thermochemical conversion, preservative removal, and inorganic extraction. Combining the use of thermal desorption with PDA extraction can support the recovery of CN components from used railroad ties and generate a high-quality biomass for thermochemical conversion processes; thereby reducing the landfilling of end-of-life ties by improving their value as a fuel source with this process. The value inherent in the carrier oil, NA, and copper recovered from rail ties after their primary service make treated wood re-use or disposal both cleaner and more commercially viable. Applying this process to treat used ties on a larger scale would provide a secondary use for this renewable fuel source while also minimizing the negative environmental impact from landfill disposal of this biomass. This extraction method using the biodegradable chelating agent PDA can also be further applied beyond CN-treated railroad ties for the lowering of ash content

from other types of biomass, which is advantageous for bioenergy producers. This application is being investigated as a follow-up to this study.

Acknowledgements

This work was supported by the IBSS Partnership which is funded by Agriculture and Food Research Initiative Competitive Grant from the USDA National Institute of Food and Agriculture [grant number 2011-68005-30410]; 2014-2015 AgResearch Innovation grant (the University of Tennessee Institute of Agriculture); and USDA Agriculture and Food Research Initiative (AFRI, [grant number 2015-6021-24121]).

Appendix

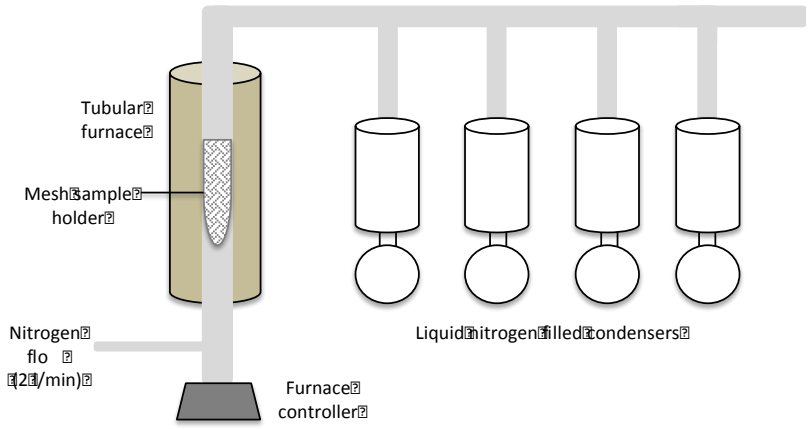


Figure S1.1. Bench-scale thermal desorption fixed bed reactor.

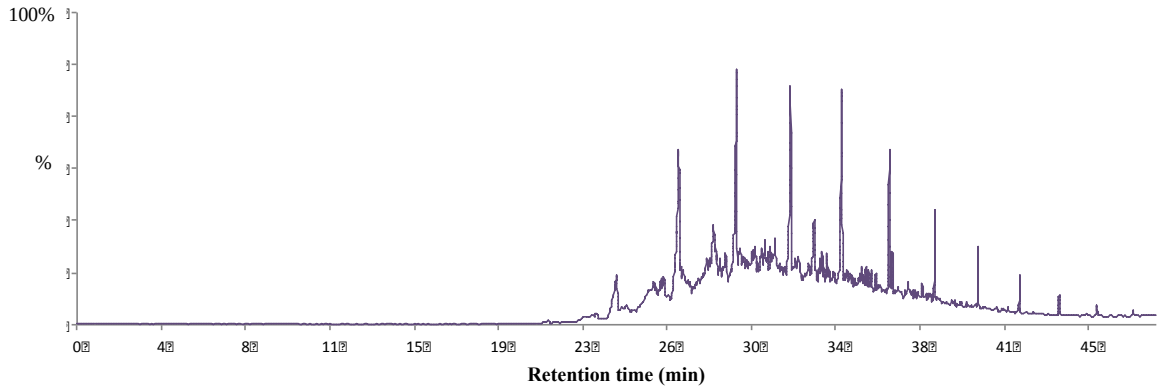


Figure S1.2. Pyrogram of 0.8 % pure liquid copper naphthenate at 500 °C for 12 seconds.

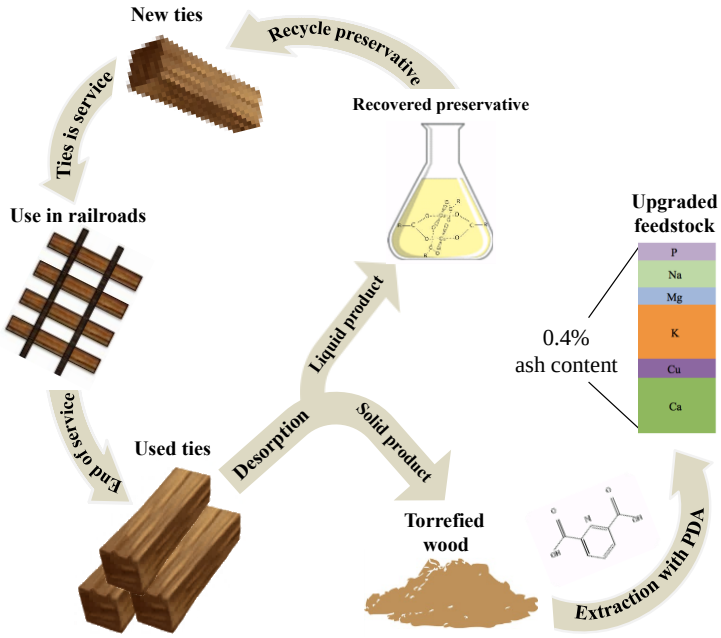


Figure S1.3. Summary graphic for Chapter II.

Table S1.1: Inorganic composition of ties thermally desorbed for 45 min under varying temperatures then extracted with EDTA, PDA, HEDP, and water

	EDTA												
	Concentration on inorganics (ppm)												
Thermal desorption temperature (°C)	Al	Ba	Ca	Cr	Cu	Fe	K	Mg	Mn	Na	P	S	Zn
Starting material	76 (0.0)	25 (0.0)	1403 (5.8)	0 (0.0)	983 (4.7)	95 (0.3)	1141 (2.2)	402 (1.9)	21 (0.1)	364 (3.7)	969 (14.1)	1067 (4.0)	0 (0.0)
Raw	1.0 (0.1)	0.3 (0.1)	104.9 (5.2)	0.0 (0.0)	99.3 (2.6)	5.0 (0.0)	98.4 (5.0)	28.6 (0.9)	2.1 (0.1)	43.9 (0.9)	86.3 (1.5)	8.3 (0.4)	2.0 (0.1)
225 °C	0.5 (0.1)	0.6 (0.2)	92.1 (14.2)	0.0 (0.0)	61.3 (2.8)	2.3 (0.5)	85.1 (6.7)	28.7 (3.0)	1.2 (0.3)	39.2 (6.2)	26.9 (1.5)	4.7 (1.0)	1.1 (0.3)
250 °C	0.4 (0.1)	1.0 (0.1)	80.6 (9.5)	0.0 (0.0)	27.4 (3.1)	1.6 (0.3)	78.0 (8.1)	25.1 (1.8)	1.2 (0.1)	38.9 (5.3)	26.1 (0.1)	4.9 (0.7)	1.1 (0.1)
275 °C	0.4 (0.1)	0.8 (0.1)	54.0 (3.1)	0.0 (0.0)	17.1 (0.8)	1.7 (0.2)	78.9 (5.4)	11.5 (1.0)	0.6 (0.1)	36.6 (1.2)	14.2 (0.1)	3.7 (0.5)	0.5 (0.1)
300 °C	0.31 (0.0)	0.5 (0.1)	33.7 (3.0)	0.0 (0.0)	9.9 (1.6)	1.1 (0.2)	65.2 (12.6)	7.9 (1.4)	0.3 (0.1)	32.3 (0.9)	11.5 (1.1)	3.7 (0.4)	0.3 (0.01)
	PDA												
Raw	1.5 (0.2)	0.9 (0.1)	159.1 (2.3)	0.0 (0.0)	86.9 (1.2)	5.0 (0.1)	126.5 (0.9)	40.4 (0.8)	2.4 (0.3)	48.7 (2.6)	86.7 (1.8)	7.6 (0.6)	2.2 (0.1)
225 °C	1.5 (0.1)	2.1 (0.1)	134.1 (0.7)	0.0 (0.0)	86.6 (1.0)	4.9 (0.9)	111.0 (1.5)	38.3 (1.0)	2.4 (0.5)	39.9 (0.2)	71.3 (0.3)	4.2 (0.6)	2.1 (0.4)
250 °C	1.3 (0.7)	1.4 (0.1)	82.7 (1.1)	0.0 (0.0)	45.1 (0.4)	2.6 (0.1)	75.2 (0.3)	23.5 (0.2)	2.2 (1.4)	34.3 (2.8)	43.3 (5.7)	2.1 (1.2)	2.1 (1.2)
275 °C	0.9 (0.1)	1.3 (0.3)	61.3 (0.4)	0.0 (0.0)	25.6 (0.3)	2.6 (0.2)	85.2 (0.2)	14.6 (0.1)	0.7 (0.1)	34.2 (0.7)	26.1 (0.8)	2.1 (0.2)	0.6 (0.1)
300 °C	0.9 (0.3)	1.2 (0.6)	44.6 (1.6)	0.0 (0.0)	25.4 (1.8)	2.0 (0.1)	80.1 (0.8)	13.4 (0.9)	0.4 (0.1)	34.0 (1.8)	25.3 (0.1)	0.5 (0.4)	0.5 (0.1)
	HEDP												
Raw	1.3 (0.2)	2.2 (0.7)	93.9 (7.4)	0.1 (0.1)	83.3 (2.3)	7.2 (0.0)	117.9 (6.7)	36.8 (6.8)	44.2 (0.3)	41.9 (1.6)	0.0 (0.0)	1.4 (0.1)	1.7 (0.1)
225 °C	1.1 (0.3)	1.9 (0.8)	59.1 (2.0)	0.1 (0.1)	37.0 (1.6)	3.5 (0.1)	107.8 (0.2)	34.4 (5.6)	4.8 (0.1)	120.8 (1.0)	0.0 (0.0)	1.3 (1.8)	1.4 (0.6)
250 °C	1.6 (0.1)	2.0 (0.1)	109.7 (5.6)	0.1 (0.1)	59.7 (3.6)	6.7 (0.1)	106.4 (1.2)	33.4 (2.3)	1.5 (0.1)	41.2 (0.5)	0.0 (0.0)	0.3 (0.1)	1.4 (0.1)
275 °C	0.9 (0.1)	1.3 (0.1)	76.2 (4.3)	0.1 (0.1)	29.7 (0.8)	5.1 (0.2)	90.8 (1.5)	20.5 (0.1)	0.7 (0.1)	41.6 (2.8)	0.0 (0.0)	0.2 (0.2)	0.8 (0.1)
300 °C	0.7 (0.3)	0.8 (0.2)	52.5 (0.9)	0.03 (0.02)	23.2 (0.1)	4.4 (0.5)	92.7 (4.3)	12.8 (0.2)	0.4 (0.1)	40.0 (1.6)	0.0 (0.0)	0.0 (0.0)	0.5 (0.2)
	H_2O												
Raw	0.4 (0.1)	0.1 (0.1)	20.4 (0.7)	0.0 (0.0)	14.2 (0.8)	0.6 (0.1)	85.8 (7.0)	7.6 (1.6)	0.1 (0.1)	34.6 (0.1)	18.0 (1.2)	5.0 (2.6)	0.2 (0.0)
225 °C	0.2 (0.03)	0.1 (0.0)	10.8 (0.7)	0.0 (0.0)	10.5 (1.3)	0.1 (0.1)	53.8 (1.6)	5.3 (0.1)	0.1 (0.0)	25.2 (5.0)	4.8 (0.1)	2.7 (0.4)	0.1 (0.1)
250 °C	0.1 (0.1)	0.1 (0.1)	7.0 (0.9)	0.0 (0.0)	3.8 (1.4)	0.1 (0.1)	47.4 (7.3)	4.2 (0.5)	0.1 (0.1)	22.2 (3.0)	0.0 (0.0)	1.9 (0.3)	0.1 (0.1)

