Comparison of direct and indirect contact heat exchange to improve recovery of bio-oil

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Abstract
This study investigates whether the rate of cooling of pyrolysis vapors affects the composition of the resulting bio-oil. Pure cellulose was pyrolyzed in a laboratory-scale fluidized bed reactor at 500 °C and the bio-oil collected in either an indirect contact heat exchange (conventional water-cooled condenser system) or a direct contact heat exchange (liquid quench) system developed in our laboratory. The liquid quench system was estimated to achieve a seven-fold increase in cooling rate compared to the water-cooled condensers. Direct contact cooling in the quench system also eliminated temperature gradients experienced by films of bio-oil running down the walls of the water-cooled condensers. The combination of these two factors helped reduce secondary decomposition of primary pyrolysis products, especially anhydrosugars such as levoglucosan. The quench system increased the yield of levoglucosan by over 20% while minimally effecting yield of other compounds.

The concept of direct contact cooling was applied to a pilot-scale, lignocellulosic biomass pyrolysis plant using water as a more practical quench media than liquid nitrogen. As with the liquid nitrogen quench, the water flashed to gas while the heavy ends of the bio-oil condensed to liquid. The quench vessel was operated above the dew point of the water to assure that it left the vessel as gas along with produced water and light ends of bio-oil, which were recovered in a condenser as an aqueous phase. In pyrolysis experiments with red oak, the quench vessel increased the yield of heavy ends by 15% compared to conventional condensers. These results encourage the design of bio-oil recovery systems that can rapidly quench products to achieve high yields and improve the quality of bio-oil.

Keywords
Cellulose, Pyrolysis, Levoglucosan, Heat exchange, Primary reaction, Secondary reaction

Disciplines
Chemical Engineering | Energy Systems | Heat Transfer, Combustion | Mechanical Engineering

Comments

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1. **Introduction**

Renewable energy and sustainable energy production are top priorities for the nation to help
provide national, economic, and environmental security. Among renewable energy sources,
biomass is the most promising for production of “drop-in fuels” that are compatible with existing
infrastructure. Biomass, like many other renewable energy sources, harnesses solar energy;
however, in contrast to many other forms of renewable energy, biomass offers the advantage of
storing that energy in chemical bonds. Biomass also offers advantages in that it can be regrown
each year almost anywhere water, soil, and nutrients are available. Because biomass removes
CO₂ from the atmosphere as it is grown, it can yield a carbon neutral or even carbon negative
fuel, which helps to mitigate concern of atmospheric carbon dioxide concentration.¹

Two main pathways exist for conversion of biomass to liquid fuels and chemicals: the
biochemical and thermochemical pathways. The biochemical pathway uses micro-organisms to
convert carbohydrates in biomass to alcohols, such as in the production of corn ethanol. The
thermochemical pathway uses heat and/or chemicals/catalysts for the conversion step. There are
several methods of thermochemical conversion and fast pyrolysis is currently gaining interest as a cost-effective approach to converting biomass into sugar rich bio-oil.²

Fast pyrolysis, or the rapid thermal decomposition of organic compounds in the absence of oxygen, is capable of producing a variety of compounds including phenolics and sugars that are suitable for upgrading to transportation fuels. Monosaccharides resulting from the depolymerization of the cellulose and hemicellulose in biomass offer advantages in that they can be directly upgraded to liquid fuels by processes such as aqueous phase upgrading³,⁴ or fermented via micro-organisms using so-called hybrid processing.⁵ In either case, the carbohydrate polymers must be depolymerized to monosaccharides before they can be utilized by microorganisms in biological conversion or upgraded to hydrocarbons in aqueous phase upgrading.

Achieving high yields of sugar-rich bio-oil is dependent on feedstock, operating conditions, and bio-oil collection systems. Previous research by Kuzhiyil et al.⁶ showed that feedstock can be optimized for sugar production by infusion of certain mineral acids. Reactor operating conditions, such as temperature and sweep gas flow rate, also contribute significantly to the overall sugar yield from biomass. Bio-oil collection has also been explored by several other researchers,⁷–⁹ although the focus has not been on sugar recovery. Several studies have revealed that molten levoglucosan is prone to polymerization and dehydration,¹⁰–¹⁵ thus implying that sugar recovery from fast pyrolysis of carbohydrates can be increased by minimizing the time that condensed levoglucosan is subject to elevated temperatures.

We have developed a novel bio-oil collection system based on direct contact heat exchange to both quickly quench the pyrolysis vapors and separate compounds based on their calculated
Laboratory-scale experiments employed liquid nitrogen as quench medium to maximize cooling rate of the pyrolysis vapors, which is hypothesized to improve sugar recovery. Although liquid nitrogen is too expensive for commercial applications, it is an excellent medium to achieve rapid quenching and testing this hypothesis. Practical applications require less expensive quench media. Based on the promising results from the laboratory-scale experiments, we also implemented the quench concept into a pilot-scale fast pyrolysis system using water as quench media. This paper describes the results obtained from both manifestations of the direct contact heat exchange concept for recovering bio-oil.

2. Materials and Methods

2.1. Materials

Pure cellulose was used as pyrolysis feedstock. The cellulose was purchased from Sigma-Aldrich under the trade name Sigmacell®, a microcrystalline cellulose powder with an approximate particle diameter of 50 $\mu$m (Sigma Aldrich SKU: S5504). Ash content was measured to be less than 0.01%.

