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Evaluation of Chemically Coagulated Swine Manure Solids as Value-Added Products

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Abstract

The objective of this research was to evaluate the chemically coagulated swine manure solids as biofuel and/or compost feedstock. Three coagulants, namely agricultural lime [$CaCO_3$], hydrated lime [$Ca(OH)_2$], and lime slurry [$Ca(OH)_2$], were added to fresh swine manure to coagulate manure solids. Four levels, *i.e.*, 0.00 (0.0X), 4.89 (0.5X), 9.77 (1.0X), and 19.77 (2.0X) gm Ca·liter^{-1}, were tested, in triplicates. Increasing the coagulant concentration increased the total solids, ash content, and pH of solid manure samples, whereas it decreased their volatile solids, chemical oxygen demand, and heating value. At the coagulant level of 2.0X rate, heating values of samples coagulated by agricultural lime, hydrated lime, and lime slurry were 2.64, 4.48, and 4.54 MJ·kg^{-1}, respectively. The heating value of raw manure solids was as high as 13.49 MJ·kg^{-1}. Increasing the coagulant concentration increased the O/C atomic ratio for all the studied coagulants. Accordingly, the high coagulant concentrations might reduce the acceptability of the feedstock as a biofuel that can be co-combusted with other feed stocks. The C/N ratio and the pH values of the solid separated swine manure increased by increasing agricultural lime and hydrated lime concentrations. The former might increase satisfactoriness for composting these solids, whereas the latter might hinder their use in the composting process. The maximum coagulant concentrations that allowed pyrolyzing the final product, based on the net energy values, were 48.80 (2.0X), 18.06 (1.0X), and 18.06 (1.0X) gm·liter^{-1} for agricultural lime, hydrated lime, and lime slurry, respectively. The maximum acceptable coagulant concentrations that allowed composting the final product, based on the pH values, were 48.80 (2.0X), 0.00 (0.0X), and 9.03 (0.5X) gm·liter^{-1} for the same three coagulants.

Keywords

Swine Manure, Solid Separation, Coagulation, Biofuel, Soil Amendment

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1. Introduction

The total number of pigs in the United States had reached 65.9 million head, as recently published in the quarterly inventory report by the USDA [1]. Daily pig manure production was estimated to be 4.67 kg·day^{-1}·animal^{-1} [2]. Thus, the total amount of swine manure generated annually is more than 110 million metric tons. Land application of excessive volumes of swine manure creates environmental issues associated with nutrient loss to water bodies following manure application on fields [3]-[5].

Traditionally, land application of swine manure is considered the most common practical and economical utilization method [6]. Manure is a valuable source of nutrients, particularly nitrogen (N), phosphorus (P), and potassium (K), to plants when utilized in an environmentally sustainable manner [7] [8]. However, repeated manure land application on the same field to meet crop N requirements results in elevated P concentrations, which may lead to P loss to the environment through surface runoff or leaching [9] [10]. Consequently, regulatory agencies require strict application plans based on soil nutrient content (N, P) before issuing permits for manure land application [11].

Typically, the moisture content and total solids of fresh swine manure are about 90% w.b. and 10% w.b., respectively [2]. Manure high moisture content limits its long distance transportation. Liquid and solid fractions of swine manure could be separated and utilized via various techniques to convert them to value-added products and minimize their harmful effects. Solid-liquid separation has been employed in wastewater treatments for decades and provided a possible management technique for phosphorus and nitrogen [12]. The method involves the separation of solids from liquid manure using sedimentation (gravity settling), centrifugation, filtration (using belt presses, screw presses, and screens), or chemical amendment. All these techniques have been demonstrated to separate solids from manure slurries [13] [14]. Ideally, the separated solid fraction is rich in nutrients, particularly P, and can be hauled for application on P-deficient soils, whereas the liquid fraction can be used to irrigate fields without elevating the soil P [3] [15]. Employing solid-liquid separation as a tool for manure treatment not only potentially improves its handling properties but also generates manure solids that can be utilized for either compost production or energy generation [16].

