

Process Water from the Hydrothermal Carbonization of Biomass: A Waste or a Valuable Product?

Harpreet Singh Kambo¹ · Jamie Minaret¹ · Animesh Dutta² 

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Abstract Hydrothermal carbonization (HTC) is a promising method for the production of energy dense coal-like material from low quality lignocellulosic biomass. The process takes place in the presence of water and therefore is unaffected by feedstocks containing a high moisture content. However, the substantial water requirement and disposal concerns for a large scale HTC plant may outweigh its advantages from an economical and environmental point of view. The work presented in this study proposes a solution to the aforementioned problem. Miscanthus feedstock was treated hydrothermally at three different reaction temperatures (190, 225, and 260 °C) for 5 min with a solid load ratio of 1:6. The liquid by-product from each experiment was characterized for chemical composition. The results show that the HTC process water was rich in organic acids (acetic, formic, levulinic, and glycolic acid), Hydroxymethyl-furfural (HMF), and total organic carbon (TOC). The acidity and the concentration of intermediate products in the HTC process water increased with an increase in reaction temperature. The HTC process water produced at 260 °C was examined for the recirculation of process water. The results show that, during successive recirculation of HTC process water, the mass yield of the hydrochar samples increases by 5–10% and the energy yield of the hydrochar samples increased up to 15% compared to the HTC-reference sample (hydrochar sample produced at initial

run). Most importantly, the HHV of hydrochars increased from 18.9 (raw biomass) to 26.6 MJ/kg (maximal value) during recirculation of process water. As a result, the recirculation of process water can increase the overall system's efficiency and reduce both the operating costs and environmental impact of a commercial HTC plant.

Keywords Hydrothermal carbonization · Organic acids · Recirculation · Process water

Introduction

The abundant amount of biomass on earth plays a substantial role in global energy production as it has been widely consumed as an alternative to fossil fuels for the purpose of generating heat and power. Lignocellulosic biomass wastes (agricultural and forest residues) and purpose grown energy crops (miscanthus, switchgrass, etc.) are favored over first generation biomass because of their nonedible characteristics; hence they do not compete with food shortage when the waste-biomasses are consumed for producing energy [1]. Therefore, the consumption of lignocellulosic biomass wastes as a resource of fuel has gained remarkable attention in the development of a clean, green renewable energy society. However, lignocellulosic biomass has inferior physicochemical properties when compared to coal, which include poor homogeneous nature, high moisture content and hydrophilic nature, poor grindability, low bulk energy density, and high alkali and alkaline earth metal content. Therefore the utilization of raw lignocellulosic biomass can be highly inefficient and expensive [2]. Treatment processes can be applied to biomass to overcome the aforementioned limitations [3]. Torrefaction, a thermal treatment

✉ Animesh Dutta
adutta@uoguelph.ca

¹ School of Engineering, University of Guelph,
Guelph N1G 2W1, Canada

² Mechanical Engineering Program, School of Engineering,
University of Guelph, Room No RICH 3509, 50 Stone Road
East, Guelph, ON N1G 2W1, Canada

process is one of the most commonly proposed options for improving the fuel quality of biomass [4]. The combustion properties of torrefied biomass are improved to some extent but are not comparable to that of coal. The high alkali and alkaline earth metallic composition in biomass ash is not removed by the torrefaction process and therefore remains a challenge during co-firing and direct combustion of biomass. Moreover, wet lignocellulosic biomass remains highly underutilized because it cannot be economically converted to biofuels with satisfying fuel qualities via conventional dry thermal treatment technologies such as torrefaction, pyrolysis, and gasification.

As an alternative to traditional conversion methods, a relatively new process called hydrothermal carbonization (HTC), also referred as wet torrefaction, demonstrates potential for converting a diverse range of feedstocks (both wet and dry) into an energy-dense solid fuel that contains significantly improved physicochemical properties. The HTC process has attracted a great deal of interest primarily because it uses water as a reaction medium, which is non-toxic, environmentally benign, and inexpensive reactant that is also inherently present in wet or freshly harvested green biomass waste [5]. Hydrochar, also referred to biochar/biocoal, is the desired solid end product in the HTC process [5]. Typically, for an HTC process the biomass is submerged in water and the mixture is heated in a confined system at elevated temperatures (180–260 °C) and high pressure (2–15 MPa) with a reaction time of 5 min to several hours [6]. Although both reaction time and temperature have been observed to influence the physicochemical characteristics of the HTC products, the reaction temperature remains the most governing process parameter [6–8]. Typically, for the HTC process, water is added to the system at a ratio of 3–10 times the dry mass of biomass [8–11].

