Hydrothermal Liquefaction Enhanced by Various Chemicals as a Means of Sustainable Dairy Manure Treatment

Junying Chen [1], Lijun Wang [2],*, Bo Zhang [2], Rui Li [2] and Abolghasem Shahbazi [2]

[1] School of Chemical Engineering and Energy, Zhengzhou University, Zhengzhou 450001, China; chenjy@zzu.edu.cn

[2] Department of Natural Resources and Environmental Design, North Carolina A & T State University, Greensboro, NC 27411, USA; bzhang@ncat.edu (B.Z.); ruilirl009@gmail.com (R.L.); ash@ncat.edu (A.S.)

* Correspondence: lwang@ncat.edu; Tel.: +1-336-334-7787

Abstract: Because of the increase in concentrated animal feeding operations, there is a growing interest in sustainable manure management. In this study, hydrothermal liquefaction (HTL) of dairy manure enhanced by various chemicals ($NH_3 \cdot H_2O$, H_3PO_4, and glycerol) was proposed as a sustainable alternative for the dairy manure management. The applications of $NH_3 \cdot H_2O$ and H_3PO_4 during HTL could significantly enhance the production of liquid chemicals. The addition of $NH_3 \cdot H_2O$ or glycerol increased the amounts of non-polar toluene, xylene, and other benzene-contained compounds, while the use of H_3PO_4 produced high amounts of acids, pyridine, 3-methyl-pyridine, 2,6-dimethyl-pyrazine, 2-cyclopenten-1-ones, and phenols. The biochars produced via HTL showed a significant increase in the surface area/pore volume and relatively higher N, P, C, and other minerals, and may serve as a good soil amendment and nutrient source. The preliminary energy analyses showed that the energy consumption of this process might be reduced to 50% of the original energy content of the feedstock, and the energy payback period was about 3.5 years. Combining all advantages, HTL of dairy manure might increase the sustainability of the farming operation via producing energy products, fine chemicals, and biochars.

Keywords: sustainable manure management; hydrothermal liquefaction (HTL); dairy manure; liquid chemicals; biochar

1. Introduction

Global livestock production has been increasingly dominated by concentrated animal feeding operations (CAFOs). As of 2016 there were 19,496 out of ~212,000 animal feeding units in the United States were CAFOs [1]. However, the development of CAFOs caused increased discharges of animal wastes into the waterway [2]. Thus, there is an increasing interest in sustainable manure management. For U.S. dairy farming alone, dairy herds hold over nine million dairy cows annually from 1950 to now [3], which resulted in a manure production of over 0.5 million tons per day [4]. A dairy cow produces an amount of manure at ~8% of its body weight per day and the water content of the manure is as high as 88% [5]. Unsanitary disposal of dairy manure has been recognized as an environmental pollution source [6]. Common practices of manure handling and disposal contribute to a main part of the operation cost [7]. The cost of manure management averaged $306.13 per cow annually [8].

The dairy manure has a relatively high content of fiber (up to 50% on a dry basis) [9], which typically contains 31% cellulose, 12% hemicellulose, 12.2% lignin, 12.5% crude protein, and 12.5% starch [10]. It has been considered as an alternative feedstock for energy and chemical production [11]. The development of new sustainable technologies and high-value applications for dairy manure could tackle the economic, environmental, and social challenges of farming operations [12].

Hydrothermal liquefaction (HTL) has been widely used as a conversion process for energy and chemical production from wet feedstock, such as algae, grass, sewage sludge, and animal manures [13]. During HTL, the feedstock is decomposed to form bio-crude oil that is sometimes called bio-oil, biochar, and gases at a moderate temperature of 280–450 °C, under an elevated pressure of 10–25 MPa, and in a water environment with a residence time typically in the range of 5–90 min [14]. Because the trend of the increase in biofuels production and consumption worldwide, further upgrading the bio-oil to biodiesel and green diesel are of interest [15,16]. The HTL technology for conversion of different feedstock has been extensively reviewed in the literature [17,18].

HTL of animal manure could represent a penitential way for the sustainable utilization of this important resource. The advantages of HTL of manure include: (1) Wet manure can be converted directly without the need of an energy-intensive drying process [19]; (2) HTL simultaneously treats and sterilizes the wastes; and (3) the bio-crude oil often possesses a higher energy content (ranging 21–35 MJ/kg) than original feedstock (8–20 MJ/kg) [20]. Comprehensive review of this topic can be found in the literature [11,21]. Studies on the HTL process of cattle (non-dairy and dairy) manure are summarized in Table 1.

Table 1. Studies on HTL of cattle manure.

