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SEPARATION OF ORGANIC ACIDS AND LIGNIN FRACTION FROM BIO-OIL AND USE OF LIGNIN FRACTION IN PHENOL-FORMALDEHYDE WOOD ADHESIVE RESIN

By

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SEPARATION OF ORGANIC ACIDS AND LIGNIN FRACTION FROM BIO-OIL AND USE OF LIGNIN FRACTION IN PHENOL-FORMALDEHYDE WOOD ADHESIVE RESIN

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Bio-oil produced from biomass by the fast pyrolysis method is promising as a renewable fuel and as sources of industrial chemicals. In this study, lower cost separation methods of organic acids such as acetic and formic acids and pyrolytic lignin fraction present in bio-oil were investigated to provide basic data needed for future industrial production procedures. The calcium oxide method and a quaternary ammonium anion-exchange resin method were studied to separate organic acids as respective salts and the methanol-and-water method was studied to separate the water-insoluble pyrolytic lignin fraction. The calcium oxide and anion-exchange methods were shown to be effective in separation of organic acids, although further improvements would be needed. The pyrolytic lignin separation method was also shown to give lignin fraction that is effective for up to 40% replacement of phenol in the oriented strand board core-layer binder PF resins.

Key words: bio-oil, pyrolytic lignin, acetic acid, formic acid, lignin-PF resin.

DEDICATION

I would like to dedicate this work to my wise and generous parents Dambadarjaa Sukhbaatar and Nyam Sanjaachultem, and my loving son Badral Zundui.

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I would like to express my sincere gratitude to my advisor Dr. Moon G. Kim for his astute and sincere help, guidance, and encouragement during this program. I would also like state my acknowledgement to my committee members Drs. Philip H. Steele and Leonard L. Ingram for their support and guidance as committee members.

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CHAPTER I

INTRODUCTION

Production of fuel and chemicals from renewable materials such as food grains, wood, and other biomass materials has been attracting high interest because of the increasing worldwide demand for petroleum and natural gas resources. The fast pyrolysis method has been one of the promising approaches for converting renewable materials to liquid, gaseous, or solid fuels (Bridgewater. A.V., 1999). Bio-oil, the liquid product obtainable from the fast pyrolysis processes, can be directly used for industrial heating and electricity generation, and also, may be useful as a source of industrial chemicals.

The Department of Forest Products at MSU has an on-going research program based on the fast pyrolysis method for producing bio-oil from wood and other biomass materials. Research is also directed toward upgrading the bio-oil for liquid fuels and chemicals. The bio-oil produced is composed of many chemical components derived from breakdown of carbohydrates and lignin components. Chemical components that were identified as potential candidates for separation are organic acids such as formic and acetic acid and pyrolytic lignin. The separation will increase the value of the pyrolysis process. The organic acids can be used in many industrial processes and the pyorlytic lignin has shown promising results as a partial replacement of phenol in manufacturing phenol-formaldehyde wood adhesive resins. However, separation of bio-oil for these useful chemicals or components involves operations using water, acids and bases, and organic solvents and also generates residual materials and waste products. The cost increases from the separation procedures can be significant and, therefore, innovative processes need to be further developed toward minimizing the overall cost of separation.

The plan of separation of bio-oil components in this work is based on the premise that once the target chemicals or components are separated, the residual stream is sent back to the main bio-oil stream of fuel use. First, two approaches were explored for separation of organic acids: (1) adding calcium oxide directly to bio-oil diluted with methanol to precipitate the calcium salts of organic acids, followed by filtration to separate the precipitates from the residual bio-oil; (2) passing bio-oil diluted in methanol through a column of a quaternary ammonium anion-exchange resin to capture the organic acids as ammonium salts of the ion-exchange resin, separate them from residual bio-oil, followed by washing the ion-exchange column with a dilute sodium hydroxide solution to obtain organic acids as sodium salts. In both approaches the salts of organic acids are then acidified with sulfuric acid to obtain the free organic acids. These approaches would be of lower cost than the methods reported in previous literature where a pre-distillation step to obtain volatile materials that includes organic acids was used before treatment with calcium oxide.

The plan of separation of pyrolitic lignin is based on a precipitation method using water and methanol as non-solvents. This method would be of lower cost than the method reported in the literature where an expensive solvent ethyl acetate was used and also involved extraction of organic acids using bases such as sodium bicarbonate from the pyorlytic lignin fraction dissolved in ethyl acetate. Since the pyrolytic lignin to be separated by using the current approach was expected to be somewhat different than that obtained from the ethyl acetate process, evaluation of the separated pyrolytic lignin as partial replacement of phenol in PF resins is also planned.

Thus, the objectives of the present work were: (1) to explore methods of separating organic acids in bio-oil using, respectively, calcium oxide and quaternary ammonium anion-exchange resin and (2) to develop a lower cost way of separating the pyrolytic lignin fraction from bio-oil by water and methanol and evaluate the lignin fraction as a partial replacement of phenol in synthesis of oriented strand board binder-type PF resins.

CHAPTER II

LITERATURE REVIEW

2.1. Production methods of bio-oils

Since the oil crisis in mid 1970s, alternative sources for fossil energy have been highly sought. Pyrolysis of renewable biomass materials such as wood and agricultural residues has shown promising results as a new source of energy and chemicals. For example, in 2000, biomass provided 3.8% electrical energy in New Hampshire (New Hampshire, 2004).

Pyrolysis of wood and biomass is the process commonly carried out at high temperatures, typically above 430°C, in the absence of oxygen. The organic materials are chemically decomposed to gas, liquid, and char products with the yields depending on the pyrolysis process types. Pyrolysis processes can be divided in two types: conventional or slow pyrolysis process and fast pyrolysis process (Mohan, 2006). The conventional pyrolysis process produces high yields of charcoal, while the fast pyrolysis process produces high yields of liquid products (Bridgewater A.V, 1999). The liquid pyrolysis products, often referred as bio-oil, are considered suitable for fuel uses.

A new “fast pyrolysis” process using a rapid heating schedule and accurate control of temperature was developed in 1980s (New Hampshire, 2002, Mohan, 2006). In this process, the decomposition of organic materials occurs very fast and, therefore, the process time is very short. Furthermore, the generated vapors in the reactor are rapidly captured by condensation using cooling columns, so that further decomposition of pyrolyzed products is greatly minimized. Comparing to the direct combustion or gasification pyrolysis methods, the fast pyrolysis procedure gives relatively high yields of liquid product, bio-oil. Typically, the fast pyrolysis process results in 75% bio-oil, 13% gas and 12% char based on the dry wood or biomass weight (New Hampshire Bio-oil, 2004). The yields of different pyrolysis products are dependent on the reactor types and, recently, several new types of reactors were reported: fluidized bed; transported; circulating fluidized bed; rotating cone; vacuum; ablative; and auger. The yields of liquid pyrolysis products from these reactors reach to 70%-80%.

The bio-oil used in the current research was obtained from an auger reactor operating at the Forest Products Department, MSU. The auger reactor operates at a comparatively low temperature of 450°C and requires no carrier gas. In this pyrolysis process, the biomass enters into the oxygen-free cylindrical tube heated at the desired pyrolysis temperature with the help of an auger. The pyrolyzed products are passed through a cooling column connected to the reactor where most of them are captured as bio-oil and char and the non-condensable gases are collected separately (Mohan D., 2006).

2.2. Characteristics of bio-oils

The liquid products obtainable from pyrolysis of wood and biomass materials have been known in various names: bio-oil, pyrolysis oil, bio-crude oil, bio-fuel oil, wood liquid, wood oil, liquid wood, liquid oil, liquid smoke, wood distillates, pyroligenious tar, and pyroligenious acid (Breadgewater. A.V, 1999). Bio-oils are dark brown, flow freely, and have pungent smoky scents and can be relatively toxic, especially, to the eye and lung, but not hazardous in minor dermal contacts. The viscosity of bio-oils varies between 40-100 cP at 40ºC and 25% water content. The different water contents of bio-oils (15-35%) are often manifested in their chemical and physical properties, such as heating values and viscosities. The heating value of typical bio-oils is about 40% of conventional fuel oil on weight basis and 60% on volume basis at 16-18 MJ/kg (Bridgewater A.V., 1999). Limited storage stability of bio-oils is one unfavorable characteristics in use; bio-oils' viscosity often increases as the storage time increases. The viscosity increase of bio-oils was explained as it arises from the polymerization of pyrolysis products (Diebold, J. P., 2000) and the polymerization reaction has been known to proceed faster in the presence of char particles (Agblevor, F.A., 1995).

Bio-oils start to boil at just below 100°C and further heating of bio-oil results in distillation of components continuously until the temperature reaches to 250-280°C, where it leaves 35%-50% nonvolatile residues. Thus, a complete volatilization of bio-oils does not occur and this is one limitation in using of bio-oils directly as a liquid fuel in internal combustion engines. Bio-oil consists of more than 400 oxygenated chemical compounds derived from the disintegration or fragmentation of wood and biomass components such cellulose, hemicellulose, and lignin. Bio-oil components have been reported to consist of 5-10% organic acids, 5-20% aldehydes and hydroxyaldexydes, 0-10% ketons and hydroxyketones, 20-30% phenolics, and 15-30% water (Czernic. S., 1999).

Elemental compositions of bio-oils also depend on the feedstock. The bio-oil produced by the research group at MSU Forest Products Department showed the following elemental compositions: 13.0% water, 52.64% C, 6.09% H, 0.09% N, 27.96% O, and 0.019% S for bio-oils made from southern pine wood; and 23.1% water, 53.99% C, 4.40% H, 0.37% N, 17.68% O, and 0.035% S for bio-oils made from southern pine bark (Mitchell, B.K., 2006). MSU bio-oils produced from pine wood commonly have a water content of 16%, 0.19% char particles, viscosity of 53 cSt at 50^{o}C, density of 1.19 g/cc, and high heating value of $21.9\text{x}10^{-3}$ MJ/kg (Ingram, L., 2008).

The various organic acids present in bio-oils have various implications in use as fuel. The organic acids in bio-oils are acetic and formic acids and other higher molecular weight acids. Phenolic hydroxyl groups are also exhibit acidic characteristics. pH values of bio-oils range between 2 and 3. Organic acids can cause corrosions to boilers, heaters, engines, and storage facility. The corrosiveness of bio-oils is more severe when the water content is high and when bio-oils are used at high temperatures (Czernic. S., 1999). This property of bio-oils must be improved for fuel applications.

2.3. Fractionation of bio-oil for obtaining organic acids

Bio-oils have been known as a source of chemicals, wood preservatives, and food flavoring (Meier D, 2002) and several approaches have been reported for the separation of desired chemical components. Separation of valuable chemicals can also add value to the overall bio-oil manufacturing processes. Among the various component chemicals in bio-oil the formic and acetic acid and lignin-rich components have been the targets of separation efforts. The water solubility of formic and acetic acids and the water insolubility of lignin-rich fraction have been used in these separation procedures. Thus, mixing bio-oil with water and separation of the water-soluble and -insoluble layers leads to the water-soluble and insoluble fractions of bio-oils. Water-soluble fractions of bio-oils contain various low molecular weight organic acids and aldehydes and one commercial product "liquid smoke" has been known to be manufactured from this type of water-soluble fraction (Czernic S., 2005).

Further, the water-soluble fraction separated from bio-oil was distilled to obtain a fraction consisting of formic and acetic acids and other volatile components. Then, the formic and acetic acids fraction obtained by distillation was treated with calcium oxide or calcium hydroxide and the calcium salts of formic and acetic acids were isolated as precipitates (Oehr, US Patent 5,264,623). It will be possible to treat the calcium salts with a low-cost inorganic acid to generate a mixture of formic and acetic acids. A distillation step is then be necessary to obtain pure grade acid materials. This separation sequence would be relatively costly and, therefore, development of a simpler and lower cost separation sequence is highly desirable. This consideration has led to the current research.

2.4. Fractionation of bio-oil for obtaining pyrolytic lignin

The water-insoluble, lignin-rich fraction (25-30%) of bio-oil also has been the target of separation research because the fraction has shown the potential of replacing phenol by up to 50% in synthesizing some phenol-formaldehyde (PF) resins (Czernic S., 2005). The lignin fraction obtainable from bio-oil is often called pyrolytic lignin from the fact that they are derived from the thermal decomposition of lignin present in wood and biomass materials.

One method reported for the separation of pyrolytic lignin used ethyl acetate, water, and sodium bicarbonate solution (Chum, H. L., U. S. Patent 4,942,269, 1990; Chum, H. L and Kreibich, U. S. Patent 5,091,499, 1992). Thus, bio-oil was first mixed in ethyl acetate in 1:1 weight ratio and the ethyl acetate-soluble layer was separated and further treated by adding an excess amount of water. The resultant mixture was separated into the ethyl acetate-rich and water-rich layers upon standing and the ethyl acetate-rich layer was then isolated and further washed with sodium bicarbonate solution to remove the residual organic acid components. Evaporation of the ethyl acetate layer resulted in the lignin fraction (~31%). This method of separation is also considered to be extensive and costly, especially due to the use of ethyl acetate as solvent. A simpler, lower cost sequence is highly desirable. This consideration has led to the current research.

2.5. Uses of pyrolytic lignin in synthesizing PF resins and in other applications

The pyrolytic lignin obtained from bio-oil was claimed to be effective as a partial replacement of phenol in synthesizing various PF resins including softwood plywood adhesive-type resins (Chum, H. L, 1990; Chum, H. L. and Kreibich, R. E., 1992). Based on this research, several companies including Louisiana-Pacific Co., Weyerhauser Co., A.C.M. Wood Chemicals, and other companies have formed a consortium to develop an industrial processes of isolating pyrolytic lignin from bio-oil and using it in manufacturing wood adhesive-type PF resins (Czernic, S., 2005). The aim was to obtain lower cost PF type resins as well as secure a more sustainable route to production of adhesives used by the wood composite manufacturing industry. The commercialization plan has not been realized. There would be various reasons for the failure, but a simpler, lower cost sequence of separation method of the lignin-rich fraction could have made a difference. A simpler separation method is one of the subjects in this thesis research as mentioned above. Another known use of the bio-oil lignin fraction is as a dust binder in the industrial handling of coal for preventing leaching of coal dust into the ground water. (Technical, Environmental and Economic Feasibility of Bio-Oil in New Hampshire's, 2002).

2.6. Characteristics of PF wood adhesive resins

Phenol-formaldehyde (PF) (resol) resins are thermosetting resins widely used in manufacturing of softwood plywood and oriented strand board (OSB) as well as in other applications by hot-pressing processes. PF resins have a good binding performance for wood and cured PF resin gluelines exhibit high durability in exterior applications (Van Epps, U. S. Patent 2,360,376, Knop, A. 1985). The various resin synthesis and curing evaluation methods have been widely known and practiced (Knop, A. 1985). Briefly, PF resins are made by reacting phenol and formaldehyde in water at an elevated temperature in the presence of a base catalyst shown in Figure 2.1. The formaldehyde/phenol (F/P) mole ratio ranges 1.8-2.5 for resins used in wood composite binder applications. In resin synthesis, the polymerization reaction between phenol and formaldehyde is stopped before the completion of reaction by cooling to room temperature (Figure 2.1.1a) and is resumed and eventually cured by heating at high temperatures, (Figure 2.1.1b)

Various PF resins used in bonding wood composite boards in industry are quite different from each other depending on the areas of application. The major difference is the resins' curing rate that becomes faster as the sodium hydroxide content and the extent of polymerization attained from phenol and formaldehyde is increased in the resin synthesis step. The polymerization reaction results in increasing the viscosity of resin which is controlled to reach between 200 cP-500 cP for ease of application on wood substrates. Additional water is often added to resin to lower the viscosity (and resin solids level) in proportion to the extent of polymerization and, therefore, the resin cure rate, resin solids level, and sodium hydroxide content are closely related properties (Lee M.S., 2007).

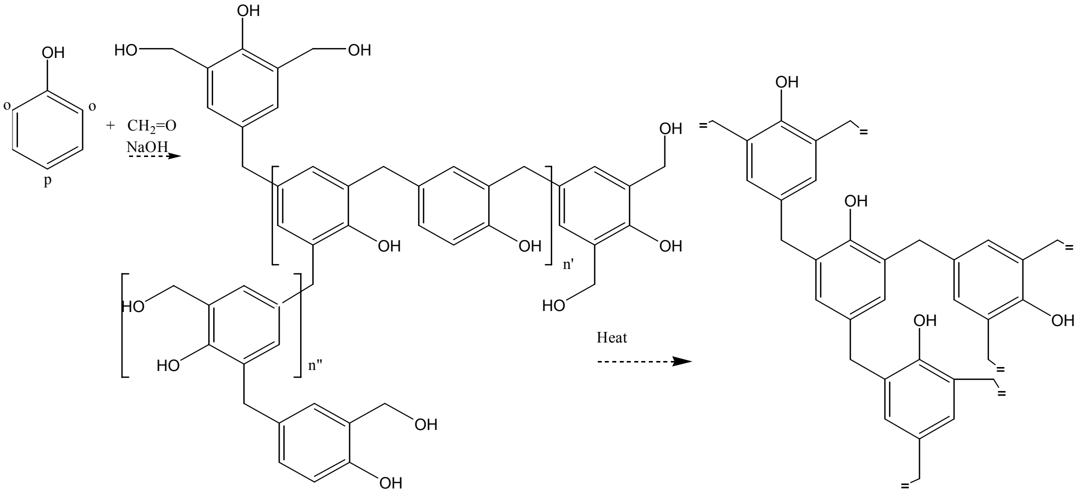


Figure 2. 1. Schematic representation of formation and curing reaction of phenol-formaldehyde resins

Specifically, oriented strand board (OSB) is bonded by hot-pressing wood mats at 400°F-440°F (204°C-226°C) using two different PF resin binders, one for the core-layer and the other for the face-layers to maximize the productivity, i.e. a short hot-press time with minimal over-cure problems in face layers of board. The core-layer binder resin's formulation is critical in that it determines the hot-press time and therefore the productivity of the plant. Materials that have a potential for partial replacement of phenol in PF resins first need to pass in this type of curing rate evaluation. Current OSB core-layer PF binder resins are commonly synthesized within a narrow range of parameters: resin solids level of ~50%; sodium hydroxide content of ~5.0%; and urea content of ~5% added as low cost diluents of solid resin (Lee, S.M., 2006). Furthermore, PF resins modified with low cost replacement raw materials need to show the effectiveness in comparison with the unmodified PF resin made by using exactly the same resin parameters except the modifying material.

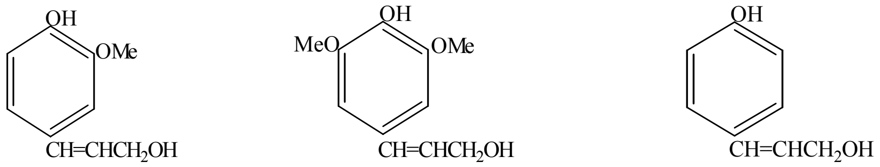
2.7. Characterization of PF wood adhesive resins

PF resins or modified PF resins have been characterized using the general industry test procedures, such as viscosity, pH, alkalinity, and solids level. The curing rate of PF resins and other similar thermosetting resins have also been conveniently measured using the dynamic mechanical analysis (DMA) method (Kim, Nieh, et. al.), although it is carried out under dry condition unlike in the hot pressing of wood composite boards. In typical DMA procedure, PF resin is impregnated in a piece of fiberglass cloth, which is then fixed to the two vibrating arms of DMA in the heating chamber. The temperature of the chamber is then increased in a controlled manner to $140^{o}C$-$160^{o}C$, followed by an isothermal run of about 10 min at the final curing temperature. The result is a measure of stiffness increases of sample vs. temperature and elapsed time, from which the curing time and the stiffness of cured sample are calculated.

Thus, DMA results are useful for comparing curing rates of different PF resins such as those obtained by modifying with low cost raw materials such as pyrolytic lignin.

2.8. Past research on using lignin in PF wood adhesive resins

One disadvantage of current PF resins is the high price of the raw material phenol derived from non-renewable crude oil. To find low cost replacements for phenol in PF resins various lignins obtained from various wood pulping processes have been extensively investigated in the form lignin-phenol-formaldehyde (LPF) resins. Lignin is abundantly available from wood and other biomass materials. Lignin is a natural polymer formed by enzyme-initiated dehydration reactions of precursor coniferyl (1), sinapyl (2) and coumaryl (3) alcohols as shown in Figure 2.2. Lignin in wood has large three-dimensional macromolecular structures as shown in Figure 2.3 and acts as binders for the cellulose and hemi-cellulose structures (Graham, G.A.).



1 2 3

Figure 2. 2. Primary lignin precursor structures.

Isolated lignins have relatively low molecular weights due to the breakage of lignin molecules occurring in the pulping processes of wood or biomass materials, but they retain phenolic rings and aliphatic chain structures having hydroxyl groups. The phenolic rings often have one unoccupied ortho carbons that can react with formaldehyde as in synthesis of PF resins. Currently, the lignin available in industrial quantities is "ligno-sulfonates" obtained from the sulfite pulping process, although its availability is also limited (Sarkanen K.V., 1971). Organo-solve lignin was available in experimental quantities from an organo-solve pulping process (Lora J.H., 1985). It has been generally accepted that phenol can be replaced with these lignins up to 40 % of resin solids without lowering the binding performance of resin for wood composite boards (Seller,T., 1990). For various reasons, however, there is currently little use of lignin as replacement of phenol in industrial manufacturing of PF wood adhesive resins. The pyrolytic lignin obtained from bio-oil appears somewhat different than lignins obtained from pulping processes and different lignin separation procedures used for bio-oils would result in somewhat different lignin products. The isolated pyrolytic lignin from MSU bio-oil using new separation procedure needed to be examined independently for suitability in replacement of phenol in PF resins.

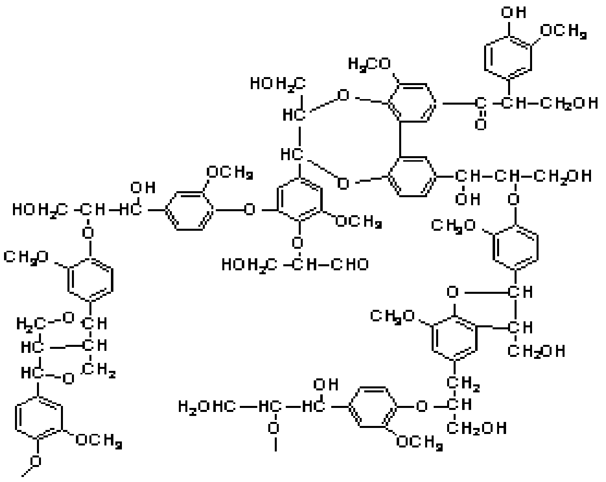


Figure 2. 3. Typical lignin molecular structures (www.lignin.org/01augdialogue.html).

2.9. Oriented Strand Board

PF resins modified with pyrolytic lignins also need to be evaluated in comparison with an unmodified PF resin by making and testing wood composite panels according to current procedures. Among various wood composite panels, oriented strand board (OSB) is a good choice to test phenol replacement raw materials in PF wood adhesive resins. OSB has been considered the most suitable as sheathing and decking materials in residential housing constructions and replaced much of softwood plywood panels traditionally used in this application. The reason for the increased uses of OSB is lower the cost from using low-grade wood and its performance and durability are comparable or better than softwood plywood made from high-grade wood (Lecture Notes, Kim. M. G, 2007). Statistics shows that the consumption of OSB reached 65 million m^3 (UNECE, 2006-2007), greater than that of softwood plywood. Although the annual production volume of OSB fluctuates according to the housing starts, it will remain to be the choice wood composite panel in future in this application. Thus, proving the suitability of the pyorlytic lignin as a partial replacement of phenol in OSB core-layer binder resin means a relatively large volume potential use of the material.

2.10. Properties of sodium and calcium acetates and formates (Merck Index 11th Edition)

Sodium acetate: chemical formula is CH_3COONa with molecular weight 82.04; hydroscopic powder; efflorescent in warm air; decomposes at high temperatures; forms tri-hydrate; very soluble in water; and moderately soluble in alcohol. For example, 1g dissolves in 0.8 ml water, 0.6 ml boiling water, 19 ml alcohol, and pH of 0.1 M aqueous solution at 25°C is 8.9.

Calcium acetate: chemical formula is $Ca(CH_3COO)_2$ with molecular weight 158.17, very hydroscopic, rod-shaped crystals; decomposes to $CaCO_3$ and acetone at 160°C or above; soluble in water; slightly soluble in methanol; and insoluble in ethanol, acetone, and benzene. pH of 0.2 M aqueous solution is 7.6. It is used in manufacturing of acetic acid and acetone and in dyeing, tanning, and curing of animal skins, stabilizing food, and inhibiting corrosion of metals.

Sodium formate: chemical formula is $HCOONa$ with molecular weight of 68.02; white crystal powder with slight odor of formic acid; decomposes at high temperatures; soluble in 1.3 parts of water; soluble in glycerol; and slightly in alcohol. The water solution is almost neutral, about pH 7 and has a buffering action. It is used in dyeing and printing of fabrics and also as precipitant of noble metals.

Calcium formate: chemical formula is $Ca(HCOO)_2$ with molecular weight of 80.11; orthorhombic crystal, slightly acidic; soluble in water; and insoluble in alcohols. It is used as a binder for fine-ore briquette, in drilling fluids and lubricants, and as preservative for food.

CHAPTER III

EXPERIMENTAL METHODS

3.1. Materials

Pine wood bio-oil produced in an auger reactor at MSU, Department of Forest Products, reagent grade calcium oxide, methanol, phenol, urea, sodium hydroxide and DOWEX-22 ion exchange resin were obtained from Aldrich Chemical Company. Also, 50% formaldehyde aqueous solution and a commercial OSB face-layer PF resin (RPPB 205C02) were obtained from Georgia-Pacific Resins, Inc., Louisville, MS. For laboratory OSB manufacture, wood strands were obtained from Norbord Corp., Guntown, MS. The wood strands consisted of approximately 90% southern yellow pine and 10 % mixed hard wood.

3.2. Gas chromatography/mass spectrometry (GC/MS)

Samples of bio-oil and treated bio-oil were analyzed on Perkin-Elmer Clarus 500 GC/MS by injecting 1.4μL of solution, followed by an injector venting for 30 sec. The injector temperature was 270°C and the carrier gas was Helium at a rate of 2mL/min. A fused silica column with 30m x 0.32mm dimensions, coated with 5% phenyl methyl polysiloxane was used. The oven temperature was maintained at 40°C during the first 4 min, then heated at a rate 5°C/min to the final temperature of 280°C, and maintained at the final temperature for 15 min. The total time for a run was 67 min. The mass spectrometer was run with electron impact ionization at 70 eV at a source temperature of 210°C and interface temperature of 225°C. The injection solutions were prepared in methanol at about 2%~ 5% concentrations of organic solids.

3.3. Determination of acetic acid concentrations in samples.

The calibration curve in Figure 3.1 was obtained from GC/MS integration values of acetic acid peak of 50, 100, 150 and 200 ppm standard solutions of pure acetic acid (99.98%) in methanol.

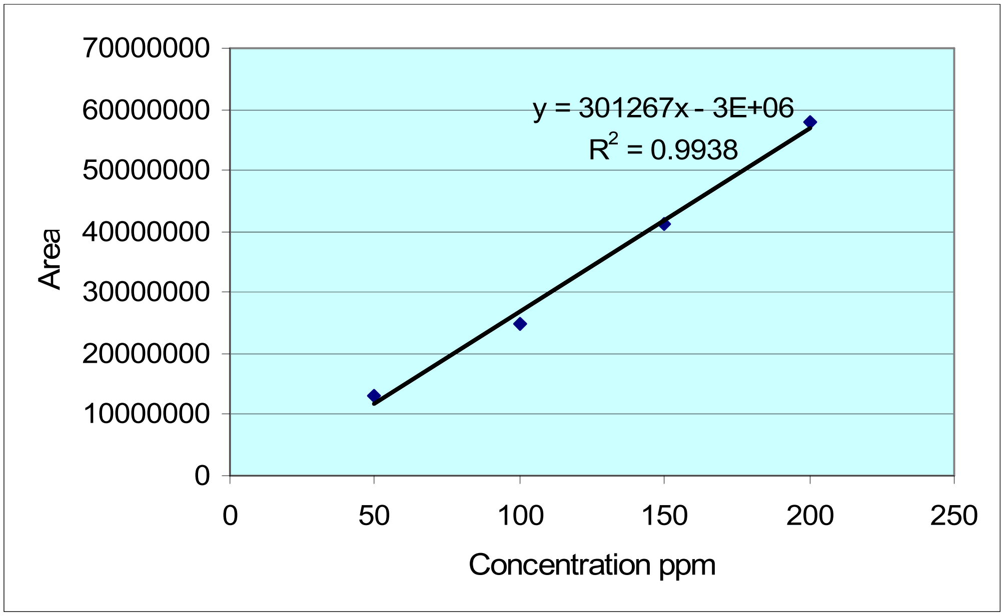


Figure 3. 1. Correlation between the concentration and integrated area of standard solutions of acetic acid.

The correlation between the acetic acid concentration and integrated area of acetic acid peak resulted in a correlation equation, y = 301267x+3E06, as shown in Figure 3.1. By using this equation, the acetic acid amount in raw bio-oil, residual bio-oil, as well as the acetic acid recovered from calcium salt or ion exchange resin was calculated while considering the dilution factors.

3.4. Exploratory experiments for separation of organic acids from bio-oil using calcium oxide

The experiments were conducted in a stirred reactor by varying the amount solvent methanol to a given weight of bio-oil and also by varying the amount of calcium oxide added according to the resultant pH value of the mixture. After the heat of neutralization has subsided, the precipitates were collected by filtration, washed with methanol, and dried for quantification as well as for transformation into free acids. Filtrates were combined and evaporated on a rotor evaporator to recover and characterize the residual bio-oil. Various parameters were observed in this sequence of experiments to obtain parameters that would allow a smooth operation for a large scale experiment as discussed in Chapter 4.

A typical procedure is described in the following: in a stirred reactor, 50 g bio-oil and 50g methanol were charged and stirring was continued for about 10 min to result in a uniform solution with the pH value reaching at about 3.61. To this solution, 1.77 g calcium oxide was added and stirring continued for approximately four hours: the temperature of the reaction mixture initially rose to 56^{o}C and reached to room temperature at the end of the period. The pH of the reaction mixture was 7.0. The formed precipitates were collected by filtration and washed with a small amount of methanol to obtain 2.22g solid organic acid calcium salt. Similar experiments were conducted to reach pH 8, pH 9, and pH 10 by adding increased amounts of calcium oxide.

3.5. Characterization of calcium salts and residual bio-oil samples

For characterization of the organic acid calcium salts, approximately one gram of sample was suspended and stirred in 10 mL methanol and 8% sulfuric acid solution was added in small amounts until the pH of the mixture reached 2.2. The mixture was then filtered to remove the calcium sulfate and the filtrate was dried over anhydrous sodium sulfate, treated with small amount of sodium bicarbonate to remove free sulfuric acid, and analyzed by GC/MS (Appendix A).

For characterization of residual bio-oil samples, GC/MS analyses were conducted as well as determination of the ash content to determine the calcium oxide/salts remained un-precipitated in the residual bio-oil. Ash contents were determined by burning approximately one gram of sample in a furnace at 800°F (427^{o}C) for 2 hours and measuring the residual ash weight.

3.6. Exploratory experiments for separation of organic acids from bio-oil using a quaternary ammonium anion exchange resin

An anion exchange resin, DOWEX-22, was used to evaluate the suitability of this type resins in capturing organic acids in bio-oil. In this method, the ion-exchange resin purchased from Aldrich Chemical Company was regenerated by stirring in 0.1N NaOH solution for two hours, converting into the quaternary ammonium hydroxide form. Then, after washing the resin with distilled water until the wash water reaches pH 7, it was filtered under light vacuum and transferred into a small amount of methanol to prevent it from drying.

A typical procedure is as follows: first, a mixture of 80 g bio-oil and 80 g methanol was made and, separately, 74 g of ion-exchange resin previously washed with 0.1N sodium hydroxide solution and some methanol were loaded in a 3.0 cm diameter 40cm long column and packed by vibration. Then, the bio-oil/methanol solution was allowed to slowly elute through the ion-exchange column by gravity and fractions were collected. During this elution period the pH of the eluting solution was monitored. The fractions were analyzed with GC/MS (Appendix B).

The small-scale ion-exchange resin column experiments were somewhat unsatisfactory due to the uneven elution of bio-oil/methanol mixture through the column. Therefore, a batch treatment method was also explored as follows: in a stirred reactor, 20 g bio-oil and 50 g methanol were charged and stirred for about 10 min to obtain a uniform solution. The pH value reached at 3.61. Then, ion-exchange resin previously washed with 0.1N NaOH solution was added in small amounts while stirring continuously until the pH of the solution reached 6.98. Then, the ion- exchange resin was collected by filtration and washed several times with a small amount of methanol to recover it in the form of organic acid salts. Organic acids were then regenerated from the recovered ion-exchange resin by stirring it in 100 mL 0.1N NaOH solution for two hours, followed by filtration, evaporation of the filtrate to obtain the residue of organic acid sodium salts, and acidifying a small amount of the residue in methanol to pH 2.2 using an 8% sulfuric acid solution. The acidified sample was dried over anhydrous sodium sulfate and the methanol solution was analyzed on GC/MS (Appendix B 26-32). The quantification of recovered acetic acid was done based on correlation equation (1) in Figure 3.1.

The original filtrate and methanol washings were combined and evaporated to give the residual bio-oil, which was analyzed on GC/MS and compared with untreated bio-oil to measure the extent of organic acid removal (Appendix B 18-25). Since ion-exchange resins are to be used repeatedly, the recovered ion-exchange resin was subjected to the same sequence experiments for two more times.

3.7. Exploratory separation of the pyrolytic lignin fraction from bio-oil

A lower cost separation procedure of pyrolytic lignin was explored by using water and methanol in comparison to the ethyl acetate solvent process reported by Chum and Kreibich (United State Patent 4,942,269; 5,091,499). The objective was to obtain a cleaner separation of the water-insoluble pyrolytic lignin fraction than by using water only. Thus, 2325g of pine wood bio-oil was mixed thoroughly with 2400g of distilled water and the mixture was allowed to stand at room temperature for two hours. After the water-rich layer was decanted off, the residue was obtained (1160g; 50% yield). This residue fraction was briefly examined by reacting with formaldehyde in the presence of sodium hydroxide according to the formaldehyde reactivity test procedure (Wooten. A. L., FPL#52, 1990). It was observed that the lignin fraction contains materials that cause an extensive foaming and phase separation during the reaction with formaldehyde. This result indicated that the fraction still contained materials that make it unsuitable as a phenol replacement material in phenol-formaldehyde resins. Therefore, the water-insoluble fraction was mixed with methanol in a 1:1 weight ratio and then the lignin fraction was precipitated by adding distilled water incrementally while stirring until no further precipitation of lignin occurred. The mixture was allowed to stand at room temperature to reach a full separation of the precipitates, which was collected by decantation, yielding 519.0g (22.0%).