For a typical industrial-scale HTC plant, the continuous supply of process water would be one of the main operational challenges. Previous experiments have shown that the hydrochar samples obtained at 260 °C have coal-like combustion properties [12]. However, to produce such a type of material, massive amounts of water may be required at full scale operation, which may not be an economical or environmentally friendly approach. For example, to produce one metric ton of dry hydrochar from miscanthus at 260 °C assuming a 50% mass yield of hydrochar and a 1:6 solid load ratio of (dry) biomass to water, would require 12 metric tons of liquid water [12]. At an industrial scale, this substantial demand for the process water may outweigh the superior properties of hydrochar in terms of production cost. Therefore the recirculation of process water is a potential method for increasing the overall efficiency of the system. Other important advantages associated with the recirculation of HTC process water are:

- i. Reduction in the waste water, which would also reduce the waste water treatment cost associated with HTC plant,
- ii. Recirculation of the process water has been suggested as the most efficient method of heat recovery and can reduce the external heat consumption by ten-folds [13],
- iii. The formation of acetic acid in the process water may further catalyze the process during recirculation and therefore can simultaneously reduce the pressure and temperature requirements,
- iv. The degraded sugar compounds from the biomass polymers present in the HTC process water might deposit in the porous structure of hydrochar, which may further augment the overall energy density of solid, and
- v. The HTC process water can also be used for the anaerobic digestion of certain types of biomass [14].

Due to the degradation of biomass polymers in the aqueous phase, the recirculation of HTC process water is expected to improve the mass yield and HHV of the hydrochar samples. Most of the research studies on HTC have been carried out with the primary focus on the production of hydrochar; there is limited literature available describing the effects of process water recirculation on HTC. Several research investigations have been performed in the past and are reported to describe the reaction mechanism of biomass degradation under hot compressed water [6, 15]. The basic reaction pathways are known for the primary components of biomass: (a) Cellulose hydrolysis primarily forms oligosaccharides and then monomeric glucose. This isomerizes and forms fructose which then dehydrates and forms hydroxymethylfurfural (HMF). Formation of HMF subsequently is assumed to polymerize to char, and or may also rehydrate to levulinic and formic acid. (2) Hemicellulose hydrolysis at first forms oligosaccharides and later monomeric xylose which then dehydrates and forms furfural which subsequently polymerizes. (3) Lignin forms several phenolic compounds which, however, readily polymerize. The recirculation of HTC process water adds benefit to the reaction mechanism as the liquid is already acidic in nature and warm, two qualities that speed up HTC reactions [7, 16, 17]. Recent investigations on the recirculation of process water show some promise. It has been demonstrated that mass yields, percentage carbon in the solid product, hydrophobicity i.e. dewatering properties of the biochar and HHVs can be improved with the recirculation of process water in HTC process [18, 19]. For an HTC process at industrial scale, recirculation of HTC process water will become significantly important factor as a mean to minimize the consumption of fresh water and the costs associated with the wastewater treatment.

Purpose grown energy crops like miscanthus represent a significant share in bioenergy development, as these crops

grow quickly and require less maintenance [20], also the pellets produced from the HTC of miscanthus have shown considerable advantages over raw white wood pellets [21]. To date there is no information available about the HTC process water produced from a quick growing energy crop. The aim of the work presented in this study is to characterize the HTC process water produced at different reaction temperatures and to demonstrate the effect of process water recirculation on the physicochemical properties of hydrochar and the chemical composition of the recycled aqueous phase.

Materials and Methods

Materials

To study the HTC process water characterization and recirculation, miscanthus (*Miscanthus × giganteus*, ‘Nagara’) feedstock was considered in this study. The feedstock was harvested in May 2013 and collected from a privately owned farm in Drumbo, Ontario. Prior to experiments, the feedstock was prepared for uniformity and was manually chopped into samples of lengths ranging from 20 to 25 mm. The prepared samples were then stored in a sealed plastic bag until treatment. Since the HTC process uses water, the samples were not dried prior to the experiment. Therefore the experiments were undergone with the as received moisture content of 10.67% dry basis (d.b.), which was determined by drying the sample at 105 °C for 24 h according to the ASTM E1756 test standard.