2.2. Fluidized Bed Reactor

A 100 g/hr bubbling fluidized bed reactor was used to pyrolyze the cellulose powder. A process diagram of the reactor is shown in Figure 1. The reactor consists of a volumetric feed system, an injection auger, the bubbling fluidized bed reactor, dual cyclones for solids separation and the bio-oil collection system.
The volumetric feeder was calibrated to provide the fluidized bed reactor with a constant feed of 100 g/hr of cellulose. The volumetric feeder delivered the cellulose into a secondary injection auger which operated at a constant 60 rpm. The injection auger introduced the cellulose directly into the bubbling fluidized bed.

The bubbling fluidized bed reactor consisted of a standard 316 stainless steel pipe that was 0.34 m in height with an inner diameter of 38.1 mm. The plenum, which was designed to both preheat the nitrogen sweep gas and provide a uniform supply of nitrogen through the porous distributor plate, was 0.17 m in height with an inner diameter of 38.1 mm. Watlow® ceramic clamshell heaters were used to maintain the plenum and reactor temperatures at 500°C.

The fluidization media consisted of 100 g of silica sand with a mean sieve size of 520 µm which corresponded to a packed bed height of approximately 55 mm. Nitrogen sweep gas was introduced into the plenum at 8 standard liters per minute (SLPM) and purged through the feed
system at 2 SLPM leading to a total flow rate of 10 SLPM. The flow rates corresponded to a superficial velocity of 36 cm/s and a ratio of superficial gas velocity to minimum fluidization velocity ($U/U_{\text{mf}}$) of approximately 2.6.

Solids separation was achieved by a series of two cyclonic separators, the first being used to remove the majority of the char (high volume) and the second used to remove any remaining char down to very fine particle size (high efficiency). The cyclones and piping up to the bio-oil collection system were heat traced with BriskHeat® heating tapes to maintain 475°C. Vapor residence time in piping prior to the bio-oil collection system was approximately 1.3 s. The bio-oil collection system employed either an indirect contact heat exchanger (conventional condenser) or a direct contact heat exchanger (liquid nitrogen quench vessel). Each of the bio-oil collection systems has distinct operating parameters including cooling rates, residence times, temperature gradients, and separation between stage fractions. Details of each are described below.

2.3. Indirect Contact Heat Exchange (Conventional Condenser) System

The conventional condenser system consisted of two water cooled condensers, an electrostatic precipitator, and a final shell and tube condenser as shown in Figure 2. Each component collects a separate fraction of bio-oil where each is labeled sequentially as a separate stage fraction (SF1, SF2, etc.). The first two condensers were stepped down in surface temperature to selectively condense higher molecular weight products in the first condenser (SF1) and lower molecular weight products in the second condenser (SF2). The condensers had enough cooling capacity to condense the bio-oil compounds; however, they were not capable of removing a majority of the aerosols formed during the cooling process which remained entrained
in the pyrolysis vapor stream. An electrostatic precipitator (SF3) was used after the condensers to collect the aerosols. The final condenser (SF4), operating with a surface temperature of -10°C was designed to collect any remaining moisture or light oxygenates.

![Image of indirect contact heat exchange bio-oil recovery system]

Figure 2. Indirect contact heat exchange (condenser) bio-oil recovery system.

### 2.4. Direct Contact Heat Exchange (Novel Quench) System

As shown in Figure 3, the quench system consisted of a quench chamber, a liquid nitrogen injection line, an electrostatic precipitator, and a final condenser. Bio-oil was collected into two stage fractions where the heavy ends collected in the electrostatic precipitator and the light ends collected in the final condenser.

Liquid nitrogen was generated and injected into the quench chamber by passing gaseous nitrogen into a heat transfer coil, which was submerged in a Dewar containing liquid nitrogen. A heavily insulated stainless-steel tube connected the heat transfer coil to a nozzle in the quench
chamber. The liquid nitrogen was sprayed from the nozzle for direct contact with the pyrolysis vapor stream immediately after leaving the reactor system. Aerosols were quickly formed from bio-oil compounds that were dropped below their dew points by the liquid nitrogen quench. An electrostatic precipitator was used to separate the aerosols from the pyrolysis vapor stream, collecting them into a distinct bio-oil fraction.

Figure 3. Direct contact heat exchange (quench) bio-oil recovery system.

The temperature of the quenched vapors was fed back into a control loop which then regulated the mass flow of nitrogen to maintain the quench temperature at 90°C. A quench temperature of 90°C was chosen as it was calculated to be just above the dew point of water and well below the dew point of levoglucosan, thereby providing a bio-oil rich in levoglucosan and low in moisture content as part of SF 1. The surface of the ESP was also heated to near 100°C both to keep the collected bio-oil flowing downward into the collection bottle and to evaporate
any condensed moisture. The remaining pyrolysis vapors at around 90°C passed into a shell-and-tube heat exchanger where they were chilled to -10°C to condense out the bio-oil aqueous phase, which consisted mostly water and light oxygenates such as carboxylic acids.

