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Characterization of Products from Catalytic Hydrothermal Carbonization of Animal Manure

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Abstract: This paper presents hydrothermal carbonization (HTC) of cow and pig manure in an acidic environment and compares the results with HTC performed without acid. HTC experiments were carried out at 170 °C for 10 min. The presence of an acid increased the extent of carbonization and energy densification for both types of manure. The heating value of the hydrochar was increased by an amount ranging from 9–21%, with sulfuric acid having a greater impact than acetic acid. The increased fuel densification may provide for more economic use as a fuel. Both acids increased the leaching of ionic species including PO₄, Ca, K, Mg, and Fe. The results demonstrated conversion greater than 90% of total phosphorous to phosphate in hydrothermal conditions. HTC with sulfuric acid resulted in increased nitrogen leaching for both types of manure and resulted in the generation of ammonia. Further analysis of the aqueous products signified the formation of acetic acid, furfural, and 3-aminopyrazine 1-oxide compounds for the sulfuric acid-catalyzed hydrothermal treatment. Analysis of the residual gas confirmed the presence of a trace amount of H₂S, NO₂, and SO₂ formation. The addition of sulfuric acid increased NO₂ significantly. Finally, detailed mass balances are presented for carbon and macronutrients (NPK).

Keywords: recycling; waste valorization; thermal hydrolysis; homogeneous catalysis; nutrient recovery



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1. Introduction

Significant environmental damage caused by livestock waste produced in large amounts is an issue of concern worldwide, especially in the United States, European Union, and China [1–3]. The problem stems mainly from two aspects of this waste. One is the potential runoff of nutrients to nearby surface waters (eutrophication), and the other is related to the emission of greenhouse gases formed during the degradation of the animal wastes (predominantly methane and ammonia) and which contributes to particulate matter (PM) formation in the atmosphere. As such, research on the treatment and valorization of animal waste has recently received significant attention.

Hydrothermal carbonization (HTC) has emerged as a promising way to utilize wastes and biomass with high moisture content to produce fuels or energy materials [4]. HTC is a thermochemical process that uses water under subcritical conditions at moderate temperatures (170–280 °C) and autogenous pressure as the reaction medium. Therefore, unlike other thermochemical processes such as pyrolysis, torrefaction, and gasification, wet feedstocks do not need to undergo a drying step before HTC. As a result, a large body of literature on HTC of various kinds of biomass such as sewage sludge, food waste, municipal solid wastes, algae, distillery grain, and many other organic wastes has formed [5–10].

The main products of HTC treatment are hydrochar (solid), process water, and a small amount of gas. The solid product, called hydrochar, is carbonaceous, friable, and hydrophobic, with characteristics similar to lignite. The process water contains some fraction of the carbon content in the form of various organic chemical species that may be suitable for resource recovery or recycling [11]. The chemistry and reaction pathways of HTC are complex and are affected by the nature of the biomass. However, some known reactions are assumed to be involved in most HTC applications, such as hydrolysis, dehydration, decarboxylation, polymerization, and condensation [12]. In addition, there are numerous studies on operation parameters influencing the HTC process and the properties of its products. Reaction temperature, reaction time, biomass to water ratio, and catalyst are widely investigated factors. Temperature seems to have the most significant effect on HTC reactions and products [13]. Increased temperature generally reduces mass yield and raises the energy value of the hydrochar by increasing the carbon content.

Several studies have focused on the impact of catalysts on the hydrothermal treatment of biomass. Karagoz et al. studied the effect of K_2CO_3 , $RbOH$, and $CsOH$ as alkaline homogenous catalysts on the distribution of products in hydrothermal liquefaction of woody biomass at 280 °C with a reaction time of 15 min and found that those catalysts reduced the production of char and favored the formation of oil products [14,15]. Mumme et al. used natural zeolite as a heterogeneous catalyst in HTC of digestate at different temperatures. They discovered that the catalytic effects of zeolite increased the degree of carbonization to the same extent as an increase in temperature of 9–29 K [16]. Ekpo et al. has investigated the extraction of nitrogen and phosphorus in process water of the hydrothermal treatment of swine manure with both acidic and alkaline catalysts at different temperatures ranging from 120 °C to 250 °C [17]. In previous work, we investigated the influence of several organic and inorganic acids on the extraction of nutrients from cow manure [18]. One recent study has focused on the influence of temperature, residence time, and acidic and alkaline condition on the fate of nitrogen and phosphorus during HTC of pig manure, where it was found that the addition of sulfuric acid or potassium hydroxide reduced P, Ca, Mg, Cl and heavy metal elements in hydrochars [19]. Lang et al. investigated the properties of the hydrochar derived from CaO-assisted HTC of swine manure and reported increased pH and yield of hydrochar. In addition, they discovered the presence of polar functional groups on the surface of the hydrochar resulting in greater hydrophilicity and well-developed porosity that improves the interaction between the hydrochar and soil when the hydrochar was used as soil amendment [20].

In this study, we aim to understand the effect of homogeneous acidic catalysts on physicochemical properties of the hydrochar produced from HTC of both cow and swine manure (e.g., carbonization and energy densification). Further, we report on the distribution and mass balances of C, N, P, and K from manures after HTC with and without acidic catalysts. An organic acid (acetic acid) and an inorganic acid (sulfuric acid) are both evaluated as HTC catalysts.

2. Materials and Methods

The cow manure was acquired from the University of Nevada Reno, Main Station Farm. The dewatered swine manure sample was obtained from a 1200-sow farrow-to-feeder and 13,000 feeder-to-finish farms in North Carolina. Both feedstocks were dried at 105 °C overnight, ground (<1 mm) and stored in sealed bags until analysis or HTC experiments.