Experimental Methods

Hydrothermal Carbonization (HTC)

HTC of biomass was carried out using a Parr 600 ml series 4560 bench top reactor (Moline, IL) fitted with a glass liner (762HC3) [21]. To characterize the HTC process water, the experiment was performed at three different operating temperatures (190, 225, 260 °C) with residence times of 5 min. The feedstock to water ratio (or solid load) was 1:6, based on the dry mass of the feedstock. However, since the feedstock used in the experiment was not dried, the as received moisture content (10.67%) was taken into account when determining how much deionized water to add to achieve the 1:6 solid load ratio. The temperature of the system was controlled using a Proportional–Integral–Derivative (PID) temperature controller. The reactor pressure was not controlled in the experiments and was kept autogenic with the vapor pressure of water at the corresponding reaction temperature. The pressure inside the reactor ranged from 1 to

5 MPa during the experiments, as indicated by the pressure gauge attached to the reactor.

Prior to the reaction, 10 g of miscanthus feedstock was mixed with deionized water in different ratios and manually stirred for 2–3 min to ensure complete wetting. The reactor was heated up to the required temperature in about 20–30 min and was then maintained to ± 5 °C for the desired time period. It should be noted that the pre-heating time for the reactor would also play an important role in the HTC reaction chemistry because a higher reaction temperature would also require longer pre-heating time. However, in this study for the data analysis purpose, the reaction temperature was defined as the isothermal holding time period (i.e., 5 min at 190, 225, and 260 °C). Later, to further quench the reactions, the reactor was immersed in cold water and was cooled down to room temperature in about 5–7 min. Once the inside temperature of the reactor dropped to room temperature, the pressure release valve was opened under a fume hood and the gaseous products were allowed to escape. The solid and liquid products were separated using filter paper (20 μm) and both the products were collected for further analysis. The hydrochar samples were dried overnight at 105 °C before analysis, where liquid samples were stored in the air tight glass bottles and were kept in refrigerator. To ensure reproducibility and consistency, the experiments were repeated three times.

Process Water Recirculation

Previous work in this area of research has shown that the physicochemical properties of the hydrochar samples obtained at 260 °C are comparable to that of coal [12, 21]. However, to produce such a material at industrial scale, the supply of fresh water will be one of the key factors. This demand for fresh water can be minimized by the recirculation of some fraction of process water after filtration of the hydrochar slurry. Therefore, to analyze the effect of process water recirculation on the mass yield, HHV, and ash content of the hydrochar samples, the liquid by-product was collected from the initial run and was used in the next cycle of the HTC experiment for a total of ten runs all at the reaction temperature of 260 °C. Sufficient amount of makeup water (de-ionized) was added to bring the total liquid mass to six times the (dry) biomass. An identical procedure was repeated for 10 recirculation experiments. For the experiments, the solid (hydrochar) and liquid phase was separated mechanically with 99.9% recovery of process water. Nearly 10 g of process water was collected from each run for analysis; and therefore for each run, the makeup water added in recirculation experiments was 17% (i.e. 10 of 60 g) of the total water required. The amount of the makeup water required for HTC experiments was calculated based on the theoretical mass of pure water. Prior to the recirculation

experiments, the raw miscanthus feedstock was mixed with process water and was manually stirred for 2–3 min to ensure complete wetting.

Analytical Methods

Mass Yield

The mass yield of each HTC experiment was determined by recording the fraction of dry mass remaining in the hydrochar sample compared to the original dry mass of the raw miscanthus.

Higher Heating Value (HHV)

The higher heating values (HHV) of raw and treated solid samples were determined using IKA C200 bomb calorimeter (Wilmington, NC). All the samples were oven dried at 105 °C for 24 h prior to analysis.