In order to determine the effect of cooling rate on the yield of sugar compounds, the temperature change across specific bio-oil collection components was divided by the residence time of the vapors within the system up to that point and termed “cumulative effective cooling rate.” The quench system collects all of the sugars in SF1; therefore, the cumulative effective cooling rate is calculated from the outlet of the reactor up to the isothermal ESP that collects SF1. The conventional system was found to collect sugars in SF1, SF2, and SF3; therefore, the cumulative effective cooling rate was calculated from the outlet of the reactor up to the isothermal ESP that collects SF3. As shown in Table 1 and Table 2, the conventional system provided a cooling rate of approximately 450°C/s whereas the quench system resulted in a cooling rate of approximately 3360°C/s. The quench system acts to increase cumulative effective cooling rate via two mechanisms; 1) increased heat transfer rate and 2) decreased residence time. The pyrolysis vapor stream encounters less thermal resistance when directly contacted with liquid quench media compared to indirect cooling in the water-cooled condensers. Liquid nitrogen, which enters the quench system at -196°C, flashes quickly to gaseous nitrogen at temperatures encountered in the quench system. The quantity of liquid nitrogen utilized to cool the pyrolysis vapor stream, once expanded to the gas phase, approximately doubles the flow rate of gases through the system, thus decreasing overall residence time. Additionally, the pyrolysis vapor stream encounters less system volume in the quench system, which also acts to decrease residence time. Accumulation of these effects lead to an almost seven-fold increase in cooling rate from the quench compared to the conventional system.
Table 1. Operating parameters for the indirect contact heat exchange bio-oil recovery system.

<table>
<thead>
<tr>
<th>Component</th>
<th>Average Flow Rate (SLPM)</th>
<th>Vapor Temperature In (°C)</th>
<th>Vapor Temperature Out (°C)</th>
<th>Wall Temperature (°C)</th>
<th>Component Residence Time (s)</th>
<th>Cumulative Residence Time (s)</th>
<th>Cumulative Effective Cooling Rate (°C/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Condenser 1</td>
<td>9.7</td>
<td>460</td>
<td>135</td>
<td>68</td>
<td>0.36</td>
<td>0.36</td>
<td>900</td>
</tr>
<tr>
<td>Condenser 2</td>
<td></td>
<td>135</td>
<td>45</td>
<td>26</td>
<td>0.57</td>
<td>0.93</td>
<td>450</td>
</tr>
<tr>
<td>ESP</td>
<td></td>
<td>45</td>
<td>45</td>
<td>54</td>
<td>12.23</td>
<td>13.16</td>
<td>30</td>
</tr>
<tr>
<td>Condenser 3</td>
<td></td>
<td>45</td>
<td>10</td>
<td>-10</td>
<td>4.31</td>
<td>17.47</td>
<td>30</td>
</tr>
</tbody>
</table>

Table 2: Operating parameters for the direct contact heat exchange bio-oil recovery system.

<table>
<thead>
<tr>
<th>Component</th>
<th>Average Flow Rate (SLPM)</th>
<th>Vapor Temperature In (°C)</th>
<th>Vapor Temperature Out (°C)</th>
<th>Wall Temperature (°C)</th>
<th>Component Residence Time (s)</th>
<th>Cumulative Residence Time (s)</th>
<th>Cumulative Effective Cooling Rate (°C/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quench</td>
<td>20.3</td>
<td>460</td>
<td>90</td>
<td>475</td>
<td>0.11</td>
<td>0.11</td>
<td>3360</td>
</tr>
<tr>
<td>ESP</td>
<td></td>
<td>90</td>
<td>90</td>
<td>100</td>
<td>5.25</td>
<td>5.36</td>
<td>70</td>
</tr>
<tr>
<td>Condenser</td>
<td></td>
<td>90</td>
<td>10</td>
<td>-10</td>
<td>1.91</td>
<td>7.27</td>
<td>60</td>
</tr>
</tbody>
</table>

2.5. Mass Balances

Mass balances for bio-oil and char were measured gravimetrically by weighing the char catches and bio-oil collection system components before and after each test. The difference in mass from before the experiment to after the experiment was used for calculating the mass balance.

2.6. Non-Condensable Gas Measurement

Concentrations of non-condensable gases in the exhaust stream were measured using a Varian® CP-4900 micro-Gas Chromatograph (microGC) interfaced with Galaxy®
Chromatography software. A split line from the main exhaust line and sampling pump were used to supply the GC with a constant flow of approximately 0.5 L/min. The microGC was programmed to sample for 30 s followed by 140 s run time for analysis. The sample line and injectors one and two were set to operate isothermally at 110°C with a 40 ms injection time. Injector three operated isothermally at 80°C with an 80 ms injection time. A thermal conductivity detector was used for gas detection on each channel. Channel one was setup with a Varian® Molesieve 5 Å column operating at 100°C with argon carrier gas at 151.7 kPa. Helium, hydrogen, oxygen, nitrogen, methane and carbon monoxide were calibrated within the expected ranges on channel one. A Varian® PoraPLOT Q column was setup on channel two operating at 58°C with helium carrier gas at 117.2 kPa. Carbon dioxide, ethylene, acetylene, and ethane were calibrated within the expected ranges on channel two. A Varian® Al2O3 column was setup on channel three operating at 60°C with helium carrier gas at 55.2 kPa. Channel three was calibrated within the expected ranges to measure propane.

Total volume of gas leaving the reactor was measured using a Ritter® TG5/4-ER-1 bar drum type gas meter. The mass of non-condensable gas produced during the reaction was then calculated using the overall gas volume and the steady-state concentrations of gases in the stream.

2.7. Water Soluble Sugar Analysis via High Performance Liquid Chromatography

Water soluble cellobiosan (1,6-anhydro-β-D-cellobiose) and levoglucosan (1,6-anhydro-β-D-glucopyranose) were quantified via a water wash method followed by analysis with High Performance Liquid Chromatography (HPLC). Approximately 0.5 g bio-oil was dissolved in 3 mL of water, well mixed with a vortex mixer, and then centrifuged at 3500 rpm for 15 min. The
supernatant was poured off and the precipitate was washed three additional times with 3 mL of deionized water to ensure the water-soluble sugars were fully dissolved. An additional 9 mL of water were then added to the accumulated supernatant to bring the total up to 18 mL. The resulting solution was then filtered through a Whatman® 0.45 µm glass microfiber filter.