3.8. Determination of formaldehyde reactivity of pyrolytic lignin

The pyrolytic lignin fraction obtained above was evaluated for its reactivity with formaldehyde according to a reported procedure (Wooten, A.L., FPL#52, 1990). Thus, 5.0 g 50% of sodium hydroxide solution, 8.94 g of 50% formaldehyde solution, and 84.0g water were loaded into a stirred reactor. Then, 5.0g of pyrolytic lignin were added and the mixture was heated slowly to 60°C. Then, 3.0g samples were taken at 0.5, 1, 2 and 3 hour of reaction. The samples were analyzed for formaldehyde content as follows: the sample was dissolved in a mixture of 20 ml methanol and 30ml distilled water and the pH was adjusted to 4.0 with 1.0N and 0.1N HCl solutions over a 5-min period. Then, 15 ml of 1M NH_2OH-HCl solution was added to the mixture and the solution stirred for 8 min. The generated acid in the solution was titrated with 0.1N NaOH solution to pH 4.0. The titration value corresponds to the amount of formaldehyde remained unreacted in the reaction mixture as follows:

$$\%\text{ Remaining } CH_2O = \frac{\text{mL(NaOH) (N of NaOH) (g mol } CH_2O\text{/L)}}{\text{g, weight of sample}}$$

3.9. ^{13}C NMR spectroscopic analyses of pyrolitic lignin and starting bio-oil

^{13}C NMR spectra of the pyrolytic lignin sample obtained above and original bio-oil were obtained on a Techmag 360 MHz NMR spectrometer at ambient temperature using a 22-μs (80°) pulse-width and 10-s delay time for maximum quantification results (Spectral Data Services, Inc., Champaign, IL) with about 400 scans accumulated. Peaks were integrated and integral values of the two spectra were compared to estimate the characteristics of the pyorlytic lignin sample.

3.10. Syntheses of OSB core-layer binder PF resins using phenol and pyrolytic lignin

OSB core-layer binder PF resins are generally known to have a formaldehyde/phenol (F/P) ratio of 1.90-2.1, NaOH content of 5.0%, resin solids level of 50.0%, urea content of 5.0%, and viscosity in the range 200cP-300cP (Kim 3.). The synthesis of control PF resin was carried out, using materials shown in Table 3.1., as follows: in a one-liter reactor equipped with a stirrer, thermometer, and condenser; 264.42 g of 99% phenol (2.78 mol), 23.76 g of 50% NaOH solution (0.3 mol) and 27.00 g distilled water were charged in the given order. The mixture was then heated to 65°C-70°C and 320.49 g of 50% formaldehyde solution (5.34 mol) were added in drops to the reaction mixture over a 30-min period while the temperature was maintained in the same range.

Then, the temperature was increased to 95°C over a period 25 min and maintained until the reaction mixture reached viscosity of I by Gardner-Holdt (G-H) scale, when the second NaOH solution (28.44g) and 71.55 g water were added. The temperature was then maintained at 85-90°C until the reaction mixture reached viscosity of H-I by G-H scale. The third NaOH solution (38.25 g) and 41.85 g water were added and the temperature was maintained in the same range until the reaction mixture reached viscosity N by G-H scale. Finally, cooling of the reaction mixture was started and 43.47 g of urea and 40.77 g of water were added to the reaction mixture at about 60°C. The finished resin was further cooled to room temperature to give a viscosity value of JK by G-H scale and 250 cP by Brookfield scale.

For syntheses of OSB core-layer resins with partial replacements of phenol with pyrolytic lignin, the procedure and materials used were the same except that 30%, 40%, and 50% of the phenol used in control PF resin were replaced with the pyrolytic lignin fraction obtained above. The amount of formaldehyde was also reduced based on the formaldehyde reactivity value determined above: 0.80 mole formaldehyde per 100 g of pyrolytic lignin. The materials charges used in the syntheses of lignin-modified resins are shown in Tables 3.2. The sodium hydroxide content of all synthesized resins were determined by titration to pH 4.0 and lignin-modified resins were found to have less than the charged values, apparently from some residual organic acids remained in the pyrolytic lignin fraction used. Therefore, calculated amounts of sodium hydroxide in comparison with the value of control PF resin were added to the lignin-modified resins. All synthesized resins were stored in a freezer until use.

3.11. Measurement of physical properties of resins

Viscosity, pH, nonvolatile resin solids, and alkalinity of all resins were measured according to the standard procedures known in the wood adhesives industry.

Table 3. 1. Material charges used in the synthesis of control PF resin as OSB core-layer binder.

	Reagents	Conc. (%)	Weight (%)	Batch wt. (g)
1	Phenol	99	29.38	264.42
2	NaOH	50	2.64	23.76
3	Water	100	3.00	27.00
4	CH_2O	50	35.61	320.49
5	Water	100	7.95	71.55
6	NaOH	50	3.16	28.44
7	Water	100	4.65	41.85
8	NaOH	50	4.25	38.25
9	Water	100	4.53	40.77
10	Urea	100	4.83	43.47
	Total		100.00	900.00

Table 3. 2. Material charges used in syntheses of OSB core-layer binder PF resins with 50%, 40%, and 30% replacements of phenol with pyrolytic lignin.

			50%P:50%L		60%P:40%L		70%P:30%L	
	Reagents	Conc. (%)	Weight (%)	Batch wt. (g)	Weight (%)	Batch wt. (g)	Weight (%)	Batch wt. (g)
1	Phenol	99	16.49	148.00	18.56	174.00	21.75	195.75
	P. lignin	100	16.49	148.00	12.37	116.00	9.22	82.98
2	NaOH	50	2.96	26.58	2.80	26.26	2.76	24.84
3	Water		3.04	27.29	7.94	74.45	5.25	47.25
4	CH_2O	50	27.90	250.43	28.44	266.68	30.5	274.50
5	Water		9.25	83.06	7.84	73.52	8.32	29.79?
6	NaOH	50	3.55	31.89	3.33	31.22	3.31	29.79
7	Water		8.14	73.09	4.65	43.6	4.87	43.83
8	NaOH	50	1.85	16.61	4.47	41.91	4.45	40.05
9	Water		5.86	52.64	4.77	44.73	4.74	42.66
10	Urea	100	4.47	40.13	4.83	45.29	4.83	43.77
	Total		100.00	897.72	100.00	937.66	100.00	900.00

3.12. Dynamic mechanical analysis (DMA) curing measurements of synthesized PF resins

DMA measurements of resins were carried out on TA Instruments DMA 983 with a procedure designed mainly to compare the curing of different PF resins under the condition closely similar to the fast temperature increasing schedule used by OSB manufacturing plants. Approximately 0.20 g of resin sample was uniformly spread on a fiberglass braid (18.5 x 11.2 x 0.12 mm), which was then clamped horizontally between the two sample holding arms. DMA runs were carried out in fixed displacement mode with 0.8 mm amplitude and 1.0 Hz oscillation frequency. The chamber temperature was increased from 30°C at a rate of 25°C/min to 140°C and 160°C, respectively, followed by an isothermal period of 15 min. From the rigidity development curve, the gel times and cure times of resin was calculated according to a reported procedure (Lee. S. M., 2007).

3.13. Strand board manufacturing procedure

Laboratory strand boards were manufactured using wood strands obtained from Norbord Company to evaluate the bonding performance of synthesized core-layer resins. Three-layer, random orientation boards were made at a target density of 42 pcf (0.6727 g/cm^3). For all boards the face-layer resin used was the commercial resin (RPPB 205C02) obtained from Georgia-Pacific Resins, Inc. The resin solids loading level was 4.0% and the emulsion-type paraffin wax solids level was 1.0% based on dry wood weight for both core-layer and face-layers of boards. Wood strands were first dried to moisture content below 2%-4% based on oven dried wood weight and a calculated amount was loaded into a rotating blender.

First, the emulsion-type wax was sprayed using a compressed-air sprayer and then the binder resin was sprayed using a disc-type atomizer spinning at 10,000 rpm into the rotating blender. Face-layer and core-layer strands were separately blended. Three-layer mats were made with random orientation of strands with measured weight of resin-applied wood strands as bottom, core and top layers in 25: 50: 25 weight ratios in a 55.7 cm x 60.7 cm forming box. The mat was then hot pressed in a Diefenbacher hot press with platen temperature of 220^{o}C using a press time of 3.0 and 3.5 min, respectively. Duplicate boards were made with total of 16 boards using the four core-layer resins. Detailed mat preparation and hot pressing data are reported in Appendix C.

3.14. Testing procedures of manufactured strand boards

Pressed strand boards were tested according to ASTM D1037 (ASTM 2000) for internal bond (IB), modulus of elasticity (MOE) and modulus for rupture (MOR), 2h and 24h water soak values. Furthermore, 2h-boil internal bond strengths were determined. Cut test specimens were equilibrated for 2 weeks in a conditioning room set at 7% EMC. The test results were compared for different core-layer resins. Board densities were measured for IB and MOR/MOE test specimens. IB and MOR/MOE strengths were measured on a Tinius Olsen universal testing machine. Boil IB values of samples were obtained by boiling specimens for 2h and drying in the oven for 6h at 103°C, followed by equilibrating to 8% moisture content. Thickness swell (TS) and water absorption (WA) values were measured by soaking specimens (15.2x15.2 cm) in water at room temperature for 2h and 24 h. Detailed data of test results are reported in Appendix C.

CHAPTER IV

RESULTS AND DISCUSSION

4.1. Exploratory separation of organic acids from bio-oil using calcium oxide

The calcium oxide approach of organic acid separation from bio-oil was based on the low solubility of calcium salts of various organic acids in methanol (Merck Index, 11th Edition, 1989). The organic acids in bio-oil are mostly in free acid form as reflected by the pH value of 2.61~3.61 when diluted with methanol. The addition of calcium oxide to bio-oil neutralizes the acids evidenced by the generation of heat with the temperature of reaction mixture rising quickly to about 60°C. The overall scheme of the approach is shown below:

Step 1 – Neutralization with calcium oxide and filtration:

Bio-oil (RCO_2H) + $CaO \rightarrow (RCO_2^-)_2Ca^{++}$ (Solid precipitates) + Residual Bio-oil

Step 2 - Regeneration of organic acids using sulfuric acid:

$(RCO_2^-)_2Ca^{++} + H_2SO_4 \rightarrow \underline{2RCO_2H} + Ca_2SO_4$ (RCO_2H: Organic acids)

Alternate Step 2 - Regeneration of organic acids using carbon dioxide:

$(RCO_2^-)_2 Ca^{++} + CO_2$ (Pressure) $\rightarrow \underline{2RCO_2H} + CaCO_3$ (Precipitates)

Alternate Step 3 - Regeneration of calcium oxide and carbon dioxide:

$CaCO_3 + \text{Heat} \rightarrow \underline{CaO} + \underline{CO_2}$

Because of the relatively high viscosity of the reaction mixture in the neutralization stage it was essential to dilute the reaction mixture with solvent. From the view point of cost and later filtration operation, methanol in an amount approximately equal to the weight of the bio-oil was found to be necessary. The reaction mixture needs to be cooled and allowed to stir several hours until the calcium salts of organic acids formed are fully precipitated. The filtration of the reaction mixture was relatively fast. The dark brown filter cake of organic acid calcium salts obtained were easily dried upon air exposure and easily crushed to fine powders. The filtrate was collected and the methanol solvent evaporated to recover the residual bio-oil.

It was observed that the pH of the reaction mixture of bio-oil and calcium oxide increases only gradually with increasing amounts of calcium oxide used. Therefore, four neutralization reactions were carried out with the target end-point of pH 7, pH 8, pH 9, and pH 10, respectively. The obtained reaction mixtures were processed for separation of organic acids and the analytical data are reported in Table 4.1 and Figure 4.1 and all GC/MS are recorded in Appendix A Figures 3-24, as indicated in Table 4.1.

Table 4. 1. Separation of organic acids with the calcium oxide method.

Reaction parameters	Target pH	pH 7	pH 8	pH 9	pH 10
	1:1 bio-oil:MeOH mixture (g)	100	100	100	100
	Initial pH	3.61	3.61	3.61	3.61
	Amount of CaO used (g)	1.77	3.27	4.75	6.20
Calcium salts obtained	Weight of organic acid salts (g)	2.22	7.95	30.14	42.09
	Recovered acetic acid (%)	0.21	0.63	2.01	1.51
	Recovered formic acid (%)	0.13	0.15	0.64	0.66
	GS/MS of recovered organic acids, Appendix A	12, 13	14, 15	16, 17	18, 19
Residual bio-oil obtained	Ash content (%)	3.60	5.45	6.26	7.90
	Acetic acid content (%)	1.9	2.4	0.46	0.6
	Formic acid content (%)	0.19	0.27	0.02	0.02
	GC/MS of residual bio-oil, Appendix A	3, 4	5, 6	7, 8	9, 10

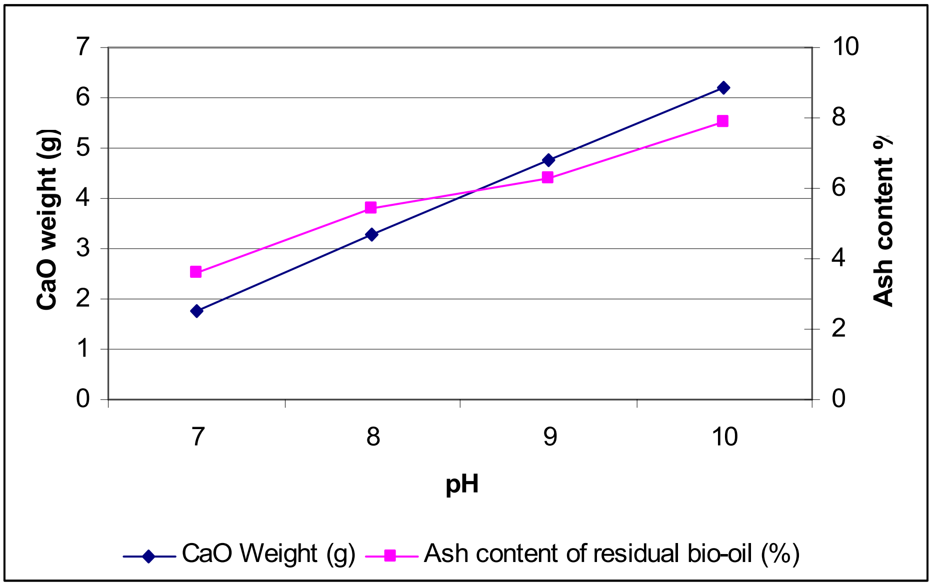


Figure 4. 1 Correlation of pH to the weight of CaO and ash of residual bio-oil.

4.1.1. Target pH, amount of calcium salts formed, acid and ash content of bio-oil

As the target pH increased with increasing amounts of calcium oxide added, the amount of calcium salt precipitates obtained was increased and the ash content of residual bio-oil also increased (Table 4.1 and Figure 4.1). These results indicated that:

(1) The formation of calcium salts occurs mostly with organic acids at target pH 7 and pH 8 with only small amounts of phenolic hydroxyl groups of pyrolytic lignin reacting to form salts,

(2) High amounts of pyrolytic lignin components in bio-oil react with calcium ion to form precipitates at target pH 9 and pH 10;

(3) The ash content of residual bio-oil is significantly high even at target pH 7 and pH 8 and it further increases as the target pH increases. This result indicates that the precipitation process is incomplete under the reaction condition, i. e. some calcium salts of organic acids and phenolic components remains in the solution of the residual bio-oil in methanol; and

(4) The acid content of residual bio-oil decreases to low values in comparison to raw bio-oil with greater reductions attained with high target pH values. The acid content values of the residual bio-oil obtained for target pH 7 and 8, about 2%, are not insignificant and need to be considered with respect to the practicality of this acid separation approach as a corrosion reduction method of bio-oil.

4.1.2. Results of the calcium oxide acid separation process with target pH 7 and 8

Acid removal from bio-oil - the experimental objective was to explore a way of removing organic acids in bio-oil to reduce the corrosiveness as well to see if the separated organic acids can add value to the overall bio-oil manufacturing process. Data in Table 4.1 indicate that the acid separation process with target pH 7 and 8 are more optimal than target pH 9 and 10. The starting bio-oil contains about 10.92% acetic acid, 3.03% of formic and small amount of other organic acids. The calcium oxide addition at these target pH levels has shown removal of significant amounts of acetic acid, down to about 2% and amount of formic acid down to 0.27%. Thus, the overall acid removal could well be more than the acetic and formic acids value would have indicated. Overall, this result would be useful in future scale-up research.

Corrosiveness of bio-oil is likely to depend on the total concentration of organic acids in bio-oil and a measure of corrosion reduction vs. acid concentration needs to be established in future. Two percent acetic acid content levels may or may not be adequate for corrosion reduction. On the other hand, the ash content of the residual bio-oil at these target pH levels, about 5.45%, would be relatively high for any liquid fuel. However, this problem of calcium salts of organic acids remaining in the residual bio-oil appears to be not insurmountable. Research would be needed regarding the amount of methanol used as diluent as well as using various coagulants to effectively cause precipitation of calcium salts and also using tighter filtration media to filtrate finer precipitate particles more effectively.

Calcium salts of organic acids and acid recovery - the amounts of calcium salts of organic acids obtained, 7.95 grams at pH 8 from 50 grams of bio-oil used, is a relatively good representative value considering the acetic acid content of starting bio-oil at 10.92% and formic acid content in that 3.03% . The obtained calcium salt of organic acids was easily dried in open air to give a free-flowing powder, easy to handle in large-scale operations. Suspending this powder in methanol also resulted in well-dispersed, low viscosity slurry and no difficulty arose during acidification by adding dilute sulfuric acid while stirring for regeneration of organic acids in methanol. The methanol solution of regenerated organic acids clearly indicated the presence of acetic acid in significant amounts in GC/MS analyses as shown in Table 4.1 (Appendix A); the recovered acetic acid values of the target pH 7 and 8 experiment were 0.21% and 0.63%, and the recovered formic acid values were 0.13% and 0.15%, respectively. The values are relatively small. Loss of organic acids appears to occur in the isolation procedure due to the handling in open air, and also, from using sodium bicarbonate needed to capture residual free sulfuric acid for preventing column deteriorations. Further research would be needed in future for distillation or other methods to isolate pure acetic/formic acids from the methanol solution to evaluate the usefulness of this separation approach as a value addition proposition to the overall bio-oil manufacturing process.

One complication observed from GC/MS results was that the acidified methanol solution also contains not only organic acids but also some other materials such as simple phenols and other pyrolytic lignin components. Since some organic acids still remain in the residual bio-oil at this target pH experiment, this result indicates that the calcium oxide neutralization has a limited selectivity between organic acids and phenolic hydroxyl groups. It was not possible to accurately quantify the amounts of these non-acid materials, but their amounts need to be minimized in future research. Overall, the procedure of obtaining organic acids from the calcium oxide precipitation appears to be useful. Especially, although it was failed to show in this study, the acidification step appears to be made to go using carbon dioxide under pressure instead of sulfuric acid. Then, the calcium carbonate formed can be burned to generate calcium oxide, resulting in a closed-loop process of recycling calcium oxide and carbon dioxide with no significant waste products being generated from the acid separation process.

4.1.3. Experimental results of target pH 9 and 10

The experiments carried with target pH 9 and 10 resulted in residual bio-oil samples having quite low organic acid concentrations. However, the amounts of precipitates of calcium salts of organic acids were very high considering the amount of bio-oil used. This indicates that much of pyrolytic lignin components have also precipitated and the amount of residual bio-oil became less and less. Therefore, this pH range would be not useful as acid separation methods. However, there is a rather drastic increase in the amount of precipitates between pH 8 and 9 and further research would be useful for looking into various different pH values between 8 and 9 to fine-tune the separation procedure discussed above in 4.1.2 for maximum acid recovery.

On the other hand, the calcium oxide method might be developed to extract a major portion of bio-oil components from bio-oil including organic acids and phenolic (pyrolytic lignin) components by carrying out the calcium oxide neutralization reaction to a high pH end point. GC/MS spectra of the recovered organic acids obtained by acidifying the calcium salts gave almost the same spectra with bio-oil itself, indicating that pyrolytic lignin components were extensively extracted by reacting with calcium oxide (Appendix A). The low experimental values for recovered acetic acid from the precipitated calcium salts, 2.01 % and 1.51%, and for formic acid 0.64% and 0.66% respectively, remain to be a question and likely to arise from losses in the isolation procedure. The residual bio-oil contained only 0.46% and 0.60% of acetic acid, and 0.02% and 0.02% formic acid, respectively. It also appears that acetic and formic acid in the recovered solution does not get accurately quantified on GC/MS analyses due to the high amounts of pyrolytic lignin components present in the samples.

4.1.4. Observations from GC/MS of recovered organic acid fractions

GC/MS of the recovered organic acids from calcium salts obtained above are reported in Appendix A11-A24. Generally all spectra are similar to each other and to bio-oil itself but the abundance of acetic and formic acid peaks varies as shown in Figure 4.2 and Figure 4.3.

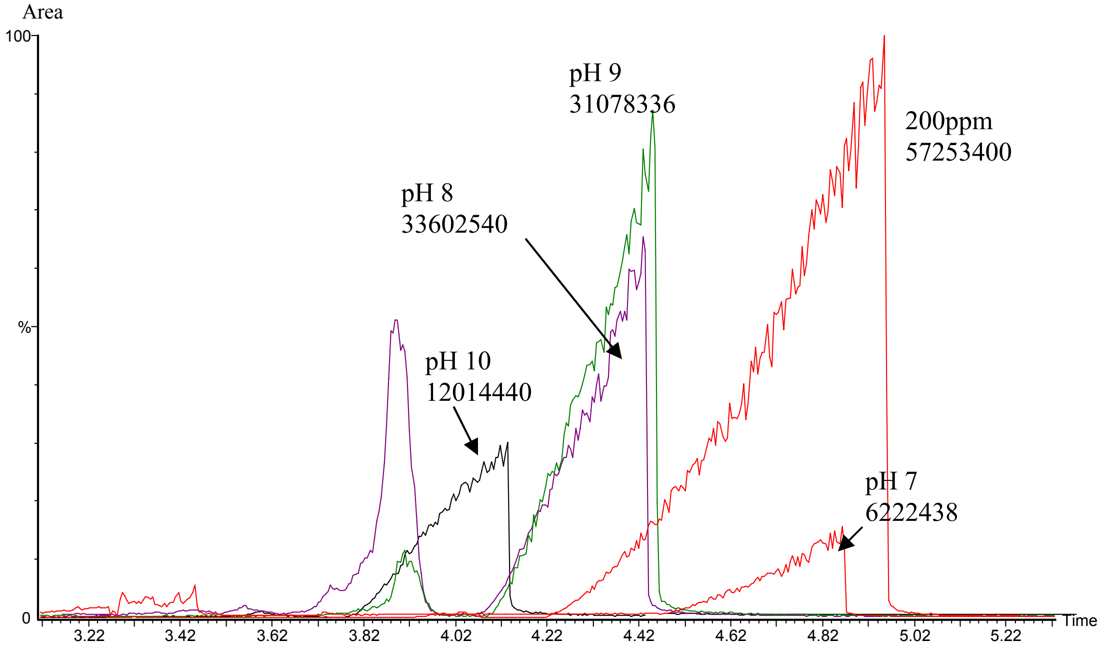


Figure 4. 2. Recovered acetic acids peaks in CaO method for different target pH and 200 ppm acetic standard solution each with integration area values.

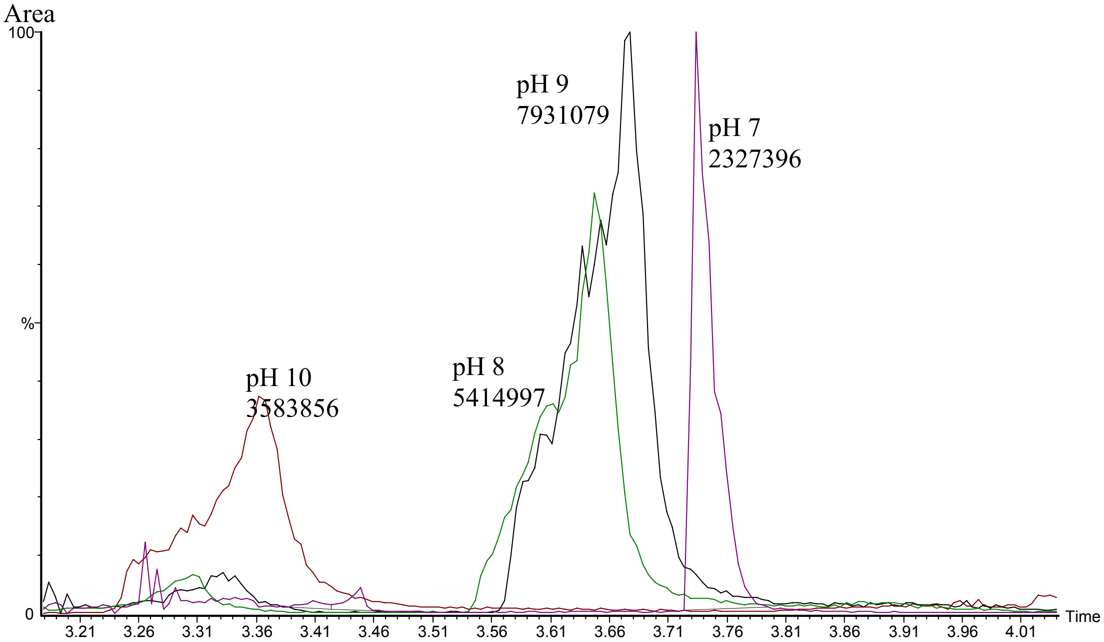


Figure 4. 3. Recovered formic acids peaks in CaO method for different target pH with integration area values.

4.2. Exploratory separation of organic acids from bio-oil using an anion-exchange resin

Since the calcium oxide method was found to give less than expected effectiveness in the separation of organic acids from bio-oil, use of an anion-exchange resin was examined to explore a way of separating organic acids in bio-oil. The overall scheme of using anion-exchange resins is as follows:

Step 1- Generation of the hydroxide form of resin:

Resin—N^+R_3--X^- + 0.1N NaOH → Resin—N^+R_3--OH^- + Na X^-

Step 2 – Reaction of the resin with acids in bio-oil and elution or filtration:

Resin—N^+R_3--OH^-+ Bio-oil (RCO_2H) →

Resin—N^+R_3—RCO_2^- (solid) + Residual bio-oil (Separated as liquid)

Step 3 - Regeneration of the hydroxide form of resin and obtaining organic acid salts:

Resin—N^+R_3—RCO_2^- (solid) + NaOH →

Resin—N^+R_3—OH^- (solid) + $\underline{RCO_2^-Na^+}$ (Separated as water soluble)

Step 4 - Generation of organic acids:

$RCO_2^-Na^+ + H_2SO_4 \rightarrow \underline{RCO_2H} + Na_2SO_4$ (RCO_2H = Organic acids)

4.2.1. Column method

The anion-exchange resins are commonly used to remove anionic components from liquid mixtures and the operation is often conducted in the column platform. In this procedure, the anion-exchange resin supplied as chloride form is transformed into the hydroxide form by treatment with sodium hydroxide solution and then packed in a column. Then, the liquid mixture is gradually sent through the column by applying some pressure or by gravitation. The eluted material is collected until the anion-exchange resin capacity is depleted and the depleted anion-exchange resins is then regenerated and used again.

In this work, sixteen consecutive fractions were collected by eluting a mixture of 80 g bio-oil and 80 g methanol from a column packed with 74 g of Dowex-22 anion exchange resin (3 cm diameter and 40 cm long). The anion-exchange resin was pre-washed with 0.1N sodium hydroxide solution and then with water until pH 7.0. During the elution of the sixteen fractions the pH of the eluting solution decreased from 6.85 to 5.44. The bio-oil fractions were analyzed on GC/MS (Appendix B 1-17) and the acetic acid concentrations were obtained as shown in Figure 4.4.

The concentration of acetic acid in the eluted bio-oil fractions was very low until the fraction #13 was collected, when the pH of the eluting solution was 5.49. Thus, this result has shown that anion exchange resins could be used in the column platform to capture organic acids in bio-oil by monitoring the pH value of eluting

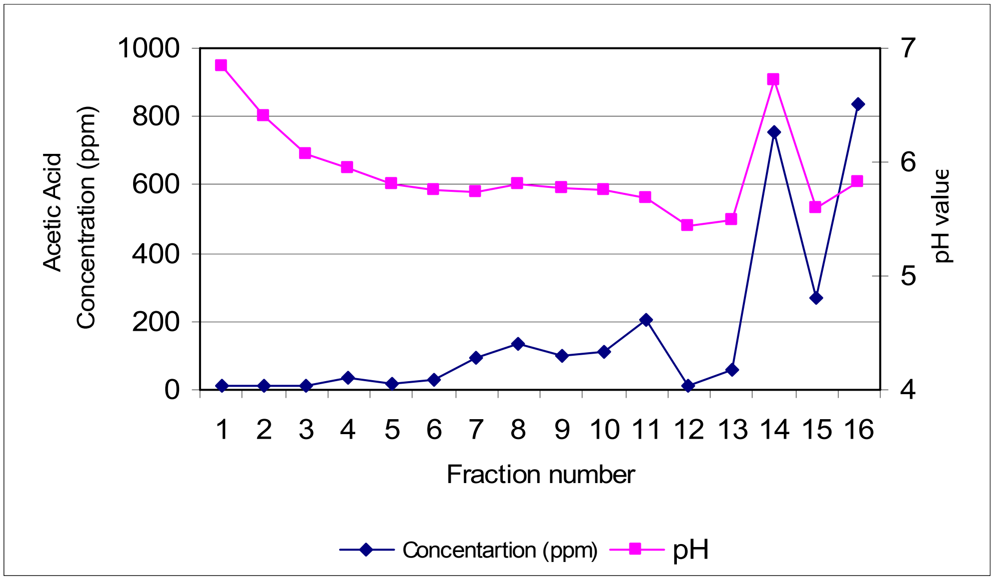


Figure 4. 4. Acetic acid concentrations (ppm) from GC/MS analyses of bio-oil fractions obtained from the anion-exchange resin column experiments.

solution. However, more quantitative data on the ion-exchange capacity and amounts of acid recovered were difficult to obtain from the column setup due to the non-uniform flow of the bio-oil/methanol solution in the column. Although the column-type loading of ion-exchange resin would be more efficient in large-scale operations, the elution control in the small scale used in this study became unsatisfactory toward the end of the fraction collection. Therefore, the batch method was explored.

4.2.2. Batch method

The batch treatment method of the anion-exchange resin was explored as follows: in a stirred reactor, 20 g bio-oil and 50 g methanol were charged and stirred for about 10 min to obtain a uniform solution. The pH value reached at 3.61. The anion-exchange resin, pre-washed with 0.1N NaOH solution and then with distilled water until pH 7, was added in small amounts to the bio-oil/methanol solution while stirring continuously until the solution reaches pH 6.98, in the first experiment. Approximately, 137 g of anion-exchange resin was needed. Then, the anion- exchange resin was collected by filtration and washed several times with a small amount of methanol to recover the resin in the form of organic acid salts. The bio-oil/methanol solution and washings were combined and evaporated on a rotary evaporator to recover the bio-oil.

Also, the expended anion-exchange resin was treated with 100 mL 0.1N NaOH solution by stirring at room temperature for two hours, followed by filtration, evaporation of the filtrate to obtain the organic acid sodium salts. The salts were acidified to pH 2.2 in 20 mL of methanol using 8% sulfuric acid solution and the solution dried over anhydrous sodium sulfate and excess of sulfuric acid was treated with sodium bicarbonate. The organic acid solution in methanol was analyzed on GC/MS (Appendix B 26-36) to estimate the acetic and formic acids content.

The recovered anion-exchange resin was used two more times in the same sequence of experiments to see if any column efficiency reduction occurs in repeated use. The analysis data are shown in Repetition II and III in Table 4.2 and Appendix B18-36. Graphic GC presentation of acetic acid determinations are also shown in Figure 4.5. Data in Table 4.2 and Figure 4.6 indicate that:

(1) In Repetition I with target pH 6.98, the recovered bio-oil has an acetic acid concentration of 0.2%, indicating that 20 grams of bio-oil need about 137 g of anion exchange resin to adequately capture most of the organic acids. The amount of acetic and formic acids recovered from the anion-exchange resin amounted to 8.9% and 1.3%,

respectively, of bio-oil used and the value appears to be reasonable although somewhat lower than the acetic and formic acids content in raw bio-oil of 10.95% and 3.03%.

(2) In Repetition II, the target pH was only 5.12 after adding all regenerated anion-exchange resin from Repetition I experiment to the same amount of bio-oil. This result indicates that the anion-exchange capacity of the resin has deteriorated as a result of the first run. A higher acetic and formic acids value in the recovered bio-oil and slightly lower acetic and formic acids recovery than in Repetition I were observed; and

(3) In Repetition III, the target pH was further decreased to 4.64 and the acetic and formic acids content in the recovered bio-oil were slightly lower than Repetition II. Also, a relatively high amount of acetic and formic acids were obtained from regeneration of the anion-exchange resins. This result also indicates some reduction in the anion-exchange capacity has occurred in each repetition.

Overall, anion-exchange resins appear to offer a convenient way of removing organic acids from bio-oil by carefully monitoring the pH of the eluting liquid. In this regard, however, better regeneration methods of the expended anion-exchange resin need to be developed in future to minimize the anion-exchange capacity reduction or to select more robust anion-exchange resins from supply houses. Using some organic solvents along with 0.1N sodium hydroxide solution may be useful to more completely removing organic materials from the expended anion-exchange resins. The batch procedure results could be similarly applicable to the column platform procedure for large scale operations.

Table 4. 2 Organic acid separation with anion exchange resin method.

Repetition		I	II	III
Treatment Parameters	Bio-oil (g)	20.0	20.0	20.0
	Methanol (g)	50.0	50.0	50.0
	Initial pH of solution	3.67	3.61	3.61
	Anion exchange resin (g)	137	137	137
	Target pH	6.98	5.12	4.64
Recovered bio-oil	Bio-oil recovered (g)	10.1	13.2	12.5
	Acetic acid content (%)	0.20	6.1	4.8
	Formic acid content (%)	0	0	0.03
	GC/MS analysis in Appendix B	18	19	20
Anion-exchange resin regeneration and organic acid salts obtained	0.1 N NaOH solution used (g)	100	100	150
	Amount of salts obtained (g)	2.87	2.82	2.81
	Amount of acetic acid recovered (%) in 20g bio-oil	8.9	6.7	5.1
	Amount of formic acid recovered (%) in 20g bio-oil	1.3	0.9	0.8
	GC/MS analyses in Appendix B	26	27	28

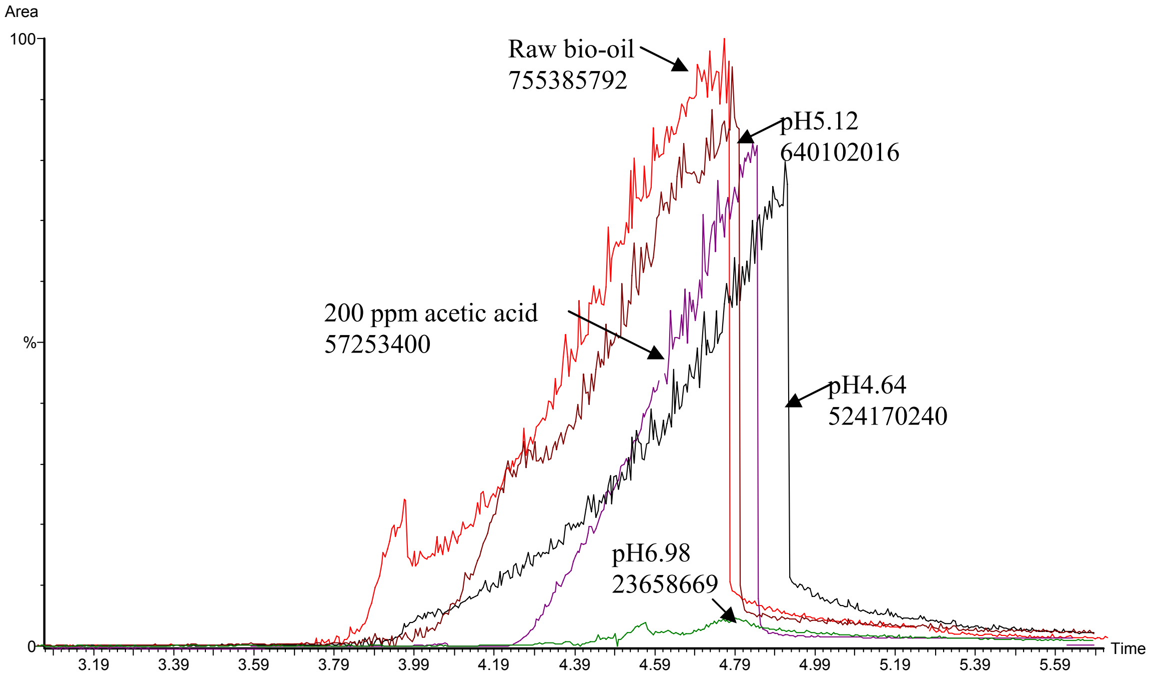


Figure 4. 5 GC/MS comparison of acetic acid peaks of recovered bio-oil at different target pH with raw bio-oil and acetic acid standard solution each.