Table S1.1 continued

	H_2O												
	Concentration on inorganics (ppm)												
Thermal desorption temperature (°C)	Al	Ba	Ca	Cr	Cu	Fe	K	Mg	Mn	Na	P	S	Zn
275 °C	0.04 (0.1)	0.04 (0.0)	5.7 (1.0)	0.0 (0.0)	1.4 (0.4)	0.04 (0.1)	55.2 (6.9)	3.2 (0.2)	0.03 (0.0)	28.3 (3.7)	0.0 (0.0)	2.5 (0.4)	0.1 (0.1)
300 °C	0.02 (0.1)	0.03 (0.1)	2.6 (0.1)	0.0 (0.0)	0.9 (0.1)	0.0 (0.0)	37.4 (1.7)	1.1 (0.6)	0.0 (0.0)	6.9 (0.4)	0.0 (0.0)	0.2 (0.3)	0.01 (0.1)

Mean (standard deviation) of replicates

Table S1.2: Effect of thermal desorption and chelating extraction on ash content of CN-treated railroad ties

Desorption temperature (°C)[a]	Chelating agent	Ash (%)	Ash removal (% change)
Raw	-	1.2 (0.1) [b]	-
225		1.0 (0.1) [b]	-
250		1.2 (0.1) [b]	-
275		1.4 (0.1) [b]	-
300		1.6 (0.1) [b]	-
Raw	EDTA	0.2 (0.2)	78.4
225		0.3 (0.4)	67.2
250		0.5 (0.1)	58.8
275		0.7 (0.1)	45.0
300		1.0 (0.1)	35.4
Raw	PDA	0.2 (0.1)	82.7
225		0.4 (0.1)	64.4
250		0.4 (0.1)	63.2
275		0.6 (0.1)	57.9
300		1.0 (0.2)	40.2
Raw	HEDP	1.0 (0.2)	78.4
225		1.4 (0.1)	67.2
250		1.3 (0.2)	58.8
275		1.5 (0.1)	45.0
300		2.8 (0.1)	35.4
Raw	Water	0.7 (0.6)	43.5
225		0.6 (0.1)	38.9
250		0.7 (0.9)	42.5
275		0.9 (0.1)	36.7
300		1.3 (0.2)	18.9

[a] All desorptions had a retention time of 45 min
[b] Thermally desorbed for 45 min at each temperature (no extraction)

Table S1.3: Percent removal of inorganics from thermally desorbed railroad ties after extraction with water, EDTA, PDA, and HEDP

Desorption Temperature	Al	Ba	Ca	Cu	Fe	K	Mg	Mn	Na	P	S	Zn
						Water						
	Percent removal (%)											
Raw	6.9	7.8	19.8	20.0	8.9	100.0	25.1	9.9	100.0	26.7	16.0	18.1
225 °C	3.1	5.6	10.4	14.8	1.2	64.8	17.6	9.9	101.7	7.1	8.7	10.7
250 °C	1.5	3.4	6.8	5.4	0.8	57.1	14.0	5.0	89.9	0.0	6.2	4.1
275 °C	0.7	2.2	5.5	2.0	0.6	66.5	10.8	2.1	100.0	0.0	8.0	4.1
300 °C	0.4	1.7	2.6	1.2	0.0	45.1	3.6	0.0	27.9	0.0	0.7	0.8
						EDTA						
Raw	17.4	15.7	100.0	100.0	60.3	100.0	95.3	100.0	100.0	100.0	26.6	100.0
225 °C	9.2	33.6	89.4	86.6	35.4	100.0	95.6	82.1	100.0	40.0	15.0	91.5
250 °C	7.1	54.9	78.2	38.8	24.7	94.0	83.5	82.8	100.0	38.8	15.6	91.5
275 °C	6.9	42.0	52.4	24.2	25.6	95.1	38.1	42.5	100.0	21.1	12.0	42.0
300 °C	5.6	27.4	32.7	13.9	16.8	78.5	26.3	22.6	100.0	17.2	11.8	21.4
						PDA						
Raw	27.0	50.4	100.0	100.0	75.8	100.0	100.0	100.0	100.0	100.0	24.2	100.0
225 °C	26.8	100.0	100.0	100.0	75.4	100.0	100.0	100.0	100.0	100.0	13.3	100.0
250 °C	23.7	78.9	80.2	63.8	39.4	90.6	78.1	100.0	100.0	64.4	6.7	100.0
275 °C	17.0	74.4	59.5	36.2	39.1	100.0	48.4	47.4	100.0	38.7	6.6	48.6
300 °C	16.1	66.0	43.3	35.9	30.1	96.4	44.6	30.4	100.0	37.6	1.6	40.4
						HEDP						
Raw	24.1	100.0	91.2	100.0	100.0	100.0	100.0	100.0	100.0	0.0	4.4	100.0
225 °C	19.8	100.0	57.4	52.4	53.3	100.0	100.0	100.0	100.0	0.0	4.0	100.0
250 °C	28.3	100.0	100.0	84.4	100.0	100.0	100.0	100.0	100.0	0.0	0.9	100.0
275 °C	15.9	74.5	74.0	42.0	78.0	100.0	68.1	49.5	100.0	0.0	0.5	69.2
300 °C	13.2	42.5	51.0	32.9	66.8	100.0	42.7	28.3	100.0	0.0	0.0	38.7

Table S1.4: Inorganics leached from thermally treated railroad ties during extraction with EDTA, PDA, HEDP and water