HTC reaction conditions were selected to optimize phosphorus extraction, as previously described [18]. All HTC experiments were conducted at 170 °C. A total of 80 g of dried biomass were mixed with 1 L of solution for every experimental run. HTC experiments were conducted with DI water, with 0.3 M sulfuric acid, and with 0.3 M acetic acid. The mixture was then placed into a glass liner and put inside a 2-L Parr reactor that was then tightly sealed. The air inside the reactor was purged with nitrogen gas through pressuring the reactor up to 20 bar and releasing the gas twice. After mounting the reactor to its stand, the heater was connected and the reactor was heated at a constant rate (5 °C/min) until

the temperature set point (170 °C) was achieved. The reactor with its contents was kept at 170 °C for 10 min. Quenching was performed by placing the sealed reactor in an ice water bath. The final pressure of the reactor was recorded at 35 °C in order to estimate the total amount of gas produced during the experiment. After cooling the reactor to room temperature, a gas sample was captured in a Tedlar bag, and all remaining gas was vented into the fume hood. Slurry from the reactor was filtered via the Buchner vacuum funnel technique using Whatman® grade 6 filter papers with a pore size of 3 µm. The hydrochar filter cake was rinsed with deionized water and dried in an oven at 105 °C for 24 h. Every experiment was carried out in duplicates and from each experiment approximately 100 mL of process water filtrate was stored at 5 °C for later analysis.

The ultimate analysis of all the solid samples (hydrochar and dried manure) was conducted in a Thermo Scientific FlashSmart, Waltham, MA, USA elemental analyzer. Each sample was ground in a mortar and three replicates were analyzed to best assess these heterogeneous solid samples. Oxygen is measured directly using this instrument.

The ICP-AES technique was employed to obtain the elemental composition of the inorganic fraction of solid samples, i.e., the ash analysis. For this analysis samples were first digested in microwave digester using a mixture of hydrochloric acid, nitric acid and hydrogen peroxide.

The proximate analysis (ash, volatile matter, and fixed carbon) of the solid samples was carried out using a TA Q500 TGA instrument. The method applied for this analysis was adopted from ASTM D7582 standard. For the analysis of nitrogen gas a flow rate of 100 mL/min was used to purge the air. The sample was heated with the ramp of 50 °C/min to 110 °C and held at this temperature for 10 min to remove the moisture. Then the temperature was increased to 950 °C with a heating rate of 40 °C/min and held there for 7 min for fixed carbon measurement. At the final step the sample was cooled to 600 °C and gas flow was changed to air in order to obtain the ash content of the sample. For each solid, three samples were analyzed. The calorific values for untreated manure and hydrochar were measured in a Parr 1108 oxygen combustion bomb in a Parr 1241 calorimeter. A total of 5–8 samples weighing in the 0.6–1 g range were used for every analysis. Results are reported on a dry-and-ash-free (daf) basis.

Total phosphorous and phosphate content in all liquid samples were measured by ascorbic acid method equivalent to EPA 365.1 using a Hach spectrophotometer [21]. Total phosphorus was obtained following an acid and persulfate digestion aimed at hydrolysis of all the forms of phosphorus and conversion to orthophosphates. The phosphate measurement procedure was similar except there was no digestion involved. Total Kjeldahl nitrogen (TKN), nitrite, nitrate and total nitrogen were measured using the Hach method 10,242. In this method, inorganic and organic nitrogen are oxidized to nitrate by digestion with peroxydisulfate. The nitrate ions react with 2,6-dimethylphenol in a solution of sulfuric and phosphoric acid to form a nitrophenol. Oxidized forms of nitrogen in the original sample (nitrite + nitrate) are determined in a second test vial and then subtracted, resulting in TKN [22]. Total nitrogen (TN) is the sum of TKN (ammonia and organic nitrogen) plus nitrite and nitrate. The salicylate method was used for ammonia quantification, in which free ammonia and hypochlorite are mixed to form monochloramine. Monochloramine further reacts with salicylate and nitroprusside which produces indosalicylate with blue color; the color is proportional to the ammonia measured at 690 ± 5 nm using a spectrophotometer [23].

Total organic carbon of the liquid samples was assessed using in Shimadzu, TOC-LCSH instrument. Samples were diluted and acidified to pH 2 with phosphoric acid. The run includes sparging for 5:30 min to remove all the inorganic carbon so that organic carbon is determined by the detector.

The liquid samples were first extracted into CH₂Cl₂ using a fourfold volume excess of solvent. This solution was analyzed using a Supelco Petrocol DH 50.2 (50 m × 0.2 mm × 0.5 µm) column in a Shimadzu QP2010 SE GC/MS. The oven program was as follows: The initial temperature was held at 50 °C for 3 min, ramped at 20 °C/min to 275 °C, with a final

hold time of 2 min. The MS was operated in electron impact (EI) mode at 70 eV. Trace gas analyses were performed on a Pfeiffer Prisma Plus residual gas analyzer. For the analyses, 1.0 mL of gas was withdrawn from a Tedlar gas bag using an air-tight syringe. This gas was then injected into a stream of He flowing into the analyzer at 35 mL/min. The gas samples were analyzed in triplicate on a HP 6890 GC fitted with a thermal conductivity detector (TCD) operating at 220 °C (493 K). Gas separation was accomplished using a Poropack Q column (Restec, Bellafonte, PA, USA) with He as the carrier gas. The column was heated as follows: 40 °C (313 K) for 2 min, ramped to 180 °C (313 K) (40 °C/min, 313 K/min), held for 5 min, ramped to 200 °C (473 K) (40 °C/min, 313 K/min), held for 10 min, and returned to 40 °C (313 K). Gas products were quantified versus the calibration of a standard gas mixture consisting of $\approx 3\%$ (w/v) each of H₂, CH₄, CO, CO₂, C₂H₆, and C₂H₄ in He (Linde North America Inc., Murray Hill, NJ, USA) and 5% (w/v) each C₃H₈ and C₃H₆ in He (ILMO Specialty Gasses, Jacksonville, IL, USA). Due to TCD signal damping effect of He on H₂, a standard gas curve for H₂ was prepared from mixtures ranging from 3 to 50% (v/v), resulting in a calibration curve of $y = 24 \times 1.5$ ($R^2 = 0.997$).

3. Results and Discussion

In this section, we present a detailed analysis of both manure feedstocks and the results of the HTC experiments with and without acid. HTC products are characterized, and a mass balance is presented.

3.1. Characterization of the Solid Products

The solid products from hydrothermal carbonization of each kind of manure were analyzed for their fuel properties, proximate, ultimate and elemental compositions of their ash. The results are presented in Figure 1 and Tables 1 and 2. All samples are labelled using the following system: the first two letters indicate the source (CM for cow manure and PM for pig manure.) If there is no suffix, then the sample is raw manure. A suffix of SA indicates a hydrochar processed with sulfuric acid catalyst, a suffix of AA indicates a hydrochar processed with acetic acid catalyst, and a suffix of DIW indicates a hydrochar processed in deionized water without any acid catalyst.