Ash Content

The ash content was measured according to the ASTM E1755 test standard, using a Thermo Scientific Thermolyne Muffle Furnace Model number F48055-60. All the samples were oven dried at 105 °C for 24 h prior to analysis. The samples were heated to 250 °C at 10 °C/min and held at 250 °C for 30 min, then heated again to 575 °C and kept at ± 25 °C for 3 h. The mass of the remaining solid was taken as the ash content.

pH

The pH values of the liquid samples were measured using a digital probe meter (Thermo Orion pH meter, model 210 A). Each reading was measured twice with an absolute error of ± 0.02 .

Total Organic Carbon (TOC), Organic Acids and Furfurals

TOC of liquid samples were measured by a Shimadzu TOC-ASI analyzer at the University of Western Ontario, London, Ontario. The concentration of organic acids (acetic acid, levulinic acid, glycolic acid, and formic acid) and HMF were measured by a Dionex Ionic chromatographer system (ICS)-3000 at the University of Western Ontario, London, Ontario. The chromatography system utilized a Waters 1525 Binary HPLC System with Waters 2487 Dual λ Absorbance Detector and a HPLC Water Sunfire C18 5.0 μm 4.6 mm \times 150 mm column. The analysis conditions for the liquid chromatography measures were: an Eluent (Mobile Phase) of 1 mmol/l H_2SO_4 + 8 mmol/l Na_2SO_4 ; a flow rate of 0.8 ml/min, and UV wavelength of 210 nm.

Ultimate Analysis

The composition of carbon, hydrogen, nitrogen, sulphur, and oxygen of the untreated and treated miscanthus were determined using the Thermo Scientific Flash 2000 CHNS/O Analyzer. These results were used to determine the H/C and O/C ratios of each sample.

Results and Discussions

HTC of Miscanthus

The chemical properties and percentage distribution of HTC product streams significantly depend upon the process operating conditions [22]. Although both reaction time and temperature have been observed to influence the physicochemical characteristics of products, the reaction temperature remains the most governing process parameter [12]. The mass yields of the hydrochar samples from miscanthus feedstock were found to be 84, 68, and 48%, at the reaction temperatures of 190, 225, and 260 °C, respectively. The considerable reduction in the mass yield of solid product with an increase in the reaction temperature is mainly caused from the decomposition and depolymerisation of cellulose and hemicellulose components into liquid and gaseous by-products, which also increases the hydrophobicity of the solid hydrochar [6, 23, 24]. The HHV of the raw miscanthus used was 18.9 MJ/kg (d.b.) and the HHV of the hydrochar samples increased to 19.6, 21.4, and 26.1 MJ/kg (d.b.) for the reaction temperatures of 190, 225, and 260 °C, respectively. HTC reaction temperature has most significant effect on the decomposition/depolymerisation of biomass components that can be hydrolyzed. Hemicellulose is almost completely hydrolyzed around 180 °C, main parts of lignin are hydrolyzed around 200 °C, where the hydrolysis of cellulose does not occur below 220 °C. Moreover, additional pyrolytic reactions might become increasingly influential at higher temperatures under subcritical conditions [6]. Under subcritical water conditions, the degradation of polymeric composition of biomass results in the formation of intermediate compounds like monomers, furfurals, and 5-Hydroxyl Methyl Furfural (HMF) [8]. These intermediate particles are characterized as aqueous soluble materials during fiber analysis, which increases with an increase in the HTC reaction temperature [24]. 5-HMF has several value-added applications in biochemical industry. The HHV of 5-HMF is about 22 MJ/kg, which is significantly higher than that of hemicellulose and cellulose, and is close to that of lignin [3]. Precipitation of such compounds in the porous structure of hydrochar may further enhance the overall energy density of a solid product [8]. Usually, a very small fraction of gaseous products

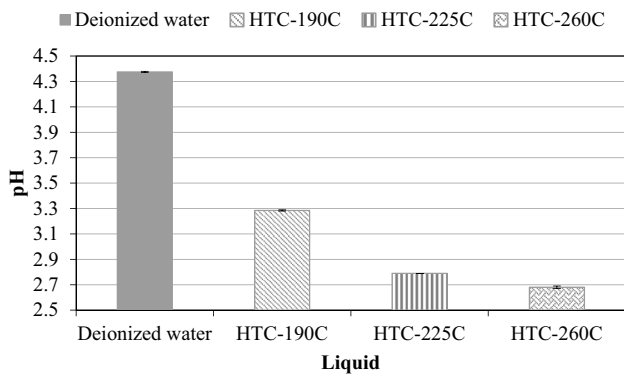


Fig. 1 Effect of the reaction temperature on the pH of HTC process water produced at different reaction temperatures

(<5–10%) are produced under HTC conditions especially when performed below 260 °C [5, 22, 25], therefore, most of the important decomposed organic compounds were expected to be present in the liquid by-product. Hence, the characterization of the HTC process water is crucial for the development of an industrial HTC plant.