Desorption Temperature	Concentration of inorganics leached (mmol/L)												
	Al	**Ba**	**Ca**	**Cu**	**Fe**	**K**	**Mg**	**Mn**	**Na**	**P**	**S**	**Zn**	**Sum**
EDTA													
Raw	0.04	0.00	2.62	1.56	0.07	2.52	1.18	0.04	1.91	2.78	0.26	0.03	13.01
225 °C	0.02	0.00	2.30	0.96	0.04	2.18	1.18	0.02	1.70	0.87	0.15	0.02	9.44
250 °C	0.01	0.01	2.01	0.43	0.03	2.00	1.03	0.02	1.69	0.84	0.15	0.02	8.24
275 °C	0.01	0.01	1.35	0.27	0.03	2.02	0.47	0.01	1.59	0.46	0.12	0.01	6.34
300 °C	0.01	0.00	0.84	0.16	0.02	1.67	0.32	0.01	1.40	0.37	0.11	0.00	4.92
PDA													
Raw	0.06	0.01	3.97	1.37	0.09	3.24	1.66	0.04	2.12	2.80	0.24	0.03	15.62
225 °C	0.05	0.02	3.35	1.36	0.09	2.84	1.58	0.04	1.73	2.30	0.13	0.03	13.52
250 °C	0.05	0.01	2.06	0.71	0.05	1.92	0.97	0.04	1.49	1.40	0.07	0.03	8.79
275 °C	0.03	0.01	1.53	0.40	0.05	2.18	0.60	0.01	1.49	0.84	0.06	0.01	7.21
300 °C	0.03	0.01	1.11	0.40	0.04	2.05	0.55	0.01	1.48	0.82	0.02	0.01	6.52
HEDP													
Raw	0.05	0.02	2.34	1.31	0.13	3.02	1.51	0.80	1.82	0.00	0.04	0.03	11.07
225 °C	0.04	0.01	1.47	0.58	0.06	2.76	1.41	0.09	5.25	0.00	0.04	0.02	11.75
250 °C	0.06	0.01	2.74	0.94	0.12	2.72	1.37	0.03	1.79	0.00	0.01	0.02	9.81
275 °C	0.03	0.01	1.90	0.47	0.09	2.32	0.84	0.01	1.81	0.00	0.00	0.01	7.51
300 °C	0.03	0.01	1.31	0.37	0.08	2.37	0.53	0.01	1.74	0.00	0.00	0.01	6.44
Water													
Raw	0.01	0.00	0.51	0.22	0.01	2.19	0.31	0.00	1.51	0.58	0.16	0.00	5.51
225 °C	0.01	0.00	0.27	0.16	0.00	1.38	0.22	0.00	1.09	0.15	0.08	0.00	3.37
250 °C	0.00	0.00	0.17	0.06	0.00	1.21	0.17	0.00	0.97	0.00	0.06	0.00	2.65
275 °C	0.00	0.00	0.14	0.02	0.00	1.41	0.13	0.00	1.23	0.00	0.08	0.00	3.02
300 °C	0.00	0.00	0.07	0.01	0.00	0.96	0.04	0.00	0.30	0.00	0.01	0.00	1.39

CHAPTER III
GENERATION OF HIGH-QUALITY BIO-OIL FROM PRESERVATIVE-TREATED RAILROAD TIES

Abstract

Copper naphthenate (CN) is a wood preservative used to extend the service life of wood through its efficacy to prevent mold, fungi, and other natural sources of deterioration. A growing amount of CN-wood waste will be generated each year as creosote and other hazardous preservatives are replaced with CN. This woody biomass can serve as a renewable pyrolysis fuel source. Thermal treatment between 230 and 290 °C and subsequent extraction with the biodegradable chelating agent pyridine-2,6-dicarboxylic acid (PDA) was used for improving the properties of CN-treated wood waste for use as a renewable thermochemical feedstock. The higher heating value of the biomass increased by 0.4 MJ/kg from combined desorption at 260 °C and inorganic removal at 70 °C. The ash content was reduced from 1.5 to 0.5 % without degradation to the wood waste matrix from extraction with PDA. Based on the characteristics of the resulting biomass, it can be estimated that the ties treated with thermal desorption and extracted with the biodegradable chelating agent would generate the highest quantity of bio-oil from subsequent fast pyrolysis, as well as the highest quality of product.

Introduction

Woody biomass has been investigated as a feedstock for thermochemical conversion processes, like pyrolysis, acting as an energy source with fewer harmful environmental impacts than traditional fossil fuels. Fast pyrolysis of lignocellulosic biomass produces three types of products, i.e. biochar, condensable bio-oil, and non-condensable gases (NCG), and is known to produce a higher bio-oil yield than slow pyrolysis.[37] Bio-oil

produced from fast pyrolysis of lignocellulosic biomass is typically acidic (~ pH 2.5) with a high water (~ 25%) and oxygen (25-40%) content.[80-81] However, the composition and quality of the bio-oil produced vary with a feedstock's physical and chemical properties, as well as with the fast pyrolysis conversion technology.[36-37]

Lignocellulosic biomass is composed of cellulose, hemicellulose, lignin, extractives, and ash, and the ratios of these components contribute to both the yields and quality of the pyrolysis products.[38] Biomass with high cellulose content has been shown to produce higher bio-oil yields with low water content and larger organic fractions.[36] Pyrolysis of hemicellulose also results in a higher bio-oil yield than that of lignin, while pyrolysis of lignin traditionally produces a larger amount of biochar.[38]

In addition to the biomass type, the inorganics present in the biomass also play a significant role in product yields. Ash has even been reported to have a larger effect than lignin content on pyrolysis and its product yields and quality.[82] Typically, higher ash content and more of certain inorganic compounds within a feedstock lower the liquid generated and increase its biochar and gas formation by acting as a catalyst during the pyrolysis process.[38] Higher ash content can also lead to physical issues within the reactor, further impairing the thermochemical conversion process.[35, 42]

Among the physical properties that influence pyrolysis product quality, particle size and water content of the biomass are some of the most significant.[37] Heat transfer is often not uniform when a feedstock with a larger particle size is used; making smaller particles more desirable to ensure uniform heating.[38] Pyrolysis of feedstocks with too small particles, however, has been shown to result in a larger number of secondary

cracking reactions that consequently cause a decrease in bio-oil yield.[83] The suggested optimal particle size varies based on differences in feedstock type and desired product distribution.

The moisture content of a feedstock for thermochemical conversion also plays an important role in the distribution and characterization of those products generated. The relatively high moisture content of biomass as a renewable fuel source, often makes it difficult to store and transport; in addition to negatively impacting the product quality and process efficiency.[39] Though overall liquid yield is augmented from biomass with greater initial water content, the bio-oil produced has higher moisture content. This bio-oil is of lower quality because of its increased viscosity and corrosiveness, as well as its decreased chemical stability.[38] In addition, all water must be removed from the bio-oil when combusted, which increases the energy requirement of the fuel and reduces the efficiency of the system.[84] Several methods have been developed that are commonly used to mitigate these negative impacts by reducing a feedstock's moisture content; including traditional drying, pelletization, and torrefaction.[85] Torrefaction is most commonly used prior to pyrolysis of lignocellulosic biomass because it not only lowers the water content, but also improves the properties of the biomass for storage and subsequent conversion.[39, 48, 86-87]

With approximately 29 tons of oil-borne CN being used to treat railroad ties alone each year, copper naphthenate-treated wood waste can serve as a readily available renewable source of woody biomass.[60] Furthermore, thermal desorption (torrefaction) pretreatment of these end-of-service ties can upgrade the wood's properties prior to use

as a thermochemical conversion feedstock.[2] Copper naphthenate (CN) is a preservative that serves as an effective and green alternative for preventing the degradation of wooden railroad ties, utility poles, and pilings.[2, 25] The more frequent usage of CN over other commonly used preservatives, like creosote and pentachlorophenol, is generating a large amount of landfilled waste.[60] Reuse of this biomass waste as a pyrolysis feedstock would reduce landfilling, as well as supply a low cost renewable fuel source. Recovery of the preservative components from the feedstock prior to conversion could provide an economic advantage, as well as makes the disposal process of the ties more sustainable. The inherent value in the recovered CN could be used to offset that of the treatment costs, and could also potentially be recycled to treat new products.

Because CN is composed of an organic fraction (naphthenic acids) and an inorganic fraction (salts of copper ions), removal of the preservative from the biomass requires two pretreatment processes; a thermal desorption and an extraction with a biodegradable chelating agent.[1] Pyridine-2,6-dicarboxylic acid (PDA) is a biodegradable chelating agent that has been shown to be effective in removal of transition metals, like copper, and other inorganics during paper pulp pretreatment, in addition for heavy metal soil remediation.[32, 55] These inorganics can have undesired effects on the pyrolysis process, promoting secondary cracking reactions and reducing bio-oil yield, if left in the feedstock.[14, 21, 82]

We have previously studied the use of several chelating agents for removing copper and other undesired inorganics from CN-treated ties following thermal treatment of the biomass at a micro- and bench-scale.[7] PDA was found to have a higher overall

extraction efficiency than both EDTA and HEDP from the torrefied wood. The pilot scale recovery of CN components from used railroad ties has not yet been investigated prior to this study, however. Estimating the quantity and quality of the products generated from fast pyrolysis of these used ties, as well as studying how their physical and chemical properties change from the suggested pretreatment methods, aims to enforce the reuse of this readily available feedstock.

Materials and Methods

Material

Wooden railroad ties pressure treated with a 0.8 % copper naphthenate (CN) solution were provided by Nisus Corporation (Rockford, TN) and then ground to a particle size of less than a 2 mm preceding analysis.