Xiu *et al*. [17] report that chemical separation of manure solids is mostly accomplished using metal salts and organic flocculants that bring solubilized nutrients out of solution as fine particles, then form agglomerates of these salts, which can then quickly precipitate. Commonly used chemical amendments are metallic salts, especially those of iron (Fe), calcium (Ca), or aluminum (Al) and/or synthetic organic polymers, such as polyacrylamide (PAM) formulations [18]. Addition of coagulants, *i.e.*, $FeCl_3$, $Fe_2(SO_4)_3$, $Al_2(SO_4)$, and $CaCO_3$, to manure results in coagulation of suspended particles by neutralizing the particles' negative surface charge and enhances P removal via coagulation of P by the cations constituting the coagulants [19]. Several studies have demonstrated that treatment of animal manure with coagulants and flocculants enhances solid-liquid separation [13] [20].

Reviewing the accessible literature reveals that there are no available data related to the energy contents and the thermal degradation behavior of the chemically coagulated swine manure solids. In addition, there are no data related to the maximum values of coagulants that will hinder the use of the final product as biofuel and/or compost feedstock. Consequently, swine producers, who practice manure-solid separation, should have interest in the determination of the optimum amount of coagulant additions and in the comparison between utilizing these solids as a biofuel or as a compost feedstock. Hence, the objective of this paper was to evaluate the chemically coagulated swine manure solids as a feedstock candidate for biofuel and/or compost.

2. Materials and Methods

2.1. Swine Manure Solids Collection and Coagulant Addition

Fresh swine manure was collected from a privately owned Arkansas farm. Three coagulants, namely agricultural lime [$CaCO_3$], hydrated lime powder [$Ca(OH)_2$], and lime slurry [$Ca(OH)_2$], were used to coagulate solids from fresh swine manure. Lime slurry was prepared by mixing the coagulant with water at the ratio of 0.3:1.0 kg·kg^{-1}, which is the mix ratio lime slurries starts behaving less as a suspension and more as a paste [21]. Mixing was accomplished using a battery powered drill and paint stirrer with less than 5 minutes of mixing needed. During the course of this study, coagulants were added to fresh swine manure in triplicates based at four levels of coagulant concentrations (0.00, 4.89, 9.77, and 19.77 gm Ca·liter^{-1}). These rates were set by mixing various volumetric ratios of the lime slurry to sub samples of the liquid manure in clear containers. Visual determination of precipitate settling identified that 5% lime slurry is an acceptable treatment rate to balance chemical use and treatment effect. Based on this the 0.0X, 0.5X, 1.0X, 2.0X treatment rates for the lime slurry was set at 0%, 2.5%, 5%, and 10% on a volumetric rate. Hereinafter, they will be referred as 0.0X, 0.5X, 1.0X, and 2.0X, respectively. The equivalent mass of chemical addition; *i.e.*, agricultural lime, hydrated lime, and lime slurry, are shown in **Table 1**. In this experiment, the specified amount of the chemical coagulant was mixed with 17 liters of fresh manure. Immediately the amended manure was poured into a second container lined with a 150-micron filter bag. The filter bag was lifted and suspended above the container to drain and naturally dry for 10 days. The coagulated, air-dried swine manure solid samples were collected and transported to the Rice Research and Extension Center lab, Stuttgart, Arkansas, for analyses.

2.2. Physical, Chemical, and Thermochemical Analyses

Physical, chemical, and thermochemical characteristics of the solid separated swine manure were determined in triplicates. Moisture content, volatile solids and ash content were determined according to the standard methods [22]-[24], respectively. Fixed carbon was obtained as the difference between dry weight and the sum of volatile solids and ash contents. The pH values of the manure samples were determined using an OMEGA Water Analyzer PHH-500 Series.