Table 1. Ultimate analysis of cow manure (CM), pig manure (PM) and hydrochar. Results are given on a daf basis.

Sample Name	N [wt.%]	C [wt.%]	H [wt.%]	S [wt.%]	O [wt.%]
CM *	2.55 ± 0.32	40.80 ± 1.3	5.25 ± 0.14	0.31 ± 0.02	27.15 ± 0.67
CM-DIW	1.69 ± 0.14	40.97 ± 2.22	5.09 ± 0.27	0.12 ± 0.02	23.64 ± 0.44
CM-SA	1.50 ± 0.06	49.52 ± 0.24	5.31 ± 0.11	3.53 ± 0.39	25.49 ± 0.25
CM-AA	1.86 ± 0.05	46.67 ± 0.76	5.73 ± 0.08	0.23 ± 0.01	30.55 ± 0.53
PM *	5.25 ± 0.21	30.98 ± 0.68	5.24 ± 0.15	1.16 ± 0.19	25.30 ± 0.81
PM-DIW	4.00 ± 0.28	34.90 ± 1.67	4.62 ± 0.22	0.94 ± 0.04	22.25 ± 1.26
PM-SA	3.84 ± 0.14	44.95 ± 0.40	5.32 ± 0.03	5.80 ± 0.29	24.33 ± 0.15
PM-AA	4.47 ± 0.20	38.98 ± 1.51	4.84 ± 0.18	0.93 ± 0.01	17.06 ± 0.43

* The error shown for manures represents the uncertainty associated with the ultimate analysis only. Other errors account for the experimental error for duplicate HTC tests.

Table 2. Energy properties and proximate analysis of cow manure, pig manure and hydrochar produced by their hydrothermal carbonization.

Sample Name	Solid Yield (% Dry wt.)	Volatiles (% Dry wt.)	Ash (% Dry wt.)	Fixed Carbon (% Dry wt.)	HHV (MJ/kg)
CM	-	63.41 ± 1.17	22.88 ± 0.66	13.71 ± 0.84	16.21
CM-DIW	86.91 ± 2.41	66.14 ± 1.33	20.45 ± 1.45	13.41 ± 1.00	17.75 ± 0.10
CM-SA	58.79 ± 0.07	59.78 ± 0.69	18.62 ± 0.85	21.61 ± 0.20	20.06 ± 0.01
CM-AA	76.69 ± 0.26	63.92 ± 1.80	21.13 ± 2.23	14.95 ± 0.44	19.35 ± 0.14
PM	-	61.33 ± 0.22	26.67 ± 0.10	12.00 ± 0.13	14.96
PM-DIW	72.35 ± 1.62	53.98 ± 0.38	35.84 ± 0.42	10.19 ± 0.06	15.37 ± 0.09
PM-SA	58.52 ± 0.47	66.87 ± 0.07	18.21 ± 0.15	14.92 ± 0.20	18.66 ± 0.24
PM-AA	66.08 ± 0.07	59.07 ± 0.18	28.56 ± 0.07	12.38 ± 0.11	17.63 ± 0.21

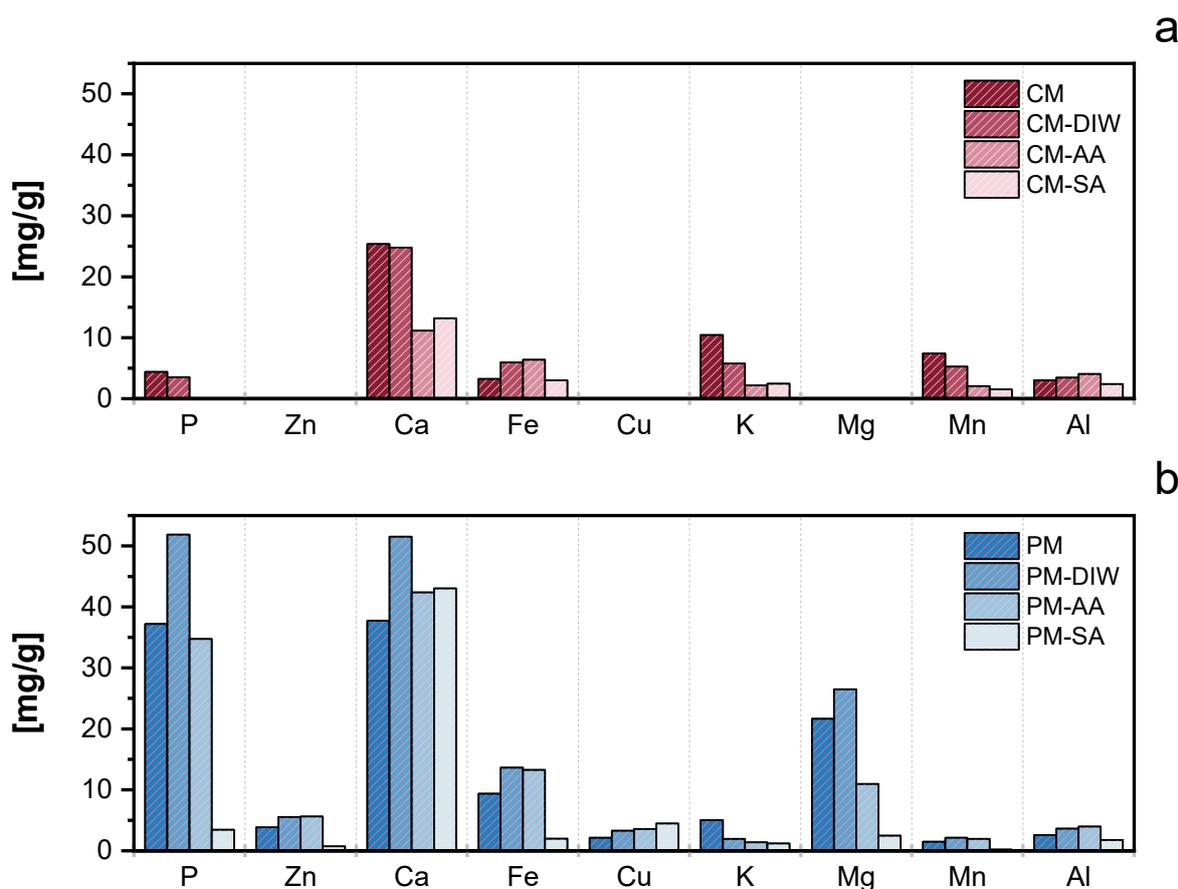


Figure 1. Ash analysis of the feedstock and hydrochar from cow manure (a) and pig manure (b).

