

AN EXPLORATORY STUDY ON THE REMOVAL OF ACETIC AND FORMIC ACIDS FROM BIO-OIL

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Bio-oil produced from fast pyrolysis of biomass contains various levels of acetic and formic acids derived from breakdown of cellulose and hemicellulose components. Removal of these organic acids from bio-oil was investigated for use as industrial chemicals as well as to improve the quality of recovered bio-oil as fuel in various applications. Calcium oxide and a quaternary ammonium anion-exchange resin were used to form acid salts of the organic acids, which were then separated, and the organic acids were generated by reacting with sulfuric acid. Both methods were found to be effective in limited ways and various difficulties encountered in this approach are discussed.

Keywords: Bio-oil; Pyrolysis of wood; Acetic acid; Formic acid; Pyrolytic lignin

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INTRODUCTION

The fast pyrolysis method has been reported to be a promising approach to the conversion of biomass materials to liquid bio-oil and gaseous and char byproducts. The fast pyrolysis method typically results in 75% bio-oil, 13% gas, and 12% char based on dry biomass weight (Bridgwater 1999; New Hampshire 2004). Bio-oils produced from various biomass were found to contain 5-10% organic acids, 5-20% aldehydes and hydroxyaldehydes, 0-10% ketones and hydroxyketones, 20-30% phenolics, and 15-30% water. In all, bio-oils are a mixture of more than 400 chemicals derived from cellulose, hemicellulose, and lignin components through their thermal breakdown (Diebold and Bridgwater 2002; Czernik and Bridgwater 2004 and 2005; Ingram et al. 2007).

Formic and acetic and other organic acid components in bio-oils have been implicated in corrosion of metals and storage instability of bio-oil in fuel uses (Agblevor 1995; Diebold and Bridgwater 2002). The corrosiveness of bio-oils is more severe when the water content is high and also when bio-oils are used at high temperatures (Czernik 1999), and removal of the acids can be a useful approach to reducing the corrosiveness. Bio-oils have also been considered as sources of various industrial chemicals (Radelin 1999), and separation of the lignin components was reported by using ethyl acetate as solvent for lignin and sodium bicarbonate solution for washing out organic acids from the solution to result in pyrolytic lignin in 31% yield based on bio-oil weight. The isolated lignin was also shown to be satisfactory as a partial replacement of phenol in synthesizing various phenol-formaldehyde resins (Chum and Black 1990; Chum and Kreibich 1992). Further, separation of the lignin fraction was investigated by using only methanol and water as a lower cost method of separation to obtain lignin in about 25% yield, and the

product was shown to be effective as a phenol replacement up to 40% in synthesizing oriented strand board core-layer binder phenol-formaldehyde resins (Sukhbataar 2008; Sukhbataar et al. 2008).

Removal of acetic and formic acids from bio-oils has also been investigated by various authors. The product “liquid smoke,” which is sold as a food processing aid, is known to derive from the water-soluble fraction of bio-oil (Meier et al. 2001; Czernic and Bridgwater 2005). The water-soluble fraction of bio-oil contains various organic acids, aldehydes, and simple phenolic components (Ingram et al. 2007). A further distillation of the water-soluble fraction was reported to give a fraction containing formic and acetic acids as well as some other volatile components, and treating it with calcium oxide led to form calcium salts of organic acids as precipitates (Oehr et al. 1993). The calcium salts could be treated with a strong inorganic acid to recover the acids or used for manufacturing other chemicals. However, the distillation process would be costly, and development of lower cost separation methods has been desirable. Removal of acetic acid from bio-oil has also been investigated by an extraction method using trioctylamine dissolved in octane, but the result indicated its impracticality due to a good amount of the tertiary amine being transferred into the bio-oil layer. In this work exploratory experiments were carried out using calcium oxide and an anion-exchange resin, with direct addition to bio-oil to form acetic and formic acid salts, aiming at a more economical way of removing and obtaining organic acids from bio-oils.

EXPERIMENTAL

Materials

Pine wood bio-oil was produced in an auger reactor at the Department of Forest Products, MSU. Reagent-grade calcium oxide and Dowex-22 anion-exchange resin were obtained from Aldrich Chemical Company.

Methods

Gas chromatography/mass spectrometry (GC/MS)

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

Determination of acetic acid concentrations in samples from GC/MS

A calibration equation was obtained from GC/MS integration values of acetic acid peaks of 50, 100, 150, and 200 ppm standard solutions of pure acetic acid in methanol.