Manure Type	Catalyst Concentration (wt %/vol %)	Reaction Condition	Results	Ref.
Cattle	None	HTL was performed a 0.6 L reactor at 260 °C for 30 min with a feedstock-to-water ratio of 1:6 (*w/w*).	The bio-oil was used as the feed of gasification.	[22]
Cattle	NaOH (4%); NaOH/Manure = 0.8:1–1:4	HTL was carried out in a 1.8 L reactor at 270–350 °C under a process gas of air, N_2, CO or H_2 for 0–40 min.	The bio-oil yield depended on the conversion temperature and the process gas. The major components of bio-oil were toluene, ethyl benzene and xylene.	[13]
Dairy	Na_2CO_3 (1%); Na_2CO_3/Manure = 1:20	HTL was done in a 0.3 L reactor at 250–350 °C under a process gas of CO for 15 min.	The maximum bio-oil yield was 24% at 350 °C using 1% Na_2CO_3 catalyst, which corresponded to 67.6% or energy contained in raw manure.	[20]
Dairy	Na_2CO_3, K_2CO_3, NaOH (1–4%); Catalyst/Manure = 1:10 to 4:10	HTL was done in a 0.3 L reactor at 350 °C under CO for 15 min.	The effect of the catalysts on bio-oil was not clear, and the highest energy recovery was 70.8%	[23]
Dairy	$NH_3 \cdot H_2O$, H_3PO_4, glycerol (1%); Catalyst/Manure = 1:10	HTL was done in a 1 L reactor at 350 °C under a process gas of N_2 for 30 min.	The applications of $NH_3 \cdot H_2O$ and H_3PO_4 during HTL significantly enhanced the production of liquid chemicals. The biochars showed a significant increase in the surface area/pore volume and relatively higher N, P, C, and other minerals, and may serve as a good soil amendment and nutrient source.	This study
Dairy	None	Cow manure was hydrothermally carbonized (HTC) at 180–260 °C for 5 and 30 min.	Ash-free HHV for hydrochar increased up to a maximum of 22.1 MJ/kg from 19.1 MJ/kg.	[24]

HTL of cattle manure has been demonstrated in few studies [13,20,23,24]. Direct liquefaction and catalytic liquefaction can convert cattle manure into liquid bio-crude oil at a temperature range of 250–350 °C with a processing time of 5–40 min under a process gas of air, N_2, CO, or H_2. The application

of alkaline catalysts such as 1–4% Na_2CO_3, K_2CO_3, and NaOH did not show clear effects on the bio-crude oil, but might enhance the energy recovery ratio.

Besides the bio-crude oil, Reza et al. studied production of biochar from dairy manure via hydrothermal carbonization [24]. Biochar with a high mineral content and surface area can be used to condition soil by recycling the minerals back to soil and increasing the soil holding capacity of water and nutrients, and thus increasing the sustainability of the farming system [25]. Moreover, recent developments in activation procedures allow a better control over the pore structure and surface property, which have widened the use of biochar to more demanding applications including catalyst precursor, energy storage, gas storage, and contaminant adsorbents [26,27]. Biochar from pyrolysis of biomass was also used as a supplement of the animal feed [28]. These high-value applications are still in their infancy, and further research and development are needed to reach commercialization.

In order to study the effects of various chemicals on HTL of dairy manure, following three chemicals: ammonium hydroxide ($NH_3 \cdot H_2O$), phosphoric acid (H_3PO_4), and glycerol were used in this study. Ammonium hydroxide is a common chemical can be formed from urine. Because cow urine contains 2.5% urea [29], a $NH_3 \cdot H_2O$ concentration of 1% might be realized in nature. The use of H_3PO_4 and glycerol is because that these two chemicals were reported to enhance production of activated carbon [30] and bio-crude oil [31], respectively.

2. Materials and Methods

2.1. Dairy Manure Samples

Fresh dairy manure samples without bedding materials were collected from the research farm at the North Carolina A&T State University (Greensboro, NC, USA) and stored in a refrigerator below 4 °C for this study. To determine the solid content, three manure samples were taken and dried at 105 °C until moisture equilibrium was reached. The solid content of dairy manure samples was approximately 20 wt %.

2.2. Hydrothermal Liquefaction of Dairy Manure

HTL of dairy manure was carried out in a 1-L Parr stainless steel continuously stirred reactor equipped with an agitation impeller, a pressure transducer, and a thermocouple (Moline, IL, USA).