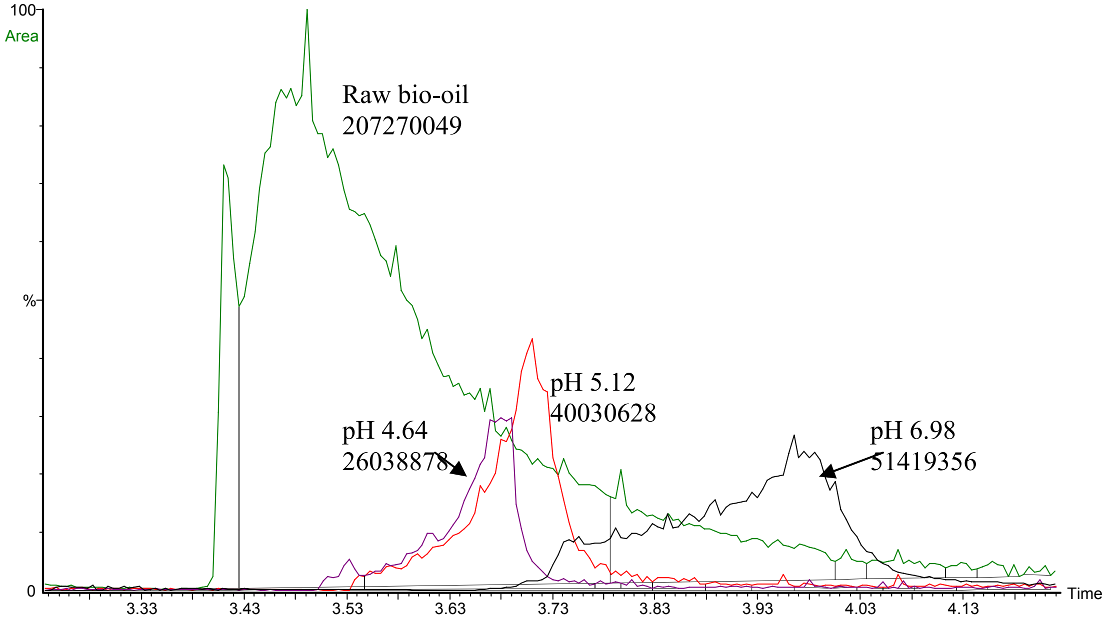


Figure 4. 6 GC/MS comparison of formic acid peaks of recovered acids at different target pH with area integration values.

4.3. Exploratory separation of pyrolytic lignin from bio-oil using water and methanol

4.3.1. Separation procedure of pyrolytic lignin fraction

It as been known that the pyrolytic lignin and neutral fraction of bio-oil are soluble in good organic solvents like ethyl acetate while the other components mostly derived from cellulose and hemi-cellulose are much more soluble in water. In one previous patent literature (Chum, H.L., 1992), the lignin and neutral fraction intended for incorporation into PF resins was obtained by taking up the bio-oil in ethyl acetate and the ethyl acetate soluble fraction taken and washed with water and subsequently with sodium bicarbonate solution to remove organic acids more completely. Finally, the ethyl acetate solution was evaporated to give the lignin/neutral fraction in 20%~25% yields depending on the source of bio-oil. A further separation of the neutral fraction was also attempted in the reported patent. The more pure lignin fraction thus obtainable will be more suitable for synthesizing PF resins since the neutral fraction will be unable to participate in the resin forming and curing reactions.

In this reported procedure, beside the desired lignin fraction, the ethyl acetate-insoluble fraction containing some ethyl acetate, sodium bicarbonate solution containing organic acid salts, and evaporated ethyl acetate solvent containing volatile bio-oil components are produced as byproducts. These byproduct materials must be processed in subsequent steps to recover ethyl acetate solvent and bio-oil components for reuse or further processing. The costs involved in these separation/recovery procedures could be significant, especially because of the relatively high cost of ethyl acetate used as solvent. Organic acids remaining in the lignin/neutral fraction could complicate the PF resin synthesis reactions due to the neutralization of sodium hydroxide added as catalyst for resin synthesis and for curing of resin in the final hot pressing step in wood composite manufacturing. The patented separation procedure would be adequate for a good removal of organic acids, but the sodium bicarbonate washing procedure could be expensive. On the other hand, it is considered that a small amount of organic acids would be tolerated in PF resin synthesis by adjusting the amount of sodium hydroxide level in the final resin.

The separation procedure of bio-oil used in this work employs water and methanol in two steps to obtain the water-insoluble components as the pyrolytic lignin fraction. This fraction may contain some neutral fraction referred in the patent literature discussed above. In a typical separation experiments, 2325g of pine wood bio-oil was separated using 2400g distilled water in the first step, and then 1000g water and 1000g methanol were used to yield 519.0g pyrolytic lignin (22.0%) as described in the Experimental Section. Since the starting bio-oil contains about 10%~15% water, the yield would amount to 25%~28% based on solid content. This yield is comparable to the yields of the reported ethyl acetate procedure. In our procedure, the water layer and methanol/water layer, which contain bio-oil components, are produced and need to be processed in subsequent steps to recover the methanol and residual bio-oil components. The materials cost in this subsequent steps appears to be lower than the ethyl acetate procedure, but the total amount of water that must be evaporated in the recovery of bio-oil components would be greater. Overall, the current procedure may provide some advantage over the ethyl acetate procedure, although details need to be explored in future.

4.3.2. Properties of the pyrolytic lignin obtained

The pyrolytic lignin fraction obtained from the water/methanol fractionation procedure contained 1%~2% methanol and was relatively fluid with the viscosity in the range of 10P~15P. The bio-oil odor was still apparent but less severe than the starting bio-oil. Filtration of the methanol solution during the procedure allowed elimination of most char particles. ^{13}C NMR spectroscopic analysis results of the pyrolytic lignin fraction and original bio-oil in Figure 33a and 33b, respectively, show the various carbon groups of bio-oils spanning the entire spectral region: aliphatic carbon region (0~50 ppm), aliphatic hydroxyl-carbon region (50~80 ppm); aliphatic dihydroxy-carbon region (81~106 ppm); olefin/aromatic carbon region (107~160 ppm); carboxylic acid carbon region (161~190 ppm); and keto/aldehydic carbon region (191~220ppm). The integral and percentage values of the carbon group regions of raw bio-oil and isolated pyrolytic lignin are reported in Table 4.3 nad Figure 4.7- 4.10. The NMR data clearly show that much of hydroxyl- and dihydroxyl-carbons of bio-oil are eliminated in the current isolation procedure of the pyrolytic lignin fraction.

Table 4. 3 ^{13}C NMR chemical shift ranges and range integral values of MSU bio-oil and isolated pyrolytic lignin.

Chemical shift range	0-49 ppm	50-80 ppm	81-106 Ppm	107-160 ppm	161-190 ppm	191-220 ppm	Total
Bio-oil	45.96	44.58	20.38	82.62	12.89	7.29	213.72
(%)	21.50	20.86	9.54	38.66	6.03	3.41	100.00
P. Lignin	120.58	18.64	2.00	300.44	7.82	10.00	459.48
(%)	26.24	4.06	0.43	65.39	1.70	2.18	100.00

Table 4. 4 Formaldehyde reactivity with lignin.

Time, h	0.5	1	2	3
0.1N NaOH, ml	26.1	16.8	14.9	13.6
Remaining CH_2O, %	2.61	1.68	1.49	1.36

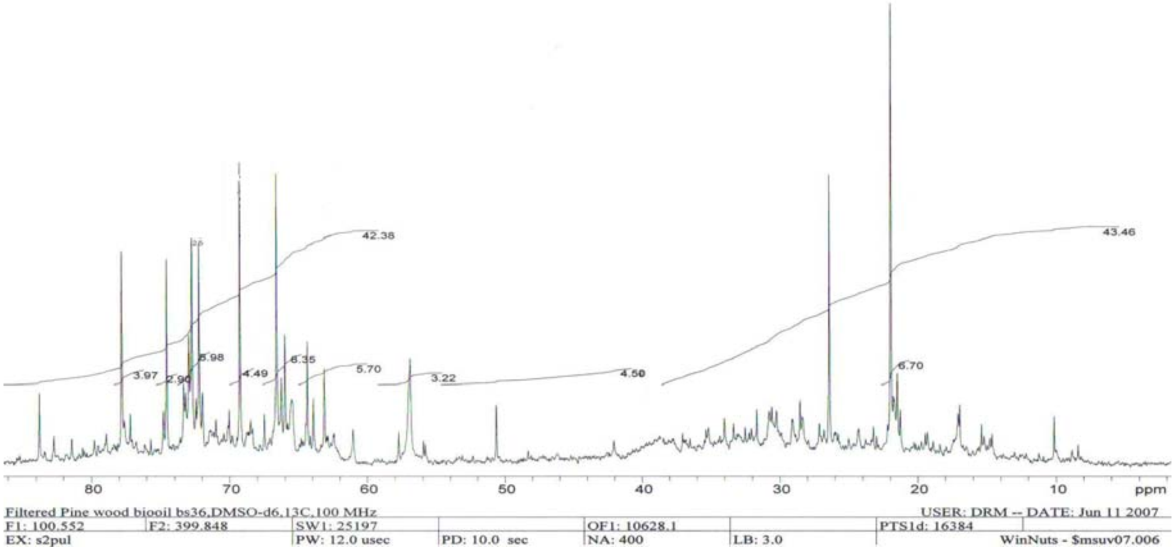


Figure 4. 7 ^{13}C NMR spectra of MSU pine wood bio-oil from 0 ppm to 86 ppm with integration values indicated. Organic solvent peak at 40 ppm was removed.

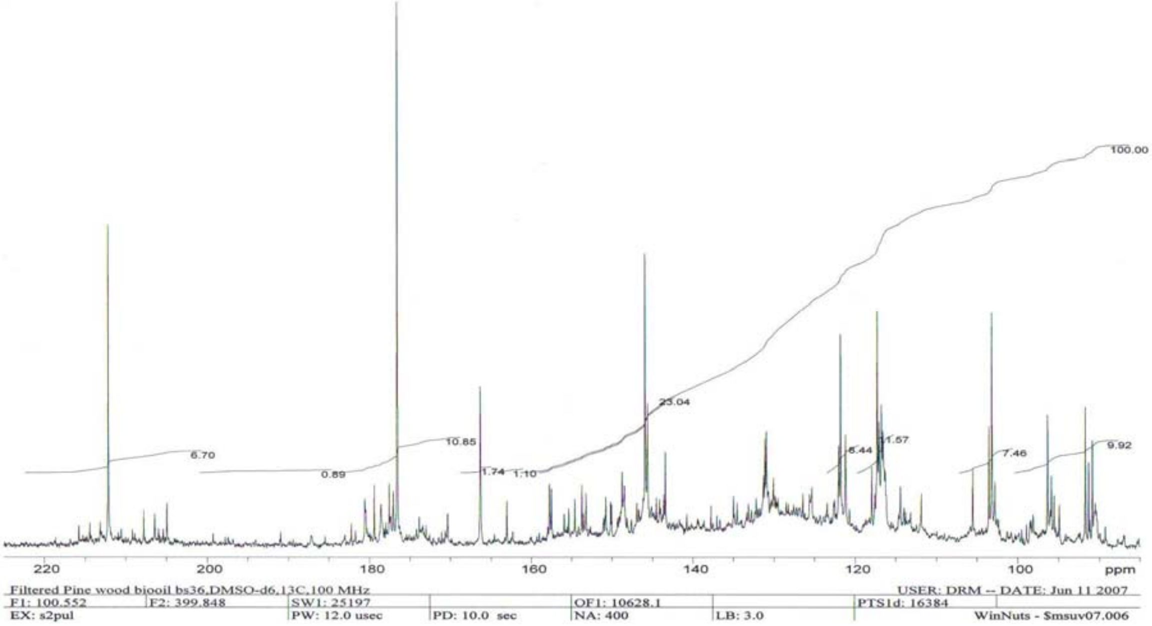


Figure 4. 8 ^{13}C NMR spectra of MSU pine wood bio-oil from 85 ppm to 220ppm with the integration values indicated.

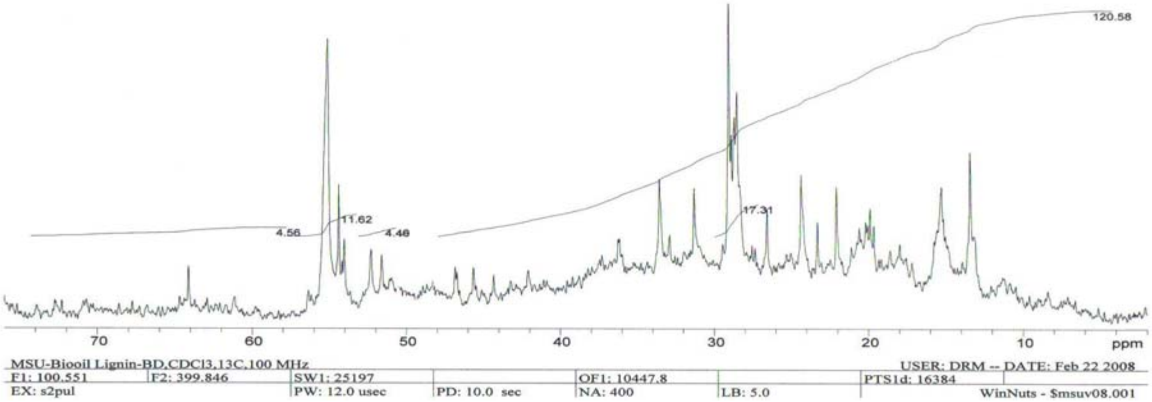


Figure 4. 9 ^{13}C NMR spectra of pyrolytic lignin of MSU pine wood bio-oil from 0 ppm to 76 ppm with integrated values indicated. Organic solvent peak at 50 ppm was removed.

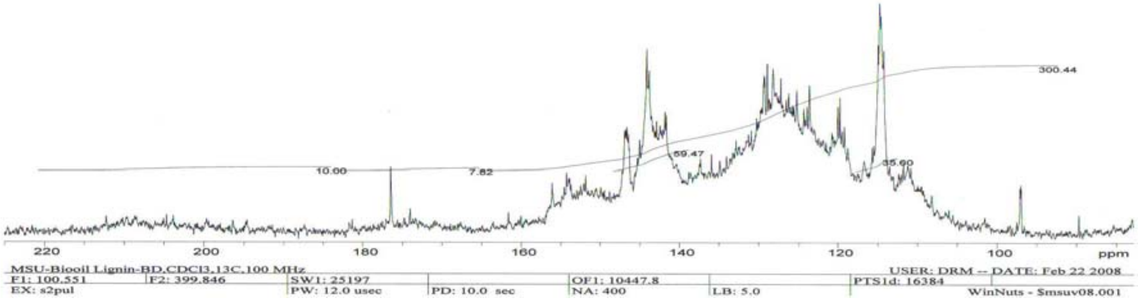


Figure 4. 10 ^{13}C NMR spectra of pyrolytic lignin of MSU pine wood bio-oil from 80 ppm to 220 ppm with integration values indicated.

Hydroxyl- and dihydroxyl-carbons in bio-oil are mostly derived from cellulose and hemi-cellulose components and they are relatively low in molecular weight and soluble in water and therefore were removed in the water/methanol separation procedure. The current separation procedure has also removed much of the carboxylic acid carbons in the 161-190 ppm region, indicating that the separation procedure has removed much of organic acids. The aliphatic mono- and di-hydroxyl as well as the carboxylic acid carbon components commonly do not have the chemical functional groups that can positively participate in the resin-forming and curing processes of PF resins and therefore undesirable. Thus, the NMR data adequately showed that the water/methanol separation procedure of bio-oil has eliminated much of the undesirable components and the aromatic carbon components were concentrated in the pyrolytic fraction.

The formaldehyde reactivity test results of the pyrolytic lignin in Table 4.4 indicated that about 0.80 mole of formaldehyde has reacted with 100 grams of pyrolytic lignin. The formaldehyde reactivity value is slightly lower than values observed for lignin obtained from wood pulping processes (Sellers T., 1994), but still indicates the potential for positive contribution of the pyrolytic lignin when incorporated in PF resins. Overall, the isolated pyrolytic lignin is a dark brown liquid with some bio-oil odor and the viscosity is in the range of 1100 cP to allow a convenient handling in uses as resin raw materials. The small amounts of methanol and water remained in the lignin fraction would have no negative effect on resin manufacturing or curing of resins in board manufacturing.

4. 4. OSB core-layer binder resins made from phenol and pyrolytic lignin

4.4.1. Resin synthesis procedures

The resin synthesis experiments with the incorporation of pyrolytic lignin went smoothly as with the control PF resin. There was no excessive foaming and no difficulty in stirring during the entire procedure. The viscosity measurement, however, had to be done with Brookfield viscometer rather than Gardener-Holdt viscometer due to dark color for lignin incorporated resins. Therefore, it appears that incorporation of the pyrolytic lignin in PF resins can be done in large scales without any handling problem.

4.4.2. Physical properties and DMA curing test results of synthesized resins

Test results of physical properties and DMA curing are reported in Table 4.5. The resin solids level and alkalinity were carefully adjusted in the resin synthesis procedure and the adjustments were reflected in the test results. The viscosity values of all synthesized resins are in the similar and spray-able range for common spinning-disc type sprayers. The uniform physical test results of resin solids levels, sodium hydroxide contents, viscosity, etc., assured that the wood composite bonding experiments would display the effects of the lignin addition effect rather than from differences in alkalinity or extent of polymerization. Furthermore, the physical property values are very close to current commercial core-layer binder PF resins (Seller T., 1994), so that evaluation of the resins by manufacturing laboratory

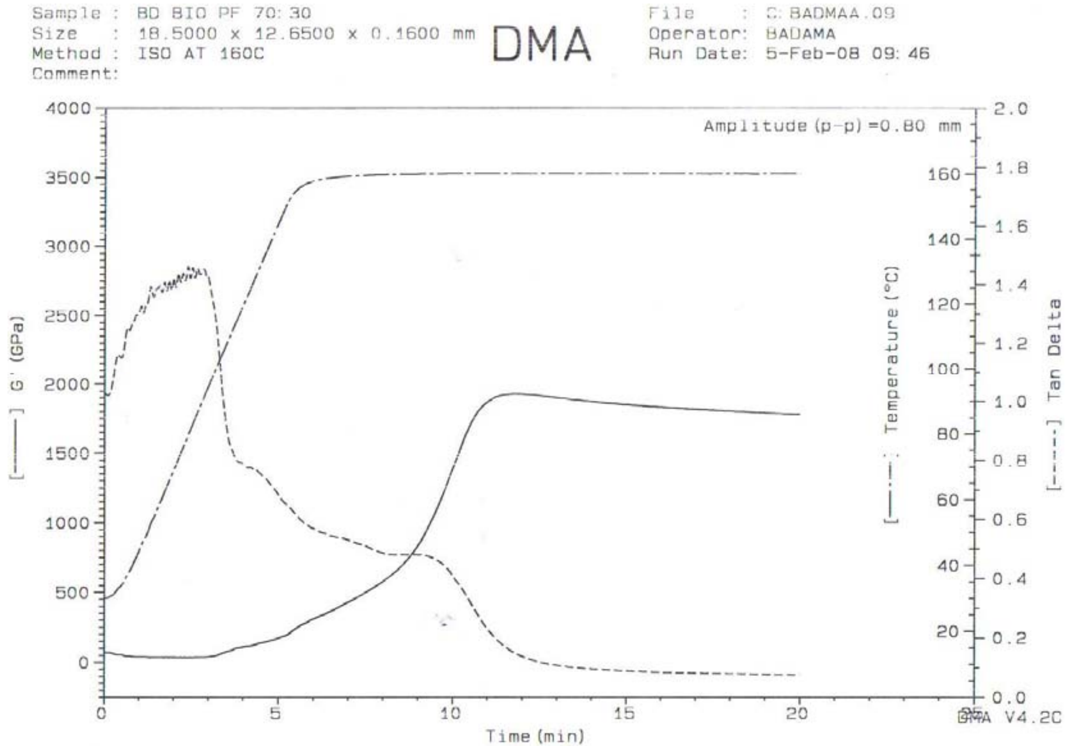


Figure 4. 11 DMA of 70/30 PF-Lignin resin at 160°C isotherm for 15 min.

oriented strand board can be carried out using the commonly used press temperature and press time parameters. The hot-pressing temperature and time parameters in OSB manufacturing determine the productivity of the plant.

The DMA cure rate and cured strength values reported in Table 4.5 reflect the differences among synthesized resins arising from the incorporation of lignin. One typical DMA result is shown in Figure 4.11 for the 70P:30L resin with the final curing temperature of 160°C. In this DMA run, the rigidity of sample stayed near zero until about 3 min (105°C) and it then started to increase but remained at low values until about 5 min (160°C). The rigidity of sample then increased somewhat rapidly reaching to about 800 GPa at 9.5 min and then very rapidly reaching to a final value of about 2000 GPa at

11.5 min. The rigidity of sample changed only very slightly during the next 18 min of isothermal run, indicating that the cured resin sample was very stable at the curing temperature. This curing profile agrees well with that of the control PF resin as well as with data of earlier reports (Lee S. M., 2007). The synthesized resins, however, showed different curing times and final rigidity values as shown in Table 4.5and Figure 4.12. Thus, it is seen that the curing rate of resins becomes slower and cured resin rigidity becomes lower as the lignin content increased, both effects rather significantly.

Furthermore, the free formaldehyde content for all resins are very small, indicating that the amounts of formaldehyde used in resin syntheses were not in excess and no formaldehyde odor problem will result in using the resins in manufacturing of boards.

Table 4. 5 Physical property and DMA curing test results of synthesized resins.

	Control	Pyrolytic Lignin PF Resins		
Properties	PF resin	70P:30L	60P:40L	50P:50L
Resin solids content (%)	49.63	49.60	49.68	47.36
Alkalinity (%)	4.76	4.76	4.76	4.76
Viscosity (cP)	310	330	450	230
pH	11.94	11.74	11.85	11.80
DMA cure rate at 140°C (min)	14.0	13.5	12..0	10.8
DMA cure rate at 160°C (min)	10.4	11.00	9.6	9.7
DMA cured strength at 140°C (GPa)	2880	1500	1450	1450
DMA cured strength at 160°C (GPa)	2500	1950	1450	1470
Free formaldehyde content (%)	0.0	0.0	0.0	0.0

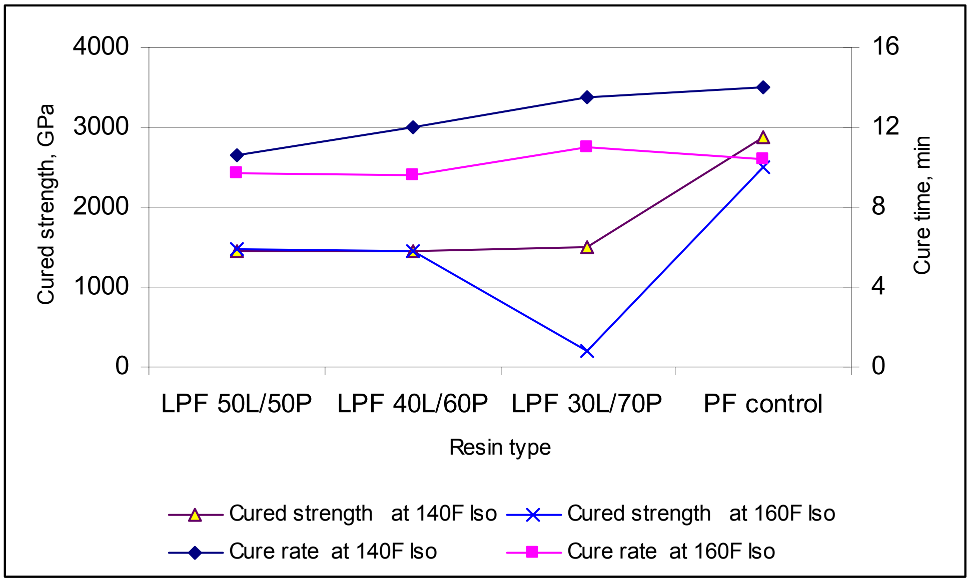


Figure 4. 12 Curing rates and cured resin strengths of synthesized resins from DMA.

4.5. Manufacturing of strand board with synthesized resins

4.5.1. Strand board mat preparation procedures

The four synthesized resins were used only as core-layer binders with a commercial PF resin (Georgia-Pacific RPPB 205C02) used as the face-layer binder for all boards. All synthesized resins behaved well during the laboratory strand board manufacturing procedures. Especially, the spraying procedure of resins on wood strands in a tumbling blender using the spinning-disc sprayer went smoothly without much build-up of resin in the sprayer or inside the blender drum. This indicates that the resins containing the pyrolytic lignin fraction would give no particular rheological problem in general handling and spraying operations such as that can arise from resin having thixotropic characteristics.

One negative characteristic observed in the process was the bio-oil odor of resins that contain pyolytic lignin, but it was mild in general. The resin droplets on wood strands were very uniform on visual inspection and the resin-loaded strands for all resins were dry to the touch at the time of mat preparation as is commonly observed with industrial PF resins used in the OSB manufacturing plants. In this work, the resin-applied wood strands were not oriented in mat formation compared to industry processes where they are oriented to the long direction of board. This orientation results in better stiffness for board, but little effect on internal bond strength. Since internal bond strength values are the key to evaluation of bonding performance of different resins, the random orientation used in this work would serve the purpose well.

4.5.2. Hot-pressing of strand board mats

The press temperature used (420°F) was chosen to be near the highest temperature used in the current OSB industry and also the press times used (3.0 min and 3.5 min) were the minimum and maximum values used in the same industry. These hot-pressing parameters were chosen to see the effects of lignin incorporation on board performances within the current application regime. The hot pressing of boards went relatively well according to the hot-pressing schedule program commonly used in this laboratory shown in the Appendix C, Figure 9-12. However, a few boards shown to experience somewhat high internal gas pressures and four boards out of the sixteen boards showed partial de-lamination. These delaminated boards were equally tested as shown in Appendix C but excluded in the calculation of average values or shown as "de-lamination" for comparative purposes. This type of delamination commonly arises from factors other than resin curing performances.

4.6. Physical performance test results of prepared strand boards

4.6.1. Density of manufactured strand boards

Physical performance test results of prepared strand boards are reported in Tables 4, 5, and 6 and in Appendix C. The average density values of IB test specimens of all prepared strand boards were in a very narrow range of 0.77 to 0.82 g/cm^3 (48~52 pcf) to indicate that the resultant IB values could be compared with each other without the common density dependence consideration. The average density values of IB specimens came out to be somewhat higher than the targeted density value of 42.0 pcf, occurred as the result of shrinkage of board thickness. Overall, however, the comparison of the effects of lignin incorporation in resins on board performances appears to be unaffected by the slightly higher average board density values.

4.6.2. Internal bond (IB) strength test results of dry and 2-h boiled strand boards

As shown in Table 4.6 and Figure 4.13, the 30%-lignin replaced resin showed comparable performance values with the control PF resin in dry and 2-h boil IB strength values, while the 40%- and 50%-lignin replaced resins showed gradually decreased dry and 2-h boil IB strength values. The decreasing trend of IB values with higher lignin contents was also reflected in the 2-h boil samples' thickness swell values. This result indicates that lignin replacement of 40% is at borderline and higher replacements will decrease the dry IB as well as lower durability of strand board.

On the other hand, the hot-pressing time of 3.0 and 3.5 min showed no difference in IB strength values, indicating lignin replacement up to 40% will have little effect on the production rate of strand board. Thus, resins made with 30%-lignin replacement can be concluded to be as effective as current PF resins in bonding the core-layers of strand board and 40%-lignin replacement can be made to be comparable with some adjustment of resin synthesis parameters. A further research on the fractionation of bio-oil and/or resin formulation may lead to resins effective as PF resins with lignin replacements at 40% or slightly.

Table 4. 6 Dry and 2h-boil internal bond strength and 2h-boil thickness

Resin	Press time	Density		Dry IB		2-h Boil IB		2-h Boil	
	Min	g/cm^3	pcf	Psi	kPa	psi	kPa	TS (%)	RS (%)
PF Control	3.5	0.7868	49.1	83.8	578	39.84	275	27.26	45.75
	3.0	0.8279	51.7	102.6	707	41.63	287	31.84	40.57
LPF 70P/30L	3.5	0.8194	51.2	98.9	682	47.72	329	31.84	46.04
	3.0	0.8026	50.1	84.4	582	40.91	282	33.83	52.29
LPF 60P/40L	3.5	0.8082	50.5	82.7	570	31.41	217	38.71	38.00
	3.0	0.8141	50.8	95.3	657	32.69	225	39.59	38.07
LPF 50P/50L	3.5	0.8005	50.0	73.9	510	24.36	168	44.23	34.03
	3.0	0.8066	50.4	66.5	459	5.94	41	41.20	9.25

TS-thickness swelling; RS- residual strength; P-phenol; L-pyrolytic lignin.

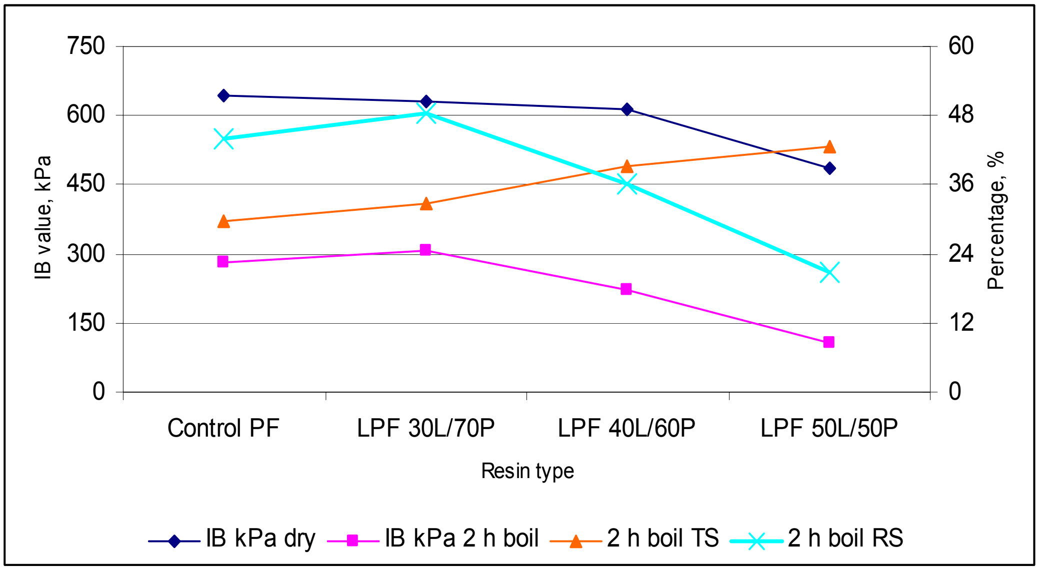


Figure 4. 13 IB, thickness swell and residual strength of the laboratory strand boards.

4.6.3. Thickness swelling (TS) and water absorption (WA) values in water soak tests

Test results in Table 4.7 and Figure 4.14 show 2-h and 24-h TS and WA values of all three lignin replaced resins are comparable with the TS and WA values of the control PF resin. This result indicates that the poor core-layer bonding obtained for the 50%-lignin replaced resin has little effect in the 2-h and 24h water soak tests. Furthermore, the lignin in the core-layer resins, overall, has little adverse effect in the water soak tests in comparison with the control PF resins. The fact that the pyrolytic lignin did not show any more tendency of absorbing water than PF resins would be an advantage over the commonly available lignosulfonate that showed the tendency of somewhat increased water absorption when used as partial replacements of phenol in PF resins (Seller.T., Jr., 1994).

Table 4. 7 2-h and 24-h water soak test results of laboratory strand boards.

Resin	Press time (min)	2-h Water Soak		24-h Water Soak	
		TS (%)	WA (%)	TS (%)	WA (%)
PF Control	3.5 3.0	3.79 3.81	7.85 8.61	8.32 8.60	35.84 38.25
LPF 70P/30L	3.5 3.0	4.26 3.25	7.47 7.44	7.96 8.68	33.96 34.48
LPF 60P/40L	3.5 3.0	2.95 2.52	7.36 7.73	7.22 8.92	36.37 37.90
LPF 50P/50L	3.5 3.0	2.84 3.19	6.86 7.57	7.79 8.93	34.07 40.96

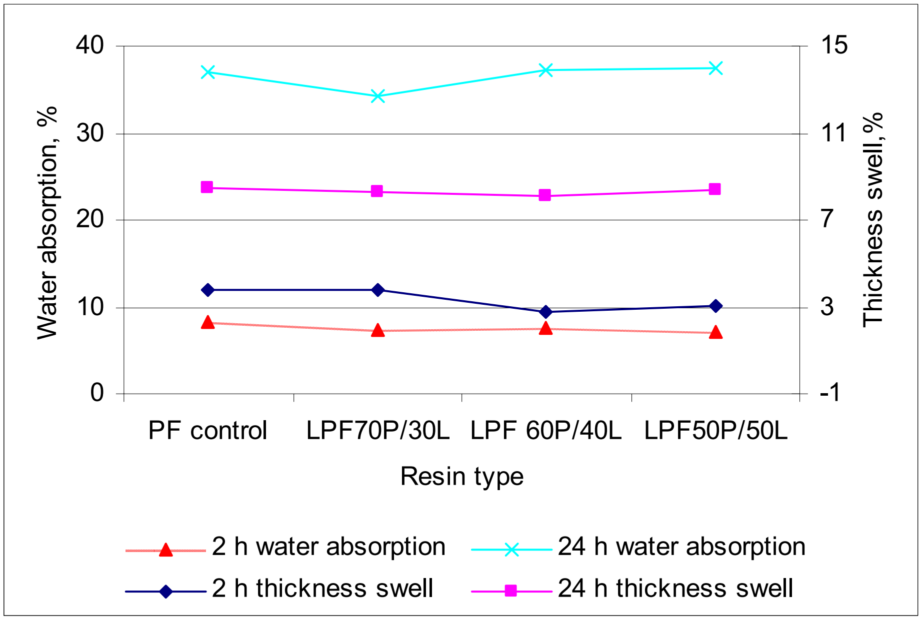


Figure 4. 14 2-h and 24-h water absorption and thickness swell of laboratory strand boards.