Chemical oxygen demand (COD) was employed in this study as an indirect measurement of soluble and insoluble organic matter in the manure samples. Samples were digested using a HACH DRB200 Digester, Germany. Following, a HACH DR7200 Spectrophotometer, Germany, was used to measure the COD. The ultimate and ash analyses were performed in a specialized diagnostic laboratory (Huffman Laboratories Inc., Golden, Colorado, USA). Samples' carbon, hydrogen, and nitrogen contents were determined according to standard ASTM D5373-14 [25], while sulfur was determined using standard ASTM D4239-14e1 [26]. The elemental analyses of the ash oxides were quantified according to standard ASTM 6349. Higher heating values were determined using an oxygen bomb calorimeter (Parr instruments, Model1241, Moline, Illinois, USA) according to ASTM Standard D5865-12 [27]. The calorimeter was used to burn a small mass of well dried feedstock samples in the presence of oxygen inside a sealed container.

2.3. Thermal Degradation

The pyrolysis of raw manure, agricultural lime, hydrated lime, and chemically coagulated samples, was investigated using a thermogravimetric analyzer (Model TGA 4000, Perkin Elmer, Inc., Waltham, Massachusetts). To ensure that the decomposition was controlled by kinetics rather than diffusion, the particle size and the sample size were kept small. The dry samples were first milled and sieved to generate a subsample with a particle size less than 0.2 mm. The sample weight was maintained at 5 mg (±0.1 mg) in all the TGA tests. The analyzer was used to determine the relationship between the temperature and weight loss for the different samples under oxy-

Table 1. Chemical coagulants utilized in manure solids separation.

Treatment	Level	Chemical[1] mass added per liter of liquid manure ($gm \cdot l^{-1}$)	Calcium mass added per liter of liquid manure ($gm \cdot l^{-1}$)
Manure	Raw	-	-
Agricultural Lime $CaCO_3$	0.5X	12.20	4.89
	1.0X	24.40	9.77
	2.0X	48.80	19.55
Hydrated Lime $Ca(OH)_2$	0.5X	9.03	4.89
	1.0X	18.06	9.77
	2.0X	36.13	19.55
Lime Slurry $Ca(OH)_2$	0.5X	9.03	4.89
	1.0X	18.06	9.77
	2.0X	36.13	19.55

[1]Mass of $CaCO_3$ and $Ca(OH)_2$ only added assuming chemicals are 100% pure.

gen-free conditions. Nitrogen was used as the purge gas (50 mL·min^{-1}), at a heating rate of 5˚C·min^{-1}. Each sample was placed in a clean, inert alumina (Al_2O_3) crucible. A blank test was conducted with an empty crucible under the regular test conditions to quantify the buoyancy of the crucible. The experimental data was then corrected by subtracting the blank test results.

2.4. Statistical Analysis

The results were analyzed using JMP® Pro software (version 11.0.0, SAS Institute Inc., Cary, North Carolina). Two-way ANOVA was used to analyze the impact of coagulant type and concentration on the characteristics of the feedstock.

3. Results and Discussion

Evaluation of the coagulated swine manure solids, as biofuel and/or composting feedstock, requires comprehensive analyses that determine the acceptable levels of the concentrations of each coagulant. The following section details the results of the lab analyses performed on the swine manure solids.

3.1. Physical, Chemical, and Thermochemical Characteristics of Coagulated Swine Manure Solids

The average total solids of raw manure were found to be 32.1% ± 4.9%, as shown in **Table 2**. The volatile solids, ash, and fixed carbon content were 54.9% ± 1.8%, 30.5% ± 1.6%, and 14.7% ± 0.4%, respectively. Increasing the concentration of the agricultural lime, hydrated lime, and lime slurry increased the total solids and ash contents in varying degrees. The highest total solids value of 68.0% ± 2.1% was achieved with the agricultural lime 2.0X, whereas the lowest total solids value of 33.1% ± 4.2% was observed with lime slurry of 0.5X. The increase in the total solids could be attributed to the rise in the chemical coagulant concentration in the manure samples. As shown earlier in **Table 1**, the mass of agricultural lime addition to fresh manure samples was higher than that added to either hydrated lime or lime slurry. These results are slightly lower than the results reported in the literature. Riano and Garcia-Gonzalez [3] found that the total solids produced from swine manure solids separated by a screw press and a coagulation-flocculation unit reached 73.3% and 85.4%, respectively. This could be attributed to the nature of the diet or the collection technique. Statistical analysis of the total solids values showed a significant effect of coagulant concentrations as compared with raw manure ($P < 0.05$). There was no significant difference between the values of total solids of both hydrated lime and lime slurry. Comparison of means showed the total solids in high coagulant concentration to be significantly greater than total solids of mixtures under low (0.5X) coagulant concentration ($P < 0.05$). Ash content, in the present study, also increased in the solid separated swine manure samples due to the rise in the inorganic component represented in coagulants. Ash concentration rose by 12.6% and 24.1% as the coagulant concentration increased from 0.5X to 2.0X for the agricultural lime and hydrated lime, respectively. Increasing lime slurry concentration did not show a