To ensure use of a procedure that has been shown to produce desirable products, most processing parameters chosen were the same as those used in literature [13,20,23,24]. For each experiment, 350 g dairy manure sample and 350 g de-ionized water were loaded into the Parr reactor, resulting in a solid content of 10 wt %. Chemicals of $NH_3 \cdot H_2O$, H_3PO_4, or glycerol were added to the reactor to make a 1 wt % concentration. The reactor was then sealed and purged with nitrogen gas to remove air existing in the headspace. The temperature of the reactor was increased to 350 °C at a heating rate of 7 °C min^{-1} and maintained at 350 °C for 30 min. The reaction pressure generated by the reactants at 350 °C was ~25 MPa for all experiments, and the agitation speed was controlled at 200 rpm. After the reaction was completed, the reactor was rapidly cooled down to the room temperature at a cooling rate of 10 °C min^{-1} by circulating the tap water in the cooling coil.

The product separation process after HTL is shown in Figure 1. The gaseous products were collected into a 1 L Tedlar bag for later gas chromatography (GC) analysis [32]. The vessel was opened to collect its contents, and the final pH of the slurry was recorded. The slurry mixture was filtered to separate the aqueous products and the solid residue. Because the solid residue composed of solid biochar and tar-like organic compounds, the residual solid was also washed with acetone during filtration until the filtrate was clear. Accordingly, the liquid products contain water-soluble and acetone-soluble chemicals [33,34]. The solid residue (i.e., biochar) was dried in an oven at 105 °C until its mass became constant, and then weighted. The mass of the gas was calculated based on the final pressure in the reactor at the room temperature and gas composition. The biochar yield was determined as the mass ratio of the solid residue to the input dry manure. The gas yield was

determined as the mass ratio of the gas to the input dry manure. The liquid yield was calculated by mass difference.

$$\text{Yield of biochar (\%)} = (\text{weight of solid residue})/(\text{weight of dry manure}) \times 100\% \quad (1)$$

$$\text{Yield of gas (\%)} = (\text{weight of gas})/(\text{weight of dry manure}) \times 100\% \quad (2)$$

$$\text{Yield of liquid (\%)} = 100\% - \text{Yield of biochar (\%)} - \text{Yield of gas (\%)} \quad (3)$$

All experiments were duplicated or triplicated. The mean values and standard deviations were reported in this paper. The statistical significance of the results was assessed using ANOVA F-test in Microsoft® Excel 2016 (Redmond, WA, USA). The statistical significance level cut-off was chosen as $p = 0.05$.
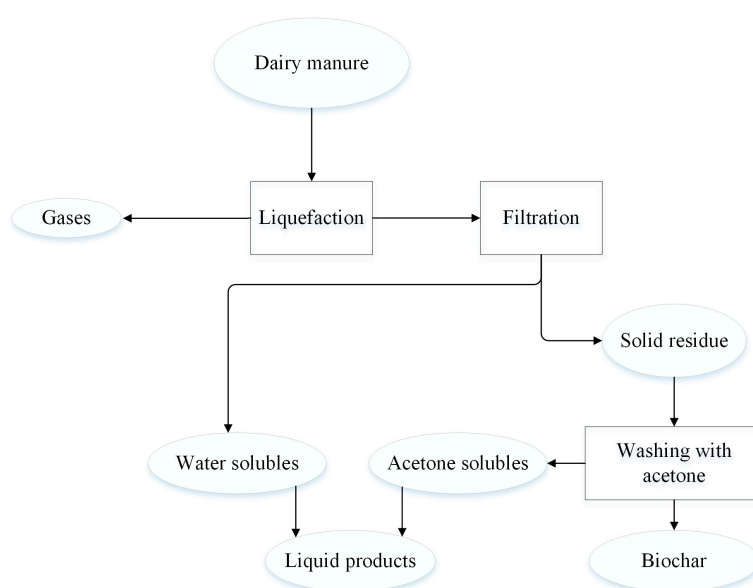

Figure 1. Process for product separation after hydrothermal liquefaction.

2.3. Chemical Composition of Produced Gases and Liquid Products

Gases produced by the HTL were quantified and analyzed by using a Varian CP-4900 Micro-GC (Santa Clara, CA, USA) to determine the contents of H_2, N_2, O_2, CO, CO_2, and ethane. The chemical composition of the liquid products was identified using an Agilent 7890-5975C gas chromatography-mass spectrometry (GC-MS) (Santa Clara, CA, USA) with a HP-5MS capillary column (Agilent Technologies, Santa Clara, CA, USA). The temperature of the GC column was programmed at 60 °C for 4 min and then increased to 280 °C at 10 °C/min, and held isothermally at 280 °C for 5 min. The injector temperature was set at 250 °C. The injection size was 1 μL. The carrier gas was helium at a flow rate of 1 mL/min. The ion source temperature of the mass selective detector was set at 230 °C. The compounds in the samples were identified by the comparison with the mass spectral database of the National Institute of Standards and Technology (Gaithersburg, MA, USA).