4.6.4. Modulus of rupture (MOR) and modulus of elasticity (MOE) values

MOR and MOE values in Table 4.8 and Figure 4.15 indicate that the 30%- and 40%-lignin replaced resins are comparable to the control PF resin in bending strength, but the 50%-lignin replaced resin show significantly decreased values. Although the bending strength of boards depend greatly on the bonding performance of the face-layer binder resins, the 50%-lignin replaced resin's poor bonding in the core layer was reflected to give poor MOR and MOE values. On the other hand, the 30%- and 40%-lignin replaced resins can be concluded to have given enough bonding strength in the core layer to little adverse effect on the bending strength of boards.

Table 4. 8 Density and MOR and MOE values of laboratory strand boards.

	Press time	Density		MOR		MOE	
Resin	min	g/cm^3	pcf	psi	MPa	kpsi	MPa
PF	3.5	0.7782	48.60	3375	23.27	580	3999
Control	3.0	0.8127	50.75	5248	36.18	798	5502
LPF	3.5	0.7751	48.39	4003	27.60	815	5619
70P/30L	3.0	0.7885	49.22	4067	28.04	802	5530
LPF	3.5	0.8052	50.28	4410	30.41	855	5895
60P/40L	3.0	0.7979	49.82	4413	30.43	659	4544
LPF	3.5	0.7585	47.36	3578	24.67	515	3551
50P/50L	3.0	0.7630	47.64	3614	24.92	593	4089

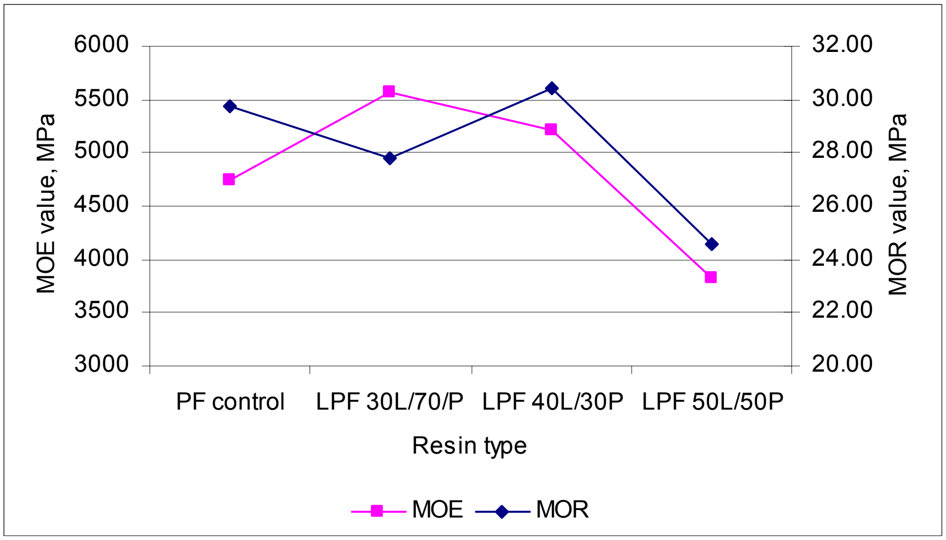


Figure 4. 15. MOR and MOE values of strand boards bonded with synthesized resins.

Overall, the performance test results of prepared strand boards indicate that resins made with 30% lignin replacement will bond strand board core-layer as good as PF resins in all testing criteria. Resins with 40% lignin replacement would give slightly lower dry and 2-h boil IB strength value while the water absorption and bending strength values would be equal to PF resins. Resins made 50% lignin replacement will not give the adequate internal bonding strength in the core-layer and this can also result in unacceptable bending strength values of strand boards.

CHAPTER V

CONCLUSION

The calcium oxide method of separating organic acids from bio-oil carried out to form organic acid calcium salts until pH 7 and pH 8, followed by filtration of the salt precipitates resulted in a recovered bio-oil having acetic acid content of 1.9% and 2.4%, respectively, in comparison to 10.92% acetic acid in raw bio-oil. The formic acid content of the recovered bio-oil was similarly reduced to 0.19% and 0.27%, respectively, from 3.03% of raw bio-oil. These residual acid values may or may not be low enough for metal corrosion prevention. On the other hand, the acetic acid value obtained from separated calcium salts was 0.21% and 0.64%, respectively, and the formic acid value was 0.19%-0.27%, respectively. These acid values were lower than expected values and it appeared to be from losses in the isolation and measurement procedures due to handling small samples in open air and from using sodium bicarbonate to capture the residual free sulfuric acid to prevent GC column deteriorations.

The calcium oxide method of organic acid separation carried out until pH 9 and 10 resulted in forming salt precipitates that also contained high amounts of phenolic compounds and, therefore, was concluded to be not suited for acid separation. The acetic and formic acid values in recovered bio-oil were 0.46%-0.6% and 0.02%-0.02%, respectively, and the acetic and formic acid values obtained from salt precipitates were

2.01% and 1.51%; and 0.64% and 0.66%, respectively. Research would be needed in future for distillation or other methods to isolate pure acetic/formic acids from the salt precipitates to evaluate more fully the usefulness of this separation approach as a value addition proposition to the overall bio-oil manufacturing process. Also, the minimum acid value of bio-oil for causing corrosiveness to metals needs to be determined to help fine-tune this acid separation method.

Furthermore, the ash contents of the recovered bio-oil at target pH of 7 and 8 were relatively high at 3.6% and 5.45%, high for any liquid fuel. Further research would be needed to investigate the calcium oxide procedure regarding the amount of methanol diluent and use of various coagulants to effectively cause precipitation of calcium salts and also use of tighter filtration media to filtrate finer precipitate particles more effectively. Overall, the experimental results of the calcium oxide methods up to pH 8 or slightly higher would be useful in future scale-up research.

The anion-exchange resin method carried out for separation of organic acids from bio-oil using the batch procedure until pH 6.98 resulted in a recovered bio-oil having insignificant amounts of acids, 0.2% acetic acid and 0% formic acid. For this result, 137 g of anion-exchange resin was found needed for treatment of 20 g of bio-oil. The procedure repeteated two more times using the spent anion-exchange resin see changes in the anion-exchange capacity of the resin indicated slightly reduced effectiveness of acid removal. The recovered acetic acid levels from the expended anion-exchange resins in repetition I, II, and III were 8.9%, 6.7% and 5.1%, respectively, and the formic acid value were 1.9%, 0.9%, and 0.8%, respectively. Research on separation and purification of organic acids from the recovered organic acid mixture as well as regeneration of the expended anion-exchange resin would be needed in future. Overall, the anion-exchange resin method can be used to remove organic acids from bio-oil that also reduces the acid contents in recovered bio-oil.

The methanol and water separation method of pyrolytic lignin of bio-oil resulted in 25%-28% yields of pyrolytic lignin fractions based on dry weight of bio-oil. The obtained lignin fraction showed only aromatic and aliphatic components in ^{13}C NMR analysis, typical of industrial lignin materials obtainable from wood pulping processes. Furthermore, the isolated lignin was successfully incorporated into PF resins at 30%, 40% and 50% phenol substitution levels. The resin synthesis procedures went werr without any problem in comparison to the common procedure.

The test results of the synthesized lignin-phenol-formaldehyde (LPF) resins as OSB core-layer binders indicated that physical properties of OSB panels at 30% substitution level were almost the same as those of the control PF resin made without any lignin substitution. The performance of the LPF resin at 40% substitution level was only slightly lower than the control resin but above the acceptable levels. The LPF resin made with 50% phenol replacement showed lower performance than the control PF resin and, therefore, it was concluded that the phenol in PF resins can be replaced with pyrolytic lignin up to about 40%. Overall, the water and methanol method was satisfactorily shown to be able to separate the desired pyrolytic lignin fraction from bio-oil that can be used in PF resin manufacture. This lignin separation method appeared to be of lower cost than reported methods that use expensive organic solvent such as ethyl acetate.

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APPENDIX A

GC/MS CHROMATOGRAMS OF BIO-OIL, RECOVERED BIO-OIL, AND ORGANIC ACID FRACTIONS FROM THE CALCIUM OXIDE METHOD

Table A. 1 Conversion of integrated areas of organic acid peaks into concentrations from the calcium oxide method

Sample	Acid	Integrated area (units)	Conc. (ppm)	Sample wt. (g) diluted in 10 ml	Conc. in sample		Conc. (%)	Total sample wt. (g)	Acetic acid in 50 g bio-oil	
					%	Dilution			G	%
Rac. pH7	acetic	6222438	30	0.2240	0.13	36	4.92	2.2	0.1	0.21
	formic	2327396	17		0.08		2.84		0.06	0.13
Rac. pH8	acetic	33602540	121	0.2339	0.52	7.69	3.98	7.95	0.32	0.63
	formic	5414997	28		0.12		0.95		0.075	0.15
Rac. pH9	acetic	31078336	113	0.2381	0.48	7.03	3.34	30.14	1.01	2.01
	formic	7931079	36		0.15		1.07		0.32	0.64
Rac. pH10	acetic	12014440	50	0.2357	0.21	8.52	1.79	42.09	0.74	1.51
	formic	3583856	22		0.09		0.79		0.33	0.66
Rec. bio. pH7	acetic	130828446	444	0.2300	1.9	1	1.9	49.57	0.96	1.9
	formic	10674752	45		0.19		0.19		0.09	0.19
Rec. bio. pH8	acetic	150056050	508	0.1929	2.6	1	2.6	45.32	1.19	2.4
	formic	14585268	58		0.3		0.3		0.14	0.27
Rec. bio. pH9	acetic	100762981	344	0.2478	1.4	1	1.4	16.61	0.23	0.46
	formic	2542984	18		0.07		0.07		0.01	0.02
Rec. bio.pH10	acetic	126409444	430	0.1923	2.24	1	2.24	14.11	0.32	0.6
	formic	1683513	15		0.08		0.08		0.014	0.02

(Rac.– recovered acid from calcium salts; Rec.bio.- recovered bio-oil)

Table A. 2 Conversion of integrated area of organic acids into concentration (Anion-exchange resin method).

Sample	Acids	Integrated area	C (ppm)	sample weight diluted in 10 ml	conc. in sample		C (%)	total sample weight (g)	acetic acid in 20 g bio-oil	
					%	dilution			M (g)	%
raw bio-oil	acetic	755385792	2517	0.2304			10.92			
	formic	207270049	698				3.03			
pH 6.98 recov. acid	acetic	362287712	1213	1.0169	1.19	10.73	12.8	13.87	1.78	8.9
	formic	51419356	181		0.18		1.91		0.27	1.3
PH 5.12 recov. acid	acetic	298424039	1001	1.0255	0.98	10.36	10.11	13.18	1.33	6.7
	formic	40030628	142		0.13		1.43		0.19	0.9
PH 4.64 recov. acid	acetic	193716681	653	1.0120	0.65	11.26	7.27	14.07	1.02	5.1
	formic	26038878	96		0.09		1.07		0.15	0.8
pH 6.98 rec.bio-oil	acetic	23658669	88	0.2322	0.38	1	0.38	10.12	0.04	0.2
	formic	0								0
pH 5.12 rec.bio-oil	acetic	640102016	2134	0.2300	9.2	1	9.2	13.24	0.93	6.1
	formic	0								0
pH 4.64 rec.bio-oil	acetic	524170240	1750	0.2300	7.61	1	7.61	12.54	0.95	4.8
	formic	912822	13		0.05		0.05		0.007	0.03

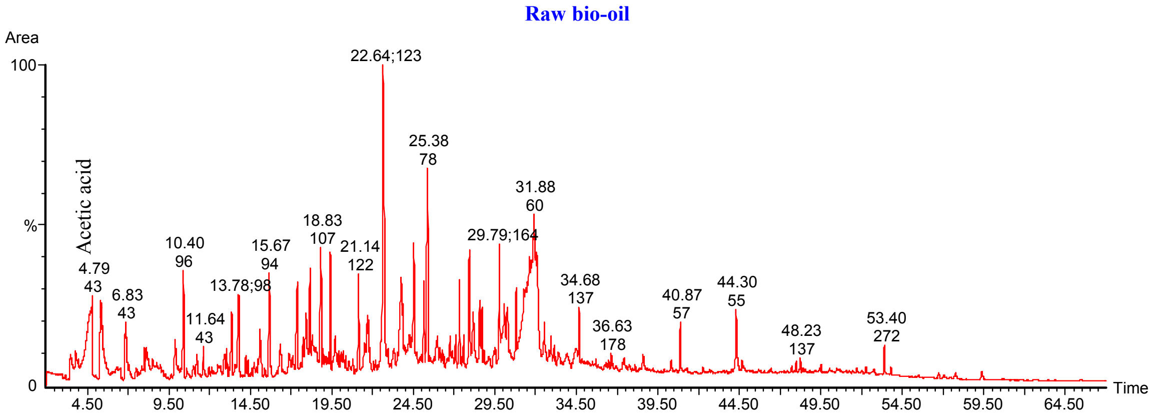


Figure A. 1 GC/MS chromatogram of MSU pine wood bio-oil. Acetic acid peak is at retention time of 4.79 min.

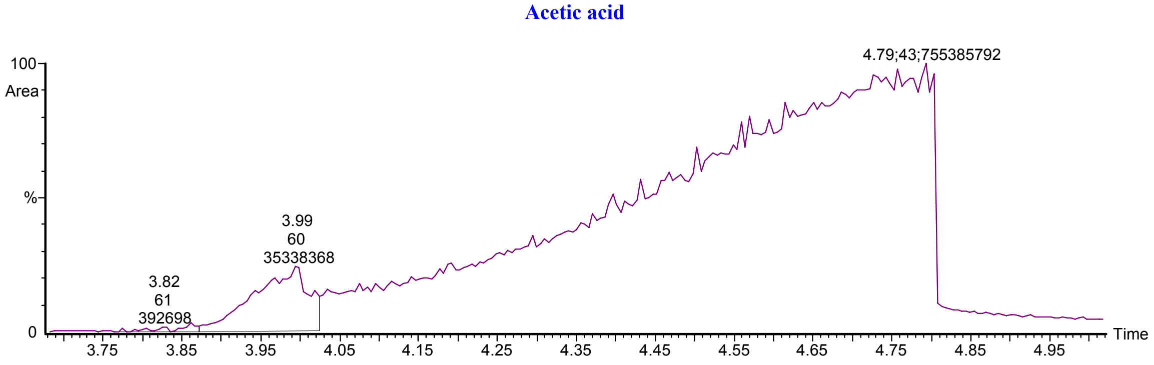


Figure A. 2 Integration of acetic acid peak of raw bio-oil at retention time of 4.79 min after expansion.

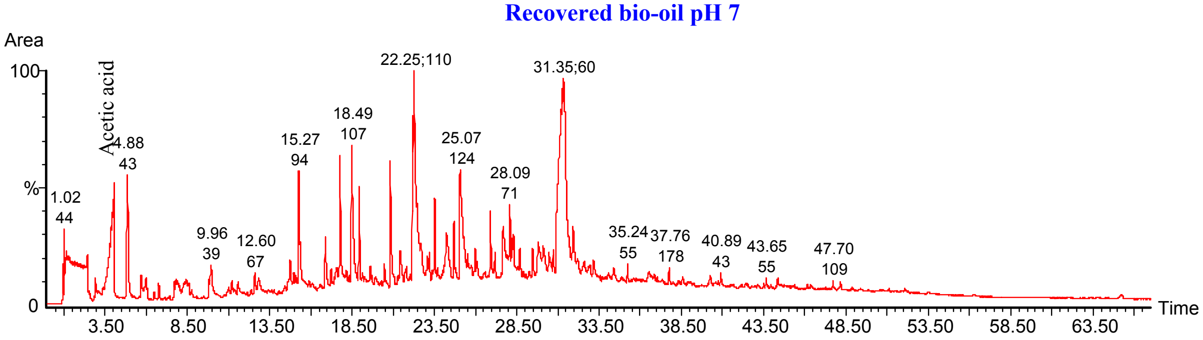


Figure A. 3 GC/MS chromatogram of recovered bio-oil from calcium oxide method at pH 7. Acetic acid is at retention time of 4.08 min.

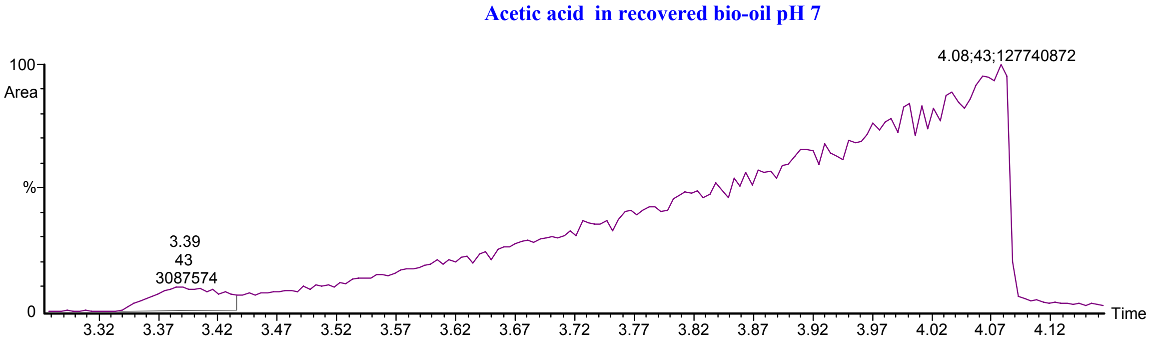


Figure A. 4 Integration of acetic acid peak of recovered bio-oil from calcium oxide method at target pH 7 after expansion.

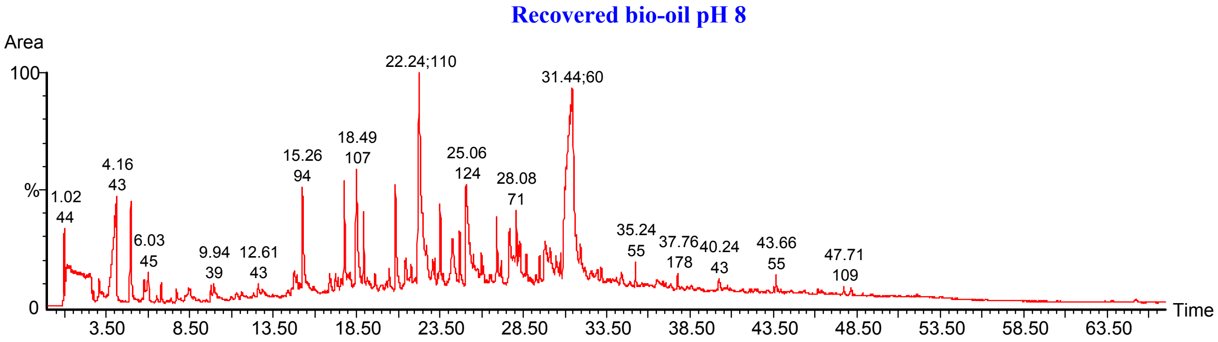


Figure A. 5 GC/MS of recovered bio-oil from calcium oxide treatment method at pH 8. Acetic acid peak retention time is 4.16.

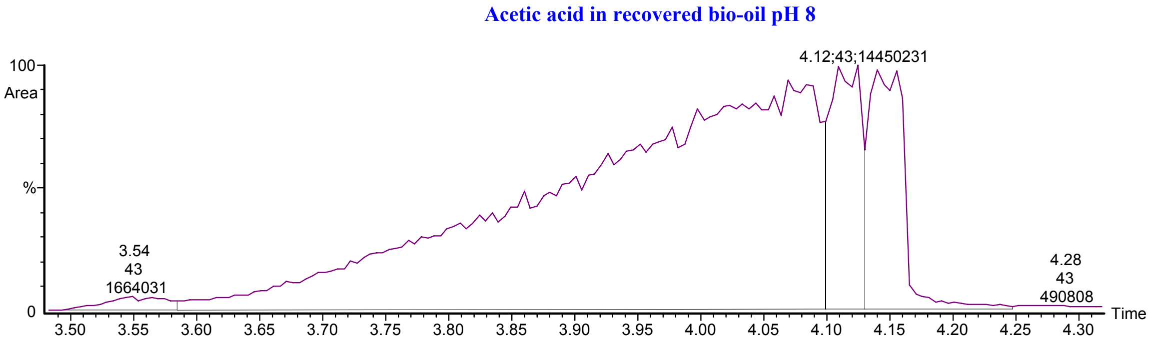


Figure A. 6 Acetic acid integrated peak of recovered bio-oil from calcium oxide treatment at pH 8.

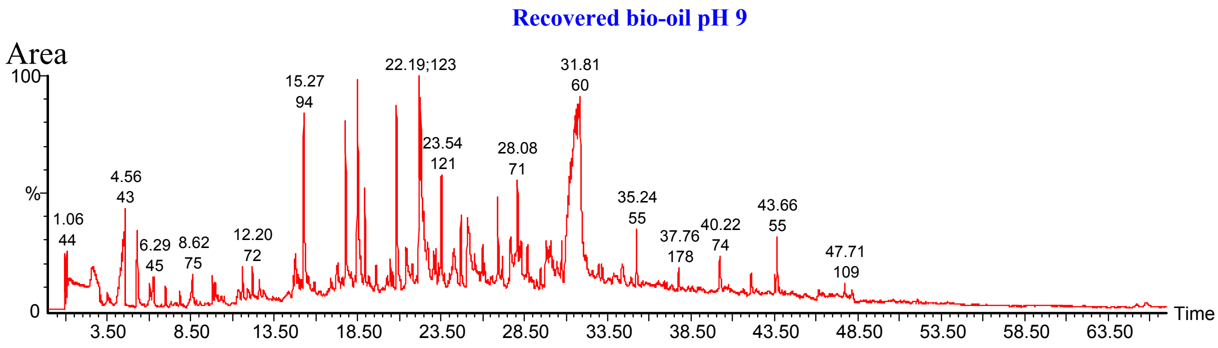


Figure A. 7 GC/MS of recovered bio-oil from calcium oxide treatment method at target pH 9. Acetic acid retention time is 4.56.

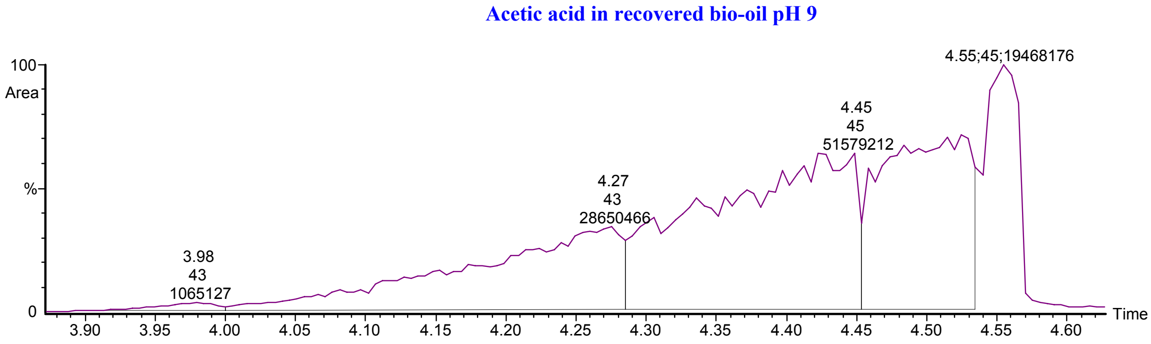


Figure A. 8 Acetic acid integrated peak of recovered bio-oil from CaO treatment method at pH 9.

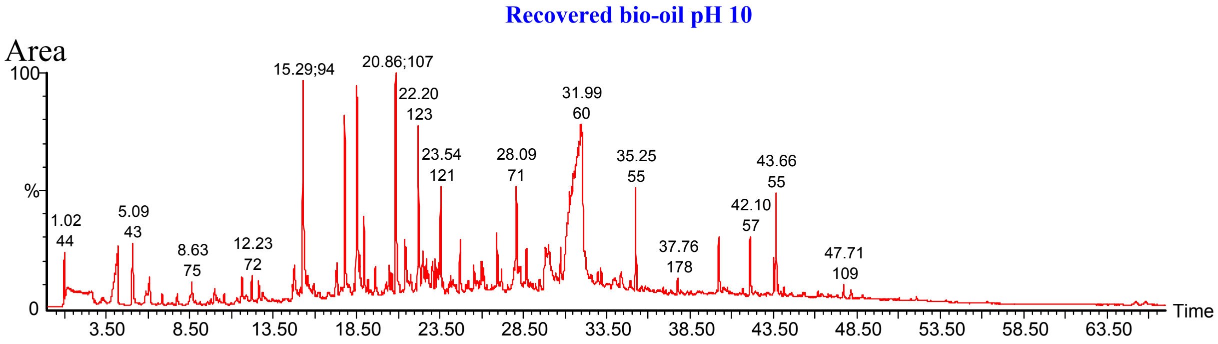


Figure A. 9 GC/MS of recovered bio-oil from CaO treatment method at target pH10. Acetic acid retention time is 4.20.

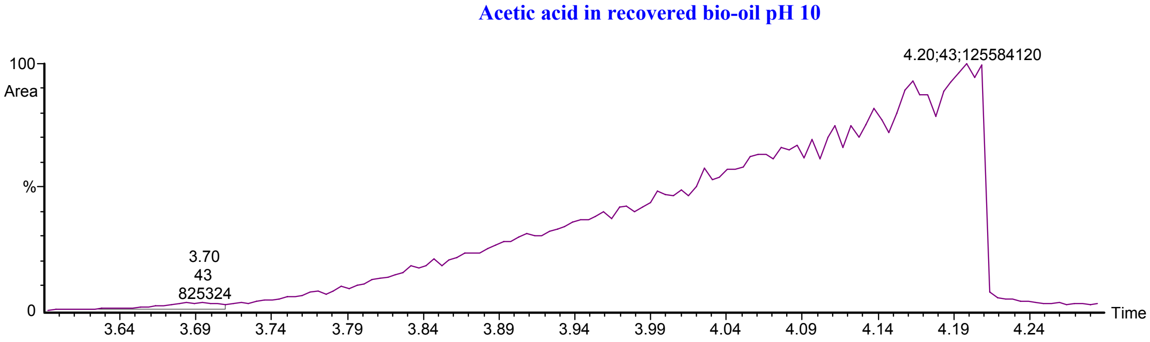


Figure A. 10 Acetic acid integrated peak of recovered bio-oil from CaO treatment method at pH 10.

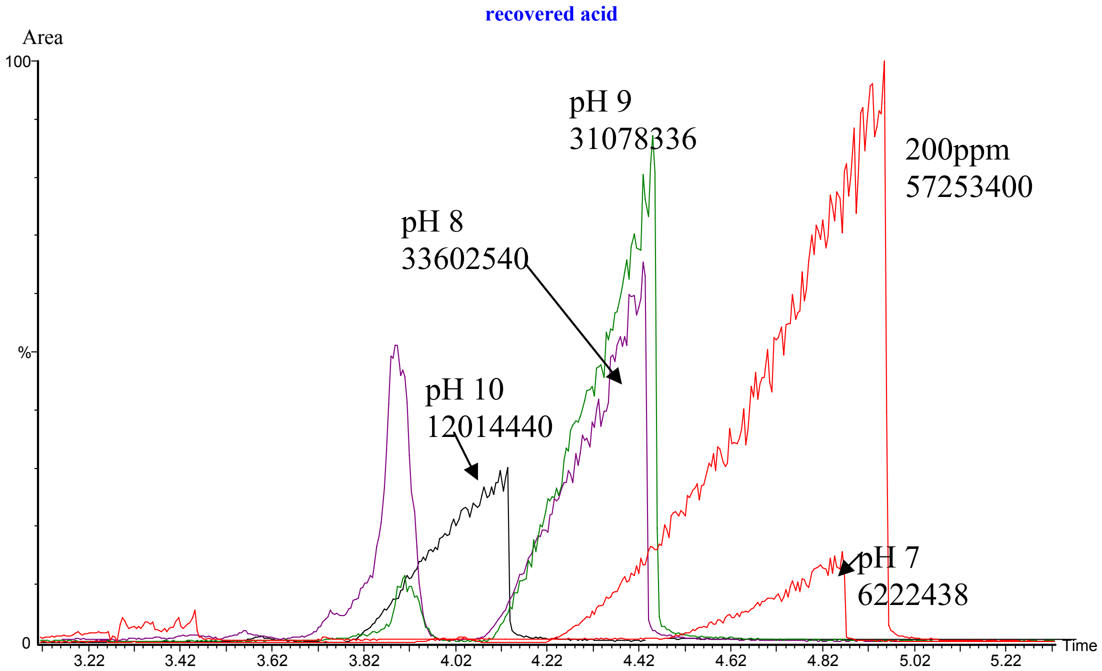


Figure A. 11 Comparison of integrated peak areas of acetic acid recovered with calcium oxide method at different target pH values compared with the acetic acid peak of 200 ppm standard solution.

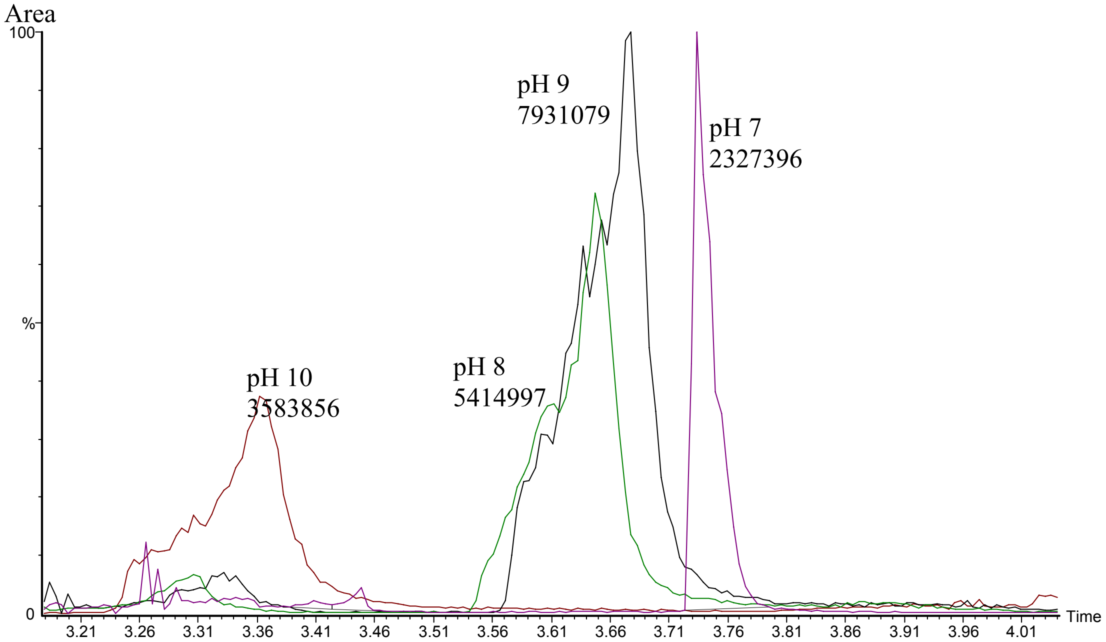


Figure A. 12 Comparison of integrated areas of formic acid recovered from calcium oxide method at different target pH values.

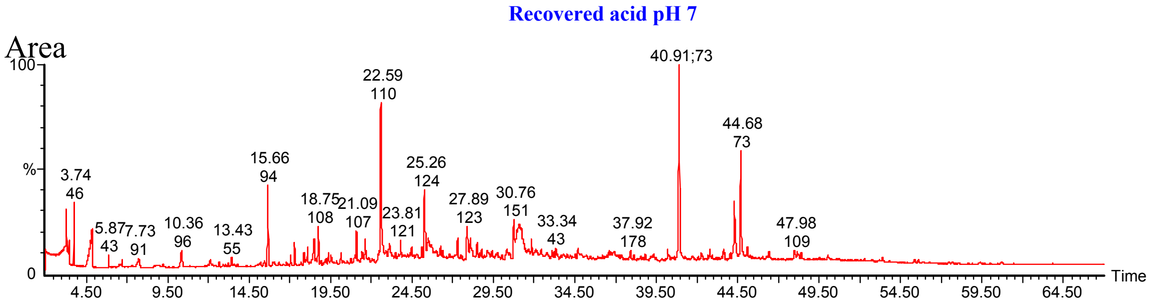


Figure A. 13 GC/MS chromatogram of recovered organic acids from calcium oxide method with target pH 7.

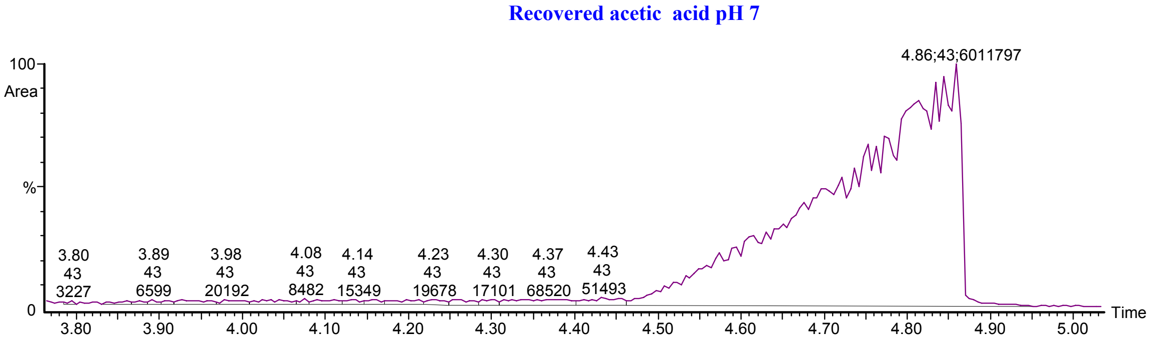


Figure A. 14 Integration of acetic acid peak from GC/MS chromatogram of recovered organic acid fraction of calcium oxide method at target pH 7.

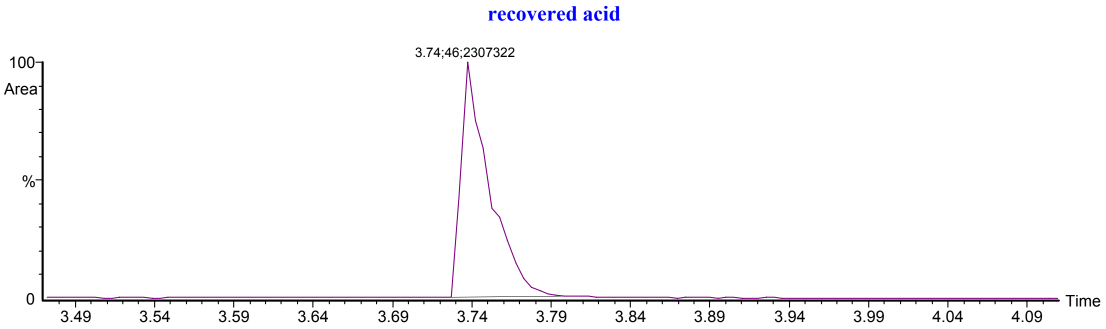


Figure A. 15 Integration of formic acid peak from GC/MS chromatogram of recovered organic acid fraction of calcium oxide method at target pH 7.