A Dionex UltiMate® 3000 high performance liquid chromatography system interfaced with Chromeleon® software and a Refractive Index (RI) detector was used to quantify water soluble sugars. Two Bio-Rad® Aminex HPX-87P columns were used in series for separation with a guard column and Micro-guard cartridge. The column compartment was held at 75°C for analysis. Ultrapure deionized water of 18.2 Mohm-cm was used as eluent at a flow rate of 0.6 mL/min. The water-soluble sugars levoglucosan and cellobiosan were calibrated from 0-10 mg/mL using a five-point calibration.

2.8. Total Sugar Analysis via Acid Hydrolysis and HPLC

Monomeric and dimeric sugars resulting from cellulose pyrolysis tend to be largely soluble in water; however, these sugars can also polymerize and form water-insoluble polysaccharides.17 In order to jointly quantify water soluble and water insoluble sugars, all sugars were first hydrolyzed to glucose and xylose via acid hydrolysis. The total sugar yield was then calculated based on the quantity of bio-oil that was capable of hydrolysis. Approximately 60 mg of bio-oil was first placed in a hydrolysis reactor vessel (HRV) and then dissolved in 6 mL of 400 mM sulfuric acid in water. A Teflon gasket and a cap were placed on the HRV which was then placed in a 125°C oil bath for 45 min. The HRV was then quickly chilled to room temperature in a freezer followed by centrifuging at 3500 rpm for 15 min. The supernatant was then filtered with a Whatman® 0.45 µm glass microfiber filter and injected into a 2 mL glass vial.
A Dionex UltiMate® 3000 high performance liquid chromatography system interfaced with Chromeleon® software was used for HPLC analysis. A 300 mm X 7.7 mm 8 µm particle size HyperRez XP Carbohydrate analytical column was used for separation of the carbohydrates. A Carbohydrate H+ cartridge was used as the guard column prior to the HyperRez XP column. The mobile phase used was 18.2 Mohm-cm deionized water which was flown at a rate 0.2 mL/min. The column compartment was held isothermally at 55°C. Further details of this method are available from Johnston and Brown.18

2.9. Moisture Analysis

Moisture analysis was performed using a Karl Fischer MKS-500 moisture titrator. Hydranal Working Medium K was used as the solvent and Hydranal Composite 5 K was used as the titrant. The instrument was calibrated using deionized water prior to sample testing.

2.10. Carboxylic Acids Analysis

Approximately 100 mg of bio-oil was dissolved in 1.5 mL methanol and 6 mL deionized water for organic acids analysis for fractions with relatively low organic acid content. To remain within the calibrated range samples with high organic acid content were diluted further where 40 mL of deionized water was used rather than 6 mL. The sample was then filtered through a Whatman® 0.45 µm glass microfiber filter.

A Dionex® ICS3000 ion chromatography system with a conductivity detector and an Anion Micromembrane Suppressor (AMMS-ICE 300) was used for analysis of the bio-oil samples. The Dionex system was interfaced with Chromeleon® software version 6.8.
Tetrabutylammonium hydroxide (TBOH) in water at a concentration of 5 mM was used to regenerate the suppressor at a flow rate of 4-5 mL/min. A mixture of 1.0 mM heptafluorobutyric acid in water was used for the eluent at a flow rate of 0.120 mL/min at 19°C. An IonPac® ICE-AS1 4x50 mm guard column in series with an IonPac® ICE-AS1 4x250 mm analytical column were used for separation. Standards of acetate, propionate, formate and glycolate were purchased from Inorganic Ventures (Christiansburg, Virginia) to calibrate the instrument. The concentrated standard was certified at 200.0 ± 1.3 mg/L for all acids and was diluted down with ultrapure deionized water to concentrations of 10, 25, 67, and 100 mg/L to achieve a 5 point linear calibration.

2.11. Gas Chromatography/Flame Ionization Detector (GC/FID) Analysis of Volatile Organic Compounds

Approximately 0.5 g of bio-oil was mixed in 1.0 g of methanol stock solution for an approximate 33% bio-oil solution. Phenanthrene was mixed in the methanol stock solution to provide an internal standard for comparison between runs. The mixture was then mixed on a vortex mixer for several minutes to ensure all of the bio-oil was dissolved. The resulting bio-oil solutions were then filtered through a Whatman 0.45 µm glass microfiber filter before analysis.

A Bruker® 430-GC Gas Chromatograph with a Varian® CP-8400 liquid injection autosampler interfaced with Galaxy® software was used for GC/FID analysis. A Zebron® ZB-1701 column of 60 m length and 0.25 mm inner diameter was used for separation of volatile species. The GC method operated with an injector temperature of 300°C at a split ratio of 30. The oven program started at 35°C, held for 3 min, ramped at 5°C/min to 300°C and held for 4 min for a total of 60 min per run. The column pneumatics was set for constant flow at 1 mL/min
helium carrier gas. The FID was set at 300°C with 25 mL/min helium makeup flow, 30 mL/min hydrogen, and 300 mL/min air flow. A four-point linear calibration was developed from known standards. Standard were not available for xylosan (1,4-anhydro-α-D-xylopyranose) or levoglucosan-furanose (1,6-anhydro-β-D-glucofuranose) and therefore were quantified using the response factor of levoglucosan. Retention time of both xylosan and levoglucosan-furanose were found by comparing chromatograms found on the FID and chromatograms from a mass spectrometer operating with identical GC conditions. Glycolaldehyde was calibrated via pyrolysis of the dimer at 500°C at different mass loadings. One major peak was found with a few minor peaks where the major peak was identified to be the glycolaldehyde monomer via GC/MS.