The correlation between the acetic acid concentration and integration area counts of acetic acid peak resulted in the following correlation equation,

$$y = 301267x + 3E06 \text{ (R}^2 = 0.994\text{)} \quad (1)$$

where x is the acid concentration and y is the integration area counts. By using this equation, the acetic and formic acid amounts were calculated in GC/MS results from various samples.

Exploratory experiments for removal of organic acids using calcium oxide

The experiment was carried out in a stirred reactor by dissolving bio-oil in an equal weight of methanol and then adding incremental amounts of calcium oxide, while the resultant pH values of the mixture was monitored using a pH meter. After the heat of neutralization subsided, the precipitates were collected by filtration, washed with methanol, dried and quantified. The precipitates were then treated in methanol with dilute sulfuric acid solution to free the acids, while the filtrates were combined, and the methanol solvent was evaporated on a rotor evaporator to recover the residual bio-oil.

A typical procedure was as follows: in a stirred reactor, 50 g bio-oil and 50g methanol were charged and mixed for about 10 min to result in a uniform solution with the pH value reaching about 3.61. To this solution, 1.77 g calcium oxide was added incrementally and stirring continued, the temperature of reaction mixture rising to 56°C. The stirring was continued for approximately 4 h, when the temperature fell to room temperature and the pH value of the reaction mixture reached 7.0. The formed precipitates were collected by filtration under water vacuum and washed with a small amount of methanol to yield 2.22g solid organic acid calcium salts. Similar experiments were conducted to reach target pH values of 8, 9, and 10 by adding increased amounts of calcium oxide.

Characterization of calcium salts and recovered bio-oil samples

Approximately one gram of calcium salt sample was suspended and stirred in 10 mL methanol, and 8% sulfuric acid solution was added in small amounts until the pH of mixture reached 2.2. The mixture was then filtered to remove the calcium sulfate, and the filtrate was dried of water over anhydrous sodium sulfate, treated with a small amount of sodium bicarbonate powder to remove free sulfuric acid, and analyzed on GC/MS. For characterization of recovered bio-oil samples, GC/MS analyses were carried out, and ash contents were also determined by burning approximately one gram of sample in a furnace at 427°C for 2 h and measuring the residual ash weights.

Exploratory experiments for removal of organic acids using an anion exchange resin

Dowex-22, an anion exchange resin, was first regenerated by stirring in 0.1N NaOH solution for 2 h and washing with distilled water until pH 7.0 to obtain the quaternary ammonium hydroxide form. The resin was filtered under light vacuum and transferred into a small amount of methanol to prevent it from drying. A typical column procedure was carried out as follows: A mixture of 80 g bio-oil and 80 g methanol was made and, separately, 74 g of ion-exchange resin and some methanol were loaded in a 3.0

cm diameter 40cm long glass column and packed by vibration. Then, the bio-oil/methanol solution was allowed to slowly elute through the ion-exchange resin column by gravity and about 10mL fractions were collected. During the elution period the pH of the eluting solution was monitored and the fractions were analyzed on GC/MS.

Since the small-scale anion-exchange resin column experiments were somewhat unsatisfactory due to the uneven elution, a batch treatment method was carried out 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 3.61. Then, anion-exchange resin was added in small amounts while stirring continuously until the pH of the mixture reached 6.98. The anion-exchange resin was collected by filtration and washed several times with small amounts of methanol to recover it as organic acid salts. The organic acids were recovered from the resin by stirring it in 100 mL 0.1N NaOH solution for 2 h, followed by filtration, evaporation of the filtrate to obtain the residues of organic acid sodium salts, and acidifying the residues in methanol to pH 2.2 using 8% sulfuric acid solution. The acidified methanol solution was dried over anhydrous sodium sulfate, treated with a small amount of sodium bicarbonate powder, and analyzed on GC/MS. The original filtrate and methanol washings were combined and evaporated to give the recovered bio-oil, which was analyzed on GC/MS and compared with raw bio-oil to measure the extent of organic acid removal. Since anion-exchange resins are to be used repeatedly, the recovered anion-exchange resin was subjected to the same sequence of experiments for two more times.