Table 2. Proximate analysis and bulk density of raw swine manure and amendment samples.

Treatment	Level	Total solids[1] (%)	Volatile solids (%)	Ash (%)	Fixed carbon (%)
Manure	Raw	32.1^{a} ± 4.9	54.9^{a} ± 1.8	30.5^{a} ± 1.6	14.7^{a} ± 0.4
	0.5X	56.7^{e} ± 3.4	34.6^{b} ± 4.1	46.8^{b} ± 1.3	18.6^{b} ± 3.2
Agricultural Lime	1.0X	66.2^{f} ± 5.6	24.5^{d} ± 2.6	50.7^{cde} ± 1.9	24.8^{c} ± 0.9
	2.0X	68.0^{f} ± 2.1	18.0^{f} ± 1.4	52.7^{e} ± 0.7	29.4^{d} ± 0.7
	0.5X	35.7^{bc} ± 0.9	33.8^{b} ± 3.3	48.6^{bcd} ± 4.1	17.6^{ab} ± 0.8
Hydrated Lime	1.0X	39.3^{cd} ± 3.5	23.9^{de} ± 1.2	57.3^{f} ± 3.0	18.7^{b} ± 2.0
	2.0X	40.8^{d} ± 1.3	21.1^{ef} ± 1.6	60.3^{f} ± 2.8	18.6^{b} ± 4.3
	0.5X	33.1^{ab} ± 4.2	35.5^{b} ± 0.9	48.1^{bc} ± 0.5	16.5^{b} ± 0.4
Lime Slurry	1.0X	35.6^{bc} ± 1.5	30.3^{c} ± 0.3	51.6^{de} ± 1.1	18.2^{b} ± 1.3
	2.0X	39.1^{cd} ± 0.2	29.9^{c} ± 0.3	47.8^{bc} ± 1.2	22.3^{c} ± 3.0

[1]Averages within a column followed by different letter are significantly different at $P \le 0.05$ level and n = 3.

clear trend. These high values of the ash contents might hinder the suitability of these feedstocks being utilized in thermochemical conversion processes. A significant effect ($P < 0.05$) was observed between samples having various coagulant concentrations. Low concentration of hydrated lime or lime slurry addition (0.5X) did not show the significant difference as compared with manure samples. However, the addition of agricultural lime showed a significant difference from hydrated lime and lime slurry ($P < 0.05$). A wide range of the ash content was reported previously in the literature. Jørgensen and Jensen [28] reported that the ash content ranged between 8.0 and 37.4%. Wnetrzak *et al*. [29] found that the ash content reached 22.2% during the testing of swine manure solid separation using chemical pretreatment and a mechanical separation system.

Conversely, for the present study, volatile solids concentrations in the manure samples decreased as the coagulant concentration increased, as shown in **Table 2**. Volatile content is the energy-rich fraction that fuels the heating necessary for both thermochemical and biological conversion processes. Increasing the coagulant concentration from 0.5X to 2.0X decreased the volatile solids from 34.6% ± 4.1% to 18.0% ± 1.4%, from 33.8% ± 3.3% to 21.1% ± 1.6%, and from 35.5% ± 0.9% to 29.9% ± 0.3% for agricultural lime, hydrated lime, and lime slurry, respectively. This is a result of the increase of coagulant concentration. Higher values of volatile solids results were reported by Xiu *et al*. [17]. They found the volatile solids to be about 65.5% when they separated solids using centrifugal force.