Characterization of HTC Process Water

The effect of reaction temperature on the pH of the HTC process water is presented in Fig. 1. Fresh deionized water was used to start the HTC of miscanthus. The deionized water has tendency to react with the CO₂ present in the air, which results in the formation of carbonic acid; this explains the reason why the deionized water has such a low pH value (Fig. 1). The result shows that the pH of HTC process water reduces with an increase in the HTC reaction temperature. This is due to the presence of acidic components in the HTC process water that were formed during the decomposition and depolymerisation reactions of biomass [5]. The HTC process water produced at 225 °C shows a sharp drop in the pH value and almost remained constant with a further increase in reaction temperature (Fig. 1). Hoekman et al. [7] observed that the concentration of the total organic acids produced during the HTC of different biomass feedstocks increases with an increase in the process reaction temperature. Also, in their study, the maximum increase in the concentration of total organic acids was observed at 215 °C compared to small fraction of acids produced at 175 °C. Hence, under subcritical conditions, the rate of conversion of polymeric compositions of biomass to organic acids increases with an increase in the reaction temperature.

The results of the pH value are consistent with the results of the organic acids characterized during the high performance liquid chromatography (HPLC) analysis (Fig. 2). It can be observed that a very small amount

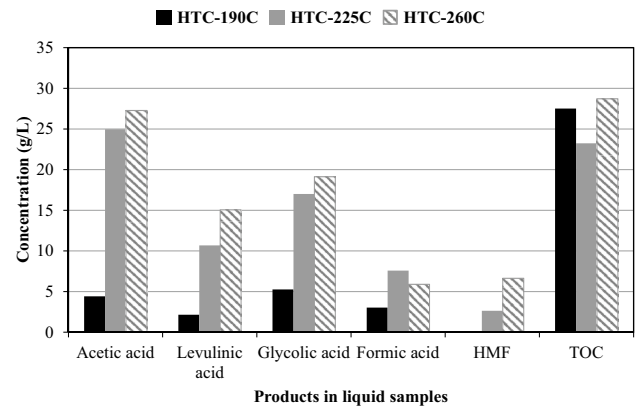


Fig. 2 Effect of reaction temperature on concentrations of different compounds in HTC process water

of organic acids were produced at a low temperature (190 °C), however, the formation of acids increased with an increase in the HTC reaction temperature (i.e., at 225 and 260 °C). Acetic acid was the most dominating component among all the organic acids characterized in this study, with the exception of the process water produced at 190 °C, which contained a slightly larger concentration of glycolic acid compared to acetic acid (Fig. 2). A slight reduction in the concentration of formic acid was observed at 260 °C compared to the concentration observed at 225 °C. This could have been due to the decomposition (oxidation) of formic acid into the gaseous products (mainly CO₂) under hydrothermal reaction conditions [26]. The concentrations of TOC in the HTC process water were found to be 27.5, 23.2, and 28.7 g/l at 190, 225, and 260 °C, respectively.

Recirculation of HTC Liquid By-product

The characterization of the HTC process water shows the formation of organic acids and important intermediate compounds in the aqueous by-product. Moreover, the addition of salt and acid in the HTC process water has also shown an improvement in the HHV of the hydrochar samples [27]. However, the supplement addition of organic acids and salts in the HTC process and the use of fresh water for every run is neither an economical nor environmental-friendly option. Recovery of organic acids and intermediate compounds from the HTC process water significantly depends on the availability of the bio-refinery industry, which is also challenging in terms of processing steps, such as; extraction, separation, and purification [6]. These aforementioned limitations of HTC can be minimized by recycling/recirculating the process water after filtration of the hydrochar slurry.