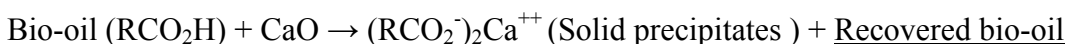
RESULTS AND DISCUSSION

Calcium Oxide Method

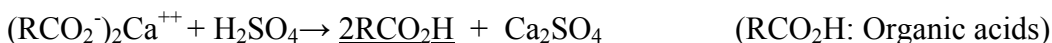
General observations on the calcium oxide method

The calcium oxide approach was based on the low solubility of calcium salts of various organic acids in methanol (Merck Index 1989). The organic acids in bio-oil are mostly in the free acid form as reflected by the pH values of 2.61~3.61 when diluted with methanol. The addition of calcium oxide to bio-oil neutralizes the acids, as 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:



Step 2 - Regeneration of organic acids using sulfuric acid:



Because of the relatively high viscosity of the reaction mixture in the neutralization stage it was necessary to dilute the reaction mixture with solvent. Based on consideration of the cost and later filtration, methanol was chosen in an amount

approximately equal to the weight of the bio-oil. The reaction is exothermic and needs to be stirred while cooling for at least 2 h 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 exposure to air and easily crushed to fine powders. The filtrate and washings were collected and solvent evaporated to recover the residual bio-oil. It was observed that the pH of the reaction mixture of bio-oil and calcium oxide increased only gradually with increasing amounts of calcium oxide added. The reactions were carried out to the target end-points of pH 7, 8, 9, and 10, respectively, and the analysis results are reported in Table 1.

Table 1. Removal 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
Residual bio-oil obtained	Weight of bio-oil (g)	49.6	45.3	16.6	14.1
	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
All percentage (%) values are based on bio-oil weights.					

Results of the calcium oxide procedure with target pH 7 and 8

The experimental results indicate that the acid removal process with target pH 7 and 8 was more optimal than with higher target pH values. The starting bio-oil contained about 10.92% acetic acid, 3.03% of formic acid, and small amounts of other organic acids. The calcium oxide additions to the target pH values of 7 and 8 showed removal of significant amounts of acetic acid to about 2.0% and of formic acid to 0.27%. This result would be useful in future scale-up research. Corrosiveness of bio-oil toward metals is likely to depend on the total concentration of organic acids in bio-oil. 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 values, at about 5.45%, would be relatively high for any liquid fuel. This problem of organic acid calcium salts remaining in the recovered bio-oil needs to be resolved in future research. One inconsistency observed in the experimental results, the low amounts of organic acids recovered appears to be due to losses in the isolation procedure as well as the organic acid calcium salts remaining in recovered bio-oil.

The obtained organic acid calcium salt precipitates were easily dried in open air to give a free-flowing, easy to handle powder. Suspending it in methanol also resulted in well-dispersed, low viscosity slurry with no difficulty arising during the acidification step for regeneration of organic acids in methanol. The methanol solution of regenerated organic acids clearly indicated the presence of acetic acid in significant amounts according to GC/MS analyses, as shown in Table 1. 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 compared with the corresponding values in the raw bio-oil. Loss of organic acids appears to occur in the isolation procedure due to the handling in open air, and also, from using sodium bicarbonate powder, which is needed to capture residual free sulfuric acid in order to prevent deterioration of the column. The organic acid calcium salts remaining in recovered bio-oil samples also contain organic acids. Further research would be needed for distillation or other methods to isolate pure acetic/formic acids from the methanol solution.

GC/MS analysis results indicated that the acidified methanol solution also contains some other materials such as simple phenols and other pyrolytic lignin components. Since some organic acids still remain in the recovered bio-oil at this target pH, this result indicates that the calcium oxide method is limited in selectivity between organic acids and other bio-oil components that have phenolic hydroxyl groups. Other bio-oil components having aldehydic and ketonic functional groups might be similarly affected, but it was not feasible to accurately quantify the amounts of these non-acid materials. These other components in the recovered acids fractions need to be minimized in future research. Overall, the procedure of obtaining organic acids from the calcium oxide precipitation appears to be useful, especially if the acidification step is to be proven, making it possible to use carbon dioxide 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 removal process.