2.12. Water Insoluble Compounds Analysis

Bio-oil resulting from cellulose was found to contain a small portion of water insoluble content, which is likely to be polysaccharides. Water insoluble content was quantified by a method developed in-house. Water was heated to 80°C prior to mixing with bio-oil at a ratio of 80:1 water to bio-oil on a mass basis. The mixture contained in a 50 mL centrifuge tube was then thoroughly mixed using a vortex mixer for one minute. Each centrifuge tube was then sonicated for 30 min to ensure proper mixing. The mixture was then centrifuged at 2500 rpm for 20 minutes. The supernatant was then filtered through a Whatman® 2 µm filter. Both the centrifuge tube and filter paper were then dried at 50°C for 24 hours. Accumulated mass on both the filter paper and centrifuge tube were then considered water insoluble content.
3. Results and Discussion

3.1. Overall Mass Balance

As shown in Table 3, mass balances for the two bio-oil collection systems were similar as might be expected since the reactor operating conditions were identical. Yield of bio-oil from the conventional recovery system averaged 87.4 wt.% whereas the quench system averaged 83.3 wt.% Mass balances and bio-oil composition were compared for each system using a Student t-Test. The t-statistic for the comparison of each mean is indicated in the column labeled “Prob > t.” A t-statistic of 0.05 indicates a 95% probability that the mean for the quench system is significantly greater than the mean for the conventional system. Similarly, a t-statistic of 0.95 indicates a 95% probability that the mean for the conventional system is significantly greater than the mean for the quench system. The t-statistic from comparing average bio-oil yields was 0.97 indicating that the conventional system resulted in a statistically significant increase in bio-oil yield. Three factors are expected to contribute to the higher bio-oil yield in the conventional system: 1) lower dew points of bio-oil compounds in the quench system, 2) higher gas velocities in the quench system, and 3) contribution of char to the bio-oil mass in the conventional system. The rapid cooling of pyrolysis vapors by the addition of liquid nitrogen to the pyrolysis vapor stream likely discouraged secondary reactions; however, the diluting effect of the nitrogen reduced the dew points of bio-oil compounds, making them more difficult to separate from the pyrolysis vapor stream. Higher gas velocity through the quench system due to the injected nitrogen may have prevented some aerosols from condensing with the cooled vapor. Subsequent tests with the quench system and an additional electrostatic precipitator after the SF2 condenser supported this hypothesis, collecting an additional 1-3 wt.% of bio-oil.
Table 3. Mass balance comparisons.

<table>
<thead>
<tr>
<th>Product</th>
<th>Quench Average (wt.% of cellulose feedstock)</th>
<th>Conventional Average (wt.% of cellulose feedstock)</th>
<th>Prob &gt; t</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bio-oil</td>
<td>83.3%</td>
<td>87.4%</td>
<td>0.97</td>
</tr>
<tr>
<td>Char</td>
<td>3.4%</td>
<td>2.5%</td>
<td>0.25</td>
</tr>
<tr>
<td>Non-Condensable Gases</td>
<td>4.2%</td>
<td>5.4%</td>
<td>0.79</td>
</tr>
<tr>
<td>Mass Closure</td>
<td>90.8%</td>
<td>95.3%</td>
<td>0.94</td>
</tr>
</tbody>
</table>

Increased production of char in the conventional bio-oil recovery system by secondary reactions is likely another contributing factor to its higher bio-oil yields. Both systems tended to produce some char in secondary reactions at the inlet to the bio-oil collection system. This is thought to occur when vapors condense or aerosols impact at relatively high temperatures on the inlet. These hot liquids polymerized and dehydrated to char, some of which ended up with the collected bio-oil and was counted toward bio-oil liquid yield. The slower cooling rate in the conventional system led to longer residence time at high temperature, which encouraged char formation by secondary reactions of the bio-oil.

The reported char yield considered only char collected in the cyclones ahead of the bio-oil collection system. Thus, the char yield does not include any secondary char produced in the bio-oil collection system. Char yield for the two systems were 3.4 wt.% for the quench system and 2.5 wt.% for the conventional system. The t-statistic of 0.25 suggests no statistically significant difference between the char yields as might be expected since the pyrolysis conditions were identical for the two systems.

Non-condensable gas yield proved to be similar for the two systems. The quench system averaged 4.2 wt.% non-condensable gases and the conventional system averaged 5.4 wt.% non-
condensable gases. The t-statistic from comparison of the means was 0.79 suggesting no statistically significant difference in the non-condensable gases for the two systems.

Overall mass closures were approximately 91 wt.% for the quench system and 95 wt.% for the conventional system. The lower mass closure for the quench system correlates directly with lower bio-oil yield. As discussed above there are several factors contributing to the higher bio-oil yield in the conventional system, also leading to the higher mass closure.

### 3.2. Bio-oil Composition

In order to determine the effect of the cooling rate on bio-oil composition, concentrations of constituents from each stage fraction were summed to provide a composite “whole bio-oil” composition. Table 4 summarizes the bio-oil composition resulting from the two bio-oil recovery systems. Approximately 90% of the total bio-oil was accounted for in each case.

Acids identified in cellulose bio-oil included acetic acid, formic acid, and glycolic acid. The quench system produced an average carboxylic acid concentration of 1.3 wt.% and the conventional system produced an average 1.9 wt.% concentration; however, variability between runs led to a t-statistic of 0.77, which indicates the difference was not statistically significant.