Effect of Recirculation on pH of Process Water

The pH of the HTC process water significantly depends on the initial pH of the fresh water that was used in the process. The pH of the process water was found in the range of 2.5–3.5 (acidic in nature). The HTC process water produced at 260 °C was chosen for the recirculation experiments because it showed the highest acidity (pH 2.68), highest acetic acid concentration (27.28 g/l), highest HMF concentration (6.64 g/l), and highest TOC concentration (28.72 g/l). The presence of such compounds in the HTC process water can significantly improve the HHV of hydrochar samples produced during recirculation. The pH of the fresh deionized water used in this study was found to be 4.37 ± 0.01 , which significantly dropped to 2.72 ± 0.01 after the first HTC run (Fig. 3). However, during the recirculation, the pH of the process water remained almost constant with the negligible drop of 0.05.

Effect of Recirculation on Mass Yield

The mass yield of the hydrochar samples, during the recirculation of process water, increased by 5–10% for the 2nd and 3rd runs when compared to the mass yield of the reference-HTC sample (the initial sample produced in HTC using fresh deionized water, Fig. 4). The mass yield of the hydrochar samples remained almost unaffected after the 4th recirculation.

The scanning electron microscope (SEM) images of raw and pretreated miscanthus showed a porous structure [27]. The formation of a considerable amount of aqueous soluble products and organic acids were observed in the HTC process water; therefore the increase in mass yield of the hydrochar samples may have been from the deposition of such intermediate compounds on the porous surface of the hydrochar particles. Alternatively, during recirculation,

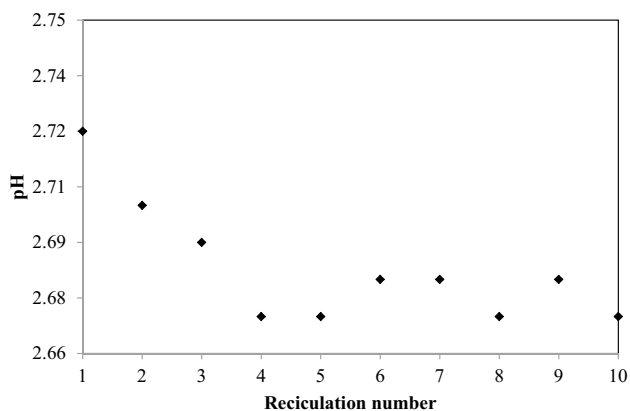


Fig. 3 Effect of recirculation of HTC process water on pH of liquid by-product

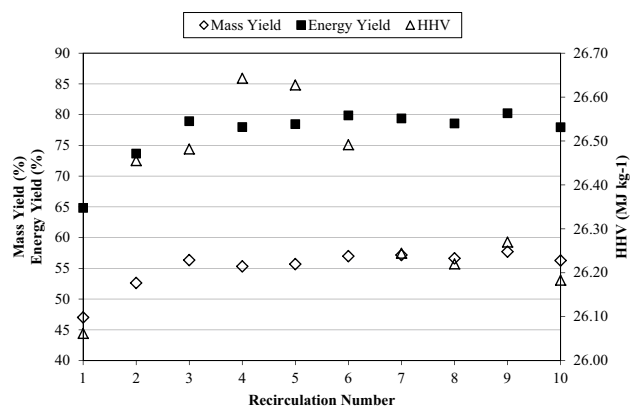


Fig. 4 Effect of recirculation of HTC process water on Mass Yield, HHV, and Energy Yield of hydrochar samples

the HTC process water from initial runs may have caused the resistance towards the diffusion of the intermediate compounds from the hydrochar surface to the bulk solution [28], causing an increase in the mass yield. Also, after the 4th recirculation run the stable pH value of the process water (Fig. 3) and the mass yield of the hydrochar samples (Fig. 4) may have been caused from the reaction mechanism reaching equilibrium during recirculation. Similar results were also reported by other studies using loblolly pine wood [28] and poplar wood samples [18]. Although the mass yield did remain fairly consistent after the 4th run, it can be observed that a slight increase occurred over the span for 4th–9th runs (Fig. 4). This is likely attributed to the polymerization of HMF into heavy compounds [29] that deposit into the structure of the hydrochar. This argument is also supported by the concentration of HMF in the process water (Fig. 5). HMF reaches a maximum concentration at the 4th run and then remains fairly consistent thereafter,