Results of the calcium oxide acid separation process with target pH 9 and 10

The target pH 9 and 10 experiments resulted in low yields of recovered bio-oil, although the bio-oils had quite low concentrations of organic acids, as expected. However, the amounts of organic acid calcium salts obtained were very high, indicating that pyrolytic lignin components having phenolic and other functional groups have also been precipitated. Therefore, this pH range would not be useful as acid removal methods. However, there was a rather rapid 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. On the other hand, the calcium oxide method might be useful for extracting the major portion of bio-oil components from bio-oil including organic acids and phenolic (pyrolytic lignin) components. GC/MS spectra of the recovered organic acids and other components obtained by acidifying these calcium salt precipitates gave very similar GC/MS spectra with raw bio-oil itself, indicating that most pyrolytic lignin components were extracted by their reaction with calcium oxide (Sukhbaatar 2008).

Anion-Exchange Resin Method

Column method

The overall scheme of using anion-exchange resins is as follows:

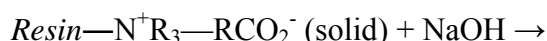
Step 1 - Generation of the hydroxide form of resin:



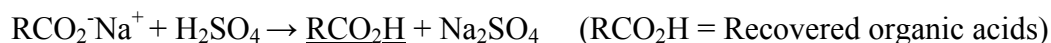
Step 2 – Reaction of the resin with acids in bio-oil and elution or filtration:



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



Step 4 - Generation of organic acids:



Anion-exchange resins are often used in a column platform in which a liquid mixture is gradually sent through the column by applying pressure or by gravity. The eluted material is collected until the anion-exchange resin capacity is depleted, and the depleted anion-exchange resin is then regenerated and used again and again. In this work, the sixteen consecutive fractions, approximately 10 mL each, collected from eluting the mixture of 80 g bio-oil and 80 g methanol through a column packed with 74 g of anion exchange resin showed the pH decreasing from 6.85 to 5.44, compared with pH of about 3.60 for the starting solution. GC/MS analyses of collected bio-oil fractions also showed that the acetic acid concentrations were very low, in the range of 10-200 ppm, until fraction #13, compared with its nearly 5% concentration in the starting solution, indicating capture of acids by the column with efficiency decreasing as the fraction collection is extended. GC/MS analyses of the collected bio-oil fractions had acetic acid concentrations as shown in Fig. 1.

Thus, anion exchange resins could be useful in the column platform to capture organic acids in bio-oil. However, more quantitative data on the anion-exchange capacity and acid recovery were difficult to obtain from the small column setup used, due to the non-uniform flow of the bio-oil/methanol solution in the column after the fraction #13. Although the column-type loading of ion-exchange resins would be more efficient in large-scale operations, the elution control in the small scale became unsatisfactory toward the end of the fraction collection.

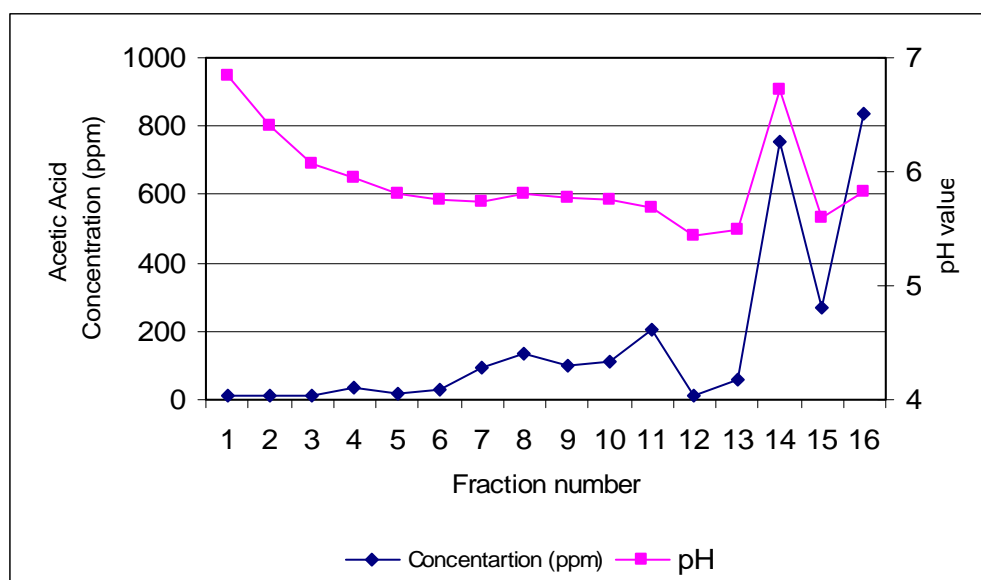


Figure 1. Acetic acid concentrations (ppm) from GC/MS analyses of bio-oil fractions obtained from the anion-exchange resin column experiments

Batch method

The results of batch experiments using the anion-exchange resin, repeated three times, are reported in Table 2. In the first experiment with the end pH value of 6.98, the recovered bio-oil had an acetic acid concentration of 0.2%, indicating that 20 grams of bio-oil needed 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 spent anion-exchange resin amounted to 8.9% and 1.3%, respectively, based on bio-oil used, which appear to be reasonably close to the acetic and formic acids' content in the raw bio-oil of 10.95% and 3.03%.