2.4. Elemental Analysis and Heating Value

The elemental analyses of carbon (C), hydrogen (H), nitrogen (N), and sulfur (S) contents of raw manure and biochars were carried out using a Perkin Elmer series II CHNS/O analyzer 2400 (Waltham, MA, USA). The oxygen (O) content was calculated as the mass difference on an ash-free basis.

The higher heating value (HHV) of samples was calculated using Equation (4) [35]:

$$\text{HHV (MJ/kg)} = 34.91 \times C + 117.83 \times H - 10.34 \times O - 1.51 \times N + 10.05 \times S - 2.11 \times \text{Ash} \quad (4)$$

2.5. Analyses of Raw Manure and Biochar

The moisture content of raw manure and the biochar was determined according to ASTM E871-82. Ash content was measured according to ASTM E1755-01.

The surface area and pore size distribution of raw manure and the biochar samples were measured with a Micromeritics ASAP 2020 surface area and porosity analyzer (Norcross, GA, USA). Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) methods were used to analyze the surface area and average pore size, respectively. The total pore volume was determined by the amount of N_2 uptake at a relative pressure of $P/P_0 \approx 0.995$.

The analysis of the phosphorus (P) availability of the biochar samples was carried out using a LaMotte NPK Soil Test Kit (Chestertown, MD, USA). The phosphorus availability has a unit of pounds per acre.

Fourier Transform Infrared (FT-IR) spectra were collected on a Varian 670 FT-IR spectrometer (Santa Clara, CA, USA). Spectra were collected from 4000–600 cm^{-1} with 0.98 cm^{-1} resolution.

X-ray diffraction technology (XRD) was used to analyze the crystal structural differences of biochar produced by HTL of dairy manure assisted with various chemicals. The XRD analysis was conducted by using an Agilent Technologies Oxford Gemini X-Ray Diffractometer (Santa Clara, CA, USA) in the range of $20 \leq 2\theta \leq 80$.

3. Results and Discussion

3.1. Product Yields of HTL of Dairy Manure in Different Solutions

The yields of biochar, liquid, and gases and the pH value of the liquid after HTL of dairy manure are summarized in Table 2. The biochar yields (i.e., solid residues) were in a range of 27–33 wt % of the original manure, while the gas yields were in a range of 5.9–14.8 wt %. The liquid yields were generally higher than 50 wt % of starting materials. The significance of the yields of the water-only and chemical assisted HTLs was analyzed via one-way ANOVA (Table S1 of the Supplementary Materials). Compared to the liquid yield (54.1 wt %) of the water-only HTL, the addition of 1 wt % $NH_3 \cdot H_2O$ and 1 wt % H_3PO_4 significantly increased the liquid yields to 67 wt % (by 23.6%) and 60.3 wt % (by 11.3%), respectively. The literature has shown that adding an alkaline catalyst such as NaOH increased HTL bio-oil yields by over 50 wt % [36], and hindered the formation of biochar [37]. The HTL assisted by $NH_3 \cdot H_2O$ showed the lowest biochar and gas production in this study. Similarly, the application of acids may produce some important intermediates like 5-(hydroxymethyl)furfural, which positively affect the HTL process and increase feedstock conversion into bio-crude oil [38]. Although crude glycerol (66.95% glycerol) was reported to enhance bio-oil production, the use of a low dosage of glycerol (1%) during HTL of dairy manure did not result in a significant difference.

The pH values of the liquid portion after HTL varied between 5–7. HTL of complex biomasses like manure involves cross-interactions among carbohydrates, proteins, lipids, their degradation products, and chemicals added, and resulting in various pH values [39,40].

Table 2. Product yields of the hydrothermal liquefaction (HTL) of dairy manure assisted with various chemicals.

Yields and pH	Water-Only	$NH_3 \cdot H_2O$	H_3PO_4	Glycerol
pH value	6	7	5	6
Liquid yield (wt %)	54.3 ± 1.7	66.9 ± 2.6	60.3 ± 3.2	54.0 ± 2.3
Biochar yield (wt %)	32.9 ± 1.2	27.2 ± 2.1	28.8 ± 1.8	31.2 ± 1.0
Gas yield (wt %)	12.8 ± 1.1	5.9 ± 0.9	10.9 ± 0.8	14.8 ± 0.5

3.2. Analyses of the Liquid Products and Reaction Scheme

HTL of dairy manure resulted in a mixture of chemicals, which were identified by using a GC-MS and summarized in Table S2 (Supplementary Materials). Table 3 shows the top 10 chemicals in the liquid products, which count for 30–62% of total area in GC profiles.