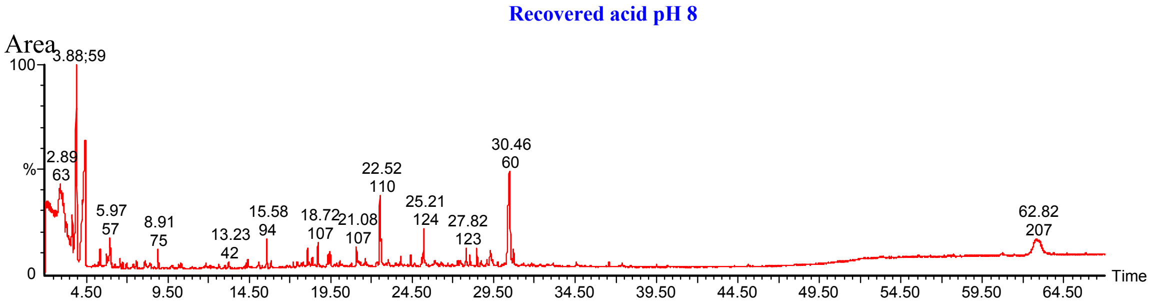


Figure A. 16 GC/MS chromatogram of recovered organic acid fraction from calcium oxide method at target pH 8.

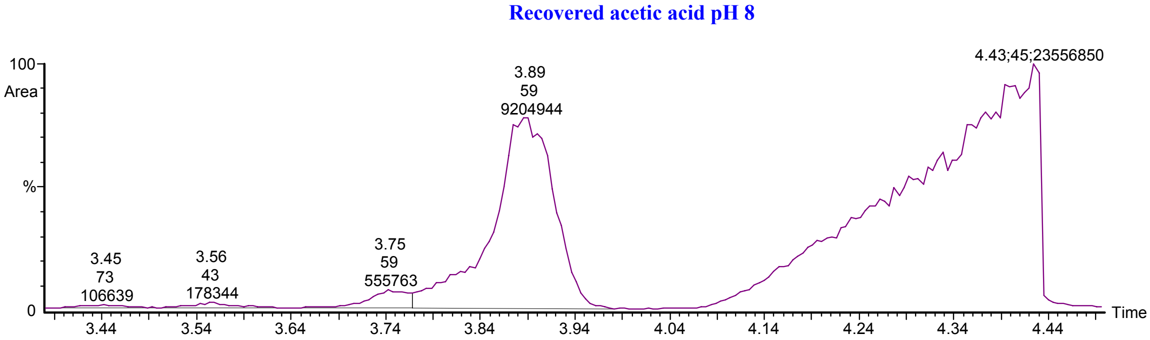


Figure A. 17 Integration of acetic acid peaks from GC/MS chromatogram of recovered organic acid fraction from calcium oxide method at target pH 8. Acetic acid came as two peaks from an unknown reason.

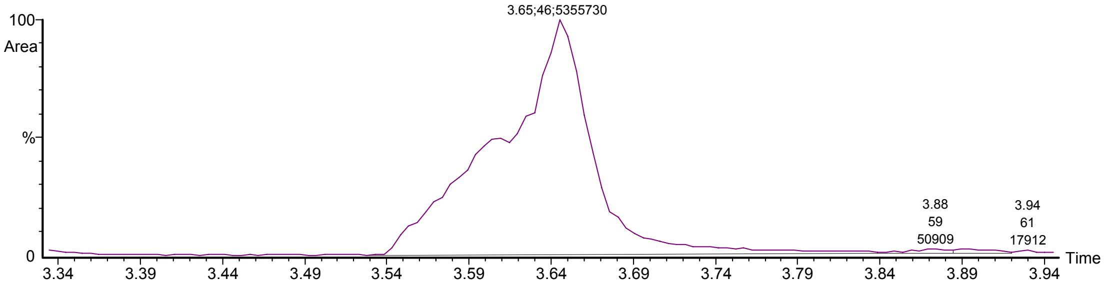


Figure A. 18 Integration of formic acid peak from GC/MS chromatogram of recovered organic acid fraction from calcium oxide method at target pH 8.

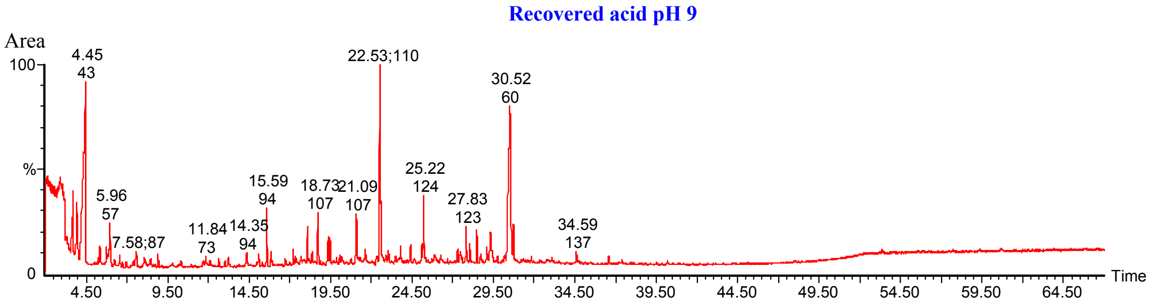


Figure A. 19 GC/MS chromatogram of recovered organic acid fraction from calcium oxide method at target pH 9.

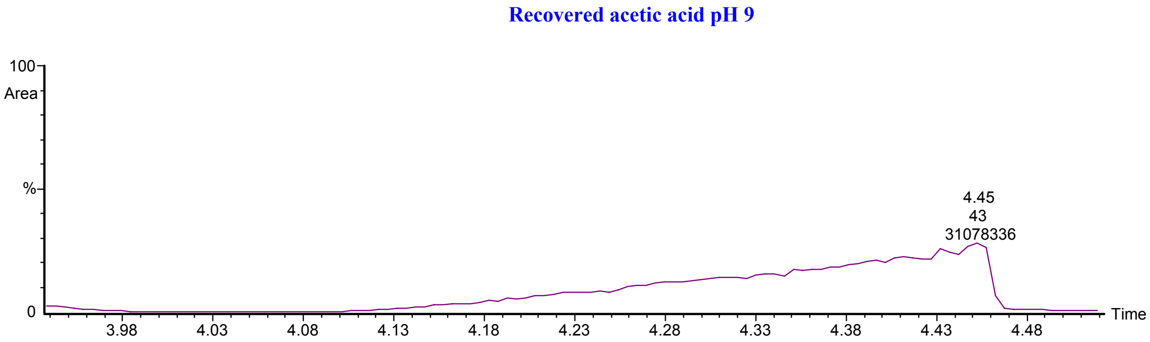


Figure A. 20 Integration of acetic acid peak from GC/MS chromatogram of recovered organic acid fraction from calcium oxide method at target pH 9.

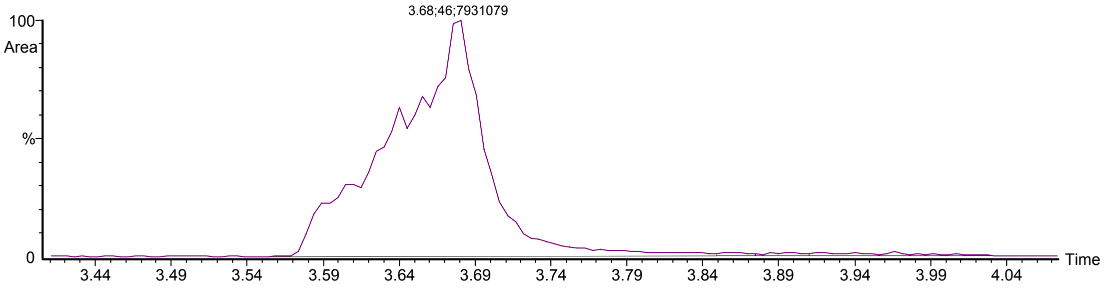


Figure A. 21 Integration of formic acid peak from GC/MS chromatogram of recovered organic acid fraction from calcium oxide method at target pH 9.

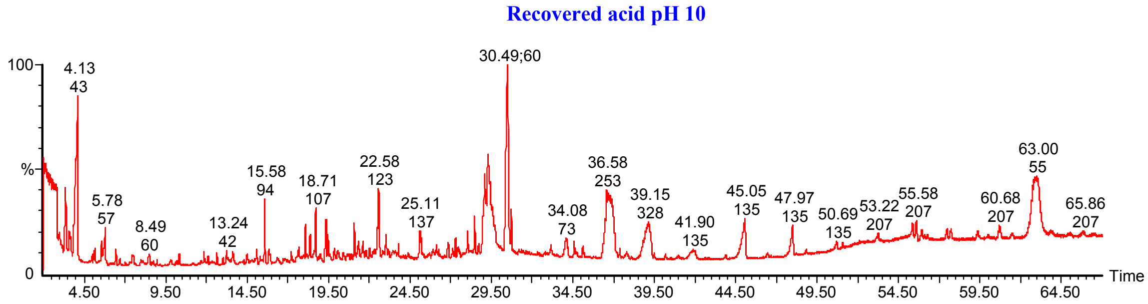


Figure A. 22 GC/MS chromatogram of recovered organic acid fraction from calcium oxide method at target pH 10.

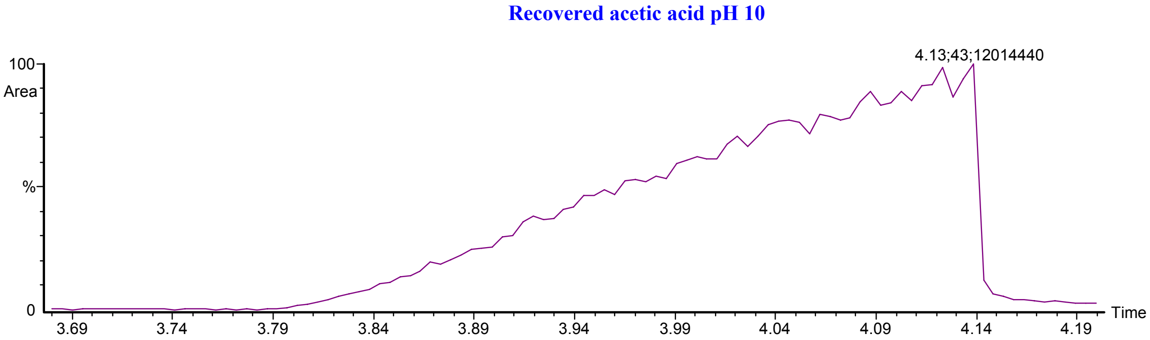


Figure A. 23 Integration of acetic acid peak from GC/MS of recovered organic acid fraction from calcium oxide method at target pH 10.

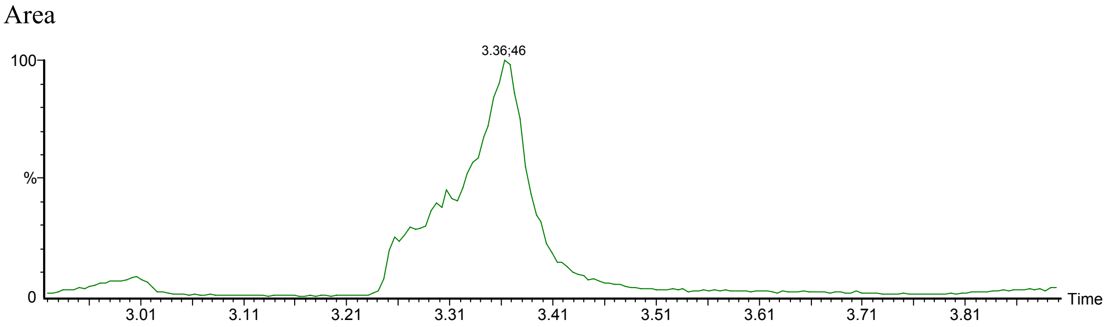


Figure A. 24 Integration of formic acid peak from GC/MS chromatogram of recovered organic acid fraction from calcium oxide method at target pH 10.

APPENDIX B

GC/MS CHROMATOGRAMS OF RECOVERED BIO-OIL AND ORGANIC ACID FRACTIONS FROM THE QUATERNARY AMMONIUM ANION-EXCHANGE RESIN METHOD

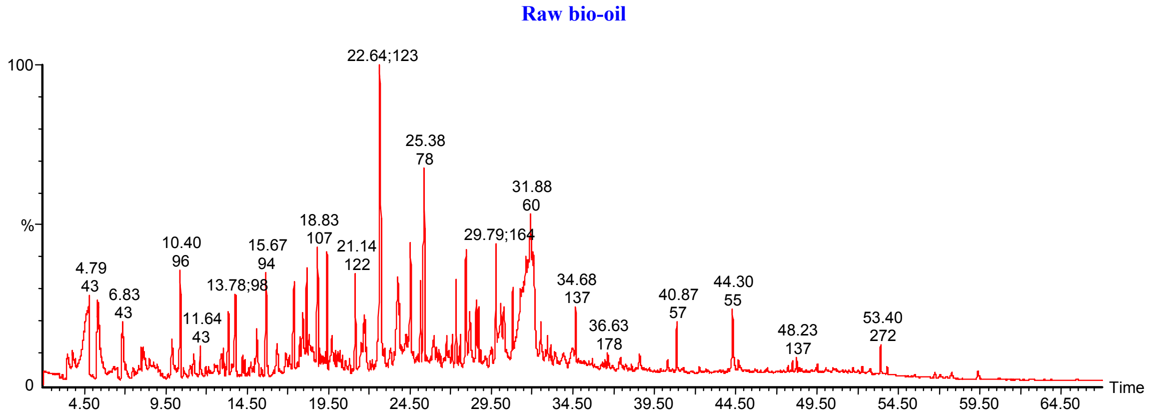


Figure B. 1 GC/MS chromatogram of MSU pine wood bio-oil.

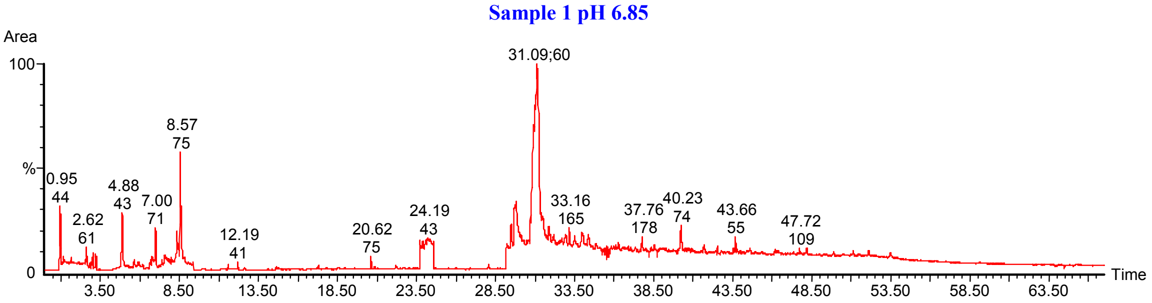


Figure B. 2 GC/MS chromatogram of bio-oil passed through quaternary ammonium anion-exchange resin at pH 6.85.

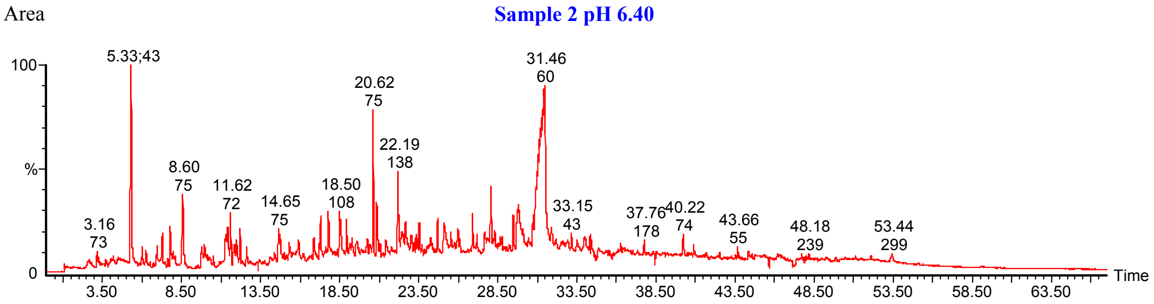


Figure B. 3 GC/MS chromatogram of bio-oil passed through quaternary ammonium anion-exchange resins at pH 6.40

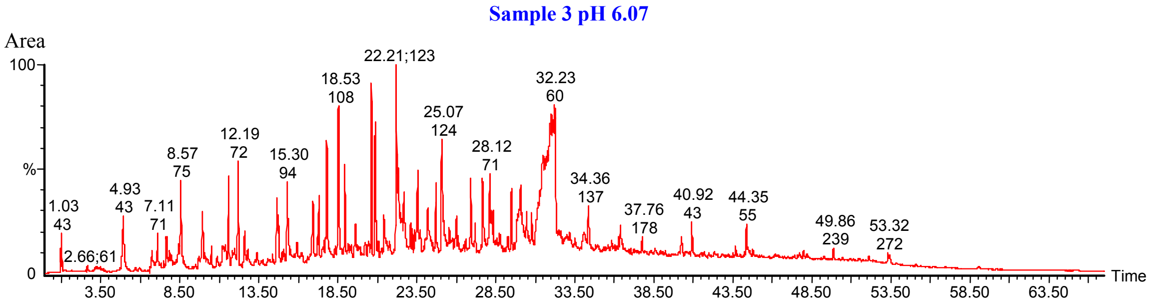


Figure B. 4 GC/MS chromatogram of bio-oil passed through quaternary ammonium anion-exchange resin at pH 6.07.

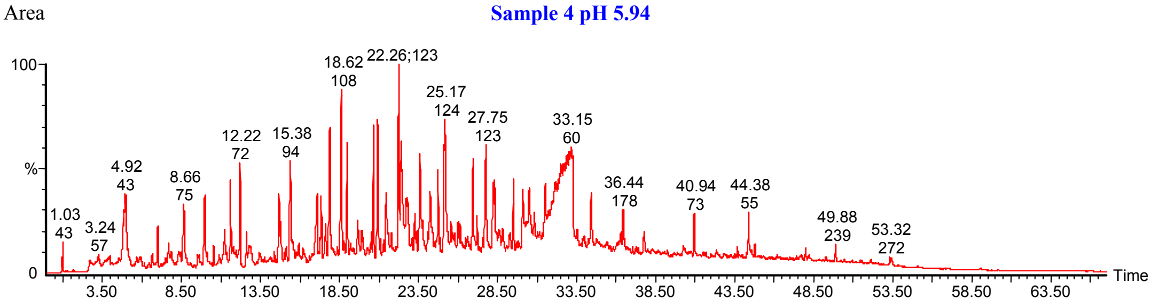


Figure B. 5 GC/MS chromatogram of bio-oil passed through quaternary ammonium anion-exchange resin at pH 5.94.

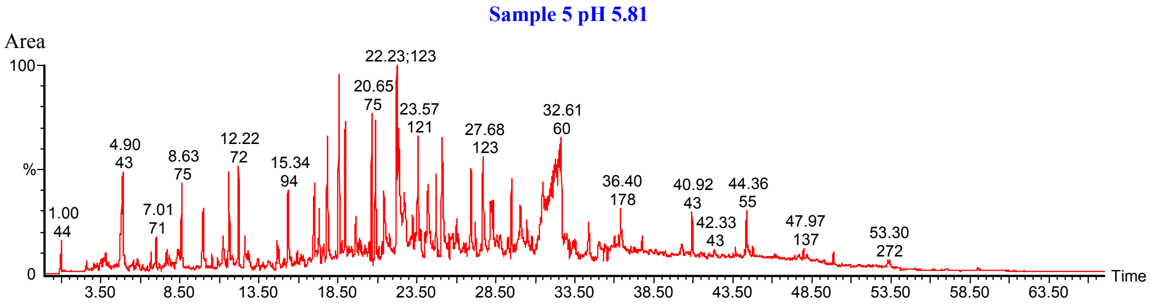


Figure B. 6 GC/MS chromatogram of bio-oil passed through quaternary ammonium anion-exchange resin at pH 5.81.

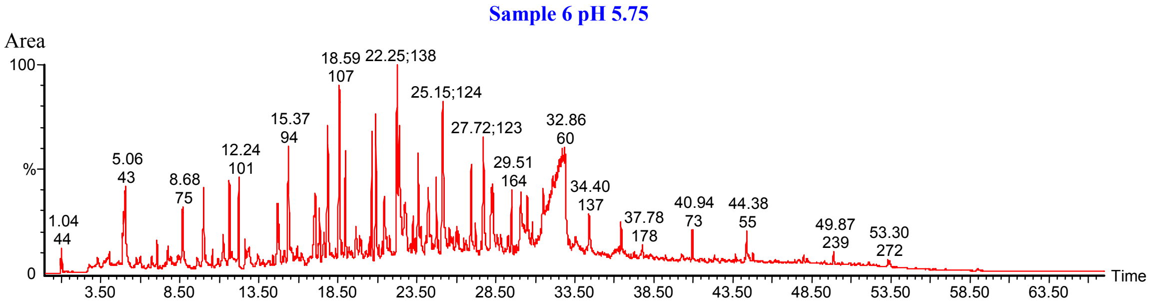


Figure B. 7 GC/MS chromatogram of bio-oil passed through quaternary ammonium anion-exchange resin at pH 5.75.

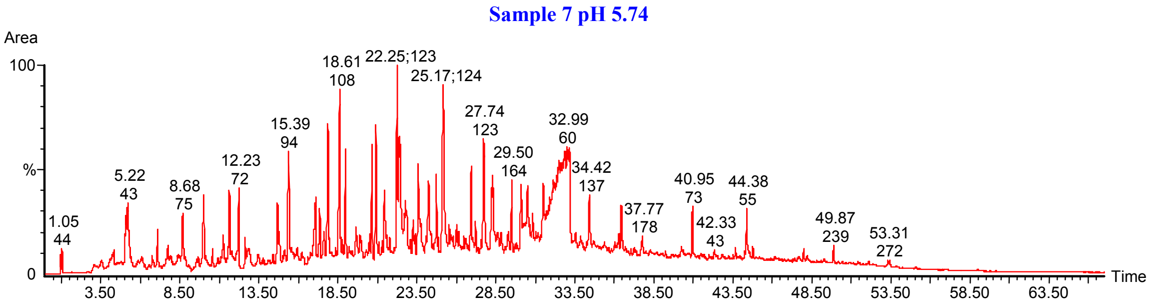


Figure B. 8 GC/MS chromatogram of bio-oil passed through quaternary ammonium anion-exchange resin at pH 5.74.

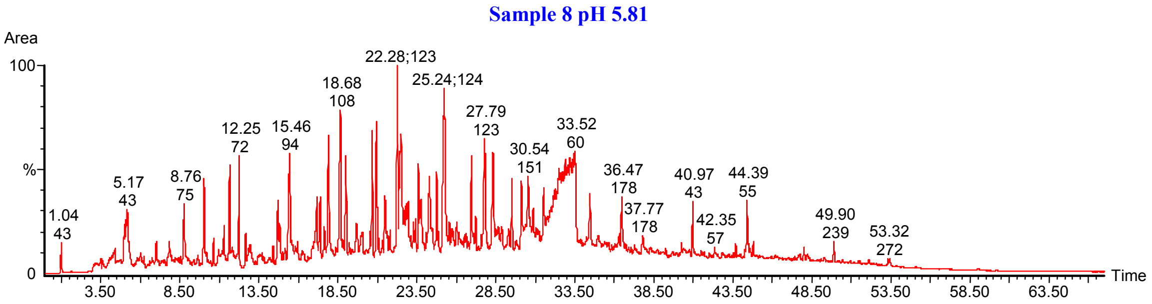


Figure B. 9 GC/MS chromatogram of bio-oil passed through quaternary ammonium anion-exchange resin at pH 5.74.

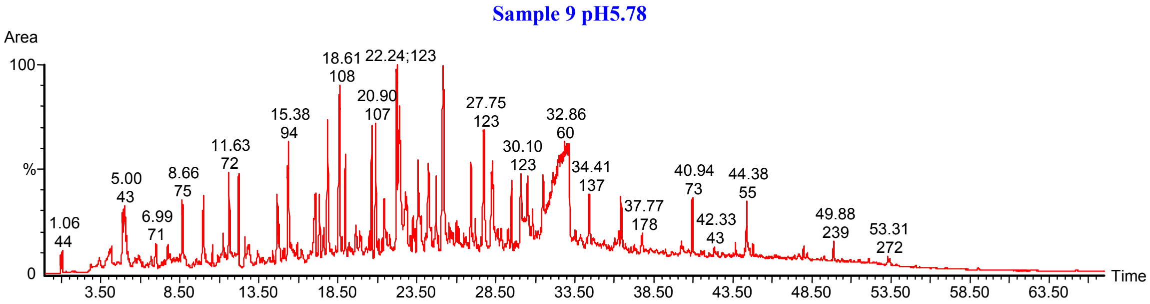


Figure B. 10 GC/MS chromatogram of bio-oil passed through quaternary ammonium anion-exchange resin at pH 5.78.

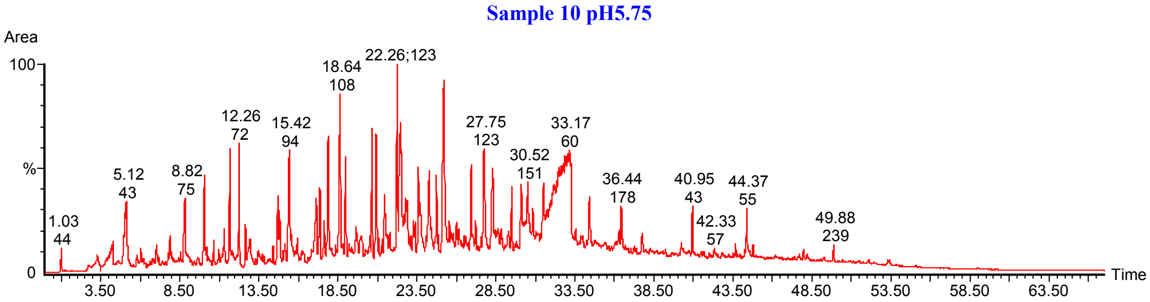


Figure B. 11 GC/MS chromatogram of bio-oil passed through quaternary ammonium anion-exchange resin at pH 5.75.

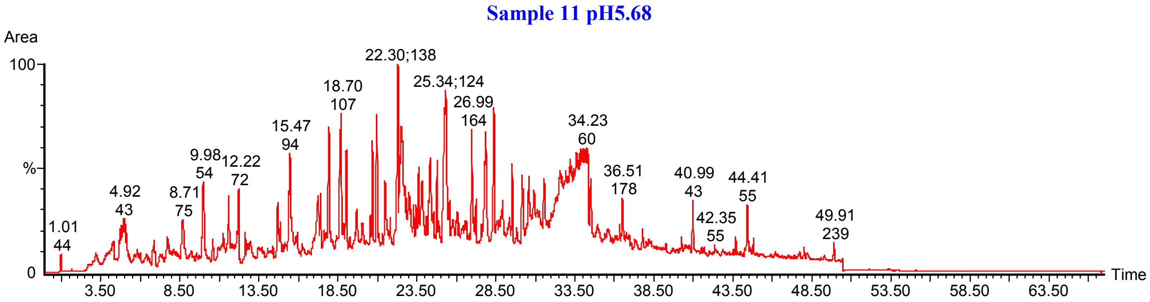


Figure B. 12 GC/MS chromatogram of bio-oil passed through quaternary ammonium anion-exchange resin at pH 5.68.

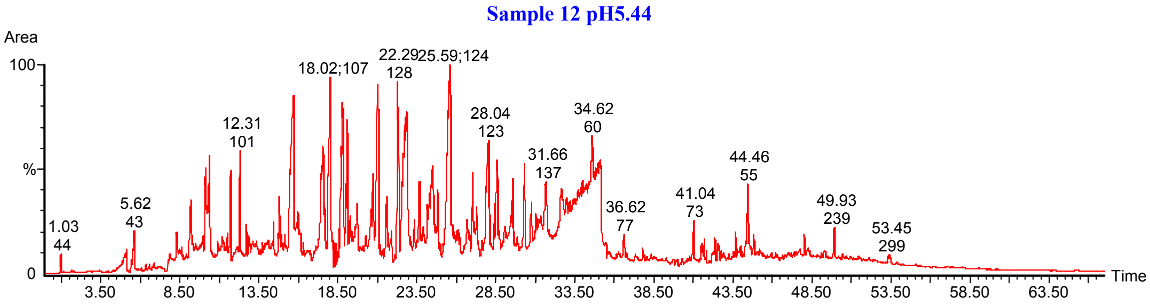


Figure B. 13 GC/MS chromatogram of bio-oil passed through quaternary ammonium anion-exchange resin at pH 5.44.

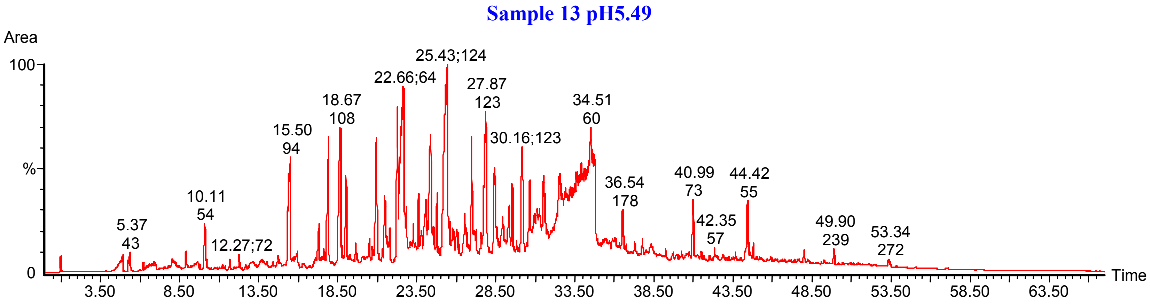


Figure B. 14 GC/MS chromatogram of bio-oil passed through quaternary ammonium anion-exchange resin at pH 5.49.

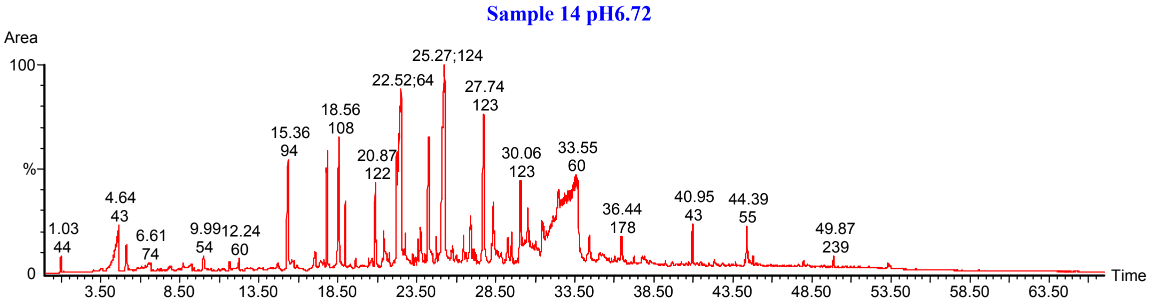


Figure B. 15 GC/MS chromatogram of bio-oil passed through quaternary ammonium anion-exchange resin at pH 6.72.

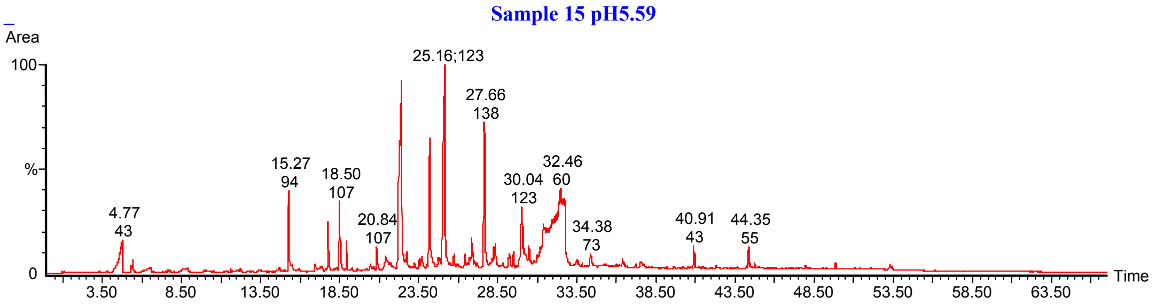


Figure B. 16 GC/MS chromatogram of bio-oil passed through quaternary ammonium anion-exchange resin at pH 5.59.

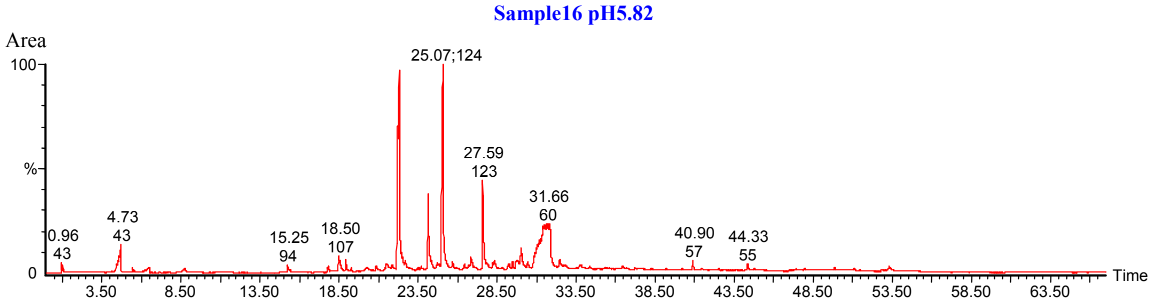


Figure B. 17 GC/MS chromatogram of bio-oil passed through quaternary ammonium anion-exchange resin at pH 5.82.

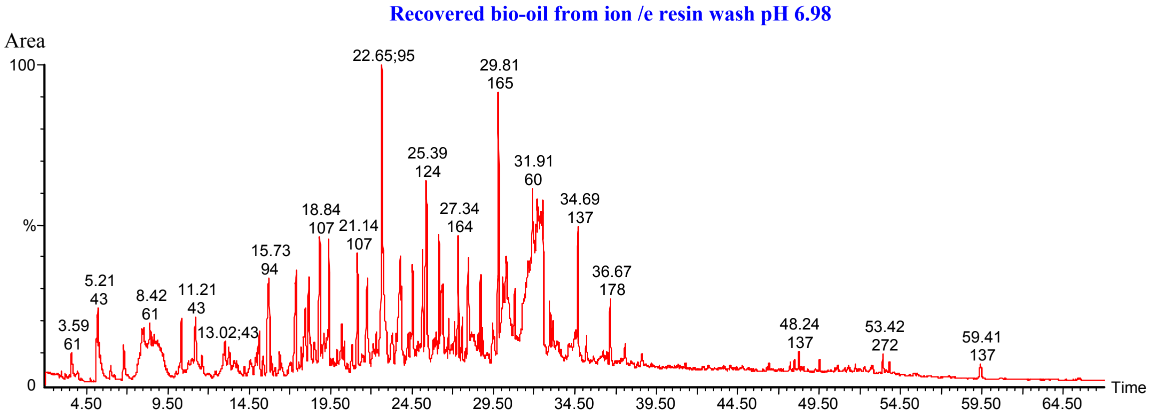


Figure B. 18 GC/MS chromatogram of recovered bio-oil from quaternary ammonium anion-exchange resin method at target pH 6.98.