Table 1 summarizes the ultimate elemental composition of the feedstock (cow and pig manure) used in this study, in addition to that of the hydrochars. Comparing two feedstocks reveals that there is a major variation in pig and cow manure composition with the most distinct difference being in their sulfur (1.16 wt.% vs. 0.31 wt.%), nitrogen (5.25 wt.% vs. 2.55 wt.%), and carbon (30.98 wt.% vs. 40.80 wt.%) contents, respectively.

The hydrochar produced from cow manure indicates very little degree of carbonization when done without adding acids. This is not surprising considering the low temperature (170 °C) applied for the hydrothermal treatment, and is consistent with previous observations [18]. However, by adding acids, a significant increase in the carbon content of the hydrochar can be observed. The influence of acid type in increasing the carbon content is significant as sulfuric acid causes more carbonization compared to acetic acid. The nitrogen content of the resulting hydrochars produced from cow manure shows small variations among each other, but each is significantly reduced below the nitrogen content of untreated manure. While CM undergoes a modest degree of deoxygenation in DI water (from 27.15% to 23.64%), the addition of acid seems to suppress (sulfuric acid) or even reverse (acetic acid) this deoxygenation. This is a remarkable result, since deoxygenation of biomass is a common result observed during HTC. Looking at the sulfur content of the hydrochar and cow manure one can notice the low percentage of this element. However, for the hydrochar produced by applying sulfuric acid the sulfur content is increased, suggesting that some of the sulfate from the acid has transferred from the solution into the hydrochar.

Unlike cow manure, hydrothermal treatment of pig manure without acid addition has resulted in noticeable carbonization of the hydrochar. This could be an indication of the high amount of inorganic carbon in pig manure which is not readily soluble in the mild hydrothermal condition (170 °C). The addition of acid to the HTC reactor enhances the carbonization of pig manure, especially the addition of sulfuric acid. Hydrothermal

treatment of pig manure does slightly decrease the nitrogen content; however, the change is not significant. Pig manure undergoes modest deoxygenation without acid, but the deoxygenation is significantly enhanced in the presence of acetic acid.

Table 2 presents the proximate analysis of manure and of the hydrochars produced from those manures, along with the mass yield (solid yield) of the hydrochar. For both types of manure the solid yield drops and the higher heating value (HHV) increases as the reaction condition changes from deionized water towards stronger acids. Comparing the heating value of cow manure versus pig manure, one can see that cow manure is slightly more energy dense. For both CM and PM, sulfuric acid reduced the ash content to the lowest measured values in the product hydrochars; in the case of PM, the reduction was substantial. This may be due to the hydrolysis and leaching effect of sulfuric acid. For cow manure hydrothermal treatment resulted in lowering the ash content for every reaction condition. However, in the case of pig manure the ash content increases and decreases, depending on the HTC conditions, with no obvious pattern.

The fixed carbon in hydrochar produced from CM is nearly unchanged during hydrothermal treatment, except in the case of the addition of sulfuric acid, in which case the fixed carbon increases markedly. Similarly, for the pig manure the fixed carbon increases substantially for the sulfuric acid runs while in the case of no acid catalyst the fixed carbon content actually drops. Apparently, labile carbon is more reactive in an aqueous environment in the presence of sulfuric acid. In terms of the volatiles one can see no specific trend among different reaction scenarios.

The elemental composition of the ash in feedstock and produced hydrochar has been determined using the ICP-AES technique and the analyses are presented in Figure 1. It can be seen that for the majority of elements their concentration in PM surpasses the values in CM. In particular, phosphorus content in PM is approximately an order of magnitude larger than that of CM. Based on the solid yield, it is possible to calculate the fraction of each element present in the hydrochar as a fraction of the amount of that specific element present in the unreacted manure. We call this fraction the hydrochar yield of each individual element, and these results are shown in Table 3. The most striking observation might be the difference between the distributions of elements when acids were added in contrast to the scenario where no acid was used. It is clear that using acids significantly improves the leaching of Ca, K, Mg and Fe elements into the process water according to these results. Moreover, for all elements and for both types of manure, sulfuric acid has shown better extraction capability with the exception of potassium in cow manure where acetic acid seemingly had better extraction performance.

Table 3. Hydrochar yield of selected elements.

Sample Name	Ca (%, wt.)	K (%, wt.)	Mg (%, wt.)	Fe (%, wt.)
CM-DIW	85.0	53.9	38.3	71.6
CM-SA	30.6	12.2	2.5	4.5
CM-AA	33.8	9.2	2.6	11.6
PM-DIW	98.8	53.4	65.3	69.6
PM-SA	66.8	27.8	3.2	0.6
PM-AA	74.3	31.0	15.7	19.8

3.2. Characterization of the Liquid and Gas Products

The process water generated during hydrothermal treatment of manure was analyzed for different chemical properties. Table 4 presents the pH of the reaction environment before and after the experiment. As expected, after adding acids into the process the pH of the solution drops however some interesting patterns appear as well. For both types of manure whenever acids were added the pH of the solution increased slightly at the end of the hydrothermal treatment, contrary to the cases where no acids were used in which pH decreased during the reaction. It can be seen that the water and cow manure mixture

is alkaline in the absence of an acid; however, after the reaction the pH moves towards neutral, due to the formation of organic acids during the hydrothermal reaction. Similarly, the water and pig manure mixture pH is in the neutral range and the mixture becomes acidic at the end. Both before and after the treatment, the pH of the solutions was identical for the cow manure and pig manure for sulfuric acid and acetic acid.

Table 4. pH of the solution before and after hydrothermal reaction.