The diet of cows is composed of some forage (grass, legumes, or silage), grain, soy, and other ingredients [41]. Thus, dairy manure is rich in cellulose, hemicellulose, and lignin, and also has sugars, lipids, proteins, and a high ammonia content [42,43]. HTL of dairy manure is based on fast hydrolysis reactions of these materials, followed by dehydration and condensation of sugars, lipids, proteins, and their degradation products in subcritical water [44]. The liquid products formed during a water-only HTL comprised degradation products of protein (like pyrazines), cellulose and hemicellulose (such as 2-cyclopenten-1-ones and organic acids), and lignin (mainly phenols). Hydrazinecarbothioamide was likely formed between ammonia and sulfur-containing compounds, while HTL reactions also produced a small number of hydrocarbons such as hexane.

The addition of 1 wt % $NH_3 \cdot H_2O$ could increase the amounts of non-polar toluene, xylene, and other benzene-contained compounds, which are components of crude oil, gasoline, and diesel. Similar results were reported in the literature for the bio-crude oil obtained by HTL of cattle manure with NaOH [13]. These aromatic compounds were formed via condensation and cyclization of unstable intermediates [45]. Meanwhile, higher production of short chain organic acids was observed, which was due to sugar degradation under alkali conditions [46].

HTL assisted with 1 wt % H_3PO_4 shifted liquid products to higher amounts of acids (acetic acid, butanoic acid, etc.), pyridine, 3-methyl-pyridine, 2,6-dimethyl-pyrazine, 2-cyclopenten-1-ones (3-methyl-2-cyclopenten-1-one, 3,4-dimethyl-2-cyclopenten-1-one, etc.), and phenols (phenol, 2-methoxy-phenol, etc.). This indicated that acid could enhance dehydration reactions of most major components of manure [40].

The application of glycerol could increase the amounts of non-polar toluene, xylene, and other benzene-contained compounds too. Methanol, ethanol and 1-propanol can be produced from HTL of glycerol through reduction or free radical reaction [47], which may react with other intermediates to form esters via esterification reactions or new chemicals via alkyl substitution reactions [48,49].

The results of analyses indicated that HTL of dairy manure could form various hydrocarbons and precursors for industrious products, such as acetic acid, pyridine, toluene, xylene, phenol, 2-cyclopenten-1-one, etc. HTL could reduce the oxygen content of original feedstock to approximately 10% in the biocrude by dehydration and decarboxylation reactions [50]. However, the liquid products resulted from HTL of dairy manure still contained high amounts of oxygenated chemicals and nitrogenated chemicals (Tables 3 and S2), which may adversely affect the product quality if it is used as the fuel [51]. Generally, the bio-crude oil requires catalytic hydrogenation to remove oxygen and other heteroatoms like nitrogen to form new C–H bonds, so that the resulting product more closely approaches the C/H ratio found in fuels (~1/2) [23,52].

Table 3. Top 10 chemicals in liquid products from the HTL of dairy manure assisted with various chemicals (area %).

Water-Only		NH$_3$·H$_2$O		H$_3$PO$_4$		Glycerol	
Hydrazinecarbothioamide	10.74	1,3-Dimethyl-benzene	12.41	2-Methyl-2-cyclopenten-1-one	9.80	Toluene	7.92
Methyl-pyrazine	10.00	Toluene	11.43	2,3-Dimethyl-2-cyclopenten-1-one	8.10	Ethylbenzene	4.81
3-Hexene	9.17	3-(Butylthio)-propanoic acid	7.26	3-Methyl-2-cyclopenten-1-one	7.90	o-Cymene	3.96
4-methyl-3-hexanol	6.93	4-Methyl-3-hexanol	3.33	Acetic acid	7.45	2,3-Dimethyl-1H-indole	2.32
2-Methyl-2-cyclopenten-1-one	3.79	o-Cymene	2.40	Methyl-pyrazine	6.95	1,3-Dimethyl-benzene	2.04
Pyrazine	3.29	3-Methyl-thiophene	2.22	2-Methoxy-phenol	6.63	2,6,10-Dodecatrien-1-ol, 3,7,11-trimethyl-, (Z,E)-	1.89
n-Hexane	2.88	6-Methyl-2-[(4-morpholinyl)methyl]-phenol	2.21	Butanoic acid	4.29	2-Methoxy-phenol	1.60
3-(Butylthio)-propanoic acid	2.67	2-Methyl-indolizine	2.08	Phenol	3.79	1-Pentadecene	1.57
Ethyl-pyrazine	2.46	Butanoic acid methyl ester	1.78	2-Methyl-pyridine	3.60	3-Hexyne	1.56
2,2-Dimethoxy-propane	2.38	1,3-Dimethyl-benzene	1.72	3-Ethyl-2-cyclopenten-1-one	3.41	2-Butenyl-benzene	1.56