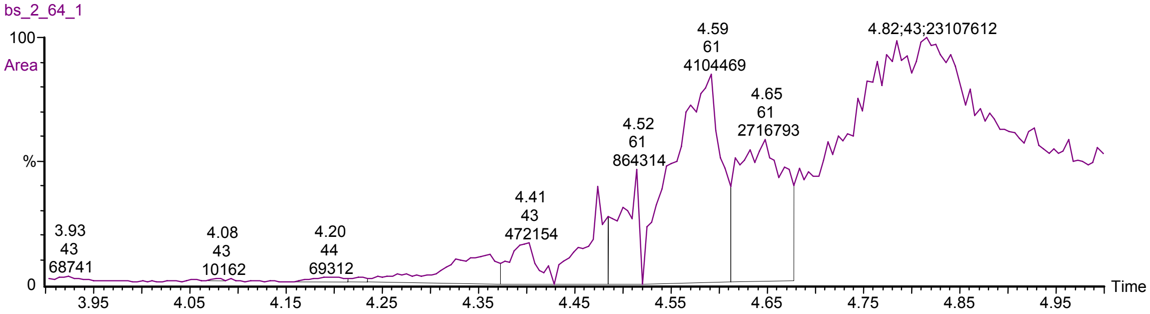


Figure B. 19 Integration of acetic acid peak from GC/MS chromatogram of recovered bio-oil at target pH 6.98 from anion-exchange resin method after expansion.

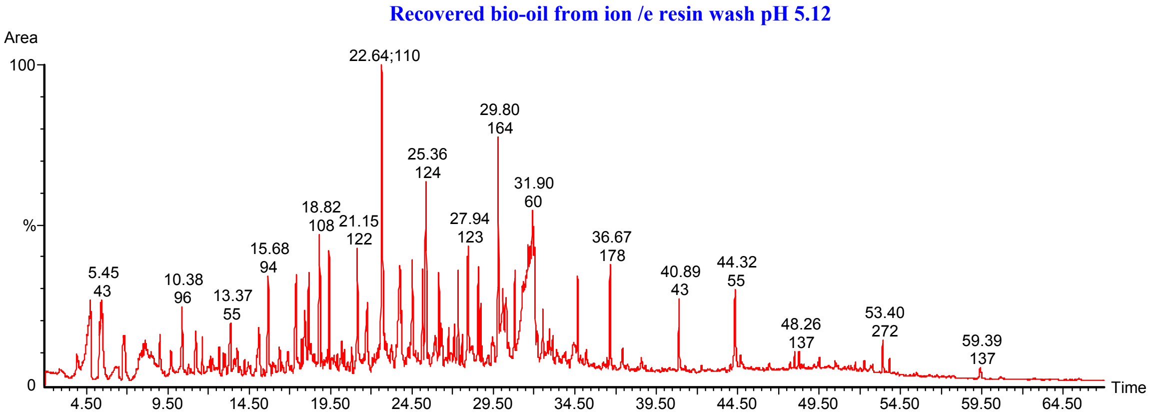


Figure B. 20 GC/MS chromatogram of recovered bio-oil from quaternary ammonium anion-exchange resin method at target pH 5.12.

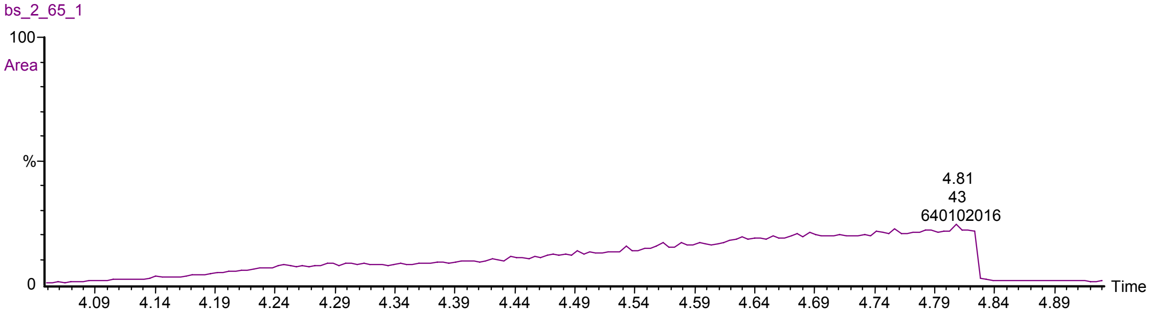


Figure B. 21 Integration of acetic acid peak from GC/MS chromatogram of recovered bio-oil at target pH 5.12 from anion-exchange resin method after expansion.

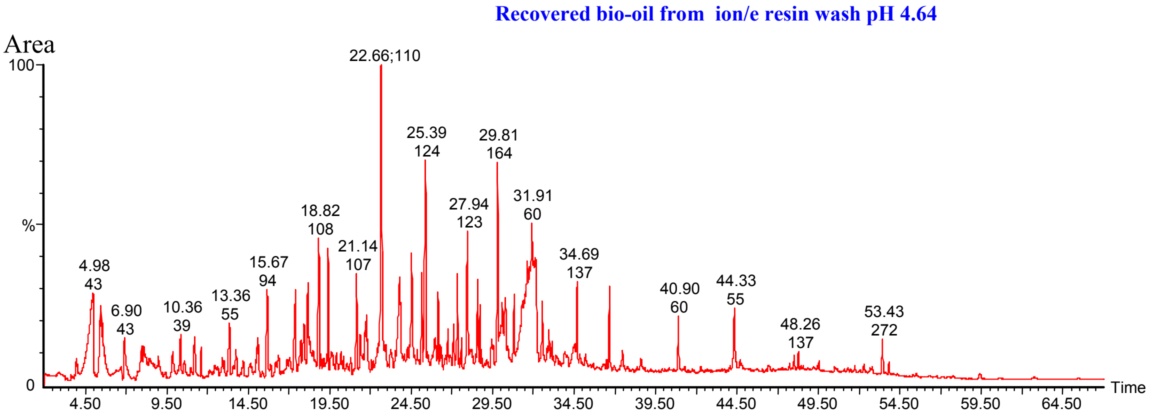


Figure B. 22 GC/MS chromatogram of recovered bio-oil from quaternary ammonium anion-exchange resin method at target pH 4.64.

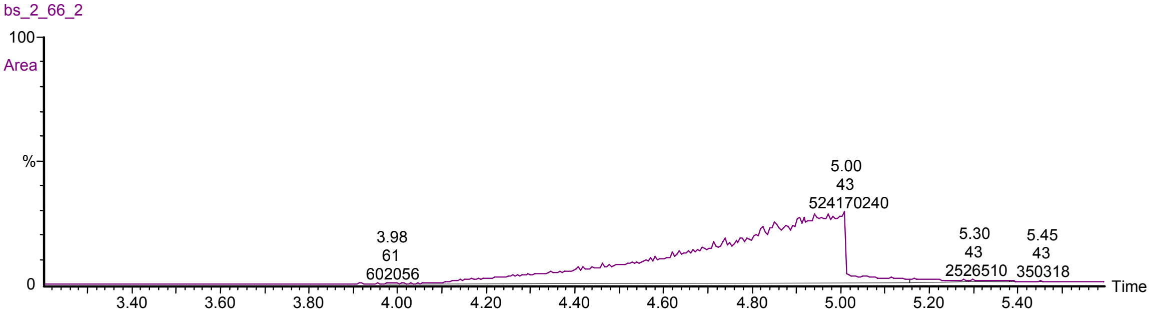


Figure B. 23 Integration of acetic acid peak from GC/MS chromatogram of recovered bio-oil at target pH 4.64 from anion-exchange resin method after expansion.

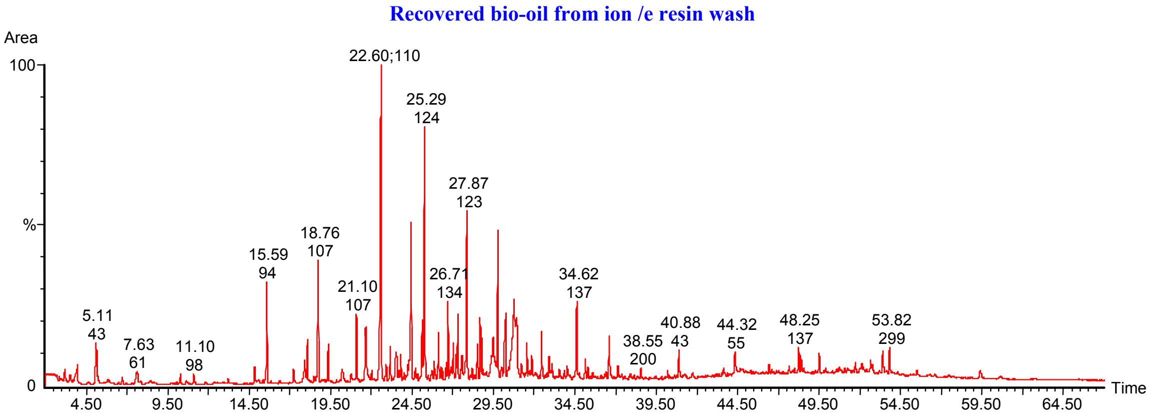


Figure B. 24 GC/MS chromatogram of methanol soluble fraction obtained by washing the anion-exchange resin after treatment of bio-oil at ending pH of 6.98.

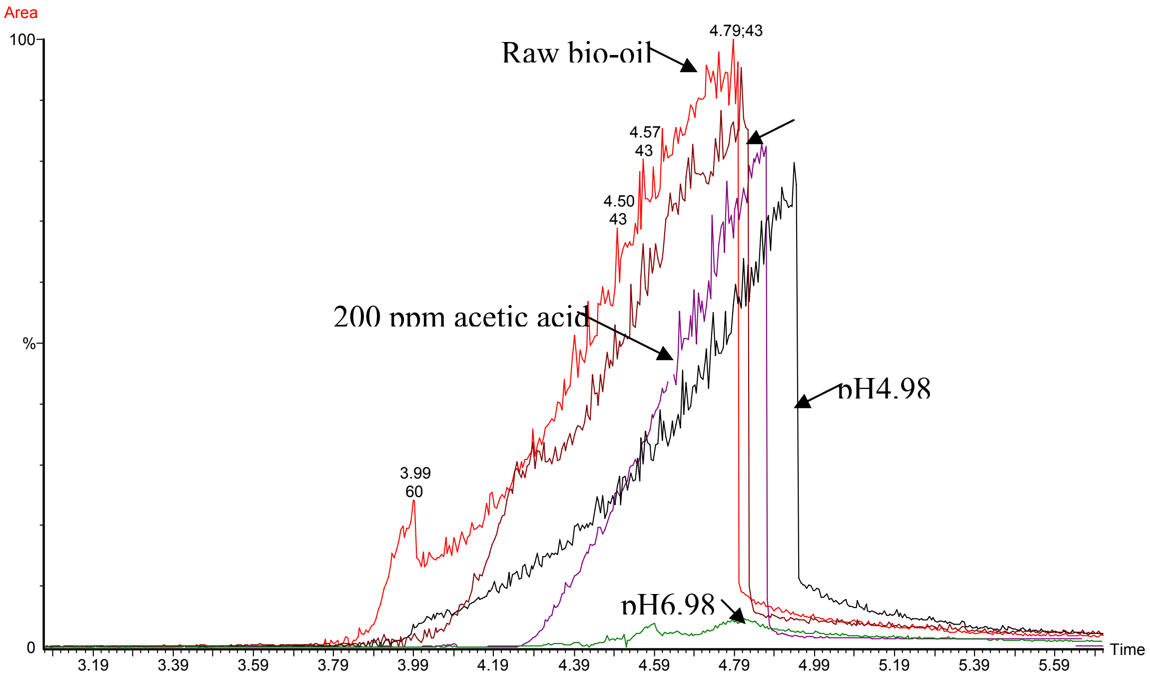


Figure B. 25 Comparison of acetic acid peaks from GC/MS chromatogram of recovered bio-oils from the batch method of using anion-exchange resin with acetic acid peak of 200 ppm standard solution.

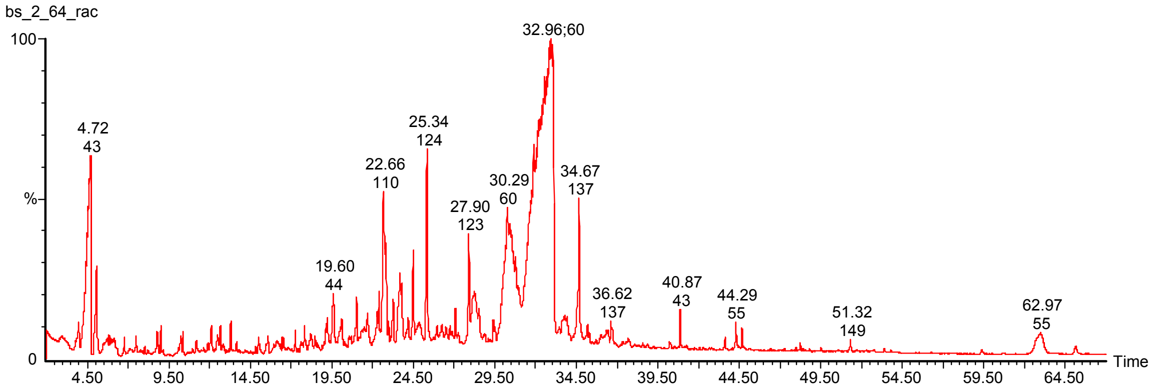


Figure B. 26 GC/MS chromatogram of recovered organic acid fraction from the batch method of using anion-exchange resin at target pH 6.98. Acetic acid is at 4.72 min and the peak at 32.96 min is levoglucosan.

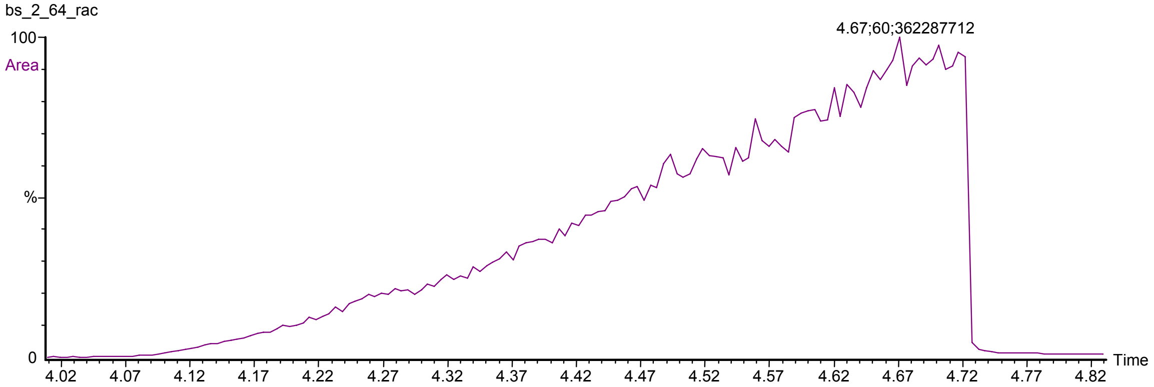


Figure B. 27 Integration of acetic acid peak form GC/MS chromatogram of recovered organic acid fraction from the batch method using anion-exchange resins at pH 6.98.

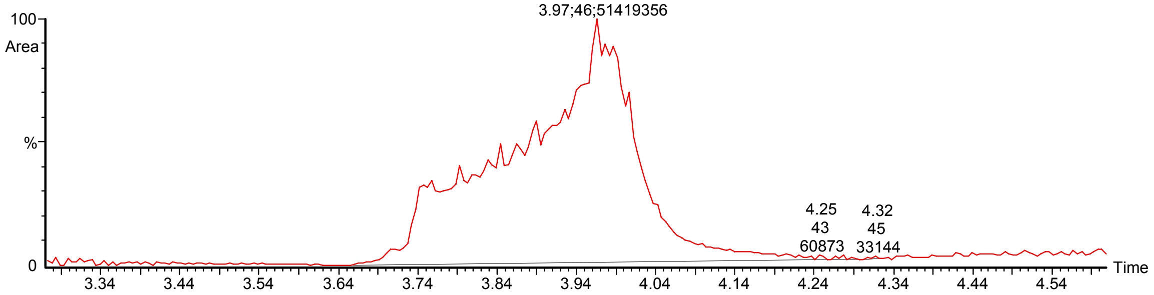


Figure B. 28 Integration of formic acid peak form GC/MS chromatogram of recovered organic acid fraction from the batch method using anion-exchange resins at pH 6.98.

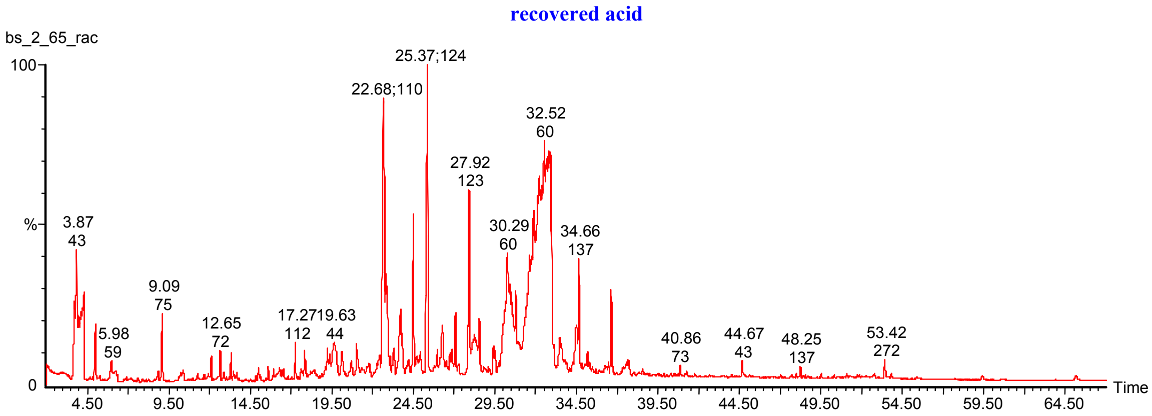


Figure B. 29 GC/MS chromatogram of recovered organic acid fraction from the batch method of using anion-exchange resin at target pH 5.12.

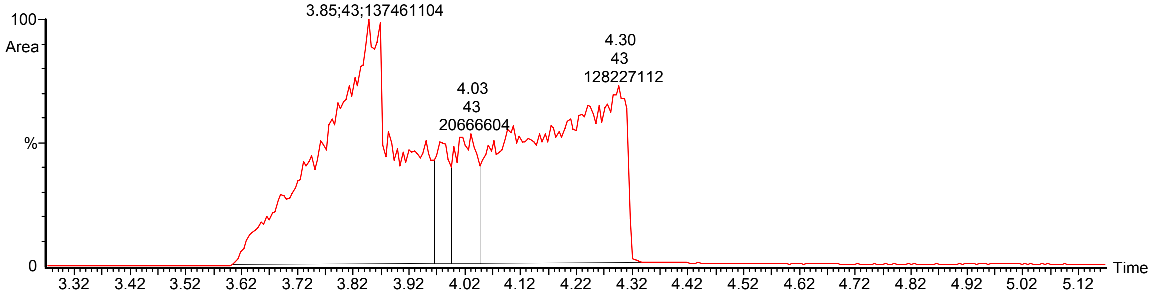


Figure B. 30 Integration of acetic acid peak form GC/MS chromatogram of recovered organic acid fraction from the batch method of using anion-exchange resins at pH 5.12.

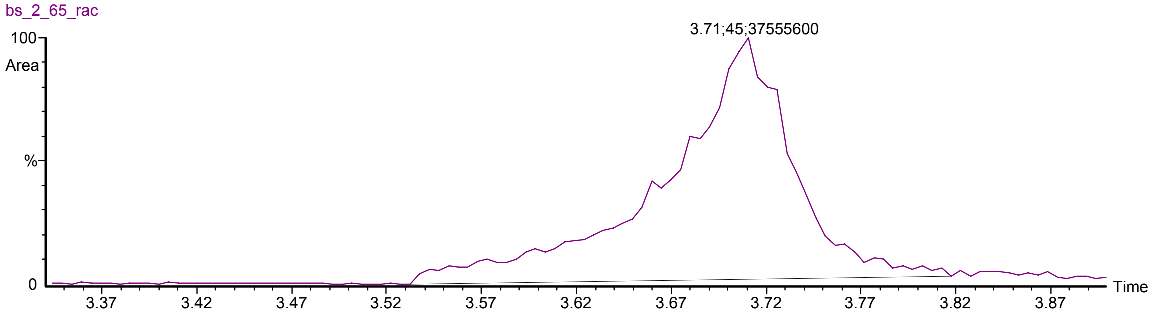


Figure B. 31 Integration of formic acid peak from GC/MS chromatogram of recovered organic acid fraction of the batch method of using anion-exchange resin at pH 5.12.

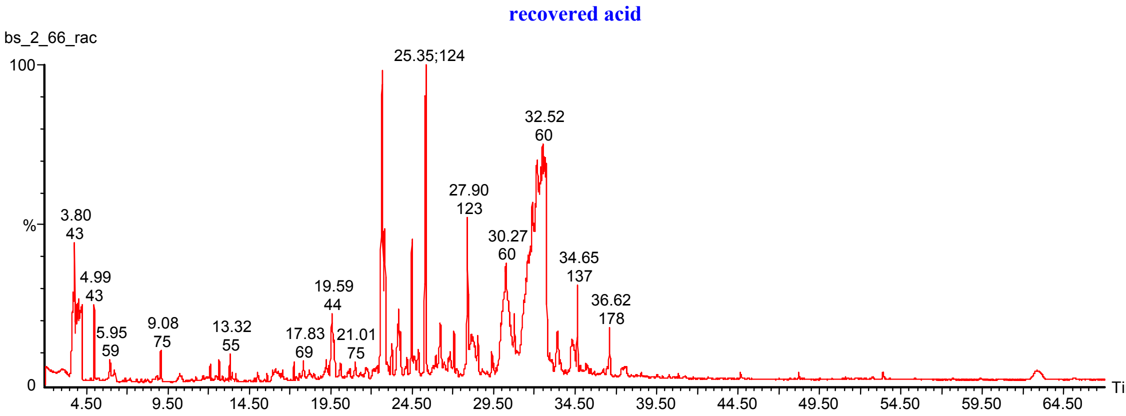


Figure B. 32 GC/MS chromatogram of recovered organic acid fraction from the batch method of using anion-exchange resin at target pH 4.64.

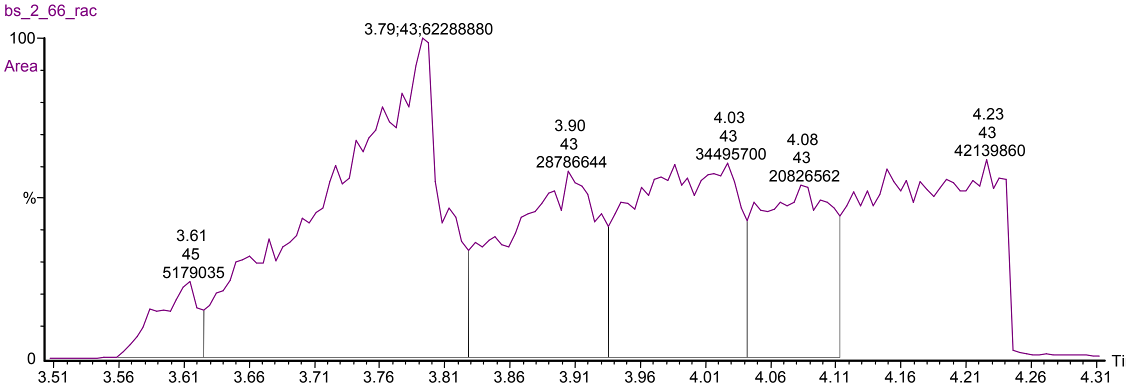


Figure B. 33 Integration of acetic acid peak from GC/MS chromatogram of recovered organic acid fraction from the batch method of using anion-exchange resins at pH 4.64.

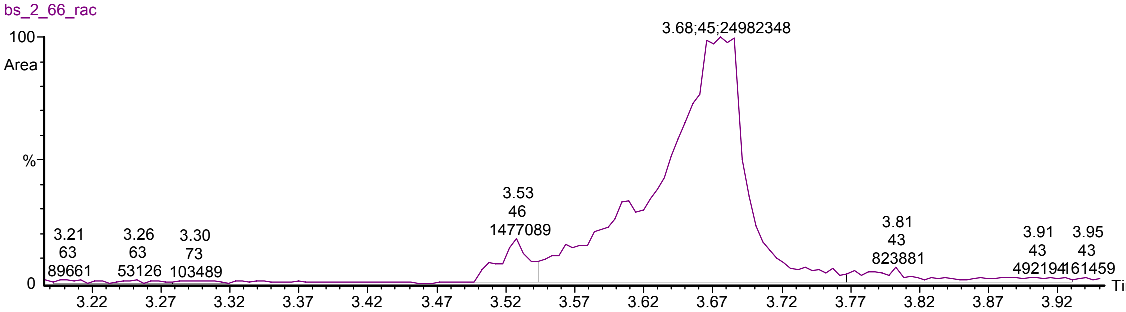


Figure B. 34 Integration of formic acid peak from GC/MS chromatogram of recovered organic acids fraction from the batch method of using anion-exchange resin at pH 4.64.

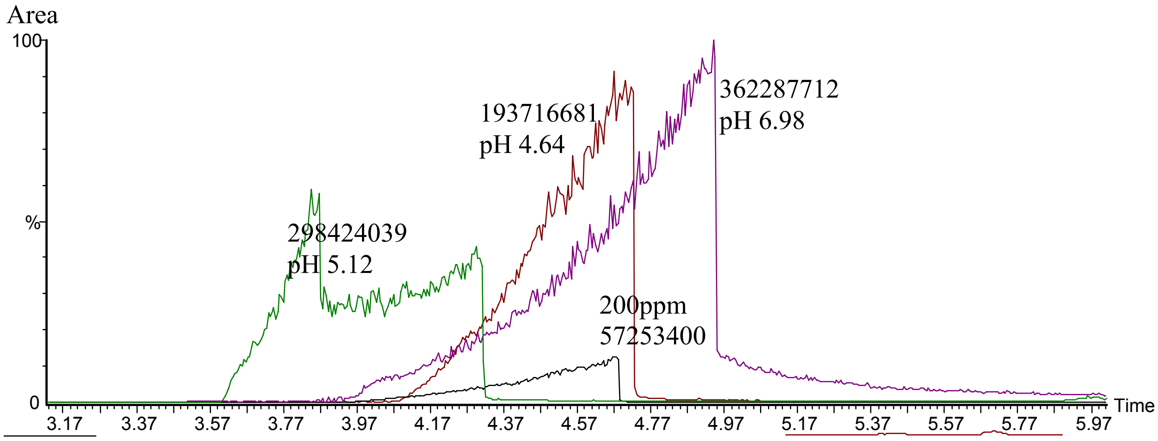


Figure B. 35 Comparison of acetic acid peak integrations from GC/MS chromatogram of recovered organic acid fractions at different target pH values compared with acetic acid peak of 200ppm standard solution.

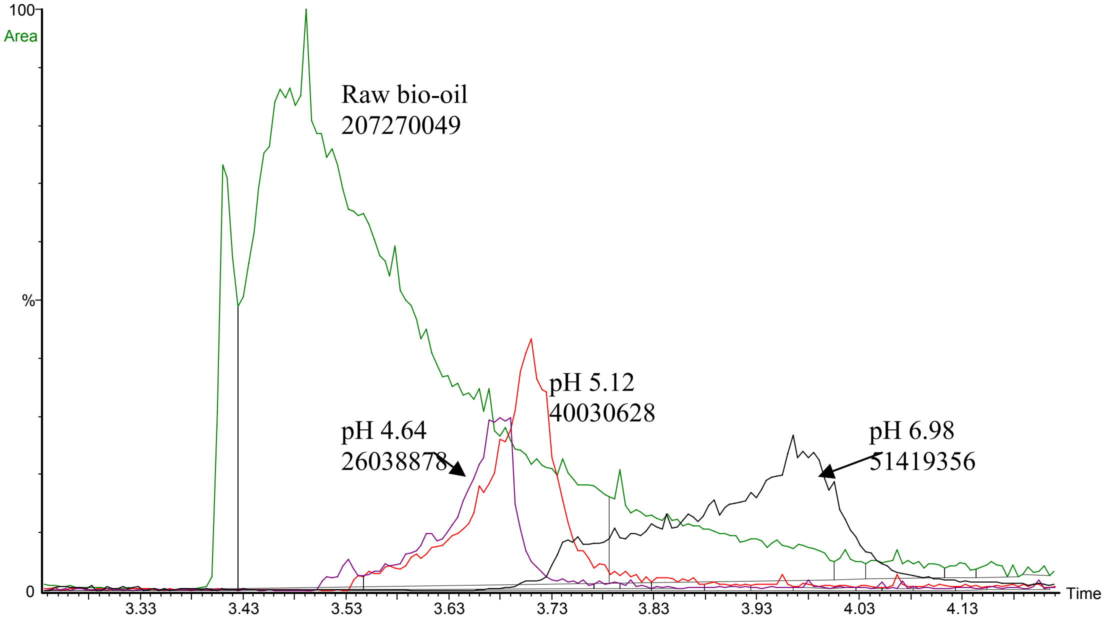
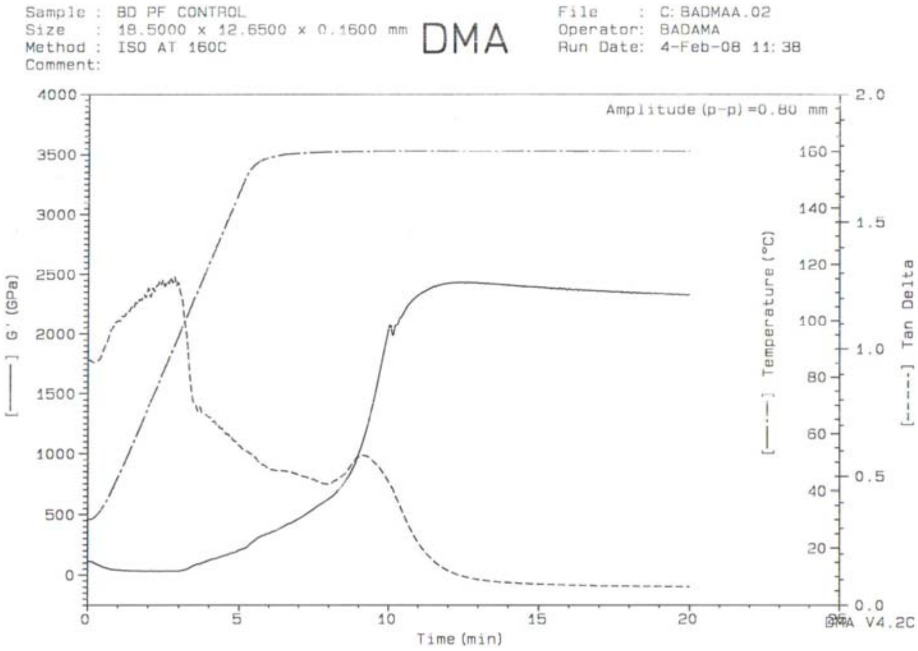


Figure B. 36 Comparison of formic acid peak integrations from GC/MS chromatograms of recovered organic acid fractions at different target pH values compared with formic acid peak of raw bio-oil.

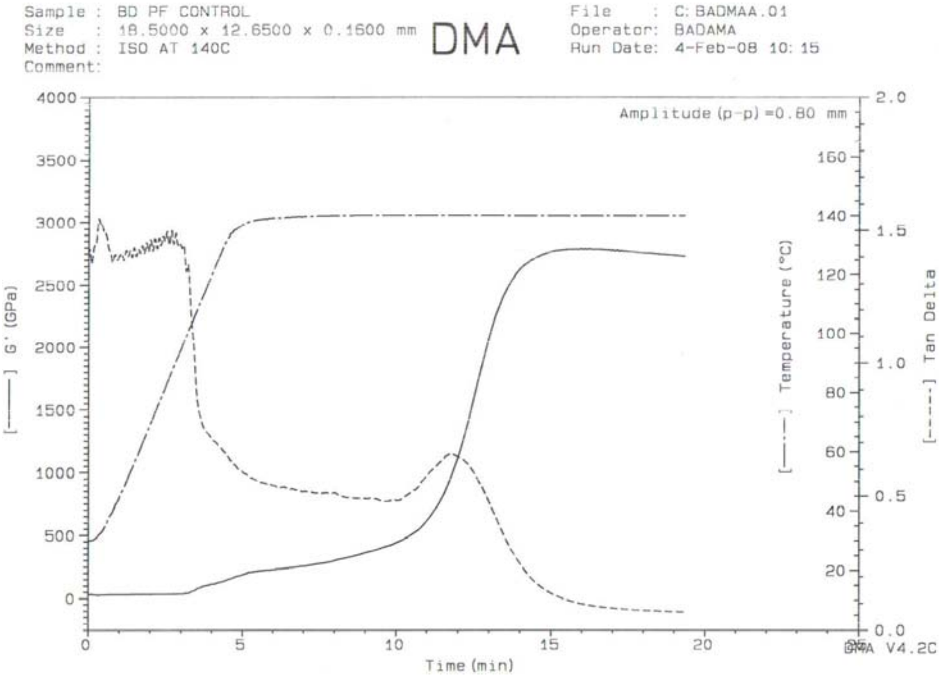
APPENDIX C

DMA RESULTS, BOARD PROCESSING DATA SHEETS, AND DATA TABLES FROM LIGNIN SEPARATION AND OSB CORE-LAYER BINDER RESIN EXPERIMENTS



Sample : BD PF CONTROL
Size : 18.5000 x 12.6500 x 0.1600 mm
Method : ISO AT 160C
Comment:
File : C:BADMAA.02
Operator: BADAMA
Run Date: 4-Feb-08 11:38

Figure C. 1 DMA of control PF resin run isothermal at 160°C for 15 min after initial heating up at 25oC/min from 30oC.



Sample : BD PF CONTROL
Size : 18.5000 x 12.6500 x 0.1600 mm
Method : ISO AT 140C
Comment:
File : C:BADMAA.01
Operator: BADAMA
Run Date: 4-Feb-08 10:15

Figure C. 2 DMA of control PF resin run isothermal at 140°C for 15 min after initial heating up at 25oC/min from 30oC.

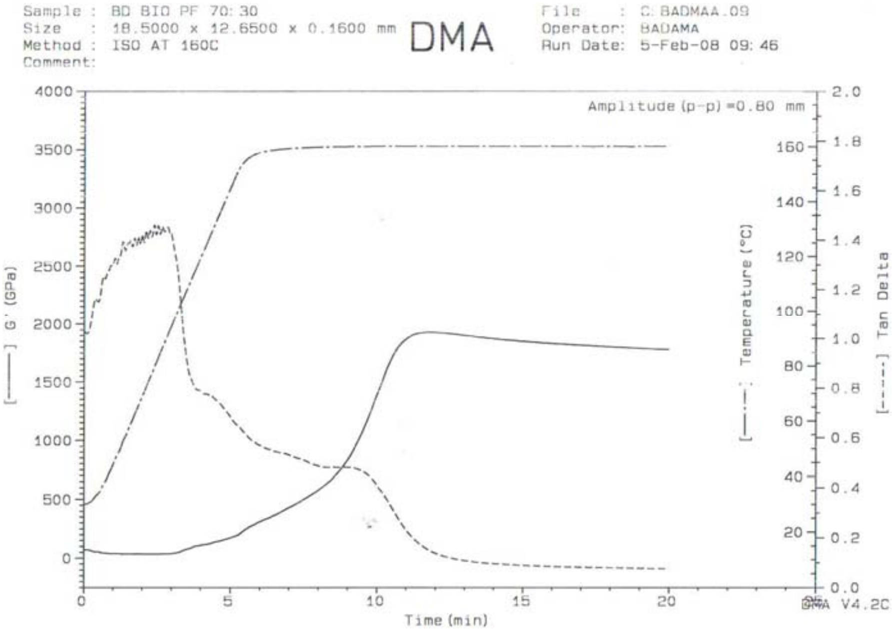


Figure C. 3 DMA of 70/30 PF-Lignin resin run isothermal at 160°C for 15 min after initial heating up at 25oC/min from 30oC.