Pyridine-2,6-dicarboxylic acid (PDA; CAS 499-83-2) was obtained as a white crystalline solid and dissolved in deionized water to prepare 1 % solutions of the chelating agent prior to batch extractions.

Characterization of the ties material

American Society for Testing and Materials (ASTM) standard method D1762 was followed for proximate analysis to determine moisture content, ash content, and the percent volatile matter of the treated wood starting material. Fixed carbon was calculated from proximate analysis values by finding the difference that summed

moisture content, ash content, and volatile matter to 100 % for the received ties sample. Ultimate analysis of the material provided was also conducted in triplicate using a CHN Analyzer (2400 Series II CHNS/O, PerkinElmer) to obtain the percentage of carbon, hydrogen, sulfur, and nitrogen within the thermally desorbed samples.

Thermal desorption with continuous auger reactor

Thermal desorption at 260 °C was applied to the extraction of preservative from the ties using a pilot scale continuous auger reactor system (Figure 2.1).[7] The ground CN-treated ties were fed into the hopper feeding system, which is connected to a single auger that then conveys the ties into the auger reactor's heated zone. Internal dual augers then move the biomass through the heated zone maintained at the desired temperature while a continuous flow of nitrogen runs through the system from both the front of the auger reactor and from the side of the bio-char collector to carry the vapors into the condensation section and to help cool the desorbed material, respectively. The residence time for the sample to be desorbed was approximately 7 minutes (one cycle). After the first cycle was completed, the desorbed material was collected and a sub sample was removed for later analysis. Then the remaining thermally treated material was again fed into reactor at the same conditions and residence time. This process was repeated a third time as well, so samples were ultimately desorbed for three 7-minute cycles at each thermal desoprtion temperature. This same procedure was repeated at both 230 and 290 °C to verify that scaling-up the process did not cause a change in the most effective treatment temperature found with the fixed bed reactor. The severity of

each of the thermal desorptions was calculated as a function of retention time and reaction temperature using Equation 1.[88]

$$\text{severity factor} = \text{time of reaction}^{[(\text{temperature of reaction}-25)/14.75]} \quad (1)$$

A particle chamber removes fine particles from the vapors before they are condensed by a set of three water circulation-cooled condensers. The thermally treated solid, as well as the condensed liquid, were collected after each cycle.

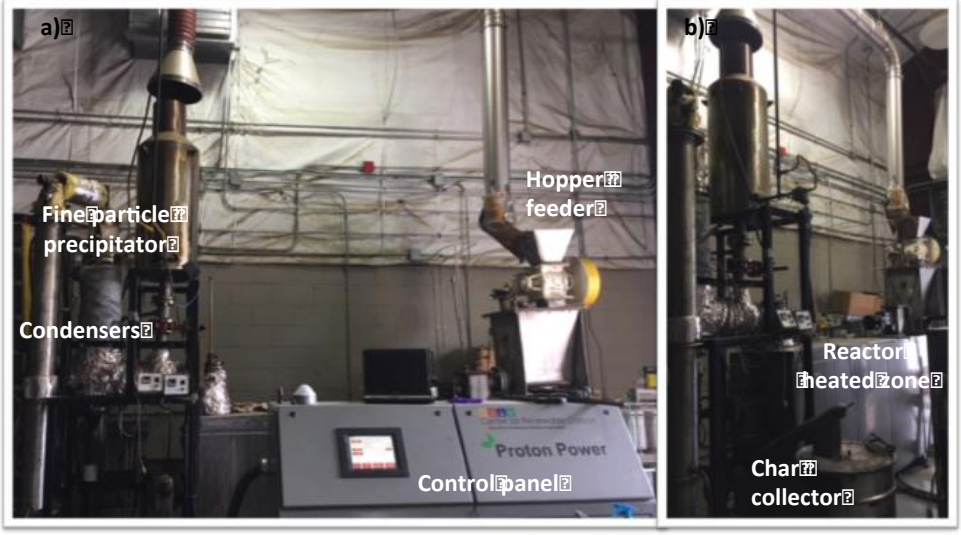


Figure 2.1. Pilot-scale continuous auger reactor used for thermal desorption of CN ties.

The two-phase liquid was divided into an aqueous and organic fraction using separatory funnels. The water content of the organic fraction was measured in triplicate using Karl Fischer titration. The variations between conditions were tested for statistical significance at a confidence level of 0.05 by completing a Duncan's Multiple Range Test using SAS statistical software. The organic liquid fraction recovered from thermal desorption was also analyzed using gas chromatography/mass spectrometry (GC/MS) to identify preservative and carrier oil components, as well as wood decomposition compounds.

Proximate and ultimate analyses of the solid fraction after thermal desorption was also conducted using the method described in the previous section, '*Characterization of the ties material'*. From CHN analysis, the higher heating value was calculated for each sample using Equation 2.[39, 89]

$$HHV = (0.1905*VM) + (0.2521*FC) \quad (2)$$

where HHV is the higher heating value of the desorbed solid (MJ/kg)

VM is the volatile matter content (wt. % db)

and FC is fixed carbon content (wt. % db)

Samples were also analyzed using a bomb calorimeter (IKA C 6000 Isoperibol), following ASTM Standard D5865-13, to determine gross calorific value of the samples.[90]

Chelation extraction with PDA

Torrefaction of woody biomass increases the ash content of the material, which has a negative effect on the quality of the wood for use as a pyrolysis feedstock.[14, 91] Some of

the inorganics that contribute to this ash can also negatively affect the pyrolysis process.[14, 21] A traditional batch extraction method using a 1% solution of 2,6-pyridine dicarboxylic acid (PDA) with pH 4 (adjusted using ammonium hydroxide) was used for removal of inorganics to reduce the ash content of the biomass. The three-hour extraction was performed at a reaction temperature of 70 °C with continuous mechanical stirring at 150 rpm.[7] The percent ash content removed during chelation was calculated.

Inductively coupled plasma-optical emission spectrometry (ICP-OES) (PerkinElmer Optima 7300 Dual View, Shelton, CT) of the liquid fraction recovered after chelation was performed to quantify the amount of inorganics extracted from the ties,. Fifteen mL of each sample were combined with one mL of nitric acid (reagent grade; 67−70%) to acidify the solutions. These solutions were then filtered (0.2 µL) and analyzed by ICP-OES. A calibration curve was constructed with commercial NIST solutions before analyzing samples.

The particle size distribution of the thermally desorbed and chelated material was measured using methods outlined in the American Society of Agricultural and Biological Engineers (ASABE) Standards S319.3/4 where 100 g of sample were shaken for 15 min at an amplitude of 60. The fraction of sample in each particle size was then determined gravimetrically. This procedure was also completed for the thermally desorbed samples as well as the starting material as provided. All determinations were done in triplicate.

Results and Discussion

Thermal desorption with continuous auger reactor

Mass loss of the ties from thermal desorption increases with desorption temperature, but decreases with retention time at each temperature (Figure 2.2). Mass loss exceeds 34 % (db) from one cycle at the highest temperature, whereas at the least severe condition (one cycle at 230 °C) the mass loss was 13 % (db). As thermal desorption temperature increases, more compounds are volatilized from the wood ties and the total volume of liquid condensed increases. This coincides with a greater mass loss from the thermally treated solid.

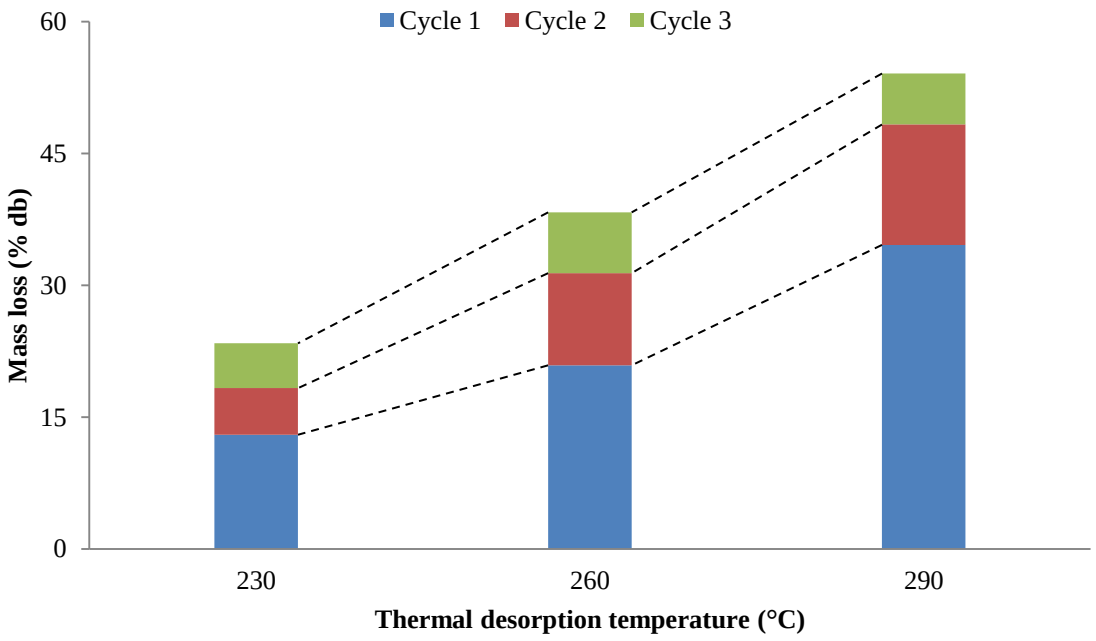


Figure 2.2. Mass loss of thermal desorbed CN ties at varied temperatures.