Sample Name	Initial pH	Final pH
CM-DIW	9.3 ± 0.01	7.2 ± 0.03
CM-SA	0.9 ± 0.01	1.0 ± 0.01
CM-AA	4.4 ± 0.01	4.4 ± 0.01
PM-DIW	7.1 ± 0.03	6.4 ± 0.04
PM-SA	1.2 ± 0.02	1.4 ± 0.01
PM-AA	4.4 ± 0.01	4.5 ± 0.02

Both total phosphorus and phosphate concentrations in the process water are presented in Figure 2. Note the difference in scale between Figure 2a,b. Clearly, there is much more phosphorus in the process water produced from PM compared to that from CM, unsurprising considering the results from the ash analysis. Nonetheless the data presented in Figure 2 demonstrate how readily the phosphorus content of those two manure types are accessible with the use of acid during HTC. Looking at these data one can clearly see that phosphorus leaching improves by increasing the acidity of the solution. Sulfuric acid as a strong inorganic acid significantly increases the extraction of phosphorus. Acetic acid indicates some extraction capability however it is not as successful as sulfuric acid. Moreover, we can compare the concentration of total phosphorus to the concentration of phosphate in each process water and see that those values are quite similar therefore it would be fair to conclude that hydrothermal treatment converts a large fraction of the total phosphorus content of feedstock into the orthophosphate form. The total phosphorus data obtained here will be used in the next section for phosphorus mass balance.

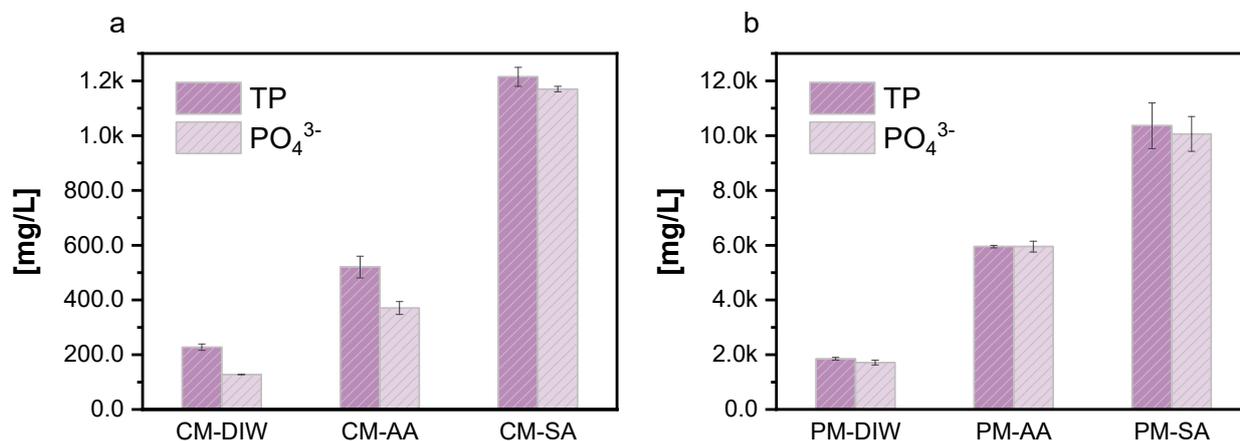


Figure 2. Total phosphorus and phosphate concentration in the aqueous product of hydrothermal carbonization of cow (a) and pig (b) manure.

The nitrogen extraction that occurs during the hydrothermal carbonization of pig and cow manure is presented in Figure 3. The fractionation of the extracted nitrogen reveals some general trends. Based on the data, it can be seen that inorganic nitrogen (NH_4 and NO_2/NO_3) constitutes the smallest fraction of the extracted nitrogen in all experimental conditions and for both types of animal manure. Apparently the nitrification reactions are limited during HTC. Although produced at a rate higher than nitrite/nitrate, ammonia is produced with a relatively small yield, never more than about 30% of the total nitrogen.

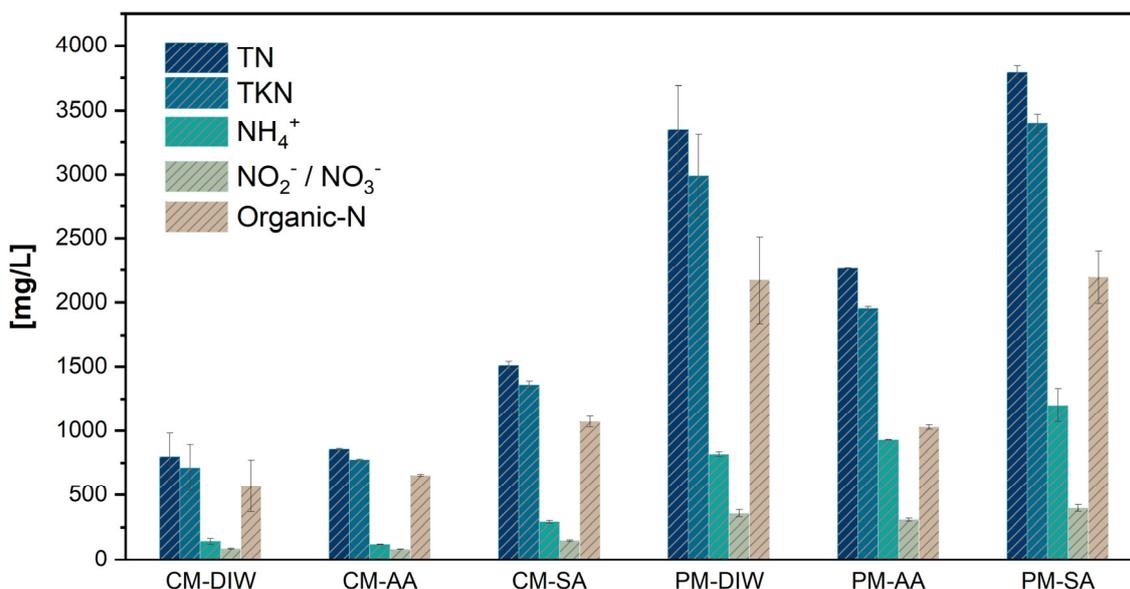


Figure 3. Total nitrogen, total Kjeldahl nitrogen, nitrite/nitrate, ammonia concentration and organic nitrogen in the aqueous products of the hydrothermal carbonization of pig and cow manure.