Furans included 2(5H)-furanone, 2-furanmethanol, 5-(hydroxymethyl)furfural, 5-methylfurfural, furfural, and methylecyclopentenolone. The quench system produced an average 0.87 wt.% furans and the conventional system produced an average 1.18 wt.% furans. Comparing the two means resulted in a t-statistic of 0.48 indicating that there is no statistically significant difference in furan yield for the two systems.
Light oxygenates including glycolaldehyde, formaldehyde, and acetol were also quantified via GC/FID. The quench system produced a bio-oil containing 13.0 wt.% light oxygenates while the conventional system averaged 12.1 wt.%. The t-statistic was 0.43 indicating no statistically significant difference in light oxygenate content for bio-oil from the two systems. Acetol concentration averaged 0.6 wt.% in the quench system and 0.1 wt.% in the conventional system with a t-statistic of 0.07 indicating there may be some statistically significant difference. Glycolaldehyde was the largest light oxygenate component of the bio-oil, at a concentration of 8 wt.% for both systems. Formaldehyde averaged 4.4 wt.% in the quench and 3.9 wt.% in the conventional system; however, this was not a statistically significant difference.

Total glucose hydrolysable sugars measured via acid hydrolysis as described in section 2.8 was 57.8 wt.% for bio-oil from the conventional recovery system and 63.2 wt.% for bio-oil from the quench system, which is a statistically significant difference (t-statistic of 0.15). It is important to note that analysis of total sugars includes water added to anhydrosugar when it was hydrolyzed to glucose. The water was not subtracted from the total sugar yield, because not all sugars were explicitly analyzed and accounted for before hydrolysis. Those sugars that were explicitly analyzed are described below.

Bio-oil from the conventional recovery system contained 37.1 wt.% of levoglucosan while bio-oil from the conventional recovery system contained 45.5 wt.% levoglucosan, which is 23% higher than the conventional recovery system. The t-statistic in comparing these results was 0.04 indicating more than 95% confidence that these differences are statistically significant.
Table 4. Bio-oil composition comparison.

<table>
<thead>
<tr>
<th>Compound/Compound Group</th>
<th>Quench System Average (wt.% bio-oil)</th>
<th>Conventional System Average (wt.% bio-oil)</th>
<th>Prob &gt; t</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carboxylic Acids</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.27%</td>
<td>1.92%</td>
<td>0.77</td>
</tr>
<tr>
<td>Acetic Acid</td>
<td>0.39%</td>
<td>0.63%</td>
<td>0.78</td>
</tr>
<tr>
<td>Formic Acid</td>
<td>0.55%</td>
<td>0.78%</td>
<td>0.77</td>
</tr>
<tr>
<td>Glycolic Acid</td>
<td>0.33%</td>
<td>0.51%</td>
<td>0.75</td>
</tr>
<tr>
<td>Furans</td>
<td>0.87%</td>
<td>1.18%</td>
<td>0.48</td>
</tr>
<tr>
<td>2(5H)-Furanone</td>
<td>0.14%</td>
<td>0.17%</td>
<td>0.59</td>
</tr>
<tr>
<td>2-Furannmethanol</td>
<td>0.03%</td>
<td>0.04%</td>
<td>0.58</td>
</tr>
<tr>
<td>5-(Hydroxymethyl)furfural</td>
<td>0.23%</td>
<td>0.55%</td>
<td>0.71</td>
</tr>
<tr>
<td>5-Methylfurfural</td>
<td>0.09%</td>
<td>0.08%</td>
<td>0.46</td>
</tr>
<tr>
<td>Furfural</td>
<td>0.30%</td>
<td>0.24%</td>
<td>0.26</td>
</tr>
<tr>
<td>Methylcyclopentenolone</td>
<td>0.08%</td>
<td>0.10%</td>
<td>0.63</td>
</tr>
<tr>
<td>Light Oxygenates</td>
<td>13.0%</td>
<td>12.1%</td>
<td>0.43</td>
</tr>
<tr>
<td>Acetol</td>
<td>0.6%</td>
<td>0.1%</td>
<td>0.07</td>
</tr>
<tr>
<td>Formaldehyde</td>
<td>4.4%</td>
<td>3.9%</td>
<td>0.45</td>
</tr>
<tr>
<td>Glycolaldehyde</td>
<td>8.0%</td>
<td>7.7%</td>
<td>0.44</td>
</tr>
<tr>
<td>Total Sugars</td>
<td>63.2%</td>
<td>57.8%</td>
<td>0.15</td>
</tr>
<tr>
<td>1,4:3,6-dianhydro-D-glucose</td>
<td>0.3%</td>
<td>0.2%</td>
<td>0.25</td>
</tr>
<tr>
<td>Cellobiosan</td>
<td>5.6%</td>
<td>8.0%</td>
<td>0.89</td>
</tr>
<tr>
<td>Levoglucosan</td>
<td>45.5%</td>
<td>37.1%</td>
<td>0.04</td>
</tr>
<tr>
<td>Levoglucosan-Furanose</td>
<td>1.5%</td>
<td>1.0%</td>
<td>0.09</td>
</tr>
<tr>
<td>Xylosan</td>
<td>2.8%</td>
<td>2.6%</td>
<td>0.31</td>
</tr>
<tr>
<td>Water</td>
<td>11.8%</td>
<td>11.9%</td>
<td>0.54</td>
</tr>
<tr>
<td>Water Insolubles</td>
<td>2.5%</td>
<td>2.4%</td>
<td>0.79</td>
</tr>
<tr>
<td>Total Accounted</td>
<td>92.6%</td>
<td>87.3%</td>
<td></td>
</tr>
</tbody>
</table>
Cellobiosan yield was also measured via HPLC. The conventional and quench systems produced bio-oil containing 8.0 wt.% and 5.6 wt.% of cellobiosan, respectively. The t-statistic in comparing the average concentration of cellobiosan was 0.89 indicating that the difference is statistically significant.