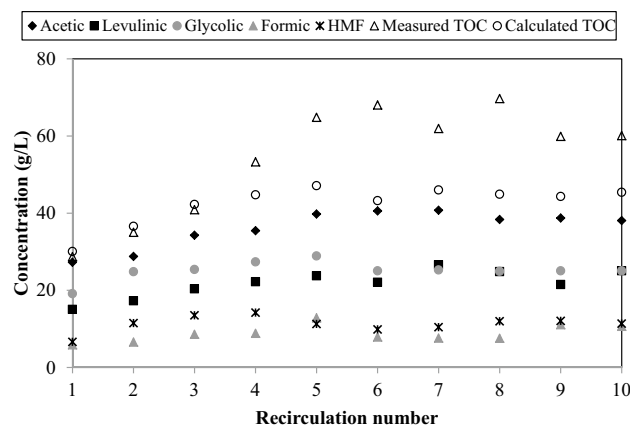


Fig. 5 Concentrations of organic compounds produced during HTC process water recirculation

meaning that the HMF was most likely being produced and polymerizing (consumed) at a similar rate.

Effect of Recirculation on HHV and Energy Yield

The HHV of hydrochar samples increased until the 4th and 5th recirculation and then started to reduce (Fig. 4). Due to the degradation of hemicellulose and cellulose in HTC, small fractions of organic acids (e.g., acetic acid, formic acid, levulinic acid, and glycolic acid) are produced in the process water (Fig. 2). The presence of these acids in the liquid phase catalyzes the reactions such as decarboxylation and dehydration [18, 28], which are the reactions that are expected to improve the carbon content of feedstock, therefore causing an increase in the HHV of the hydrochar samples [6]. The increase in HHV of the hydrochar samples was also observed during the addition of acetic acid in the HTC process [27]. However, after the 4th recirculation, the small reduction in the HHV of the hydrochar samples might have been due to the excessive formation of acetic acid, which caused the reactions to reach to an equilibrium state. The high quality intermediate compounds like HMF particles are produced during the HTC process, however, the presence of an acidic surrounding in HTC rehydrates these HMF particles to low HHV compounds such as levulinic acid and formic acid [30]. Therefore the rehydration HMF particles cause a reduction in the overall HHV of the hydrochar samples. Another study performed on the recirculation of the HTC process water using loblolly pine as the feedstock, suggested that the organic acids (acetic acid, formic acid, and levulinic acid) produced during HTC are highly oxygenated compounds, which have relatively low HHV compared to the deoxygenated hydrochar carbon particles [28]. Hence, any deposition of oxygenated compounds on the surface of hydrochar particles will most likely reduce the overall HHV of the product. Energy yield, which is an important measure during any thermochemical conversion pre-treatment of biomass, is defined below; the results for energy yields are shown in the Fig. 4 and it is very important to note that the overall energy yield of hydrochar significantly increased from about 65 to 80% with the process water recirculation.

Energy Yield = Mass Yield \times Energy Densification Ratio
 where; Energy Densification Ratio = $\frac{\text{HHV of dried Hydrochar}}{\text{HHV of Raw dry Biomass}}$

Effect of Recirculation on the Chemical Composition of Process Water

The formation of organic acids, TOC, and HMF particles in the HTC process water produced during the recirculation experiments are presented in Fig. 5. The concentration of organic compounds in the HTC process water was

expected to increase with each recirculation because of the production of organic compounds from the degradation and depolymerisation reactions; however a different trend was observed. The concentration of organic compounds in the process water increased during the first five recirculation, and thereafter remained almost constant. These unexpected results may have been due to the interaction between the solid and liquid reaction chemistry in the HTC experiments [28]. During HTC of biomass, organic compounds are produced in the liquid phase and at the same time deposition of those organic compounds takes place on the solid particles. As a result, the final concentration of organic compounds in the liquid phase significantly depends upon the rate of production and the rate of deposition. Therefore, the plateau in the increase of the organic compounds in the HTC process water (Fig. 5) could have been due to the increased deposition of organic compounds onto the hydrochar particles. These findings are consistent with [18], who carried out HTC water recirculation experiments with poplar wood chips at 220 °C. Organic concentrations have been used to determine a calculated TOC in order to compare the value to the experimentally measured value. The difference will inform about the amount of organics which have not been identified by HPLC analysis. For the first three recirculation tests, the measured TOC was within a reasonable range of error compared to the measured TOC. However, after the 4th recirculation the calculated TOC was found to have at least a 25% difference compared to the measured TOC. This indicates that after the 4th recirculation additional organic compounds were produced that were not identified by HPLC analysis. To gain a better understanding of the rate at which different organic acids are produced and the rate at which they deposit onto solid particles will require future studies with a more narrow focus into the reaction kinetics of the HTC reaction.