The organic nitrogen (ON) is found from the difference between total Kjeldahl nitrogen (TKN) and ammonia/ammonium. The results show that ON is produced in higher amounts than ammonia. It is likely that amino acids and other organic nitrogen molecules are first formed from the decomposition of protein in manure. Ammonia/ammonium are then likely produced from the deamination reaction of ON during HTC. Pig manure contains twice the nitrogen of cow manure, and it is insightful to compare the nitrogen extractions for similar HTC conditions. The fraction of ammonia in the total nitrogen from pig manure is relatively high with respect to that in cow manure. In both cases of PM and CM, the use of sulfuric acid during HTC results in the highest amounts of TN, NH₄⁺, and ON compared to either acetic acid or DI water. Surprisingly, the use of acetic acid in the HTC of pig manure reduced the total extraction of nitrogen compared to no acid, and reduced the ON fraction substantially. In fact, the highest ratio of ammonia to TKN was achieved with this experimental condition. The use of sulfuric acid with PM not only improved the raised nitrogen extraction but also increased TKN, ammonia and inorganic nitrogen as well. In general nitrogen extraction from cow manure appears to alter significantly with the reaction condition compared to pig manure.

Results of the liquid phase GC analysis are presented in the Supplementary Materials (Figure S7 and Tables S1 and S2). All samples show the presence of acetic acid, while samples processed with sulfuric acid also show peaks for furfural and 3-aminopyrazine 1-oxide. The acetic acid and furfural are likely the result of hydrolysis and dehydration reactions catalyzed by the strong acid. Acetate esters are common in the plants of cattle feed. Xylan is found both in dicotyledons and grasses and is highly acetylated. Hydrolysis of xylan would yield the acetic acid and dehydration of the xylose monomers of xylan would produce furfural. The origin of 3-aminopyrazine 1-oxide is not obvious but it has been reported to be present in some pyrolysis oils [24,25].

The GC analysis of the gas samples collected at the end of each experiment are presented in Figures S1–S6, and showed predominantly CO₂ and N₂ for all experimental conditions. Nitrogen appeared due to the use of N₂ gas to purge oxygen from the reactor in the beginning of the experiment. The average volumetric amount of CO₂ produced from pig manure was slightly higher than that of cow manure. Moreover, the variability of CO₂ production across the different experimental conditions with pig manure was quite high compared to cow manure. The residual gas analysis of the samples by using MS revealed some trace gaseous products like NO₂, SO₂ and H₂S. Qualitative comparison of

the obtained results showed an interesting trend. With the exception of sulfuric acid, in all other experimental conditions applied to both type of manure, H₂S was the most abundant compound followed by NO₂ and SO₂, respectively. However, when sulfuric acid was used as a catalyst to treat both cow and pig manure, NO₂ gas was present at higher levels. No explanation for this observation is apparent, and these data clearly indicate the necessity of additional research.

3.3. Mass Balances

Mass balances for four key elements (C, N, P, and K) are presented in Figures 4–7. The mass of carbon in the solid was determined using the measured carbon content and the yield of hydrochar, and carbon in the liquid was determined from measured TOC. While cooling, the reactor pressure was recorded when the temperature decreased to 35 °C. In combination with the mole fraction of CO₂ (measured by GC analysis), the moles of CO₂ produced by the reaction were estimated with use of the ideal gas law. The average carbon mass balance for all of six experimental scenarios was 99.7%, with a standard error of 2.6%. The mass balance of nitrogen (Figure 5) was closed at an average of 113.5% with a standard error of 6.8%. Balancing the nitrogen for the experiments with pig manure was challenging with large deviations from 100%. For phosphorus the average mass balance was 102.2% with a 0.9% standard error. In the case of potassium, the average mass balance was 110.0% with a standard error of 5.3%. The raw data for these mass balances can be found in the Supplementary Materials.

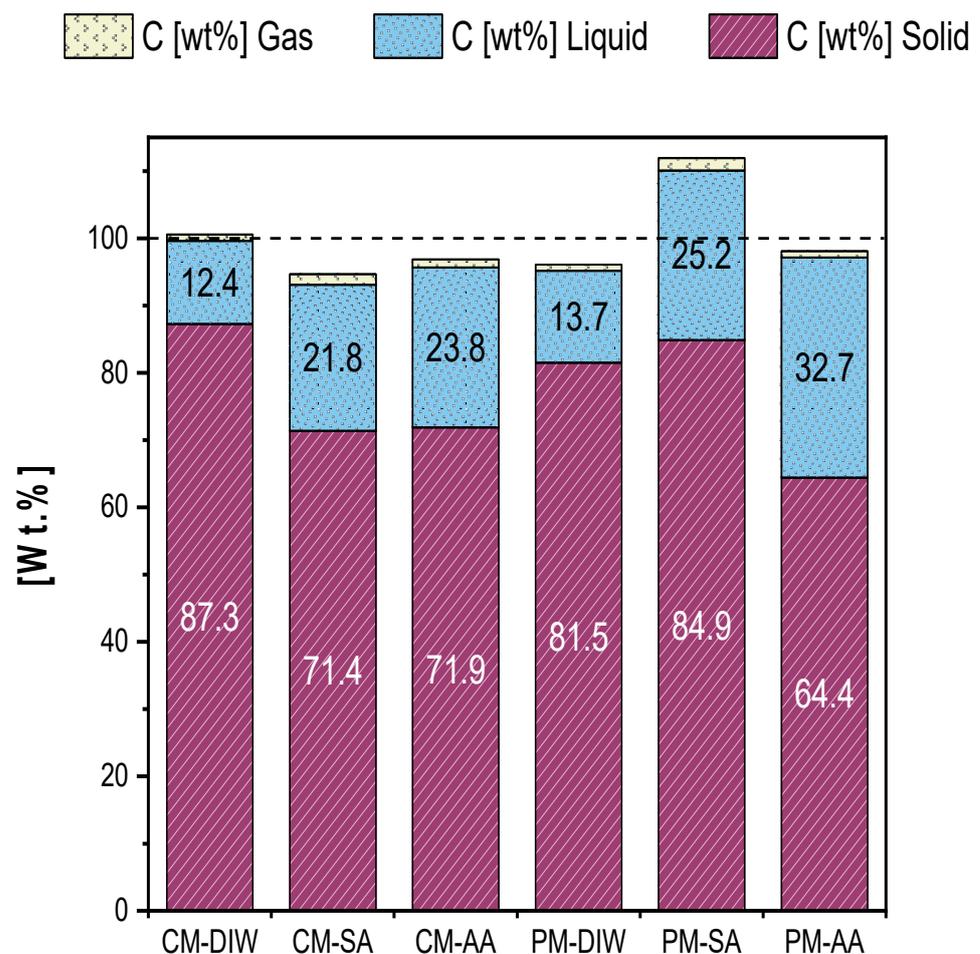


Figure 4. Carbon distribution among the solid, liquid, and gas products of hydrothermal carbonization of cow and pig manure.