Proximate analysis of the starting material (wooden ties treated with CN) and the thermally desorbed ties was completed using the ASTM standard methods and the higher heating value (HHV) was also calculated for each. The HHV of the starting material, 17.2 MJ/kg, increases with thermal desorption at all conditions (Table 2.1). An increase of 2.8 MJ/kg is achieved from desorption at 290 °C. The HHV represents the amount of energy released when a material is combusted, so an increase in this parameter is beneficial for use as a pyrolysis feedstock.[92] Thermal treatment also results in a decrease in moisture content, by as much as 7 % (on dry basis), further upgrading the biomass for use as a thermochemical conversion fuel source. Lower feedstock moisture content has been shown to result in bio-oil that is less viscous and less corrosive, as well as has an improved chemical stability.[38,39, 48, 86]

Though the ash content rises slightly as a result of thermal desorption at the more severe conditions, the value remains relatively low in all conditions, not exceeding 1.6 % after any treatment. Additionally, desorption with the pilot scale auger reactor does not affect the ash content of the ties when run at 230 °C (all cycles) or the first cycle at 260 °C. This suggests that at 230 °C, thermal desorption is removing mainly water from the ties and supports the need for a higher temperature for preservative removal. Hydrogen (Table 2.1) and oxygen content (Table S2.1) decreases with increasing desorption temperature, supporting that more water is being volatilized from the biomass. This trend is in agreement with results seen when using thermal desorption to remove preservatives from used railroad ties on a smaller scale as well.[7-8]

Table 2.1. Characterization of thermally desorbed solid samples

Temperature (°C)	Cycle[a]	Severity factor[b]	MC (% dry basis)	Volatile matter (% dry basis)	Ash (% dry basis)	Fixed carbon[c] (% dry basis)	HHV[c] (MJ/kg)	C (% dry basis)	H (% dry basis)
Raw sample (untreated)	-	-	9.6 (0.3)	85.2 (1.1)	1.2 (0.1)	4.0 (0.4)	17.2 (0.3)	50.5 (0.2)	6.7 (0.3)
230	1	4.7	7.3 (1.0)	84.4 (0.4)	1.1 (0.1)	9.3 (2.2)	17.9 (0.5)	50.5 (0.8)	6.5 (0.1)
	2	5.0	6.2 (0.2)	82.6 (0.4)	1.1 (0.2)	10.1 (0.1)	18.3 (0.1)	50.6 (0.1)	6.5 (0.1)
	3	5.1	5.8 (0.2)	81.2 (0.9)	1.2 (0.1)	11.7 (1.1)	18.4 (0.1)	51.0 (0.1)	6.5 (0.04)
260	1	5.6	6.2 (0.4)	80.4 (0.7)	1.2 (0.1)	12.2 (0.5)	18.4 (0.1)	51.1 (0.3)	6.4 (0.1)
	2	5.9	4.3 (0.4)	77.9 (0.8)	1.4 (0.1)	16.4 (0.9)	19.0 (0.1)	53.2 (0.4)	6.2 (0.1)
	3	6.0	2.6 (0.3)	69.6 (1.2)	1.5 (0.1)	26.5 (1.0)	19.9 (0.1)	52.5 (0.2)	6.0 (0.03)
290	1	6.4	3.4 (0.5)	78.2 (0.7)	1.3 (0.2)	16.9 (0.7)	19.2 (0.03)	52.0 (0.02)	6.2 (0.04)
	2	6.7	2.3 (0.2)	69.5 (0.1)	1.6 (0.1)	26.7 (0.4)	20.0 (0.1)	56.2 (0.4)	5.7 (0.03)
	3	6.9	2.6 (0.3)	68.3 (0.5)	1.6 (0.1)	27.5 (0.9)	20.0 (0.1)	56.3 (0.5)	5.7 (0.02)

[a]each cycle ~ 7 minutes

[b]severity factor[88]= time of reaction$^{[(\text{temperature of reaction}-25)/14.75]}$

[c] HHV[89] = 0.1905*VM + 0.2521*FC

Thermal desorption results in two products, a thermally treated solid fraction and a liquid fraction composed of two phases: an aqueous and organic phase. This phase separation occurs automatically. The aqueous phase is composed of mainly water, while the major components of the organic phase include naphthenic acids, carrier oil compounds, as well as some of the wood decomposition products. Table 2.2 describes the composition of the liquid fractions. The total liquid recovered increases with increasing thermal desorption temperature, as well as with subsequent cycles at each temperature. This mirrors the trend seen in the solid mass loss data (Figure 2.2). However, the majority of liquid is recovered during the first cycle at each temperature. For example, 0.16 g of liquid is recovered per gram of biomass desorbed at 230 °C during the first cycle, but only 0.03 g and 0.02 g are collected in the second and third cycles, respectively.

The water content of the organic fraction recovered from auger desorption was measured in triplicate using Karl Fischer titration (Table 2.2). Samples desorbed at 260 °C have slightly higher water content for each cycle, followed by those desorbed at 290 °C, and then at 230 °C. Little variation exists between samples, varying by less than 0.04 % in all cases. These variations were determined to be statistically significant, however, using a two-way repeated measure ANOVA conducted with SAS 9.4 statistical software. A Duncan's Multiple Range Test was then used; identifying that desorption temperature had a significant effect on the organic fraction's water content, while both the number of cycles and the interaction between the two factors did not.

Additionally, the very small amount of water (< 0.08 % for all conditions) contained in the recovered organic fraction supports its possible reuse. This meets the requirement set out by the AWPA standard (P36-16) for commercial copper naphthenate. Under this standard, copper naphthenate concentrate cannot contain greater than 0.5 % water.[3] Therefore, no further processing to reduce water content would need to be done prior to recycling the recovered preservative for use in treating new ties.

This very low water content is also advantageous for storage and processing of the preservative. It has been documented that if the water content of copper naphthenate solutions exceeds 1-2 %, an increase in temperature can cause the formation of black copper oxide, which leads to emulsion and slugging issues within storage and treating tanks.[1] The recovered naphthenic acid does not meet or exceed this limit under any thermal desorption conditions; thus, further supporting its reuse.

Table 2.2. Liquid products recovered from thermal desorption

Thermal desorption temperature (°C)	Retention time (min)	Severity factor	Aqueous phase (g recovered liquid/g biomass desorbed)	Organic phase (g recovered liquid/g biomass desorbed)	Total liquid (g recovered liquid/g biomass desorbed)	Water content of organic phase (%)
230	7	4.7	0.12	0.04	0.16	0.05 A[a]
	14	5.0	0.02	0.01	0.03	0.05 A
	21	5.1	0.01	0.01	0.02	0.05 A
260	7	5.6	0.19	0.08	0.27	0.08 B
	14	5.9	0.07	0.03	0.09	0.06 B
	21	6.0	0.02	0.02	0.04	0.07 B
290	7	6.4	0.22	0.10	0.32	0.06 A
	14	6.7	0.08	0.01	0.09	0.06 A
	21	6.9	0.01	0.00	0.01	0.06 A

[a] Values followed by the same letter are not statistically different.

The organic liquid fraction recovered from thermal desorption with the pilot scale auger reactor was also analyzed using gas chromatography/mass spectrometry (GC/MS) to identify preservative and carrier oil components, as well as wood decomposition compounds. Figure 2.3 shows GC/MS chromatograms of the first cycle of thermal treatment at each of the three temperatures tested. As the number of cycles increases at a constant temperature, the intensity of peaks attributed to carrier oil compounds decreases. These compounds include decane and its isomers. A decrease in the size of these alkanes demonstrates that less carrier oil is extracted with subsequent cycles at the same temperature. Peaks attributed to anthracene and phenanthrene are also present in the fraction recovered from thermal desorption at 260 °C, which are not present in that collected from treatment at 230 °C. These compounds are likely components of the carrier oil that is used to help copper naphthenate penetrate the wood cell wall during impregnation of the ties.[93-94] This supports that more of the carrier oil can be removed at these higher temperatures. Finally, peaks identified as syringol and furfural also increase in intensity with higher thermal desorption temperature and decrease as cycle number increased. Both of these compounds are products of the thermal decomposition of the wood structural matrix; furfural from the breakdown of hemicellulose and syringol from that of lignin.[36, 50] This trend demonstrates that a larger breakdown of the wood matrix occurred at higher temperatures; however, the majority of the breakdown occurs during the first cycle.