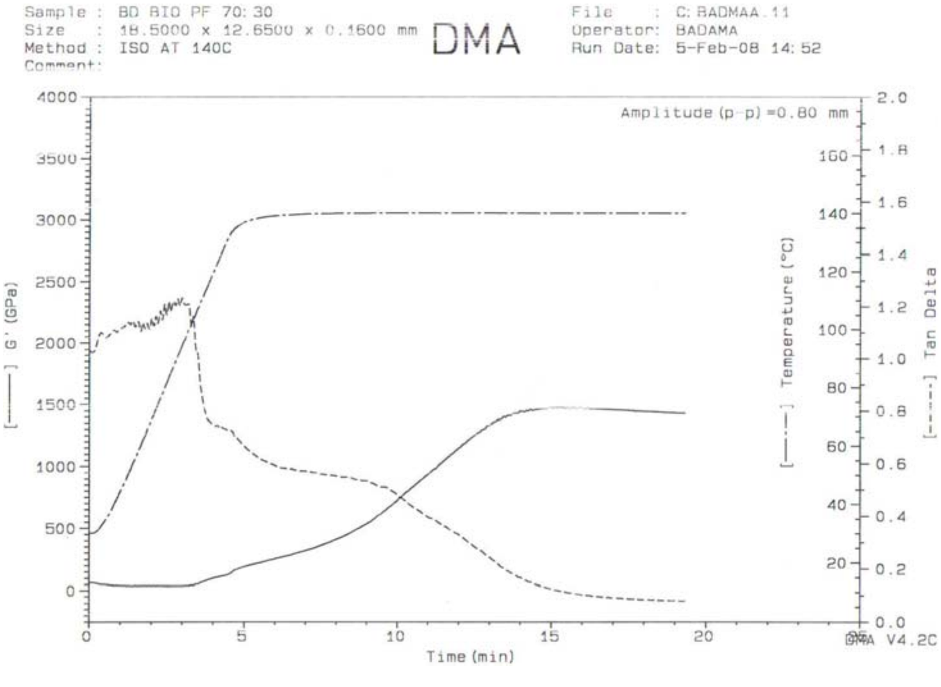


Figure C. 4 DMA of 70/30 PF-Lignin resin run isothermal at 140°C for 15 min after initial heating up at 25oC/min from 30oC.

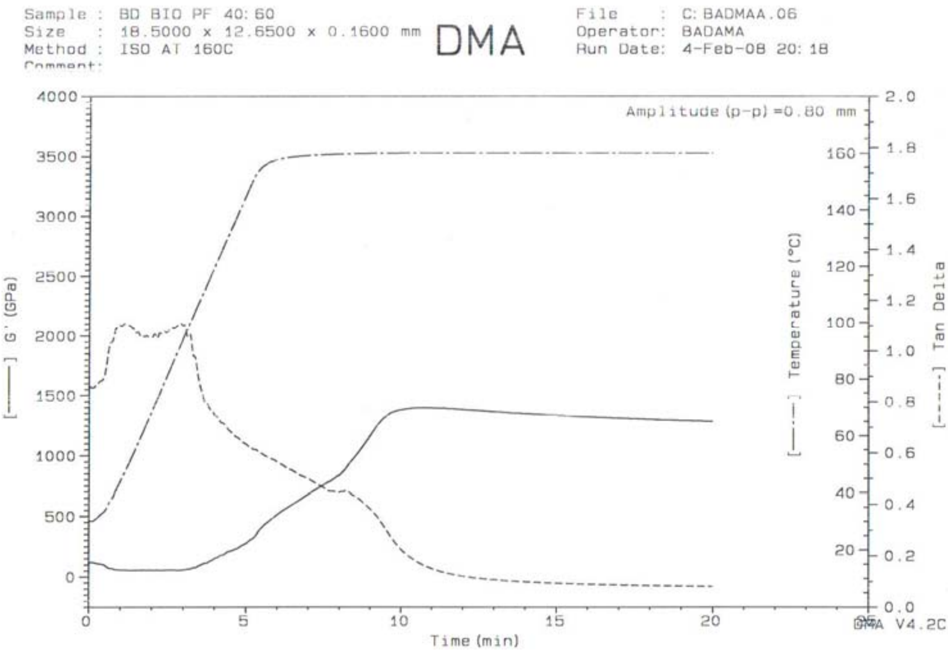


Figure C. 5 DMA of 60/40 PF-Lignin resin run isothermal at 160°C for 15 min after initial heating up at 25oC/min from 30oC.

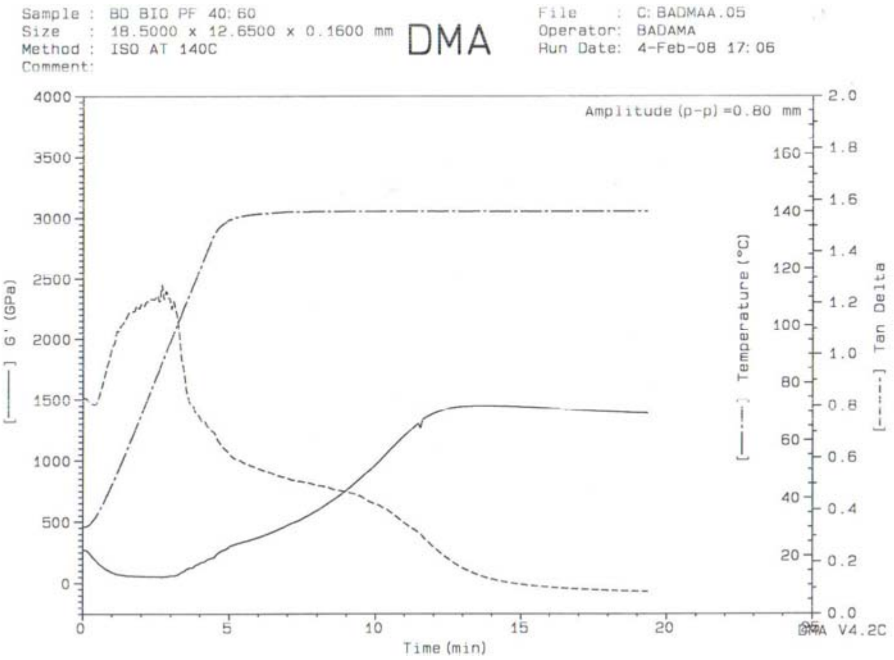


Figure C. 6 DMA of 60/40 PF-Lignin resin run isothermal at 140°C for 15 min after initial heating up at 25oC/min from 30oC.

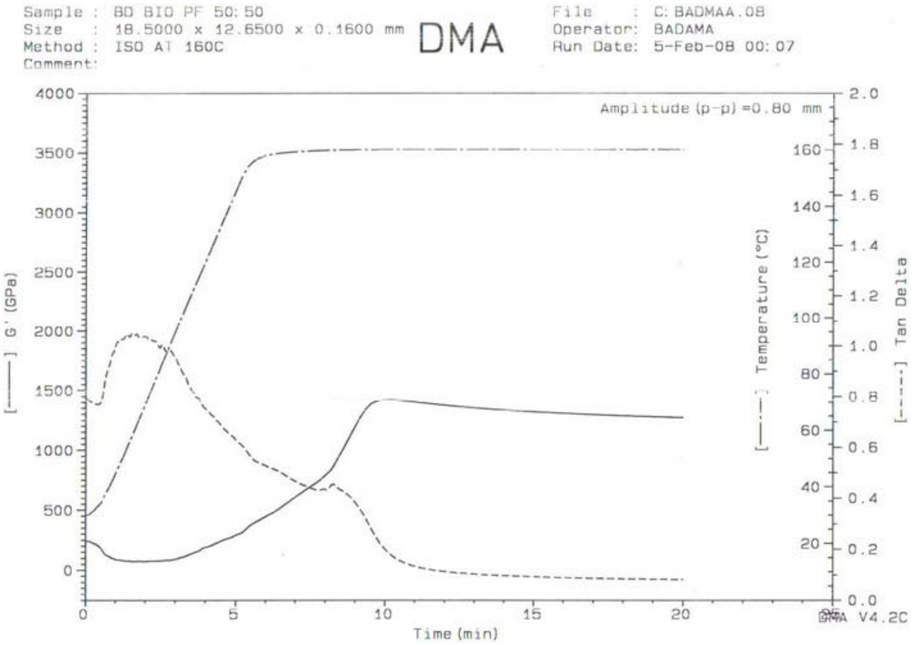


Figure C. 7 DMA of 50/50 PF-Lignin resin run isothermal at 160°C for 15 min after initial heating up at 25oC/min from 30oC.

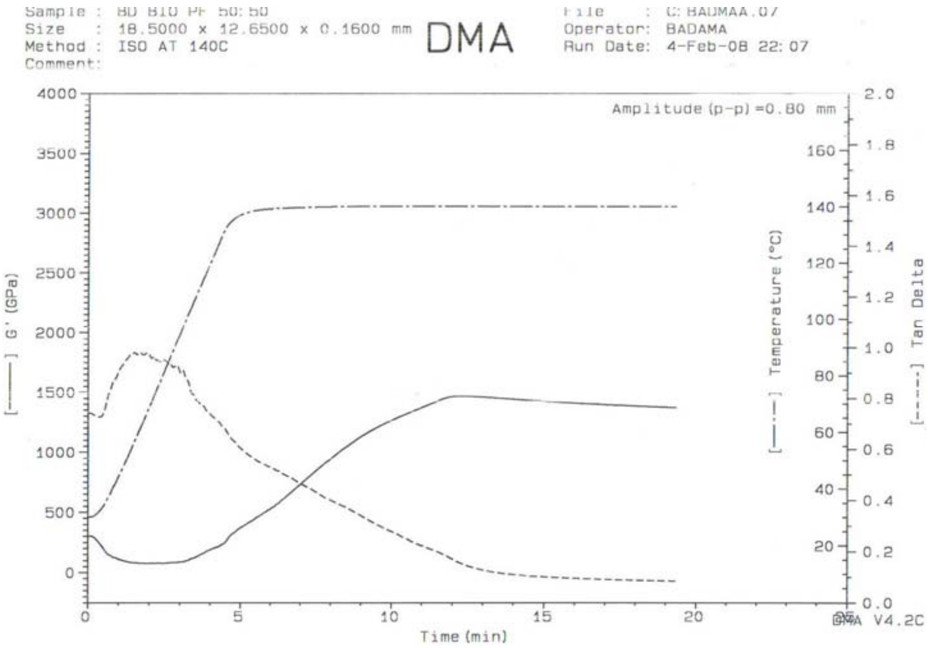
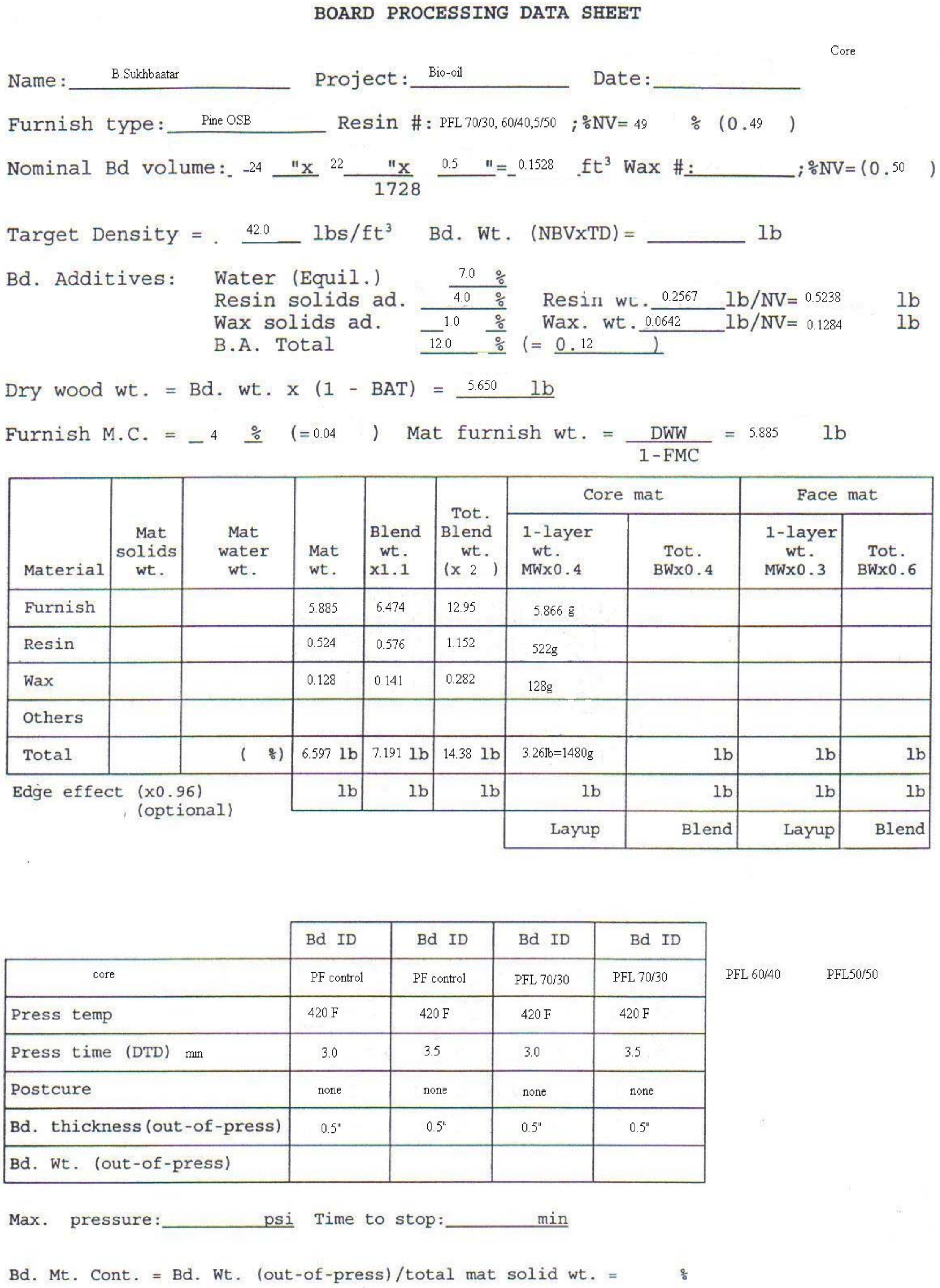


Figure C. 8 DMA of 50/50 PF-Lignin resin run isothermal at 140°C for 15 min after initial heating up at 25oC/min from 30oC.

Table C. 1 Board processing data sheet for OSB core-layer mat.



BOARD PROCESSING DATA SHEET

Core

Name: B.Sukhbaatar Project: Bio-oil Date:

Furnish type: Pine OSB Resin #: PFL 70/30, 60/40,5/50 ; %NV= 49 % (0.49)

Nominal Bd volume: 24 "x 22 "x 0.5 "= 0.1528 ft³ Wax #: ; %NV= (0.50)
1728

Target Density = 42.0 lbs/ft³ Bd. Wt. (NBVxTD) = lb

Bd. Additives: Water (Equil.) 7.0 %
Resin solids ad. 4.0 % Resin wt. 0.2567 lb/NV= 0.5238 lb
Wax solids ad. 1.0 % Wax. wt. 0.0642 lb/NV= 0.1284 lb
B.A. Total 12.0 % (= 0.12)

Dry wood wt. = Bd. wt. x (1 - BAT) = 5.650 lb

Furnish M.C. = 4 % (= 0.04) Mat furnish wt. = DWW / 1-FMC = 5.885 lb

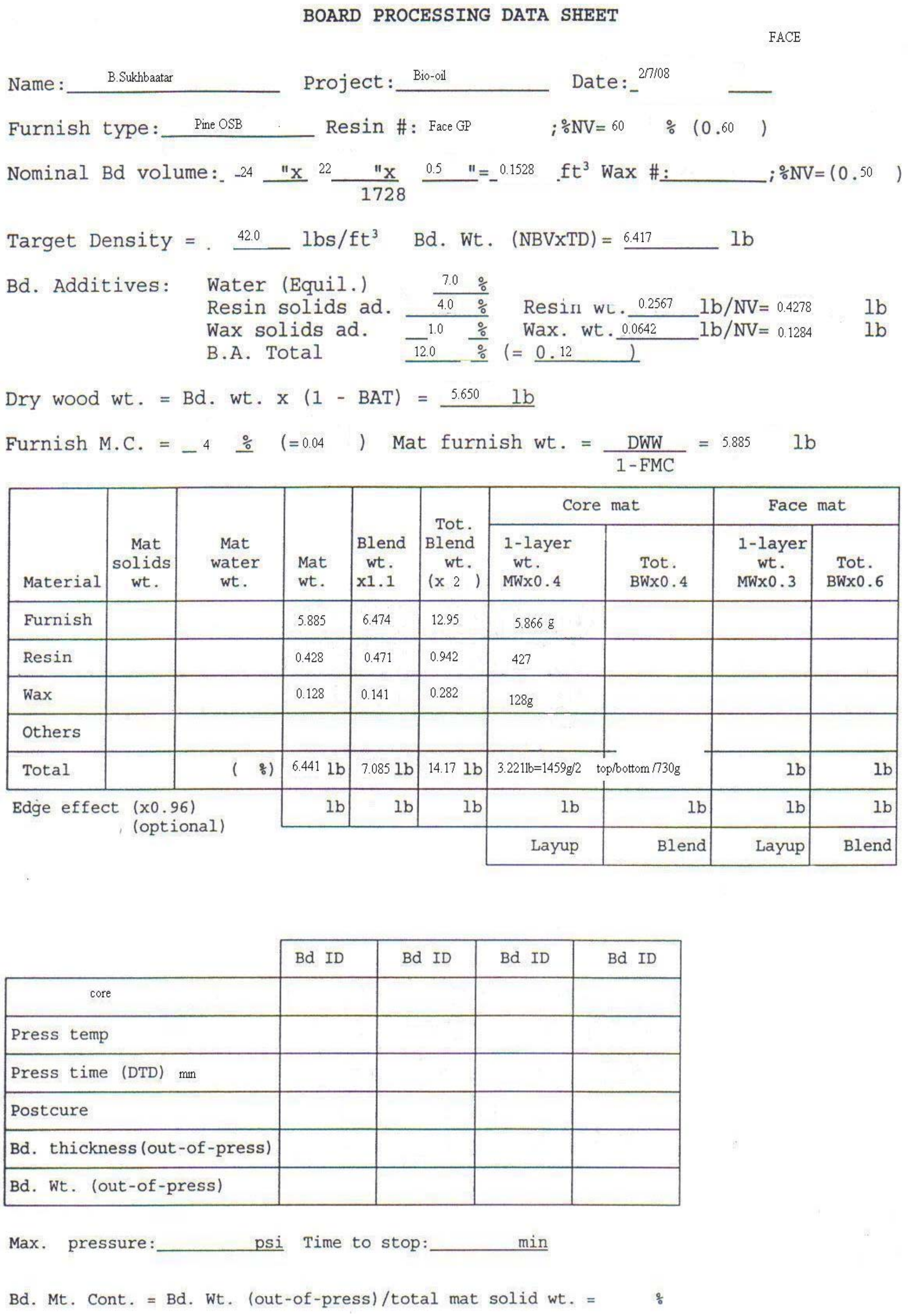
						Core mat		Face mat	
Material	Mat solids wt.	Mat water wt.	Mat wt.	Blend wt. x1.1	Tot. Blend wt. (x 2)	1-layer wt. MWx0.4	Tot. BWx0.4	1-layer wt. MWx0.3	Tot. BWx0.6
Furnish			5.885	6.474	12.95	5.866 g			
Resin			0.524	0.576	1.152	522g			
Wax			0.128	0.141	0.282	128g			
Others									
Total		(%)	6.597 lb	7.191 lb	14.38 lb	3.26lb=1480g	lb	lb	lb
Edge effect (x0.96) (optional)			lb	lb	lb	lb	lb	lb	lb
						Layup	Blend	Layup	Blend

	Bd ID	Bd ID	Bd ID	Bd ID		
core	PF control	PF control	PFL 70/30	PFL 70/30	PFL 60/40	PFL50/50
Press temp	420 F	420 F	420 F	420 F		
Press time (DTD) mn	3.0	3.5	3.0	3.5		
Postcure	none	none	none	none		
Bd. thickness (out-of-press)	0.5"	0.5"	0.5"	0.5"		
Bd. Wt. (out-of-press)						

Max. pressure: psi Time to stop: min

Bd. Mt. Cont. = Bd. Wt. (out-of-press)/total mat solid wt. = %

Table C. 2 Board processing data sheet for OSB face-layer mat.



BOARD PROCESSING DATA SHEET

FACE

Name: B.Sukhbaatar Project: Bio-oil Date: 2/7/08

Furnish type: Pine OSB Resin #: Face GP ;%NV= 60 % (0.60)

Nominal Bd volume: $\frac{24'' \text{x } 22'' \text{x}}{1728}$ 0.5 "= 0.1528 ft^3 Wax #: ;%NV=(0.50)

Target Density = 42.0 lbs/ft^3 Bd. Wt. (NBVxTD)= 6.417 lb

Bd. Additives: Water (Equil.) 7.0 %
Resin solids ad. 4.0 % Resin wt. 0.2567 lb/NV= 0.4278 lb
Wax solids ad. 1.0 % Wax. wt. 0.0642 lb/NV= 0.1284 lb
B.A. Total 12.0 % (= 0.12)

Dry wood wt. = Bd. wt. x (1 - BAT) = 5.650 lb

Furnish M.C. = 4 % (=0.04) Mat furnish wt. = $\frac{\text{DWW}}{\text{1-FMC}}$ = 5.885 lb

Material	Mat solids wt.	Mat water wt.	Mat wt.	Blend wt. x1.1	Tot. Blend wt. (x 2)	Core mat 1-layer wt. MWx0.4	Core mat Tot. BWx0.4	Face mat 1-layer wt. MWx0.3	Face mat Tot. BWx0.6
Furnish			5.885	6.474	12.95	5.866 g			
Resin			0.428	0.471	0.942	427			
Wax			0.128	0.141	0.282	128g			
Others									
Total		(%)	6.441 lb	7.085 lb	14.17 lb	3.221lb=1459g/2	top/bottom /730g	lb	lb
Edge effect (x0.96) (optional)			lb	lb	lb	lb	lb	lb	lb
						Layup	Blend	Layup	Blend

	Bd ID	Bd ID	Bd ID	Bd ID
core				
Press temp				
Press time (DTD) mn				
Postcure				
Bd. thickness (out-of-press)				
Bd. Wt. (out-of-press)				

Max. pressure: psi Time to stop: min

Bd. Mt. Cont. = Bd. Wt. (out-of-press)/total mat solid wt. = %

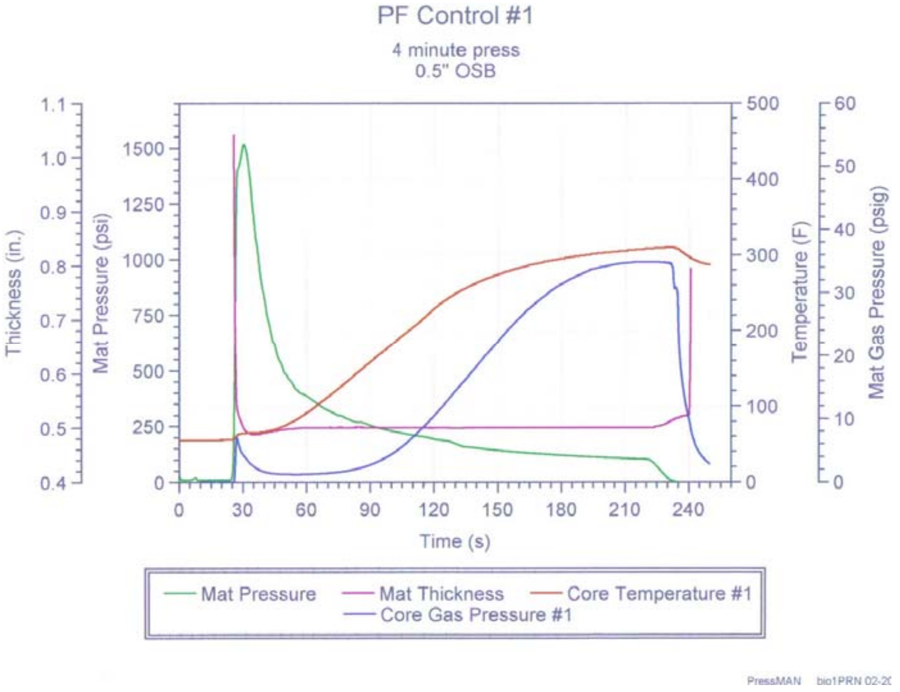


Figure C. 9 Hot-pressing data for Control PF resin in the core-layer mat.

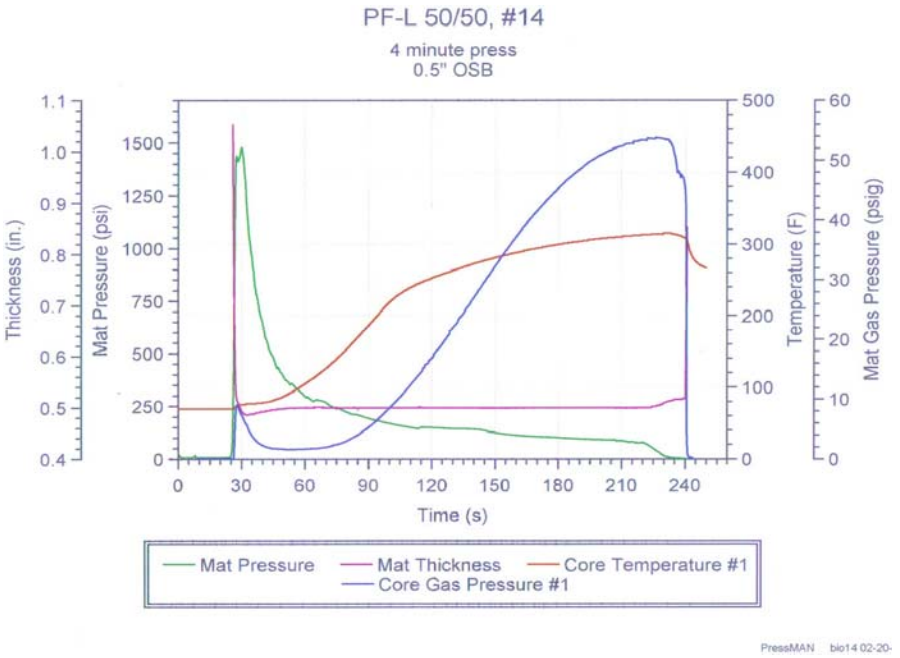


Figure C. 10 Hot-pressing data for 50/50 LPF resin in the core-layer mat.

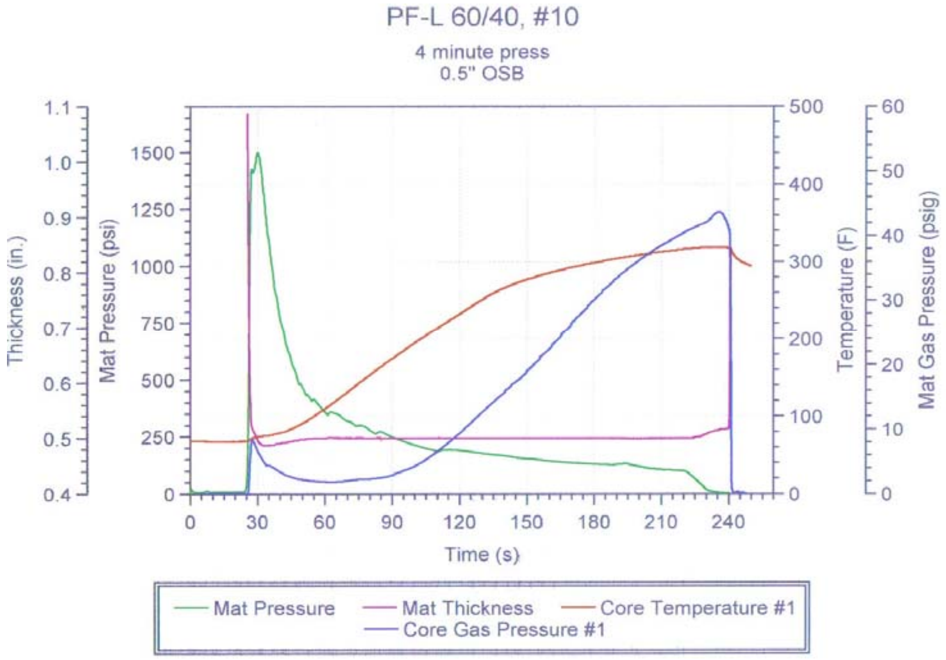
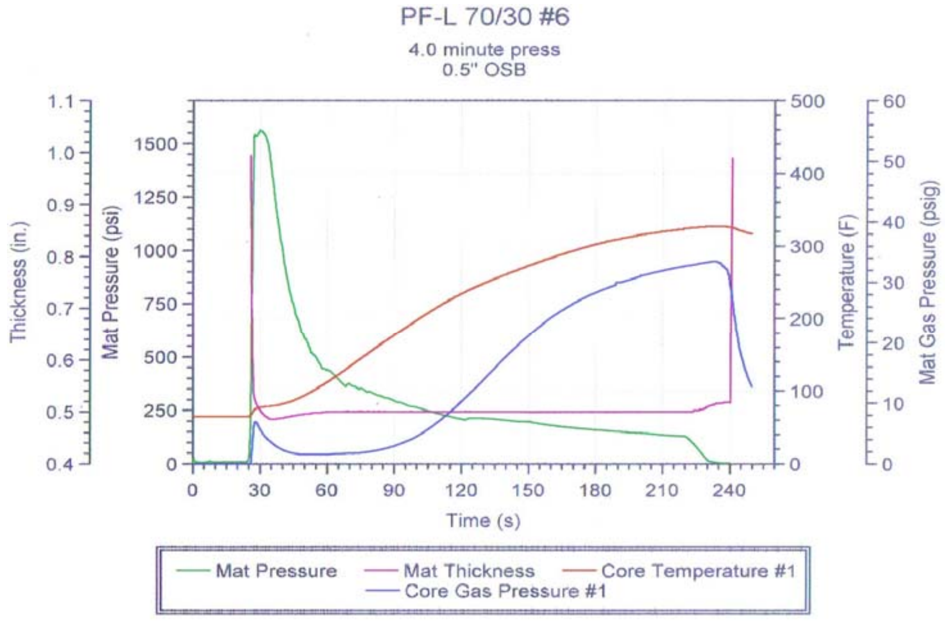


Figure C. 11 Hot-pressing data for 60/40 LPF resin in the core-layer mat.



PressMAN bio6 02-20

Figure C. 12 Hot-pressing data for 70/30 LPF resin in the core-layer mat.