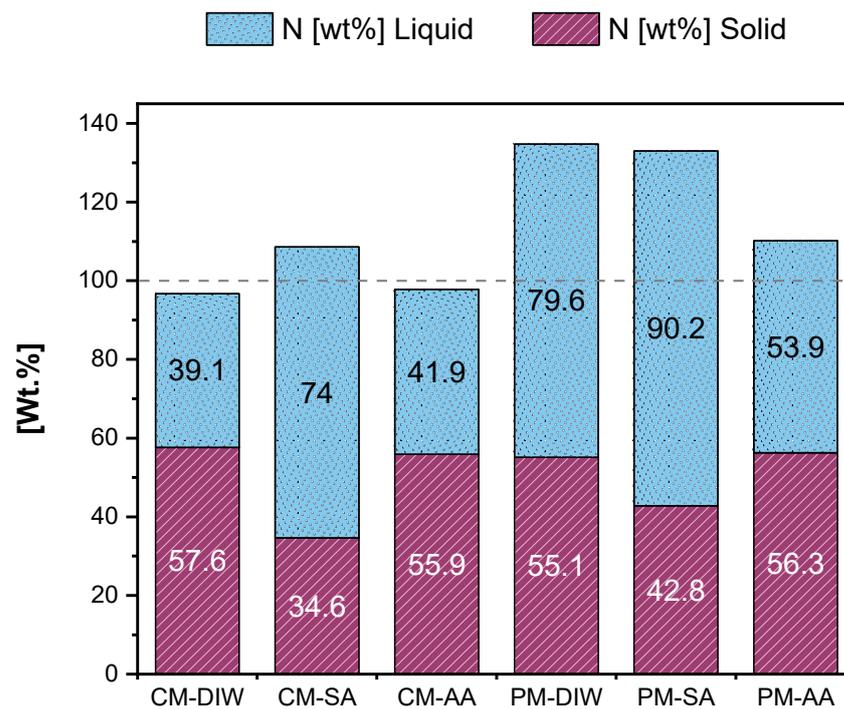


Figure 5. Nitrogen distribution among the solid and liquid products of hydrothermal carbonization of cow and pig manure.

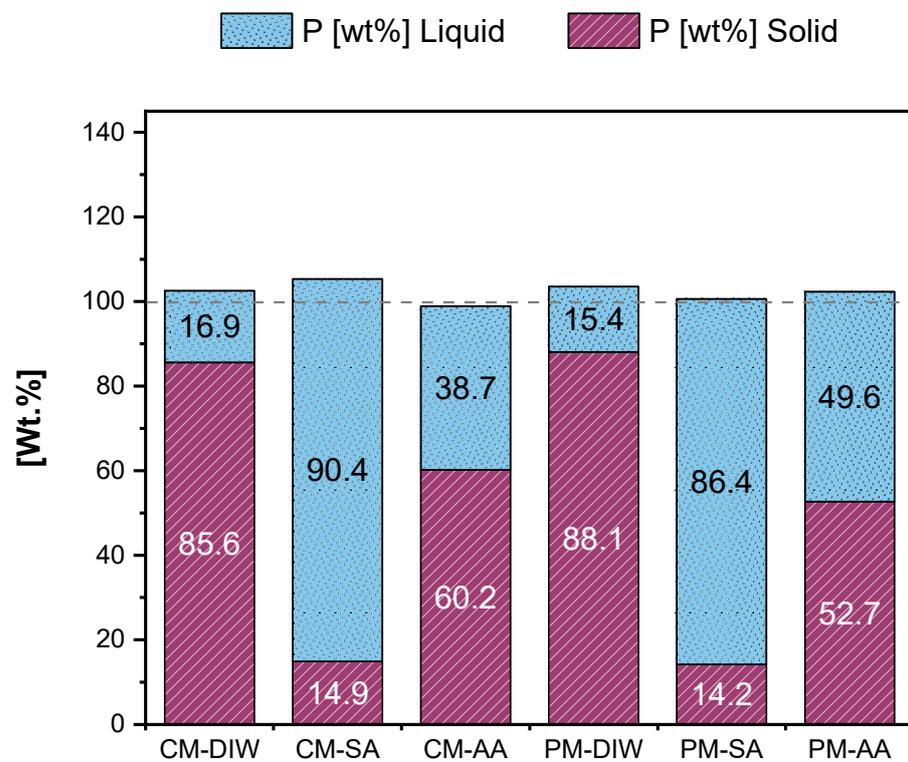


Figure 6. Phosphorus distribution among the solid and liquid products of hydrothermal carbonization of cow and pig manure.

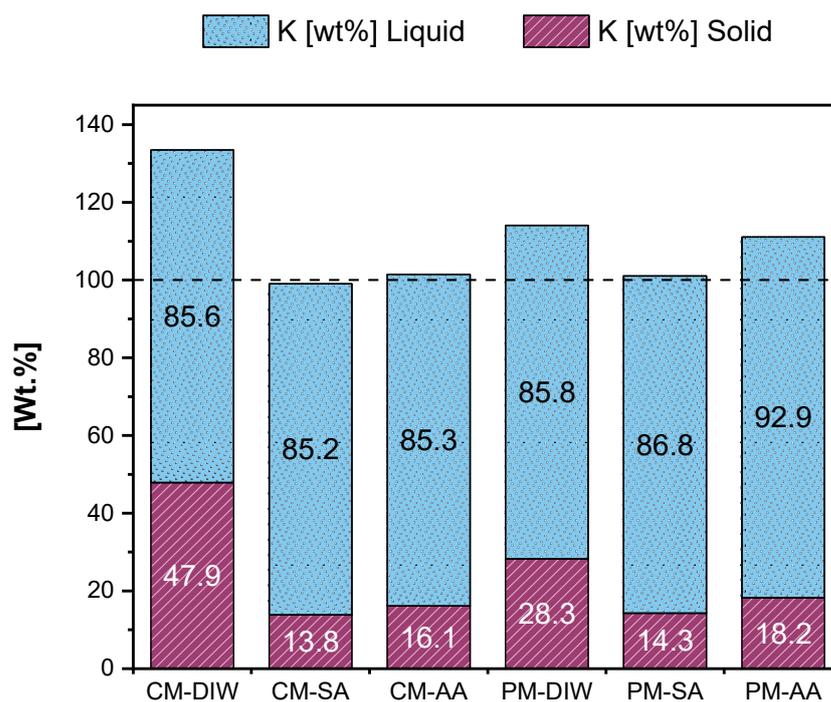


Figure 7. Potassium distribution among the solid and liquid products of hydrothermal carbonization of cow and pig manure.