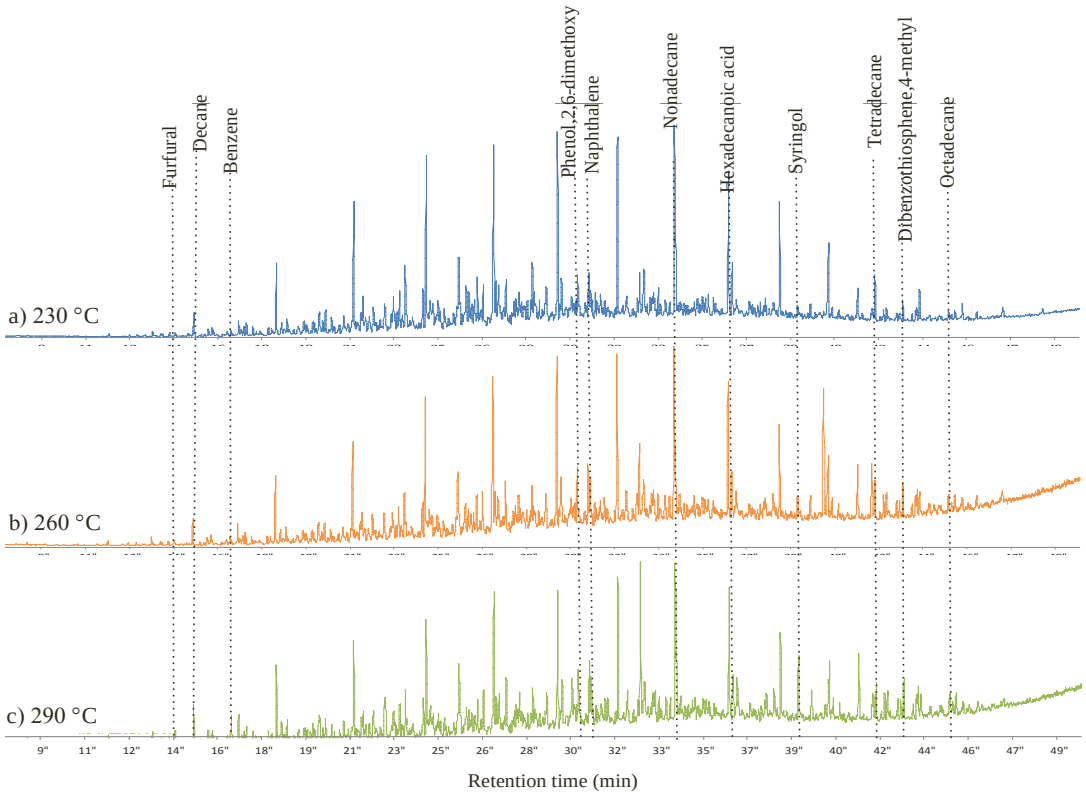


Figure 2.3. GC/MS of organic fraction recovered from thermal desorption of CN ties (diluted 1:10 with methanol) at a) 230, b) 260, and c) 290 °C for one cycle (7 min)

Chelation extraction with PDA

Thermal desorption of the used ties was followed by an extraction step with the biodegradable chelating agent, PDA, to remove undesired inorganics that could negatively affect thermochemical conversion. Most of these inorganics do not volatilize in the selected temperature range, so the pyrolysis of biomass with a high inorganic content produces a larger amount of char and gas and generates a lower quantity of liquid.[38, 82] Although the ash content of the ties only increased slightly as a result of thermal desorption, extraction with PDA decreased it to a value much lower than that before any treatment (Table 2.3). A net reduction of 0.7 % was achieved, lowering the ash content to approximately 0.5 % from 1.2 % in the raw material, and from 1.5 % from the desorbed material. This is equivalent to more than half of the total ash within the raw sample.

Analysis to determine the gross calorific value, or HHV, of the solid biomass after both pretreatment methods was also conducted using a bomb calorimeter (Table 2.3). The HHV of the biomass increases slightly after thermal desorption, but does not change after subsequent extraction with PDA. This difference from the untreated sample was determined to be statistically significant using SAS statistical software. This suggests that pretreatment has a positive effect on the biomass as a thermochemical conversion feedstock; however, there is no difference between the effects of each different treatment on this property. A decrease in ash content, coupled with no change in HHV, also demonstrates that undesired inorganics are being removed from the ties during PDA extraction while not causing carbon loss from the wood matrix. More energy would

be produced from combustion of the treated ties than from that of the raw material, further supporting the recycling of this wood waste product.

In addition to variations in ash content, the particle size distribution of the solid changed as a result of treatments as well. Average particle size decreases from thermal desorption with the continuous auger reactor (Figure 2.4). Subsequent chelation also increases the amount of smaller particles within the sample, having the largest portion of particles between 2 and 0.4 mm. Particle size is one of the most influential physical properties that effects pyrolysis products of biomass.[37] Smaller average particle size has been shown to ensure more uniform heating of the feedstock and increase the pyrolysis liquid product yield, but particles that are too small can encourage a decrease in the bio-oil produced for example.[38,83] Very small feedstock particles can splice one another and inhibit biomass cracking, thus increasing the char produced while reducing the liquid and gaseous products.[92]

Table 2.3. Biomass ash content after thermal desorption and inorganic extraction pretreatment

Treatment of sample	Ash content (%)	HHV (MJ/kg)
Raw sample (untreated)	1.2 (0.10)	20.8 (0.10) A[b]
Thermally desorbed at 260 °C[a]	1.5 (0.06)	21.2 (0.10) B
Thermally desorbed at 260 °C[a] and chelated with PDA	0.5 (0.08)	21.2 (0.03) B

[a] three cycles
[b] Values followed by the same letter are not statistically different at an alpha value of 0.05

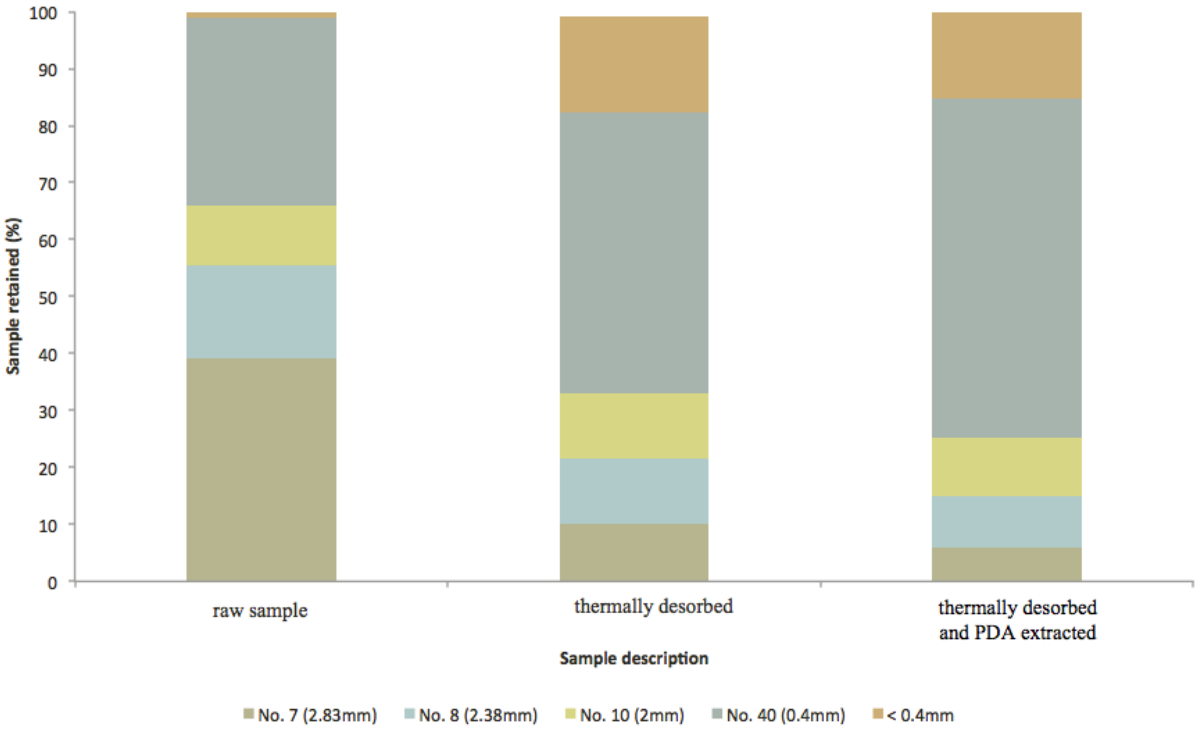


Figure 2.4. Particle size distribution of used CN railroad ties as provided and after various pretreatments.

It has been suggested that particles < 2 mm in size are optimal for fast pyrolysis using a fluidized bed specifically.[38] From this, it can be assumed that the greatest yield of bio-oil is to be expected from pyrolysis of the ties that have been both thermally desorbed and extracted with chelating agents. However, there is still a lack of consensus among the suggested particle size for producing the greatest amount of bio-oil based on biomass type and pyrolysis conditions.