Levoglucosan is known to thermally polymerize when subjected to elevated temperatures especially above 280°C. Kawamoto et al. found that the oligosaccharides formed from levoglucosan can be reversibly pyrolyzed to again produce levoglucosan; however once they begin to dehydrate and fragment they tend to carbonize and release decomposition products such as furans and light oxygenates. Levoglucosan exposed to temperatures of 250°C or higher will either volatilize or polymerize depending upon reaction conditions.

A major difference between the two bio-oil recovery systems that influences levoglucosan behavior is the more gradual temperature gradient that exists in the shell and tube condensers of the conventional bio-oil recovery system. The formation of char is commonly observed at the high temperature inlet to water-cooled condensers in conventional condenser systems. The temperature of the pyrolysis vapor stream changes gradually along the heat transfer surface of a condenser, reaching the minimum outlet temperature just before the vapors leave the condenser (see Figure 4). Bio-oil will likely condense on the heat transfer walls via film wise condensation where the film establishes a large temperature gradient between the wall and the hot gas stream. The wall temperature was close to 68°C while the gas stream temperature ranged anywhere from 460°C at the condenser inlet to 135°C at the outlet. The film of bio-oil flowing down the wall of the condenser likely reached temperatures exceeding 250°C under some circumstances, depending upon the velocities of the film and the gas stream, subjecting the liquid levoglucosan to both evaporation and polymerization. The higher molecular weight oligosaccharides and
polysaccharides resulting from the thermal polymerization of levoglucosan, similar to the caramelize process of other carbohydrates, would also be expected to increase the glass transition temperature and viscosity of the bio-oil. The higher viscosity of the resulting polysaccharides would impede their downward flow through condenser, providing time for them to dehydrate too char, water, and non-condensable gases.

![Figure 4. Illustration of the temperature gradient encountered in water cooled condensers.](image)

Another possibility is that levoglucosan vapors condensed to liquid aerosols and polymerized in the gas stream. Levoglucosan and other anhydrosugars are known to have a small but appreciable vapor pressure at pyrolysis temperatures, which allows them to escape the pyrolysis reactor as vapor. The low vapor pressure of levoglucosan may have resulted in liquid levoglucosan forming from cellulose faster than it could evaporate. At the high temperatures existing in a pyrolyzer this liquid would be subject to the competitive processes of volatilization and thermal polymerization. Under some circumstances, the pyrolysis product stream might
have become saturated with levoglucosan due to its relatively low saturation vapor pressure. Since the vapor stream tends to cool in transport lines, nucleation of vapor to aerosols are a distinct possibility. If the temperature remains higher than 250°C, the liquid levoglucosan might polymerize to cellobiosan and other polysaccharides within the aerosols.

Minor sugar components, including 1,4:3,6-dianhydro-D-glucose, levoglucosan-furanose, and xylosan, were measured via GC/FID and collectively made up around 5 wt.% of the bio-oil for each collection system. There was no statistically significant difference in the amount of 1,4:3,6-dianhydro-D-glucose or xylosan found in the bio-oil for the two recovery systems, with t-statistics of 0.25 and 0.31, respectively. The furanose isomer of levoglucosan accounted for 1.5 wt.% and 1.0 wt.%, respectively, of bio-oil from the quench and conventional systems, a statistically significant difference at the 90% confidence level (t-statistic of 0.09). The increase in levoglucosan-furanose is directly correlated with the increase the pyranose isomer of levoglucosan.

Moisture in the bio-oil was measured via Karl Fischer titration and was nearly identical between the two systems with bio-oil from the conventional system producing 11.9 wt.% and the quench system producing 11.8 wt.%.

Water insoluble content was 2.5 wt.% for the quench system and 2.4 wt.% of bio-oil for the conventional system. Water insoluble content from pyrolysis of cellulose is expected to be polysaccharides. Polysaccharides of sufficient size to be insoluble in water may come from direct mechanical expulsion from the pyrolyzing cellulose or may be formed via secondary polymerization reactions of levoglucosan during transport from the reactor to the bio-oil collection system. It should be noted that only bio-oil collected in the collection bottles at the
bottom of the condensers was tested with this analysis. Any additional water insoluble content arising from thermal polymerization near the inlet of the condensers would not be quantified due to difficulty in separation of the intrinsically mixed bio-oil and char/water insoluble content at the top of the condensers. Additional char and water insoluble content contained on the walls could make up a portion of the unaccounted fraction.

As shown in Table 4, the total accounted mass is 5.3 wt% higher for the quench system than for the conventional system. This corresponds very closely to the difference in total sugars yields for the two bio-oil recovery systems (5.5 wt%). This suggests that the improved mass balance for the quench system is due to less sugar being lost as char deposits within the collection system, which typically represents most of the unaccounted mass loss in the experiments.

3.3 Pilot Scale Validation

Although proven to be an effective method for increasing the recovery of sugar, the use of liquid nitrogen as quench media is clearly not practical for a commercial system. However, the concept of direct contact heat exchange using liquid quench media that flashes to gas could be implemented with water instead of liquid nitrogen as a more practical manifestation. Furthermore, the very large enthalpy of vaporization of water compared to liquid nitrogen allows relatively small volumes of ambient temperature water to be employed. Ideally, the injected water completely evaporates and remains above its dewpoint as it leaves the quench vessel while the heavy ends condense to liquid. This temperature control can be achieved by adjusting the flow rate of water and monitoring the entering and exiting temperature of the quench vessel.