3.3. Analyses of the Biochar

Formation of biochars generally follows three steps: (a) Depolymerization of biomass, (b) decomposition of biomass monomers, and (c) recombination of reactive fragments. Infrared spectroscopy provided information on the change of surface chemical functional groups of dairy manure after HTL (Figure 2) [53]. The intensity of O-H groups (3400 cm^{-1}) of biochar was much lower than that of the raw dairy manure. Less hydrogen bonding attributes to the depletion of oxygen in the biochar. The intensities of bands (2900–2850 cm^{-1}) were associated with alkane C-H stretching vibration, and these peaks in the biochar become more intensive, suggesting that the structure of cellulosic biomass was destroyed by HTL reactions. The bands (1750–1680 cm^{-1}) suggested the presence of oxygen groups (C=O vibrations corresponding to aldehyde, ketone, ester, carboxylic groups) on biochars. The peaks (1680–1450 cm^{-1}) were attributed to the C=C stretching vibration in aromatic ring in lignin, and preserved in all samples. Biochars generated under different conditions showed the significantly different FTIR spectra at the dominant C–O (1000 cm^{-1}) stretch that is associated to the β-glycosidic bond in cellulose and hemicellulose. The intensity of this peak follows: Biochar−NH$_3$·H$_2$O > Biochar−Water ≈ Biochar−H$_3$PO$_4$ > Biochar−Glycerol.
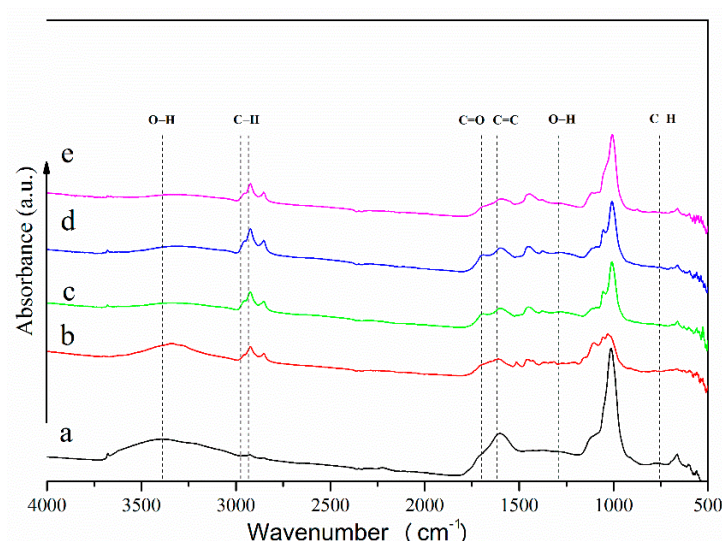

Figure 2. FT-IR spectra of raw dairy manure and biochar produced by the HTL of dairy manure assisted with various chemicals ((**a**) Dry dairy manure, (**b**) Biochar–Glycerol, (**c**) Biochar–H$_3$PO$_4$, (**d**) Biochar–Water, (**e**) Biochar–NH$_3$·H$_2$O).

The XRD analyses further confirmed the crystal changes of dairy manure (Figure S1). Raw dairy manure showed several diffraction peaks due to the presence of cellulose, hemicellulose, and other materials such as grains. After HTL treatments, materials with the crystalline structures disappeared, and the biochars showed an amorphous phase.

The BET surface area, pore volume, and pore diameter of biochars and related ANOVA analyses are shown in Tables 4 and S3, respectively. The original dairy manure has a low surface area of 1.85 m^2/g. Because the biochars are produced via recombination of reactive intermediates, different reaction pathways under acidic or basic conditions resulted in the biochars with unique property. The biochars did show a significant increase in all three characteristics. The biochar obtained by using HTL assisted with 1 wt % NH$_3$·H$_2$O had the highest surface area of 63.88 m^2/g and the highest pore volume of 0.24 cm^3/g. The high surface area and high pore volume of the biochar indicated a better holding capacity of water/nutrients and a better potential as the fertilizer.

Table 4. Surface area and porosity of the raw dairy manure and biochar produced by the HTL of dairy manure assisted with various chemicals.