Estimating pyrolysis products of the treated feedstocks

Analyses of the railroad ties as provided, after thermal desorption, and after combined thermal treatment and PDA extraction were used for estimation of product yields from their fast pyrolysis. Table 2.4 summarizes the studies used for the estimation process. These studies were chosen because they are newly published with pretreatment processes similar to that completed for this study (techniques, temperature ranges, etc.). Because the ties are composed of a mixture species, but the exact wood composition is unknown, several different wood feedstock types are included in the analysis.

Torrefaction of both hardwood and softwood species between 250 and 270 °C in the literature was demonstrated to decrease bio-oil yield.[49, 95-96] Impregnation of the biomass with both potassium and phosphorus also caused less bio-oil to be generated than from the untreated sample.[97] An increase in yield after acid leaching for inorganics removal after torrefaction pretreatment also demonstrates an undesired effect of inorganics on the pyrolysis process.[95] The ash content of hardwood chips increased from 0.9 to 1.1 % and the HHV rose from 18.9 to 21.5 MJ/kg from torrefaction at 265 °C.

Similarly, changes of 1.2 to 1.5 % and 20.8 to 21.2 MJ/kg occurred from pilot scale thermal desorption of the CN-treated ties at 260 °C. Ultimate analysis of the feedstocks also demonstrated similar values for C, H, N, and O concentration (%). For example, our ties torrefied at 260 °C contained 52.5 % carbon after treatment. This content is very similar to that of hardwood chips torrefied at 265 °C (53.3 %) and loblolly pine chips torrefied at 270 °C (55.0 %), and *Pinus radiata* torrefied at 270 °C (49.1 %). Hydrogen, oxygen, and nitrogen content are also similar. Based on these similarities in feedstock characteristics, it can be estimated that fast pyrolysis of the CN-treated ties that have been thermally desorbed within the optimal temperature range of 250 to 275 °C would produce a bio-oil yield of 27 to 54.5 %. The yield from untreated samples among these studies varies from 44 to 70.7 %.

Though the amount of bio-oil produced decreased from thermal pretreatment, the quality did improve. Water content was lowered and the HHV rose in all studies. The largest rise in HHV demonstrated was 1.2 MJ/kg as a result of torrefaction at 270 °C. Similar increases were seen with hardwood samples as well. Water content within the bio-oil fell by as much as 17 %, resulting in a product that would be less corrosive and more chemically stable. Higher carbon content along with lower hydrogen and oxygen content are also beneficial results of thermal treatment within this temperature range prior to pyrolysis. The same trends in effect of pretreatment were seen with combined inorganic removal and torrefaction. These effects can be expected from pyrolysis of the thermally desorbed ties as well as those that have also been extracted with PDA. Water content of the bio-oil produced from samples torrefied between 265 °C and 270 °C

ranged from 8.1 to 26.2 %; the range within which bio-oil generated from the thermally desorbed ties would expect to fall. Biomass that had been torrefied after inorganic leaching resulted in a product with an even smaller content (4.1 %); having a higher quality than the product after only thermal treatment and, thus, supporting combined pretreatment of the biomass.

From this review of literature, it can be estimated that our ties treated with thermal desorption and extracted with PDA, would generate the highest quantity of bio-oil from subsequent fast pyrolysis. The highest quality of bio-oil would also be expected from this feedstock. Additionally, we can predict a higher increase in yield between the raw ties and those after combined desorption and extraction compared to that seen in the summarized studies. Carbon loss from acid leaching accompanied the removal of inorganics in Wigley's study, demonstrating decomposition of the wood structure from this extraction method that would negatively effect thermochemical conversion. The use of PDA, however, did not cause structural damage to the ties.

Table 2.4. Summary of studies for estimating pyrolysis products

Study	Louwes et al. (2017)[96]			Meng et al. (2012)[49, 98]		Banks (2014)[97]			Wigley (2015)[95]	
Biomass type	Hardwood chips			Loblolly pine chips		Beech wood			*Pinus radiate*	
Pretreatment	- [a]	Torr.[b] at 250°C	Torr. At 265°C	-	Torr. at 270°C	-	Impreg.[b] with 1 % K	Impreg.[b] with 1 % P	-	Torr. at 270°C	Leached[c] then torr. at 240°C
Ash of biomass (%)	0.9	1.0	1.1	0.56	0.62	0.95	2.62	9.03	NP[d]	NP	NP
Biomass HHV (MJ/kg)	18.9	21.4	21.5	20.0	22.7	19.81	NP	NP	20.9	21.6	20.9
C (% wb) of biomass	46.0	52.9	53.3	50.5	55.0	49.66	NP	NP	39.1	49.1	48.74
H (% wb) of biomass	6.0	5.7	5.6	6.26	5.94	6.29	NP	NP	7.3	6.7	6.2
N (% wb) of biomass	0.1	0.1	0.1	0.09	0.11	< 0.10	NP	NP	0.3	0.7	0.9
O (% wb) of biomass	47.8	41.2	41.0	42.6	38.3	43.95	NP	NP	53.2	43.5	44.2
Bio-oil yield (%)	44	36	27	67.2	54.5	70.7	40.4	52.8	46.9	46.3	57.9
HHV of bio-oil (MJ/kg)	19.1	19.9	21.1	21.0	21.2	18.6	26.5	22.4	20.9	22.1	21.3
Water content of bio-oil	29.5	26.9	26.2	21.8	18.7	7.3	15.2	18.2	24.0	8.1	4.5
Viscosity of bio-oil at 25 °C (mPas)	17.8	24.7	24.8	11.0	24.1	58.0	45.0	145.0	37	414.2	NP
C (% wb) of bio-oil	46.9	48.9	51.7	50.1	54.1	46.2	59.4	52.3	39.1	49.4	50.0

Table 2.4 continued

Study	Louwes et al. (2017)[96]			Meng et al. (2012)[49, 98]			Banks (2014)[97]			Wigley (2015)[95]	
H (% wb) of bio-oil	6.6	6.5	6.7	6.7	6.4	7.9	8.8	9.4	7.3	6.6	6.3
N (% wb) of bio-oil	0.7	0.8	0.7	0.53	0.44	0.2	0.1	0.2	0.3	1.0	0.8
O (% wb) of bio-oil	45.7	43.8	41.3	42.7	39.1	45.7	31.8	38.3	52.3	43.0	42.8

[a] No pretreatment (raw sample)
[b] Impregnated with 1 % solution
[c] Acid leached with 1% solution of acetic acid at 90 °C for 4 hours
[d] Data not provided by study

Conclusion

Both pilot scale thermal desorption and subsequent batch extraction with PDA improved the quality of the CN-treated ties for use as a pyrolysis feedstock. The HHV increases, while the moisture content decreases, with treatment at all thermal desorption conditions. Temperature was shown to be more important than retention time for thermal desorption. The majority of the mass loss, as well as liquid product and preservative component recovery, occur during the first cycle at each temperature. Additionally, the organic phase of the liquid product recovered satisfies water content formulation requirements for commercial CN and for limiting physical storage and treatment issues like reactor slagging. This further encourages its possible reuse to treat new ties; thus making that process more sustainable and economically viable. Subsequent extraction with PDA reduced the ash content of the biomass to 0.5 % with no degradation to the ties resulting from this treatment method. It can be predicted that the greatest quality of bio-oil is to be expected from pyrolysis of the ties that have been both thermally desorbed and extracted with PDA, followed by the thermally desorbed ties, and finally by the untreated sample based on comparison of the feedstock physical and chemical properties to prior studies in the literature.

Appendix

Table S2.1. Nitrogen, sulfur, and oxygen content of thermally desorbed ties

Thermal desorption temperature (°C)	Retention time (min)	Severity factor	N (%)	S (%)	O[a] (%)
230	7	4.7	0.03 (0.02)[b]	0.40 (0.07)	42.6
	14	5.0	0.02 (0.03)	0.10 (0.04)	42.7
	21	5.1	0.04 (0.01)	0.05 (0.07)	42.4
260	7	5.6	0.04 (0.04)	0.03 (0.03)	42.4
	14	5.9	0.05 (0.01)	0.04 (0.01)	40.5
	21	6.0	0.02 (0.00)	0.00 (0.00)	41.5
290	7	6.4	0.06 (0.03)	0.01 (0.00)	41.7
	14	6.7	0.09 (0.07)	0.08 (0.06)	38.0
	21	6.9	0.05 (0.01)	0.00 (0.01)	38.0

[a]found by difference (100 – [C (%) + H (%) + N (%) + S (%)] = O (%))
[b]average (standard deviation) of triplicates

CONCLUSIONS AND RECOMMENDATIONS

Conclusions

This thesis investigated the recovery of CN from used railroad ties and the recycling of the woody biomass as a thermochemical conversion feedstock after preservative removal. Thermal desorption was demonstrated as an effective method for removal and recovery of the organic fraction of CN from treated ties. The carrier oil used to help increase preservative retention in the wood could also be volatilized from the ties and condensed into the liquid product. Naphthenic acids were volatilized from the wood at all temperatures within the range tested (225-300 °C). This pretreatment method mimics traditional torrefaction and was conducted at three scales; a micro scale using pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS), a bench scale with a fixed-bed reactor, and a pilot-scale desorption using a continuous auger reactor. Optimal conditions were found to be between 250 and 275 °C with Py-GC/MS, as well as with the bench-scale reactor. Removal of the preservative components were maximized with minimal degradation of the wood matrix at 260 °C using a pilot-scale setup. Though more naphthenic acids could be removed at higher temperatures in all cases, severe degradation of the wood also occurs at those conditions. Therefore, higher temperatures are recommended if only removal of CN is important. When using the ties as a feedstock for subsequent thermochemical conversion processes, however, a tradeoff between maximizing this volatilization and minimizing the breakdown of the biomass must be taken into consideration.