Comparison of the proposed water quench system for bio-oil recovery to a conventional condenser system was performed in a pilot-scale fast pyrolysis system previously described by
As shown in Figure 5, the system consisted of a 15.4-cm diameter fluidized bed of sand using nitrogen (8.38 kg/h) as the fluidizing agent heated to 500°C and continuously fed with red oak (*Quercus rubra*) sized to approximately 3 mm diameter at 6 kg/h. Pyrolysis products, including vapors, non-condensable gases, and biochar, exited the bed through a pair of gas cyclones that removed particulate matter. The original bio-oil recovery system included six stages of bio-oil collection: a condenser (Figure 6) controlled to a pyrolysis gas exit temperature of 125°C followed by an electrostatic precipitator operated at 125°C to collect the heavy ends of bio-oil; a second condenser/ESP combination designed to reduce pyrolysis gas temperature to 70°C and collect an intermediate molecular weight bio-oil; and a final condenser/ESP combination operated at 21°C and 17°C respectively to collect the aqueous phase of bio-oil.

![Figure 5. Schematic of the fast pyrolysis pilot plant with original condenser-based bio-oil recovery system.](image)

A quench vessel was constructed and installed in place of the conventional condenser system to evaluate the efficacy of the direct contact heat exchange concept using water as the quench.
medium. The quench vessel (see Figure 6) was constructed from 21.9 cm OD pipe and featured a vertically opposed water injection nozzle positioned 45.7 cm below the vapor inlet port. The interchangeable nozzle was laser cut to a small orifice size and was supplied using a high-pressure syringe-type metering pump to produce a water spray with fine atomization. Water flow rate was modulated to obtain the desired bulk stream temperature of 125°C prior to gas exiting the vessel as monitored by a thermocouple located 46 cm below the water injection nozzle. The quench vessel was followed by an ESP operating at 40 kV and 125 °C to capture heavy end aerosols. The rest of the system, designed to collect the aqueous phase of the bio-oil, was similar to the conventional condenser system with a few differences: a condenser was used to cool the gas stream to 15 °C followed by a stainless-steel wire mesh demister pad and a wet ESP operating at 15 kV and 15 °C to collect aqueous phase existing as fine aerosol.

Figure 7 compares the mass balances for the conventional condenser system and the water quench vessel to recover bio-oil. Quench water has been subtracted from the light ends to make a direct comparison between products derived from the biomass feedstock. The quench system recovered 30 wt% heavy ends compared to only 26 wt% for the conventional condenser system. This 15% gain is attributable to two causes. First, the rapid cooling of pyrolysis vapors in the quench reactor reduces secondary reactions that decarbonylates sugars into small organic molecules and carbon monoxide.28 Evidence for this is the 29% reduction in non-condensable gases, primarily carbon monoxide, for the direct contact heat exchange system. Second, the walls of the quench vessel are warmer than the plenum and tube sheet of the heavy ends condenser, which results in less viscous and faster flowing oil, reducing the opportunity for the oil to polymerize and dehydrate to char. This charring phenomenon was observed for the indirect contact heat exchange system and is illustrated in Figure 8. Accordingly, the direct
contact heat exchange system not only increases the recovery of the heavy ends of bio-oil, it eliminates troublesome fouling of the bio-oil recovery system. Furthermore, the turndown ratio for the direct contact heat exchange system is easily controlled by simply modulating the water injection rate to match the cooling load without costly changes to the vessel geometry or the need for additional surface area.

Figure 6. Cut–away views of the original shell and tube condenser (left) and the quench vessel (right) used to compared indirect contact heat exchange and direct contact heat exchange with water as the quench media, respectively, in a fast pyrolysis pilot plant.
Figure 7. Pyrolysis product yield comparison between conventional condenser and quench vessel for bio-oil recovery.

Figure 8. Dehydration of bio-oil to char on the tube sheet plenum of the heavy ends condenser for the indirect contact heat exchange bio-oil recovery system.
4. Conclusions

The cooling rate of pyrolysis vapors plays a significant role in sugar recovery. The novel bio-oil collection system described in this work was shown to increase levoglucosan recovery from fast pyrolysis of pure cellulose by more than 20% compared to a conventional condenser system. The increased sugar recovery is attributed to reduced decomposition of sugars during the recovery process. This is accomplished by reducing the residence time of the pyrolysis vapors at high temperature, decreasing the concentration of levoglucosan in the cooling vapor stream, and eliminating the temperature gradient encountered in the condensation film of the conventional condenser system. These results encourage the design of bio-oil recovery systems that can rapidly quench products to improve the recovery and quality of bio-oil. A practical implementation of this concept using water as quench media was designed and installed into a pilot scale, lignocellulosic biomass pyrolyzer. It similarly showed improvements in recovery of bio-oil attributable to reduced decomposition of the heavy ends of bio-oil. Our future work includes designing a water quench vessel for recovery of the heavy ends of bio-oil in a 50 ton per day demonstrate-scale pyrolysis plant.

5. Acknowledgements

The authors would like to thank the Phillips 66 Company and the National Advanced Biofuels Consortium for their generous financial support of this project. We would also like to thank Marjorie Rover, Patrick Johnston, and Ryan Smith of the Bioeconomy Institute at Iowa State University for assistance with many aspects of the project. The authors would also like to thank undergraduate research assistants Jordan Donner, Sean Smith, Chris Quinett, and Nick Miller for helping run the experiments and analyze samples.
6. References