Sample	BET Surface Area (m^2/g)		Pore Volumes (cm^3/g)	Average Pore Diameter (nm)
	On Total Mass Basis	On a Dry and Ash Free Basis		
Dry dairy manure	1.48	1.85	0.0049	13.39
Biochar–water	15.74	21.76	0.0506	12.85
Biochar–$NH_3 \cdot H_2O$	41.80	63.88	0.2439	23.33
Biochar–H_3PO_4	11.09	17.64	0.0441	15.92
Biochar–Glycerol	12.31	16.13	0.0497	16.54

The results of elemental composition and proximate analysis of raw dairy manure and biochars and related ANOVA analyses are summarized in Tables 5 and S4. The C, N, and H contents of the biochars obtained via HTL were lower than those of the raw manure. The possible reason is that the organic components in manure were converted to the liquid products. Among all biochars, the biochar obtained by the HTL assisted with 1 wt % $NH_3 \cdot H_2O$ showed the highest N content of 4.17%, and it reserved a relatively high C content of 41.15%. In addition, all biochars contained a higher amount of ash (minerals) that was in a range of 23.67–37.14%, compared to 20.02% for the manure. In terms of P availability, the raw dairy manure did not show positive results, while biochar samples showed P availability of <40, <40, 40–60, and 40–60 of pounds per acre for HTL assisted with water-only, $NH_3 \cdot H_2O$, H_3PO_4, and glycerol, respectively. In summary, the biochar generated via HTL of dairy manure may serve as a good source of nitrogen, phosphorus, and carbon.

Table 5. Elemental and proximate analyses of dairy manure and biochar produced by HTL of dairy manure with various chemicals.

	Dairy Manure	Biochar			
		Water	$NH_3 \cdot H_2O$	H_3PO_4	Glycerol
Elemental analysis (wt % on a dry and ash-free basis)					
C	47.11	37.61	41.15	33.44	36.12
H	6.84	6.52	5.90	5.09	5.90
N	6.90	2.71	4.17	2.77	2.59
S	1.28	0.76	0.76	0.75	0.75
O	37.87	52.40	48.01	57.95	54.64
Proximate analysis (%)					
Water content (wt %)	78.76				
Solid content (wt %)	21.24				
Volatile content (wt %)	72.67	37.10	48.33	59.09	40.65
Ash content (wt %)	20.02	27.65	34.56	37.14	23.67
HHV (MJ/kg)	16.06	10.58	9.99	6.58	10.15
P availability (pounds per acre)	-	<40	<40	40–60	40–60

3.4. Compositions of Gaseous Products

The composition of gases produced by the HTL of dairy manure assisted with various chemicals and related ANOVA analyses are given in Table 6 and Table S5, respectively. The addition of chemicals did not show significant effects on the gaseous products. The dominant gas from all HTL processes was CO_2, which was from 54.1% to 64.5% by volume.

Among all gaseous products, CO, CO_2, and CH_4 are considered as greenhouse gases and contribute to global warming. When comparing to pyrolysis of manure [54], emission of greenhouse gases or the global warming potential was about 50–75% lower. However, a detailed life cycle analysis

should be performed to comprehensively evaluate the global warming potential caused by this process. Scrubbing units for removal of these off-gases may be necessary [6].

Table 6. Analysis of gases * produced by the HTL of dairy manure assisted with various chemicals.

Concentration of Gases (% by Volume)	Water-Only	$NH_3 \cdot H_2O$	H_3PO_4	Glycerol
H_2	2.2	2.8	1.4	2.3
CO	7.8	6.7	6.5	3.7
CH_4	1.3	1.5	1.4	1.1
CO_2	61.8	54.1	64.5	63.1
Ethane	1.1	0.9	0.9	0.7
Environmental emission (g/g manure)				
CO release	0.01	0.01	0.01	0.02
CH_4 release	0.03	0.01	0.02	0.03
CO_2 release	0.08	0.04	0.06	0.09

* O_2 and N_2 were excluded from the analysis.