Table C. 3 OSB internal bond (IB) test data of 2 h boil samples.

		thickness (in)	thickness 1 (in)	load (pound)	TS (%)	IB (psi)	IB avg (psi)
1	1	0.453	0.626	100.00	38.19	25.00	
	2	0.462	0.591	143.00	27.92	35.75	
	3	0.465	0.602	128.00	29.46	32.00	
	4	0.469	0.546	100.00	16.42	25.00	
	5	0.458	0.568	206.00	24.02	51.50	
	6	0.458	0.559	200.00	22.05	50.00	
	7	0.458	0.557	160.00	21.62	40.00	
	8	0.449	0.600	158.00	33.63	39.50	
	avg	**0.459**	**0.581**	**149.38**	**26.66**	**37.34**	
2	1	0.462	0.564	104.00	22.08	26.00	
	2	0.457	0.582	242.00	27.35	60.50	
	3	0.454	0.587	212.00	29.30	53.00	
	4	0.457	0.588	135.00	28.67	33.75	
	5	0.456	0.624	118.00	36.84	29.50	
	6	0.458	0.572	256.00	24.89	64.00	
	7	0.457	0.543	175.00	18.82	43.75	
	8	0.458	0.618	113.00	34.93	28.25	
	avg	**0.457**	**0.585**	**169.38**	**27.86**	**42.34**	39.84
3	1	0.465	0.656	113.00	41.08	28.25	Partially blown
	2	0.468	0.671	10.00	43.38	2.50	
	3	0.469	0.640	58.00	36.46	14.50	
	4	0.505	0.670	10.00	32.67	2.50	
	5	0.483	0.672	16.00	39.13	4.00	
	6	0.467	0.640	66.00	37.04	16.50	
	7	0.468	0.613	88.00	30.98	22.00	
	8	0.469	0.642	126.00	36.89	31.50	
	avg	**0.474**	**0.651**	**60.88**	**37.20**	**15.22**	
4	1	0.464	0.620	243.00	33.62	60.75	
	2	0.443	0.565	172.00	27.54	43.00	
	3	0.455	0.637	169.00	40.00	42.25	
	4	0.453	0.632	255.00	39.51	63.75	
	5	0.455	0.572	80.00	25.71	20.00	
	6	0.460	0.609	238.00	32.39	59.50	
	7	0.462	0.649	90.00	40.48	22.50	
	8	0.454	0.523	85.00	15.20	21.25	
	avg	**0.456**	**0.601**	**166.50**	31.84	**41.63**	41.63
5	1	0.452	0.625	198.00	38.27	49.50	
	2	0.451	0.571	200.00	26.61	50.00	
	3	0.447	0.576	136.00	28.86	34.00	
	4	0.454	0.578	296.00	27.31	74.00	
	5	0.451	0.565	240.00	25.28	60.00	

Table C. 3 (continued)

	6	0.461	0.603	136.00	30.80	34.00	
	7	0.450	0.587	190.00	30.44	47.50	
	8	0.459	0.593	155.00	29.19	38.75	
	avg	**0.453**	**0.587**	**193.88**	29.60	**48.47**	
6	1	0.450	0.648	140.00	44.00	35.00	
	2	0.451	0.621	155.00	37.69	38.75	
	3	0.499	0.579	120.00	16.03	30.00	
	4	0.452	0.614	235.00	35.84	58.75	
	5	0.453	0.665	228.00	46.80	57.00	
	6	0.450	0.592	215.00	31.56	53.75	
	7	0.450	0.566	205.00	25.78	51.25	
	8	0.451	0.617	205.00	36.81	51.25	
	avg	**0.457**	**0.613**	**187.88**	34.08	**46.97**	47.72
7	1	0.463	0.614	188.00	32.61	47.00	
	2	0.451	0.579	253.00	28.38	63.25	
	3	0.457	0.555	165.00	21.44	41.25	
	4	0.438	0.555	175.00	26.71	43.75	
	5	0.457	0.616	168.00	34.79	42.00	
	6	0.457	0.625	96.00	36.76	24.00	
	7	0.456	0.672	198.00	47.37	49.50	
	8	0.461	0.641	225.00	39.05	56.25	
	avg	**0.455**	**0.607**	**183.50**	33.43	**45.88**	
8	1	0.456	0.555	130.00	21.71	32.50	
	2	0.453	0.598	168.00	32.01	42.00	
	3	0.450	0.590	96.00	31.11	24.00	
	4	0.451	0.582	145.00	29.05	36.25	
	5	0.454	0.680	66.00	49.78	16.50	
	6	0.453	0.635	135.00	40.18	33.75	
	7	0.452	0.621	154.00	37.39	38.50	
	8	0.451	0.598	256.00	32.59	64.00	
	avg	**0.453**	**0.607**	**143.75**	34.23	**35.94**	40.91
9	1	0.450	0.600	118.00	33.33	29.50	
	2	0.454	0.634	136.00	39.65	34.00	
	3	0.450	0.693	100.00	54.00	25.00	
	4	0.456	0.677	103.00	48.46	25.75	
	5	0.460	0.603	126.00	31.09	31.50	
	6	0.460	0.617	102.00	34.13	25.50	
	7	0.447	0.583	124.00	30.43	31.00	
	8	0.453	0.628	196.00	38.63	49.00	
	avg	**0.454**	**0.629**	**125.63**	**38.71**	**31.41**	
10	1	0.446	0.587	188.00	31.61	47.00	Partially blown
	2	0.457	0.564	80.00	23.41	20.00	
	3	0.460	0.663	120.00	44.13	30.00	

Table C. 3 (continued)

	4	0.500	0.646	10.00	29.20	2.50	
	5	0.451	0.542	95.00	20.18	23.75	
	6	0.450	0.581	152.00	29.11	38.00	
	7	0.460	0.633	25.00	37.61	6.25	
	8	0.455	0.613	132.00	34.73	33.00	
	avg	**0.460**	**0.604**	**100.25**	**31.25**	**25.06**	31.41
11	1	0.452	0.605	150.00	33.85	37.50	
	2	0.445	0.652	80.00	46.52	20.00	
	3	0.451	0.680	180.00	50.78	45.00	
	4	0.468	0.626	180.00	33.76	45.00	
	5	0.465	0.703	84.00	51.18	21.00	
	6	0.463	0.645	130.00	39.31	32.50	
	7	0.460	0.619	162.00	34.57	40.50	
	8	0.452	0.573	80.00	26.77	20.00	
	avg	**0.457**	**0.638**	**130.75**	**39.59**	**32.69**	
12	1	0.545	0.728	10.00	33.58	2.50	Partially blown
	2	0.525	0.724	10.00	37.90	2.50	
	3	0.525	0.813	10.00	54.86	2.50	
	4	0.500	0.741	10.00	48.20	2.50	
	5	0.474	0.699	158.00	47.47	39.50	
	6	0.500	0.689	46.00	37.80	11.50	
	7	0.455	0.676	160.00	48.57	40.00	
	8	0.458	0.602	58.00	31.44	14.50	
	avg	**0.498**	**0.709**	**57.75**	**42.48**	**14.44**	32.69
13	1	0.457	0.697	140.00	52.52	35.00	
	2	0.452	0.678	102.00	50.00	25.50	
	3	0.449	0.648	104.00	44.32	26.00	
	4	0.449	0.679	66.00	51.22	16.50	
	5	0.443	0.657	132.00	48.31	33.00	
	6	0.465	0.662	124.00	42.37	31.00	
	7	0.444	0.639	135.00	43.92	33.75	
	8	0.451	0.631	60.00	39.91	15.00	
	avg	**0.451**	**0.661**	**107.88**	**46.57**	**26.97**	
14	1	0.525	0.661	10.00	25.90	2.50	
	2	0.446	0.662	68.00	48.43	17.00	
	3	0.454	0.656	122.00	44.49	30.50	
	4	0.459	0.704	104.00	53.38	26.00	
	5	0.456	0.625	50.00	37.06	12.50	
	6	0.448	0.683	80.00	52.46	20.00	
	7	0.461	0.593	152.00	28.63	38.00	
	8	0.452	0.654	110.00	44.69	27.50	
	avg	**0.463**	**0.655**	**87.00**	**41.88**	**21.75**	24.36
15	1	0.452	0.685	50.00	51.55	12.50	own

Table C. 3 (continued)

	2	0.463	0.637	10.00	37.58	2.50	
	3	0.450	0.687	10.00	52.67	2.50	
	4	0.452	0.653	10.00	44.47	2.50	
	5	0.495	0.709	70.00	43.23	17.50	
	6	0.471	0.670	60.00	42.25	15.00	
	7	0.562	0.725	10.00	29.00	2.50	
	8	0.536	0.753	28.00	40.49	7.00	
	avg	**0.485**	**0.690**	**31.00**	**42.65**	**7.75**	
16	1	0.490	0.744	26.00	51.84	6.50	Partially blown
	2	0.520	0.671	10.00	29.04	2.50	
	3	0.535	0.770	10.00	43.93	2.50	
	4	0.530	0.670	10.00	26.42	2.50	
	5	0.512	0.655	10.00	27.93	2.50	
	6	0.550	0.784	10.00	42.55	2.50	
	7	0.472	0.686	26.00	45.34	6.50	
	8	0.455	0.687	30.00	50.99	7.50	
	avg	**0.508**	**0.708**	**16.50**	**39.75**	**4.13**	5.94

Table C. 4 OSB MOR and MOE test data.

		weight g	thickness inch	width inch	length inch	density g/cm^3	density pcf	0.1" deflection	max load,p	P_1 pound	MOR psi	MOE kpsi	avg MOR psi	avg MOE kpsi
1	1	255.00	0.465	2.938	14.125	0.8083	50.4710	48.00	143.00	48.00	4052	702.0		
	2	265.00	0.471	2.957	14.125	0.8238	51.4372	44.00	139.00	44.00	3814	615.1		
	avg	260.00	0.468	2.948	14.125	0.8162	50.9541	46.00	141.00	46.00	3933	658.6		
2	1	238.00	0.450	2.923	14.125	0.7836	48.9258	33.00	87.00	33.00	2646	535.3		
	2	216.00	0.454	2.953	14.125	0.6977	43.5657	30.00	101.00	30.00	2987	469.1		
	avg	227.00	0.452	2.938	14.125	0.7403	46.2458	31.50	94.00	31.50	2817	502.2	3375	580.4
3	1	245.00	0.460	2.929	14.125	0.7873	49.1573	50.00	141.00	50.00	4094	757.5	partially blown	
	2	225.00	0.455	2.942	14.125	0.7277	45.4389	40.00	115.00	40.00	3398	623.5		
	avg	235.00	0.46	2.94	14.125	0.7576	47.2981	45.00	128.00	45.00	3746	690.5		
4	1	259.00	0.457	2.920	14.125	0.8406	52.4839	40.00	168.00	50.00	4959	775.2		
	2	242.00	0.453	2.947	14.125	0.7849	49.0090	42.00	186.00	52.00	5536	820.0		
	avg	250.50	0.455	2.933	14.125	0.8127	50.7465	41.00	177.00	51.00	5248	797.6	5248	797.6
5	1	221.00	0.438	2.939	14.125	0.7434	46.4192	35.00	108.00	45.00	3448	787.2		
	2	247.00	0.445	2.907	14.125	0.8269	51.6319	37.00	112.00	47.00	3503	792.7		
	avg	234.00	0.442	2.923	14.125	0.7852	49.0255	36.00	110.00	46.00	3475	790.0		
6	1	227.00	0.448	2.912	14.125	0.7534	47.0441	40.00	132.00	50.00	4065	824.9		
	2	235.00	0.448	2.925	14.125	0.7764	48.4790	52.00	163.00	52.00	4997	854.0		
	avg	231.00	0.448	2.919	14.125	0.7650	47.7616	46.00	147.50	51.00	4531	839.5	4003	814.75
7	1	233.00	0.437	2.940	14.125	0.7852	49.0254	51.00	139.00	51.00	4456	897.8		
	2	245.00	0.445	2.938	14.125	0.8113	50.6576	45.00	117.00	45.00	3619	750.8		
	avg	239.00	0.441	2.939	14.125	0.7984	49.8415	48.00	128.00	48.00	4037	824.3		
8	1	229.00	0.445	2.918	14.125	0.7636	47.6753	45.00	121.00	45.00	3769	755.9		
	2	244.00	0.449	2.966	14.125	0.7933	49.5298	50.00	147.00	50.00	4424	804.4		

	avg	236.50	0.447	2.942	14.125	0.7786	48.6026	47.50	134.00	47.50	4097	780.2	4067	802.25
9	1	249.00	0.442	2.920	14.125	0.8355	52.1698	50.00	167.00	50.00	5270	856.8	partially blown	
	2	232.00	0.442	2.933	14.125	0.7750	48.3925	50.00	113.00	50.00	3550	853.0		
	avg	240.50	0.442	2.926	14.125	0.8052	50.2812	50.00	140.00	50.00	4410	854.9		
10	1	222.00	0.446	2.944	14.125	0.7320	45.7071	49.00	122.00	49.00	3749	810.4		
	2	229.00	0.448	2.934	14.125	0.7544	47.1017	50.00	130.00	50.00	3974	818.7		
	avg	225.50	0.447	2.939	14.125	0.7432	46.4044	49.50	126.00	49.50	3862	814.6	4410	854.9
11	1	237.00	0.443	2.929	14.125	0.7910	49.3902	40.00	142.50	40.00	4463	678.7	partially blown	
	2	246.00	0.452	2.929	14.125	0.8047	50.2450	40.00	145.00	40.00	4362	639.0		
	avg	241.50	0.448	2.929	14.125	0.7979	49.8219	40.00	143.75	40.00	4413	658.8		
12	1	238.00	0.448	2.919	14.125	0.7880	49.2039	41.00	151.00	41.00	4639	674.8		
	2	217.00	0.428	2.931	14.125	0.7489	46.7631	35.00	122.00	35.00	4090	657.9		
	avg	227.50	0.438	2.925	14.125	0.7689	48.0066	38.00	136.50	38.00	4364	666.3	4413	658.8
13	1	222.00	0.435	2.920	14.125	0.7569	47.2613	25.00	125.50	30.00	4089	539.3		
	2	227.00	0.444	2.923	14.125	0.7575	47.2951	38.00	124.00	38.00	3874	641.7		
	avg	224.50	0.440	2.921	14.125	0.7572	47.2787	31.50	124.75	34.00	3981	590.5		
14	1	228.00	0.434	2.946	14.125	0.7723	48.2210	37.00	138.00	37.00	4477	663.8		
	2	236.00	0.468	2.918	14.125	0.7484	46.7306	15.00	66.50	15.00	1873	216.7		
	avg	232.00	0.451	2.932	14.125	0.7598	47.4428	26.00	102.25	26.00	3175	440.2	3578	515.35
15	1	230.00	0.442	2.907	14.125	0.7750	48.3914	38.00	111.00	38.00	3518	653.9	partially blown	
	2	225.00	0.424	2.953	14.125	0.7780	48.5789	32.50	111.00	32.50	3763	623.7		
	avg	227.50	0.433	2.930	14.125	0.7764	48.4760	35.25	111.00	35.25	3640	638.8		
16	1	226.00	0.442	2.907	14.125	0.7616	47.5563	32.00	122.50	32.00	3883	550.7	partially blown	
	2	215.00	0.435	2.903	14.125	0.7371	46.0258	30.00	100.50	30.00	3293	542.3		
	avg	220.50	0.439	2.905	14.125	0.7495	46.7978	31.00	111.50	31.00	3588	546.5	3614	592.65

P_1 - load at 0.1" deflection

Table C. 5 OSB water-soak test data.

		thickness	dry weight	2 h water soak						24 h water soak					
		inch	gram	wet wt., g	wet th, in	TS, %	wt,%	avg TS, %	avg wt, %	wet wt., g	wet th, in	TS, %	wt,%	avg TS, %	avg wt,%
1	1	0.452	193.00	208.00	0.470	3.98	7.77			263.00	0.487	7.74	36.27		
	2	0.445	177.00	194.00	0.462	3.82	9.60			257.00	0.493	10.79	45.20		
	avg	0.449	185.00	201.00	0.466	3.90	8.69			260.00	0.490	9.26	40.73		
2	1	0.458	209.00	223.00	0.470	2.62	6.70			268.00	0.498	8.73	28.23		
	2	0.465	205.00	220.00	0.487	4.73	7.32			274.00	0.493	6.02	33.66		
	avg	0.462	207.00	221.50	0.479	3.68	7.01	**3.79**	**7.85**	271.00	0.496	7.38	30.94	**8.32**	**35.84**
3	1	0.471	216.00	243.00	0.488	3.61	12.50			331.00	0.555	17.83	53.24		
	2	0.477	210.00	235.00	0.506	6.08	11.90			325.00	0.555	16.35	54.76		
	avg	0.474	213.00	239.00	0.497	4.84	12.20			328.00	0.555	17.09	54.00		
4	1	0.462	211.00	226.00	0.480	3.90	7.11			277.00	0.500	8.23	31.28		
	2	0.457	188.00	207.00	0.474	3.72	10.11			273.00	0.498	8.97	45.21		
	avg	0.460	199.50	216.50	0.477	3.81	8.61	**3.81**	**8.61**	275.00	0.499	8.60	38.25	**8.60**	**38.25**
5	1	0.462	186.00	203.00	0.482	4.33	9.14			260.00	0.498	7.79	39.78		
	2	0.457	214.00	229.00	0.471	3.06	7.01			278.00	0.485	6.13	29.91		
	avg	0.460	200.00	216.00	0.477	3.70	8.07			269.00	0.492	6.96	34.85		
6	1	0.452	212.00	224.00	0.469	3.76	5.66			273.00	0.483	6.86	28.77		
	2	0.443	198.00	214.00	0.469	5.87	8.08			272.00	0.492	11.06	37.37		
	avg	0.448	205.00	219.00	0.469	4.82	6.87	**4.26**	**7.47**	272.50	0.488	8.96	33.07	**7.96**	**33.96**
7	1	0.454	219.00	235.00	0.473	4.19	7.31			290.00	0.493	8.59	32.42		
	2	0.460	214.00	229.00	0.467	1.52	7.01			284.00	0.489	6.30	32.71		
	avg	0.457	216.50	232.00	0.470	2.85	7.16			287.00	0.491	7.45	32.57		
8	1	0.461	207.00	223.00	0.472	2.39	7.73			282.00	0.497	7.81	36.23		
	2	0.450	208.00	224.00	0.472	4.89	7.69			284.00	0.504	12.00	36.54		
	avg	0.456	207.50	223.50	0.472	3.64	7.71	**3.25**	**7.44**	283.00	0.501	9.90	36.39	**8.68**	**34.48**

9	1	0.457	196.00	211.00	0.469	2.63	7.65			272.00	0.497	8.75	38.78		
	2	0.457	212.00	227.00	0.472	3.28	7.08			284.00	0.483	5.69	33.96		
	avg	0.457	204.00	219.00	0.471	2.95	7.36			278.00	0.490	7.22	36.37		
10	1	0.453	192.00	208.00	0.470	3.75	8.33			267.00	0.493	8.83	39.06		
	2	0.458	204.00	219.00	0.465	1.53	7.35			274.00	0.484	5.68	34.31		
	avg	0.456	198.00	213.50	0.468	2.64	7.84	**2.95**	**7.36**	270.50	0.489	7.25	36.69	**7.22**	**36.37**
11	1	0.456	217.00	231.00	0.475	4.17	6.45			286.00	0.498	9.21	31.80		
	2	0.463	200.00	218.00	0.467	0.86	9.00			288.00	0.503	8.64	44.00		
	avg	0.460	208.50	224.50	0.471	2.52	7.73			287.00	0.501	8.92	37.90		
12	1	0.468	195.00	213.00	0.484	3.42	9.23			282.00	0.518	10.68	44.62		
	2	0.464	222.00	235.00	0.480	3.45	5.86			285.00	0.494	6.47	28.38		
	avg	0.466	208.50	224.00	0.482	3.43	7.54	**2.52**	**7.73**	283.50	0.506	8.57	36.50	**8.92**	**37.90**
13	1	0.447	220.00	231.00	0.460	2.91	5.00			277.00	0.479	7.16	25.91		
	2	0.452	208.00	222.00	0.470	3.98	6.73			276.00	0.478	5.75	32.69		
	avg	0.450	214.00	226.50	0.465	3.45	5.87			276.50	0.479	6.46	29.30		
14	1	0.445	196.00	209.00	0.462	3.82	6.63			267.00	0.478	7.42	36.22		
	2	0.462	210.00	229.00	0.465	0.65	9.05			297.00	0.512	10.82	41.43		
	avg	0.454	203.00	219.00	0.464	2.23	7.84	**2.84**	**6.86**	282.00	0.495	9.12	38.83	**7.79**	**34.07**
15	1	0.467	215.00	231.00	0.468	0.21	7.44			304.00	0.530	13.49	41.40		
	2	0.455	206.00	222.00	0.465	2.20	7.77			285.00	0.478	5.05	38.35		
	avg	0.461	210.50	226.50	0.467	1.21	7.60			294.50	0.504	9.27	39.87		
16	1	0.455	199.00	217.00	0.484	6.37	9.05			300.00	0.491	7.91	50.75		
	2	0.454	216.00	229.00	0.472	3.96	6.02			288.00	0.496	9.25	33.33		
	avg	0.455	207.50	223.00	0.478	5.17	7.53	**3.19**	**7.57**	294.00	0.494	8.58	42.04	**8.93**	**40.96**

TS- thickness swell
WT- water soaked

Table C. 6 OSB internal bond (IB) test data

		thickness inch	length mm	Length Inch	width mm	width inch	weight g	dencity g/cm3	dencity d, p/f^3	breaking load pound	IB psi	avg (psi)	avg1 IB (psi)
1	1	0.460	50.72	1.998	50.44	1.987	24.00	0.8035	**50.1705**	374.00	**94.17**		
	2	0.462	50.67	1.996	50.46	1.988	22.00	0.7338	**45.8176**	190.00	**47.87**		
	3	0.461	50.36	1.984	50.66	1.996	20.00	0.6700	**41.8339**	220.00 c	**55.55**		
	4	0.455	50.60	1.994	50.21	1.978	22.00	0.7498	**46.8188**	370.00	**93.81**		
	5	0.455	50.44	1.987	50.52	1.990	22.00	0.7476	**46.6791**	160.00 c	**40.45**		
	6	0.455	50.30	1.982	50.66	1.996	21.00	0.7136	**44.5579**	359.00	**90.75**		
	7	0.446	50.76	2.000	50.53	1.991	20.00	0.6888	**43.0104**	316.00	**79.36**		
	8	0.457	50.44	1.987	50.76	2.000	25.00	0.8418	**52.5626**	370.00 c	**93.09**		
		0.456	**50.54**	**1.991**	**50.53**	**1.991**	**22.00**	**0.7436**	**46.4314**	**294.88**	**74.38**	62.38	
									42.0000		**66.67**		
2	1	0.455	50.69	1.997	50.44	1.987	25.00	0.8467	**52.8665**	490.00	**123.45**		
	2	0.462	50.64	1.995	50.74	1.999	22.00	0.7302	**45.5917**	546.00	**136.89**		
	3	0.458	50.72	1.998	50.39	1.985	25.00	0.8415	**52.5413**	478.00	**120.48**		
	4	0.455	50.80	2.002	50.82	2.002	23.00	0.7715	**48.1690**	300.00	**74.86**		
	5	0.455	50.64	1.995	50.64	1.995	25.00	0.8442	**52.7097**	404.00	**101.48**		
	6	0.453	50.69	1.997	50.39	1.985	28.00	0.9534	**59.5310**	244.00 c	**61.54**		
	7	0.461	50.59	1.993	50.67	1.996	24.00	0.8002	**49.9625**	378.00	**94.99**		
	8	0.452	50.48	1.989	50.64	1.995	25.00	0.8525	**53.2278**	335.00	**84.42**		
		0.456	**50.66**	**1.996**	**50.59**	**1.993**	**24.63**	**0.8300**	51.8249		99.76	105.22	83.8
									42.0000		**117.05**		
3	1	0.468	50.59	1.993	50.64	1.995	23.00	0.7558	**47.1925**	10.00	**2.51**	Partially blown	
	2	0.461	50.39	1.985	50.88	2.005	23.00	0.7667	**47.8724**	232.00	**58.29**		
	3	0.467	50.39	1.985	50.64	1.995	24.00	0.7935	**49.5457**	296.00	**74.72**		
	4	0.463	50.67	1.996	50.44	1.987	21.00	0.6992	**43.6578**	200.00	**50.41**		
	5	0.468	50.73	1.999	50.27	1.981	26.00	0.8583	**53.5924**	296.00	**74.77**		
	6	0.470	50.69	1.997	50.10	1.974	22.00	0.7262	**45.3434**	296.00	**75.08**		

	7	0.484	50.73	1.999	50.49	1.989	22.00	0.6992	**43.6573**	6.00	c	**1.51**		
	8	0.473	50.31	1.982	50.71	1.998	26.00	0.8489	**53.0047**	336.00	w	**84.84**		
		0.469	**50.56**	**1.992**	**50.52**	**1.991**	**23.38**	**0.7685**	**47.9833**			**52.77**		
									42.0000			**37.95**		
4	1	0.451	50.60	1.994	50.39	1.985	25.00	0.8566	**53.4833**	424.00		**107.12**		
	2	0.448	50.44	1.987	50.62	1.994	22.00	0.7578	**47.3148**	428.00	c	**107.98**		
	3	0.465	50.54	1.991	50.44	1.987	26.00	0.8642	**53.9585**	296.00	c	**74.80**		
	4	0.464	50.66	1.996	50.49	1.989	25.00	0.8299	**51.8204**	438.00	c	**110.31**		
	5	0.459	50.60	1.994	50.29	1.981	23.00	0.7759	**48.4432**	408.00	wood	**103.28**		
	6	0.461	50.69	1.997	50.34	1.983	24.00	0.8038	**50.1908**	450.00		**113.60**		
	7	0.465	50.63	1.995	50.31	1.982	26.00	0.8649	**54.0018**	326.00	c	**82.44**		
	8	0.460	50.64	1.995	50.54	1.991	26.00	0.8701	**54.3296**	482.00	c	**121.32**		
		0.459	**50.60**	**1.994**	**50.43**	**1.987**	**24.63**	**0.8279**	**51.6928**			**102.61**	102.61	102.61
									42.0000	119.80		**110.85**		
5	1	0.461	50.38	1.985	50.54	1.991	19.00	0.6378	**39.8207**	234.00		**59.20**		
	2	0.456	50.59	1.993	50.39	1.985	23.00	0.7796	**48.6747**	380.00		**96.02**		
	3	0.451	50.52	1.990	50.85	2.003	25.00	0.8502	**53.0834**	550.00	w	**137.92**		
	4	0.455	50.68	1.997	50.50	1.990	25.00	0.8459	**52.8142**	442.00	w	**111.25**		
	5	0.453	50.26	1.980	50.07	1.973	23.00	0.7949	**49.6340**	262.00	c	**67.07**		
	6	0.451	50.69	1.997	50.57	1.992	24.00	0.8179	**51.0704**	418.00		**105.04**		
	7	0.454	50.66	1.996	50.49	1.989	26.00	0.8822	**55.0803**	512.00		**128.95**		
	8	0.456	51.02	2.010	50.60	1.994	26.00	0.8702	**54.3334**	422.00		**105.30**		
		0.455	**50.60**	**1.994**	**50.50**	**1.990**	**23.88**	**0.8098**	**50.5639**			**101.34**	91.95	
									42.0000			**68.64**		
6	1	0.453	50.48	1.989	50.62	1.994	26.00	0.8850	**55.2565**	612.00		**154.28**		
	2	0.453	50.59	1.993	50.88	2.005	27.00	0.9123	**56.9644**	456.00		**114.12**		
	3	0.453	50.83	2.003	50.67	1.996	26.00	0.8780	**54.8219**	430.00		**107.55**		
	4	0.456	50.44	1.987	50.86	2.004	21.00	0.7073	**44.1624**	350.00		**87.89**		
	5	0.446	50.41	1.986	50.87	2.004	23.00	0.7923	**49.4725**	280.00		**70.34**		
	6	0.449	50.26	1.980	50.69	1.997	26.00	0.8955	**55.9155**	480.00		**121.37**		

	7	0.454	50.64	1.995	50.57	1.992	24.00	0.8133	**50.7830**	416.00		**104.64**		
	8	0.452	50.63	1.995	50.69	1.997	22.00	0.7472	**46.6556**	348.00		**87.35**		
		0.452	**50.54**	**1.991**	**50.73**	**1.999**	**24.38**	**0.8289**	**51.7540**			**105.94**	105.94	98.945
									42.0000			**68.69**		
7	1	0.455	50.46	1.988	49.89	1.966	22.00	0.7567	**47.2498**	292.00		**74.72**		
	2	0.448	50.55	1.992	50.16	1.976	20.00	0.6937	**43.3135**	288.00		**73.17**		
	3	0.453	50.60	1.994	49.88	1.965	24.00	0.8271	**51.6399**	346.00	c	**88.31**		
	4	0.454	50.57	1.992	48.97	1.929	22.00	0.7710	**48.1386**	306.00		**79.60**		
	5	0.446	50.08	1.973	50.62	1.994	24.00	0.8363	**52.2203**	450.00		**114.35**		
	6	0.457	50.50	1.990	49.02	1.931	26.00	0.9055	**56.5382**	286.00	c	**74.42**		
	7	0.457	50.55	1.992	49.59	1.954	27.00	0.9286	**57.9805**	295.00		**75.81**		
	8	0.456	50.57	1.992	49.27	1.941	25.00	0.8670	**54.1314**	256.00	c	**66.19**		
		0.453	**50.49**	**1.989**	**49.68**	**1.957**	**23.75**	**0.8232**	**51.4015**			**80.82**	82.91	
									42.0000			80.02		
8	1	0.450	50.46	1.988	50.72	1.998	23.00	0.7868	**49.1291**	336.00		**84.57**		
	2	0.457	50.44	1.987	50.49	1.989	24.00	0.8125	**50.7299**	302.00		**76.39**		
	3	0.451	50.41	1.986	50.67	1.996	23.00	0.7866	**49.1172**	320.00		**80.70**		
	4	0.452	50.34	1.983	50.55	1.992	22.00	0.7536	**47.0543**	258.00		**65.31**		
	5	0.447	50.31	1.982	50.67	1.996	25.00	0.8644	**53.9731**	424.00		**107.14**		
	6	0.458	50.57	1.992	50.29	1.981	23.00	0.7780	**48.5778**	398.00		**100.81**		
	7	0.443	50.62	1.994	50.52	1.990	23.00	0.7999	**49.9446**	218.00	c	**54.91**		
	8	0.460	50.39	1.985	50.52	1.990	20.00	0.6729	**42.0159**	140.00	c	**35.43**		
		0.452	**50.44**	**1.987**	**50.55**	**1.992**	**22.88**	**0.7819**	**48.8177**			**75.66**	85.82	84.365
									42.0000			**52.09**		
9	1	0.457	50.57	1.992	50.38	1.985	20.00	0.6768	**42.2583**	200.00		**50.57**		
	2	0.462	50.82	2.002	50.41	1.986	27.00	0.8988	**56.1203**	456.00		**114.66**		
	3	0.452	50.68	1.997	50.30	1.982	24.00	0.8207	**51.2410**	332.00		**83.90**		
	4	0.461	50.48	1.989	50.46	1.988	24.00	0.8053	**50.2798**	340.00		**85.98**		
	5	0.464	50.55	1.992	50.21	1.978	23.00	0.7695	**48.0450**	382.00		**96.95**		

	6	0.448	50.40	1.986	50.21	1.978	23.00	0.7993	**49.9090**	380.00		**96.73**		
	7	0.452	50.34	1.983	50.76	2.000	25.00	0.8528	**53.2496**	300.00		**75.63**		
	8	0.458	50.62	1.994	50.44	1.987	25.00	0.8423	**52.5929**	225.00		**56.77**		
		0.457	**50.56**	**1.992**	**50.40**	**1.986**	**23.88**	**0.8082**	**50.4620**			**82.65**	82.65	
									42.0000			**59.24**		
10	1	0.454	50.59	1.993	50.46	1.988	21.00	0.7139	**44.5760**	376.00		**94.88**	Partially blown	
	2	0.450	50.71	1.998	50.36	1.984	24.00	0.8228	**51.3770**	380.00		**95.85**		
	3	0.452	50.31	1.982	50.69	1.997	24.00	0.8203	**51.2207**	310.00		**78.31**		
	4	0.448	50.54	1.991	50.39	1.985	26.00	0.8979	**56.0616**	428.00		**108.26**		
	5	0.442	50.21	1.978	50.59	1.993	25.00	0.8773	**54.7788**	310.00		**78.62**		
	6	0.450	50.25	1.980	50.73	1.999	22.00	0.7556	**47.1801**	40.00		**10.11**		
	7	0.457	50.21	1.978	50.50	1.990	23.00	0.7820	**48.8292**	364.00		**92.48**		
	8	0.457	50.30	1.982	50.54	1.991	24.00	0.8139	**50.8208**	402.00	c	**101.87**		
		0.451	**50.39**	**1.985**	**50.53**	**1.991**	**23.63**	**0.8105**	**50.6055**			**82.55**		82.65
									42.0000	57.27		**92.02**		
11	1	0.485	50.46	1.988	50.74	1.999	27.00	0.8567	**53.4902**	332.00		**83.53**		
	2	0.452	50.34	1.983	50.64	1.995	23.00	0.7865	**49.1057**	408.00		**103.10**		
	3	0.450	50.36	1.984	50.45	1.988	21.00	0.7237	**45.1866**	234.00	c	**59.33**		
	4	0.443	50.39	1.985	50.64	1.995	25.00	0.8714	**54.4061**	408.00		**103.00**		
	5	0.455	50.35	1.984	50.63	1.995	24.00	0.8152	**50.9029**	220.00	c	**55.59**		
	6	0.459	50.33	1.983	50.59	1.993	25.00	0.8428	**52.6242**	392.00		**99.17**		
	7	0.460	50.24	1.979	50.90	2.005	24.00	0.8039	**50.1921**	398.00		**100.26**		
	8	0.454	50.41	1.986	50.82	2.002	24.00	0.8130	**50.7638**	330.00		**82.98**		
		0.457	**50.36**	**1.984**	**50.68**	**1.997**	**24.13**	**0.8141**	**50.8339**	57.40		**85.87**	95.34	
									42.0000			**101.21**		
12	1	0.451	50.77	2.000	49.68	1.957	25.00	0.8659	**54.0660**	308.00		**78.66**	Partially blown	
	2	0.455	49.55	1.952	50.66	1.996	23.00	0.7934	**49.5401**	282.00		**72.37**		
	3	0.457	50.83	2.003	50.41	1.986	26.00	0.8748	**54.6223**	440.00		**110.62**		
	4	0.460	50.53	1.991	49.08	1.934	20.00	0.6907	**43.1289**	118.00	c	**30.65**		

	5	0.460	49.78	1.961	50.57	1.992	23.00	0.7826	**48.8621**	278.00		**71.14**		
	6	0.460	50.48	1.989	50.19	1.977	19.00	0.6423	**40.1060**	90.00		**22.88**		
	7	0.462	50.68	1.997	50.29	1.981	26.00	0.8700	**54.3204**	166.00		**41.96**		
	8	0.459	50.54	1.991	50.10	1.974	21.00	0.7119	**44.4512**	276.00		**70.22**		
		0.458	**50.40**	**1.986**	**50.12**	**1.975**	**22.88**	**0.7790**	**48.6371**			**62.31**		95.34
									42.0000			**44.63**		
13	1	0.442	50.50	1.990	50.41	1.986	25.00	0.8754	**54.6587**	420.00		**106.28**		
	2	0.450	50.67	1.996	50.44	1.987	21.00	0.7194	**44.9190**	216.00		**54.44**		
	3	0.432	50.62	1.994	50.34	1.983	23.00	0.8232	**51.3994**	374.00		**94.55**		
	4	0.443	50.38	1.985	50.82	2.002	23.00	0.7990	**49.8863**	290.00	c	**72.96**		
	5	0.446	50.73	1.999	50.36	1.984	25.00	0.8645	**53.9764**	440.00		**110.95**		
	6	0.438	50.77	2.000	50.45	1.988	24.00	0.8429	**52.6282**	410.00		**103.12**		
	7	0.442	50.68	1.997	50.35	1.984	22.00	0.7685	**47.9859**	290.00	c	**73.21**		
	8	0.450	50.54	1.991	50.36	1.984	23.00	0.7912	**49.4019**	268.00		**67.83**		
		0.443	**50.61**	**1.994**	**50.44**	**1.987**	**23.25**	**0.8105**	**50.6070**			**85.42**	89.53	
									42.0000			**33.03**		
14	1	0.456	50.19	1.977	50.36	1.984	24.00	0.8204	**51.2263**	292.00		**74.42**		
	2	0.445	50.11	1.974	50.52	1.990	24.00	0.8394	**52.4099**	374.00		**95.17**		
	3	0.445	50.07	1.973	50.63	1.995	23.00	0.8033	**50.1571**	358.00		**90.97**		
	4	0.452	50.44	1.987	50.67	1.996	26.00	0.8868	**55.3680**	212.00	c	**53.43**		
	5	0.521	50.33	1.983	50.54	1.991	25.00	0.7433	**46.4077**	50.00		**12.66**		
	6	0.459	50.52	1.990	49.98	1.969	21.00	0.7139	**44.5756**	202.00		**51.53**		
	7	0.489	50.73	1.999	50.24	1.979	24.00	0.7587	**47.3737**	50.00		**12.64**		
	8	0.450	50.52	1.990	50.30	1.982	22.00	0.7580	**47.3291**	280.00		**70.98**		
		0.465	**50.36**	**1.984**	**50.41**	**1.986**	**23.63**	**0.7905**	**49.3559**			**57.73**	58.34	73.935
									42.0000			**27.07**		
15	1	0.461	50.77	2.000	50.44	1.987	25.00	0.8344	**52.0963**	210.00		**52.83**	Partially blown	
	2	0.452	50.53	1.991	50.46	1.988	21.00	0.7179	**44.8264**	180.00		**45.48**		
	3	0.450	50.57	1.992	50.58	1.993	24.00	0.8215	**51.2952**	140.00	c	**35.26**		

	4	0.450	50.48	1.989	50.31	1.982	24.00	0.8274	**51.6624**	260.00		**65.95**		
	5	0.442	50.76	2.000	50.25	1.980	23.00	0.8038	**50.1877**	396.00		**100.01**		
	6	0.452	50.40	1.986	50.73	1.999	23.00	0.7841	**48.9603**	340.00		**85.66**		
	7	0.448	50.29	1.981	50.55	1.992	24.00	0.8303	**51.8418**	360.00	c	**91.22**		
	8	0.451	50.46	1.988	50.67	1.996	23.00	0.7859	**49.0685**	250.00		**62.99**		
		0.451	**50.53**	**1.991**	**50.50**	**1.990**	**23.38**	**0.8007**	**49.9923**			**67.42**	72.02	
									42.0000			**47.66**		
16	1	0.455	49.27	1.941	50.19	1.977	24.00	0.8404	**52.4747**	214.00		**55.75**	Partially blown	
	2	0.453	50.64	1.995	50.58	1.993	26.00	0.8829	**55.1255**	298.00		**74.95**		
	3	0.426	50.26	1.980	50.80	2.002	22.00	0.7969	**49.7596**	260.00		**65.60**		
	4	0.445	50.41	1.986	50.49	1.989	23.00	0.8001	**49.9569**	230.00		**58.21**		
	5	0.446	50.63	1.995	50.46	1.988	21.00	0.7261	**45.3397**	160.00	c	**40.34**		
	6	0.448	50.49	1.989	50.49	1.989	24.00	0.8280	**51.6978**	350.00		**88.44**		
	7	0.453	50.63	1.995	50.24	1.979	24.00	0.8206	**51.2395**	230.00	c	**58.25**		
	8	0.440	50.36	1.984	50.85	2.003	23.00	0.8043	**50.2167**	184.00	c	**46.29**		
		0.446	**50.34**	**1.983**	**50.51**	**1.990**	**23.38**	**0.8124**	**50.7263**			**60.98**	60.98	66.5
									42.0000			**46.48**		

average 1- average of IB excluding boards due to curve; and excluding blown boards