In the second repetition, the end pH was only 5.12 after adding all the regenerated anion-exchange resin from the first repetition experiment to the same amount of bio-oil. This result indicates that the anion-exchange capacity of the resin had deteriorated as a result of the first run. Higher acetic and formic acid values in the recovered bio-oil and slightly lower recovery values of acetic and formic acids than in the first repetition were also observed. In the third repetition, the end pH was further decreased to 4.64, and the acetic and formic acids content in the recovered bio-oil were slightly lower than in the second repetition. Relatively high amounts of acetic and formic acids were obtained from regeneration of the anion-exchange resins. This result also indicates that some reduction in the anion-exchange capacity has occurred in each repetition.

In all three experiments the yields of recovered bio-oil were reasonable but somewhat low compared with the starting amounts of bio-oil, although about 10%-15% of starting bio-oil was water. The total acetic and formic acids contents (remaining in bio-oil and isolated) were 9.1%, 12.8%, and 9.9 %, respectively, for the three repetitions, somewhat lower than values of raw bio-oil.

Table 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
	pH after treatment	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
Anion-exchange resin regeneration & recovered organic acids	0.1 N NaOH solution used (g)	100	100	150
	Sodium salts obtained (g)	2.87	2.82	2.81
	Acetic acid weight as % of 20g bio-oil	8.9	6.7	5.1
	Formic acid weight as % of 20g bio-oil	1.3	0.9	0.8

It was apparent that some bio-oil components, including organic acids, strongly adhered to the anion-exchange resin and did not come off in the regeneration step, resulting in loss of bio-oil materials as well as reduction in the anion-exchange capacity discussed above. The anion-exchange resins approach needs improvements. The batch procedure results could be transferable to the column platform procedure. GC/MS data of raw bio-oil and recovered bio-oil from the anion exchange resin method were clearly different in the organic acid regions, but other regions of spectra were too complex to present in a table format, and readers are referred to the thesis (Sukhbaatar 2008).

Overall, the experimental approaches used in this research have never been reported, perhaps because of the complexity expected in the neutralization, filtration of salts, or in regeneration of anionic resins in comparison with the method of distillation of low boiling components and capturing acids from the distillates (Oehr et al. 1993). However, distillation to separate out a small weight fraction of bio-oil as acid fractions would incur high energy consumption as well as undesirable reactions among bio-oil components. The present research results therefore appear to serve well as a starting point in further research.

CONCLUSIONS

1. The calcium oxide approach for removal of organic acids from bio-oil carried out to target pH 7 and pH 8 resulted in a recovered bio-oil having an acetic acid content of 1.9% and 2.4%, respectively, in comparison to 10.92% in raw bio-oil, but the ash contents of recovered bio-oil were relatively high at 3.6% and 5.5%, respectively, indicating the need of method improvements in future. With target pH 9 and 10, the calcium oxide method resulted in forming calcium salt precipitates that also contain high amounts of pyrolytic lignin components and therefore was deemed unsuited for removal of organic acids from bio-oil.
2. The anion-exchange resin approach for removing organic acids in bio-oil carried out until the end pH of 6.98 resulted in a recovered bio-oil having 0.2% acetic and 0% formic acid contents. One hundred thirty-seven grams of anion-exchange

resin were needed for treatment of 20 g bio-oil. In repeating experiments the regenerated anion-exchange resin showed lowered anion-exchange capacities. In all experiments the yields of recovered bio-oil were reasonable but somewhat low due to adsorption of bio-oil components on resin particles. The results indicate the need of improvements for the anion-exchange resin technology for this purpose. Recovery of organic acids in the three consecutive experiments were relatively high with acetic acid values of 8.9%, 6.7% and 5.1% and formic acid values of 1.9%, 0.9%, and 0.8%, respectively, based on bio-oil weight used.

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