3.5. Analyses of Energy Comsuption and Energy Payback

A preliminary analysis of energy consumption on the HTL process of dairy manure was conducted. In this scenario, a manure slurry of 700 g with 10% solid content was hydrothermally treated in subcritical water at 2500–3000 psia and 350 °C. This manure slurry contains approximately 70 g dry dairy manure, which possesses 1.12 MJ energy. The specific heat of dairy manure (wet basis) increased with increase in both moisture content and temperature in the ranges of 20–82% and 40–70 °C, respectively, from 1.9925 to 3.606 kJ/kg·°C [55]. As a simplifying assumption, the specific heat capacity of the manure slurry was approximated to be equal to that of pure water (4.18 kJ/kg·°C) [56]. According to the steam table, the specific enthalpies of water (saturated liquid) at 20 °C and 350 °C (~ 17 MPa/2500 psia) are 83.9 kJ/kg and 1690 kJ/kg, respectively [57,58]. Energy required for heating 0.7 kg slurry from 20 °C to 350 °C can be calculated as:

$$z = 0.7 \times (1690 - 83.9) = 1124 \text{ kJ} = 1.12 \text{ MJ} \tag{5}$$

The energy required for processing this slurry is roughly equal to the energy content of the original feedstock. To minimize the energy usage for this process, the use of the original manure with 20% solid content is preferred, which will reduce the energy consumption by 50% to 0.56 MJ/batch

To evaluate the energy payback period, the Equation (6) is used:

$$\text{Energy Payback Period} = \frac{\text{Total Energy}}{\text{Excessive Energy Production Rate}} \tag{6}$$

The weight of the complete assembly of the 1-L Parr reactor is 245 lb (111 kg) [59]. As the embodied energy of steel is 42 MJ/kg [60], the Total Energy was estimated as 4662 MJ. The energy recovery ratio for HTL of dairy manure was about 60% [20], which gave a 0.67 MJ/batch energy recovery and 4 MJ/day (six batches per day). Thus, the energy payback period is about 1166 days (3.5 years), if the system was assumed to be operated for 11 months per year. The energy payback period of HTL is 50% lower than that of anaerobic digestion (AD), which was reported as seven years [61]. Since a simplified scenario is used here, a separate study is suggested to completely analyze the energy issues, environmental impacts, and economic benefits associated with the HTL process for manure management.

4. Conclusions

Hydrothermal liquefaction (HTL) of dairy manure assisted by chemicals of $NH_3 \cdot H_2O$, H_3PO_4, and glycerol was proposed as a sustainable alternative for the animal manure management.

HTL significantly reduced the mass of the original manure. Compared to the water-only HTL, the applications of $NH_3 \cdot H_2O$ and H_3PO_4 during the HTL of dairy manure could significantly enhance the production of liquid chemicals. The addition of $NH_3 \cdot H_2O$ or glycerol increased the amounts of non-polar toluene, xylene, and other benzene-contained compounds, while HTL assisted with H_3PO_4 produced high amounts of acids, pyridine, 3-methyl-pyridine, 2,6-dimethyl-pyrazine, 2-cyclopenten-1-ones, and phenols. Therefore, it is possible to produce target chemicals from dairy manure via HTL assisted with various chemicals.

The biochars produced via HTL showed a significant increase in the surface area and pore volume, which indicated a better holding capacity of water/nutrients. The biochar obtained by using HTL assisted with $NH_3 \cdot H_2O$ had the highest surface area of 63.88 m^2/g and the highest pore volume of 0.24 cm^3/g. In addition, the biochars had relatively higher N, P, C, and other minerals, and may serve as a good source of nutrients. FT-IR and XRD analyses showed that the structure of manure was destroyed by HTL reactions such as depolymerization of feedstock, decomposition of feedstock monomers, and recombination of reactive fragments. The preliminary energy analyses showed that the energy consumption of this process might be reduced to 50% of the original energy content of the feedstock, and the energy payback period was about 3.5 years. Combining all advantages, HTL of dairy manure might increase the sustainability of the farming operation via producing energy products, fine chemicals, and biochars. Future studies including a complete process design, pilot scale experiments, economic analysis, and life cycle analysis are still required to further explore this concept.

Supplementary Materials: The following are available online at www.mdpi.com/2071-1050/10/1/230/s1, Table S1: Results of one-way ANOVA analysis of liquid yields, Table S2: GC-MS analysis of liquid products from HTL of dairy manure assisted with various chemicals (% in area), Table S3: *p*-Values of ANOVA analysis of biochar samples, comparing to dry dairy manure and water-only HTL (Data in Table 4), Table S4: *p*-Values of ANOVA analysis of biochar samples, comparing to dry dairy manure and water-only HTL (Data in Table 5), Table S5: *p*-Values of ANOVA analysis of gases produced during HTL, comparing to water-only HTL (Data in Table 6), Figure S1: XRD curves of raw dairy manure and biochar produced by the HTL of dairy manure assisted with various chemicals (a Dry dairy manure, b Biochar–Glycerol, c Biochar–H_3PO_4, d Biochar–Water, e Biochar–$NH_3 \cdot H_2O$).

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