Effect of Recirculation on Atomic Ratios (H/C–O/C) of Hydrochar Samples

To analyze the variation in elemental compositions, the atomic ratios of hydrogen to carbon (H/C) and oxygen to carbon (O/C) of both raw and hydrochar samples produced during recirculation are presented in Fig. 6 (VanKrevelen diagram [31]). The “Van Krevelen diagram” provides the general information about atomic ratios (O/C–H/C) of typical fuels, such as biomass, peat, and different types of coals. A solid fuel with the low O/C–H/C atomic ratio is considered to be favorable because of the decreased smoke, water vapor and energy losses experienced during combustion [11]. Raw biomass has a very low carbon content and high oxygen content compared to coal (Fig. 6). However, due to the removal of water and carbon dioxide, the HTC hydrochar contains low O/C–H/C atomic ratios when compared

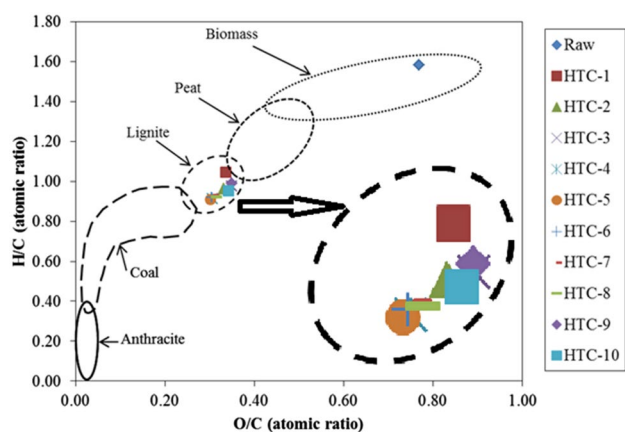


Fig. 6 Atomic H/C–O/C ratios of raw and hydrochar samples from recirculation experiments

to raw biomass and therefore is more a coal-like product. In addition, the O/C–H/C atomic ratio of hydrochar samples decreases with an increase in the number of process water recirculation. The presence of organic acids formed during the recirculation experiments might have catalyzed the dehydration and decarboxylation reaction mechanisms, which are the reactions mainly responsible for the reduction in the oxygen content and increase in carbon content of the hydrochar. The ash content of the hydrochar samples produced during recirculation experiments increased from 0.8 to 1.54% for the 1st and 10th recirculation experiment, respectively. This increase in the ash content of the hydrochar samples produced during recirculation is mainly from the re-deposition of inorganic elements in the porous structure of hydrochar samples.

Conclusions

The results show that the HTC process water is highly acidic in nature (with a pH between 2.7 and 3.3) and contains some organic acids, of which acetic acid is the highest fraction. Additionally, the process water was observed containing small fraction of intermediate chemical compounds like 2,5-HMF that have several value added applications in the chemical and bio-refinery industry. The process water was also found rich in total organic carbon (TOC). The concentration of organic acids, TOC, and HMF particles in the HTC process water increases with an increase in the process reaction temperature. All these compounds are expected to improve the HHV of hydrochar samples during the recirculation of process water. The results show that the mass yield of hydrochar samples increased by 5–10% during the 2nd and 3rd recirculation, and then remained almost constant for the successive recirculation runs. The HHV

of all the hydrochar samples produced during the recirculation experiments remained higher than that of the reference-HTC sample (26.06 MJ/kg). A maximum HHV of the hydrochar was attained for the sample produced at the 4th recirculation (26.64 MJ/kg). Energy yield of the hydrochar samples significantly increased from about 65–80% with the recirculation of process water. All these findings show that the HTC process water is composed of chemical reaction compounds, which can catalyzed the dehydration and decarboxylation reaction mechanisms and therefore can significantly improve the system's overall efficiency.

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