Carbon fractionation among the reaction products of the hydrothermal treatment of cow and pig manure presented in Figure 4 suggests that for all experimental conditions the vast majority of carbon lays in the solid hydrochar; the smallest share of the carbon belongs to the gas phase which for all cases is below 2%. With the addition of acid, the amount of carbon present in the liquid phase increases in all cases. Although carbon distribution is similar when comparing the HTC of cow manure to pig manure, the effect of acid on the production of aqueous soluble carbon seems to be more pronounced in the case of pig manure.

Figure 5 shows nitrogen distribution among the liquid and solid products of the hydrothermal carbonization of pig and cow manure. For cow manure, HTC with no acid addition led to the fixation of nearly 60% of the nitrogen into the solid product. A slight increase in the nitrogen portion in liquid can be seen by applying acetic acid, the use of sulfuric acid brings the nitrogen extraction to 74%. It is more difficult to interpret the results of the N mass balance in the case of the PM, due to apparent large systematic error. Generally, it seems that the nitrogen in PM is more readily available in the aqueous phase. Similar to CM, the use of sulfuric acid resulted in the highest amount of nitrogen transferred into the liquid product. The mass balance of N in the case of CM was between 97% and 109%, which seems reasonable. With a much higher nitrogen content, closing the mass balance in the case of PM was more challenging, with total mass balance ranging between 110% and 135%.

The phosphorus mass balance is summarized in Figure 6. In the absence of any acid, nearly 90% of the phosphorus remains in the solid phase for both CM and PM. The use of either acetic acid or sulfuric acid causes most of the phosphorus to dissolve into the aqueous phase for both types of manure. Also for both types of manure, sulfuric acid was quite effective at extracting phosphorus in the aqueous phase, 90% for CM and 86% for PM, similar to results reported previously [17]. The total mass balance ranged from a minimum of 98.9% (CM, acetic acid) to a maximum of 105.3% (CM, sulfuric acid).

The potassium mass balances are presented in Figure 7. As expected for an alkali metal, most of the potassium is partitioned in the aqueous phase during HTC, with and without acid addition. That being said, applying acid catalysts further increased the solubilization

of potassium. In all cases, HTC of manure with acid addition (sulfuric acid or acetic acid), resulted in a hydrochar containing less potassium than hydrochar produced from HTC without acid addition.

Previous studies on animal manure treatment with HTC suggest an increase in the C content of hydrochar [26–28]. On the other hand, CaO-assisted HTC of swine manure conducted by Lang et al. reported higher hydrochar yield and near 100% P retention in the hydrochar, which contrasts with the results shown in Figures 2 and 6. Considering the fact that in that study, the reaction temperature (180 °C) was relatively close to our reaction temperature of 170 °C, it is clear that the use of acid during HTC is responsible for transferring P into the liquid phase [20].

However, in terms of hydrochar ash content, a divergence is seen between the results of this study and other studies. Previous studies reported increased ash content due to HTC treatment when no acidic catalyst was applied [29–32]. As shown in Table 2, hydrochar produced in water without acid shows increased ash in the case of pig manure but slightly decreased ash in the case of cow manure. The reduced ash may be due to the low reaction temperature and relatively mild reaction conditions, with hydrochar having very similar characteristics to the untreated manure but without readily dissolved species such as alkali metals. We note that use of acetic acid during HTC has little impact on ash content in both the case of PM and CM, as shown in Table 2. In both cases, the overall ash content is actually higher in the case of using acetic acid compared to the case of no acid addition at all. However, the addition of sulfuric acid, a strong acid, causes a substantial fraction of inorganic ash to dissolve, perhaps via acid hydrolysis of the inorganic content, transferring reduced cations in the aqueous phase.

Regarding nitrogen and phosphorus extraction, our results presented overlapping implications of sulfuric acid application, as reported by Ekpo et al. [17]. That is, the extraction of phosphorus was strongly dependent on the presence of an acidic catalyst. In contrast, even though the extraction was improved for nitrogen, the impact of an acidic catalyst was not as remarkable. This can be attributed to the increased solubility of phosphate salts in acidic solutions, which is less of a factor with nitrogen salts.

4. Conclusions

In this study, we investigated the hydrothermal carbonation of pig and cow manure using sulfuric and acetic acids at 170 °C. Our findings indicate that acid acts as a homogeneous catalyst during HTC of manure. Acid addition promotes enhanced carbonization, enhanced energy values of the produced hydrochar, and resulted in a smaller yield of hydrochar. Similar effects to these can be achieved without acid addition but with increased reaction temperature and corresponding reaction pressure. However, the acid clearly functions as a catalyst, allowing similar reaction results at a lower temperature. Moreover, we have shown that employing acids increases the hydrothermal leaching of the phosphorus, while a modest increase in nitrogen solubilization was observed for sulfuric acid. Overall, our results demonstrate a strong effect of an inorganic acid, such as sulfuric acid, on the fractionation of the extracted nitrogen in the hydrothermal aqueous product. With reduced ash and reduced nitrogen content, and enhanced energy densification, the hydrochar product may well be better suited as a fuel than that produced without acid catalyst. In addition, these findings provide future information about the partitioning of minerals such as Ca, K, Mg and Fe across different products during hydrothermal treatment of pig and cow manure.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/agronomy13092219/s1>, Figures S1–S6: Residual analysis of gas samples; Figure S7: GC analyses of aqueous products; Table S1: Relative areas for GC analyses of aqueous products; Table S2: Concentration of acetic acid in the six aqueous samples analyzed using GC analysis; Tables S3–S6: Mass balances of C, N, P, and K, respectively.

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