After thermal desorption, the inorganic fraction of CN, as well as other naturally present inorganics, persist in the biomass. These inorganics can have detrimental effects on the pyrolysis process. Biodegradable chelating agents with efficiencies comparable to and exceeding that of EDTA were identified for extraction. Use of readily biodegradable chelating agents, like 2,6-pyridine dicarboxylic acid (PDA), in combination with thermal desorption can support the recovery of CN components from end-of-life railroad ties and produce a feedstock with improved qualities to that of the raw material. This in turn reduces the landfilling of petroleum-contaminated ties, making their disposal more sustainable. The value of the components encourages this reuse method, potentially using the recovered preservative to treat new ties.

Thermal desorption using optimized conditions, followed by extraction with PDA, resulted in the recovery of both CN fractions and production of an upgraded thermochemical conversion feedstock. Both the higher heating value and carbon content of the biomass was improved, while the oxygen content was lowered. The two-step extraction process also lowered the ash content significantly without causing a breakdown of the wood matrix, further improving the quality of the feedstock. It can be speculated that the quantity and quality of bio-oil produced from fast pyrolysis of this feedstock would be greater than that of the untreated sample or the sample that had only undergone thermal pretreatment.

Recommendations for Future Work

The following are recommendations for future work that would further investigate topics related to, but outside the scope of, this thesis study.

1. Investigate removal of pentachlorophenol using thermal desorption and extraction with biodegradable chelating agents. Pentachlorophenol (PCP) is a fungicide applied as a wood preservative to treat wooden utility poles. This compound is a chlorinated hydrocarbon, which would require the use of this two-step process for removal. Though its use is declining because of its toxicity to humans, a large amount of PCP treated-wood waste is still generated regularly and poses a threat to humans and the environment.
2. Optimize the PDA extraction conditions; varying conditions such as time, temperature, and chelating agent concentration to assess their effect on extraction efficiency. Conditions determined most effective in the literature were used for extraction in the work completed for this thesis. Optimized conditions, however, would ensure the greatest yields and best quality products are generated from pyrolysis of the ties prior to industrial scale-up.
3. Investigate the extraction efficiency of PDA for removing inorganics from other feedstocks with higher initial ash contents.

Preliminary investigations into this recommendation have been completed as part of this work and are included in Table 1. Batch extractions were performed at room temperature (25 °C), 50 °C, and 70 °C for three hours each with constant agitation at 150 rpm. The biomass:PDA solution ratios used were 1:15 or 1:10, and all PDA

solutions were 1 % concentration. Biomass samples tested include CN-treated railroad ties, transgenic switchgrass, pine tree residues, and 6 year-old whole pine trees. The 6 year-old whole tree samples were harvested at the University of Tennessee. The pine residues samples include material taken from where the trunk of the tree is 3 inches in diameter or smaller. All samples were ground to 40-mesh particle size before extraction. After completion of the extraction, the solid biomass was filtered from the liquid solution and then dried in an oven at 40 °C for 48 hours. The ash content was then measured using NREL standard methods at 575 °C in a furnace overnight. Initial ash content was the highest in the switchgrass samples, followed by the pine residue, CN-treated ties, and 6 year-old whole trees. Overall extraction efficiency was highest from the ties and then from the whole tree sample; achieving maximum ash removal of 91.7 % and 80 % respectively. However, treatment condition efficiency trends vary among samples. It is not conclusive which conditions are optimal among those tested. The ash content varies slightly from one another among different temperatures and solution ratios, but this results in a very large change in percent removal of inorganics because the initial content was relatively low. This same trend holds true when comparing inorganic composition of particular inorganics left within each biomass after PDA extraction (Table 2). Calcium, potassium, magnesium, and sodium in particular are known to act as undesired catalyst during pyrolysis. Though the efficiency of PDA again does not vary in a conclusive trend between extraction conditions, the extraction of these undesired inorganics is successful from all samples. Therefore, in order to verify optimum conditions, it is recommended that future work remove inorganics from biomass

samples with larger initial ash contents (higher inorganic content) to make any trends more pronounced. Examples of higher ash feedstocks include rice straw, sugarcane bagasse, grasses, and wheat straw.[56, 82]

Table 3.1. Extractions of several biomass types with PDA at varying conditions.

Biomass type	Treatment conditions	Ash (%)	Percent ash removal from raw
CN Ties	As provided [a]	1.2 (0.1)	-
	Extraction at 25 °C, 1:15	0.25 (0.05)	79.2
	Extraction at 50 °C, 1:15	0.16 (0.08)	86.7
	Extraction at 50 °C, 1:10	0.13 (0.09)	89.2
	Extraction at 70 °C, 1:15	0.21 (0.04)	82.5
	Extraction at 70 °C, 1:10	0.10 (0.09)	91.7
Switchgrass	As provided	7.2 (0.07)	-
	Extraction at 50 °C, 1:15	4.3 (0.01)	40.7
	Extraction at 50 °C, 1:10	4.3 (0.5)	40.2
	Extraction at 70 °C, 1:15	5.0 (0.2)	31.0
	Extraction at 70 °C, 1:10	4.6 (0.2)	37.0
Pine residue samples	2 inch pine residue as provided	2.2 (0.2)	-
	Extracted at 25 °C, 1:15	1.13 (0.03)	48.6
	Extracted at 50 °C, 1:15	1.4 (0.1)	36.7
	Extracted at 50 °C, 1:10	1.4 (0. 2)	35.7
	Extracted at 70 °C, 1:15	1.13 (0.01)	48.6
	Extracted at 70 °C, 1:10	1.3 (0.1)	43.0
	6 year old whole pine tree as provided	1.0 (0.1)	-
	Extracted at 25 °C, 1:15	0.2 (0.1)	80.0
	Extracted at 50 °C, 1:15	0.2 (0.1)	80.0
	Extracted at 50 °C, 1:10	0.28 (0.07)	71.8
	Extracted at 70 °C, 1:15	0.35 (0.001)	64.6
	Extracted at 70 °C, 1:10	0.39 (0.01)	61.4

Table 3.2. Composition of inorganics detrimental to pyrolysis remaining in biomass samples after extraction with PDA at varying conditions.

Switchgrass					
	As provided	50 °C, 1:15	50 °C, 1:10	70 °C, 1:15	70 °C, 1:10
Inorganic	Concentration				
Ca 315.887	19280.9	1414.54	1721.71	2525.1	1664.80
K 766.490	13081.8	2264.28	2672.58	3962.4	2559.35
Mg 285.213	11905.2	919.44	1035.50	1365.4	1002.33
Na 589.592	236.3	59.22	67.41	104.3	81.74
6 year old whole tree					
	As provided	50 °C, 1:15	50 °C, 1:10	70 °C, 1:15	70 °C, 1:10
Inorganic	Concentration (ppm)				
Ca 315.887	1395	370.86	500.04	247.10	30.11
K 766.490	1995	135.14	462.05	290.77	566.22
Mg 285.213	431	91.99	127.07	78.38	130.82
Na 589.592	1.3	2.15	0.34	0.69	2.48
3-inch pine residue					
	As provided	50 °C, 1:15	50 °C, 1:10	70 °C, 1:15	70 °C, 1:10
Inorganic	Concentration (ppm)				
Ca 315.887	4485	370.86	500.04	1584.64	Ca 315.887
K 766.490	1198	135.14	462.05	327.46	K 766.490
Mg 285.213	641	91.99	127.07	200.23	Mg 285.213
Na 589.592	11	2.15	0.34	45.95	Na 589.592

4. Perform a techno-economic analysis of the two-step extraction process implemented at an industrial scale to assess its economic viability. It would be beneficial to assess the expense of implementing this process at an industrial scale and compare that to the cost recouped from preservative reuse. Comparing the monetary benefit gained from being able to recycle the CN components to treat new ties would verify that it could offset the additional treatment costs associated with this method and assert its economic viability; thus encouraging its implementation.
5. Investigate bio-oil production from pyrolysis of the pretreated biomass. Generating bio-oil from the raw and pretreated samples would allow for a verification of the predictions in Chapter III, as well as the process as a whole. The pilot-scale continuous auger reactor that was used for thermal desorption in this study can also be used for pyrolysis of the preservative-free ties if run at higher temperatures. Utilizing this same system for desorption, as well as thermochemical conversion, would demonstrate the ability to implement the process at no additional equipment cost to the consumer currently using this type of system. This ensures ease of application and improves the economic viability of the preservative recovery process.

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