Table 3 summarizes the effects of coagulant type and concentration on the pH and chemical oxygen demand of solid coagulated swine manure. Raw swine manure pH value was 7.1 ± 0.2 (slightly greater than the neutral value of 7.0). For the amended samples, the lowest observed pH values were found with the addition of agricultural lime as compared with the other two chemical coagulants, *i.e.*, hydrated lime and lime slurry. Hydrated lime addition increased the pH values of the samples to 12.3, 12.5, and 12.6 under the coagulant concentrations of 0.5X, 1.0X, and 2.0X, respectively. Marchetti *et al*. [30] also reported that adding a chemical coagulant to separate swine manure solids increased the pH values towards the alkaline levels. They mentioned that the pH value of raw manure before and after the chemical treatment were8.00 and 9.65, respectively. Significant differences ($P < 0.05$) were observed between all the tested coagulant concentration levels as well as between the coagulant types for pH values.

Chemical oxygen demand of manure samples (**Table 3**) was used to measure the oxygen equivalent of the solid separated swine manure subjected to oxidation by a strong chemical oxidant. Adding 0.5X hydrated lime and lime slurry to manure increased the chemical oxygen demand (COD) from 1777.5 ± 406.3 $mg \cdot kg^{-1}$ to 2916.7 ± 376.3 $mg \cdot kg^{-1}$ and 2777.3 ± 508.4 $mg \cdot kg^{-1}$, respectively. Conversely, adding 0.5X agricultural lime concentration to fresh manure decreased the COD significantly. With further increase of the agricultural lime concentration, the COD values continued to decrease significantly ($P < 0.05$). Vanotti *et al*. [31] reported a significant decrease (83%) of the COD concentration of manure treated with a polymer and filtered through sand.

The highest heating value of 13.49 ± 0.42 $MJ \cdot kg^{-1}$ was observed with the raw manure sample (**Table 3**). Tsai *et al*. [32] reported the heating value of manure solids to be as high as 19.4 $MJ \cdot kg^{-1}$. Additionally, Park *et al.* [33] reported higher heating values of 22.3 $MJ \cdot kg^{-1}$. In contrast, Wnetrzak *et al.* [29] reported the higher heating value

Table 3. Chemical and the thermochemical characteristics of raw swine manure and amendment samples.

Treatment	Level	pH[1] (-)	Chemical oxygen demand ($mg \cdot g^{-1}$)	Higher heating value ($MJ \cdot kg^{-1}$)
Manure	Raw	$7.1^{a} \pm 0.2$	$1777.5^{d} \pm 406.3$	$13.49^{f} \pm 0.42$
	0.5X	$7.1^{b} \pm 0.0$	$1003.5^{abc} \pm 129.0$	$5.79^{cd} \pm 0.68$
Agricultural lime	1.0X	$7.4^{c} \pm 0.2$	$950.0^{ab} \pm 140.0$	$4.51^{b} \pm 0.46$
	2.0X	$7.5^{c} \pm 0.0$	$640.0^{a} \pm 17.3$	$2.64^{ba} \pm 0.68$
	0.5X	$12.3^{e} \pm 0.1$	$2916.7^{f} \pm 376.3$	$7.39^{e} \pm 0.38$
Hydrated lime	1.0X	$12.5^{fg} \pm 0.0$	$1886.7^{d} \pm 118.5$	$5.81^{cd} \pm 0.33$
	2.0X	$12.6^{g} \pm 0.0$	$1316.7^{bc} \pm 40.4$	$4.48^{c} \pm 0.70$
	0.5X	$8.7^{d} \pm 0.1$	$2773.3^{ef} \pm 508.4$	$7.60^{g} \pm 0.09$
Lime slurry	1.0X	$12.4^{ef} \pm 0.0$	$2343.3^{e} \pm 134.3$	$6.38^{f} \pm 0.07$
	2.0X	$12.5^{g} \pm 0.0$	$1440.0^{cd} \pm 52.9$	$4.54^{a} \pm 0.04$

[1]Averages within a column followed by a different letter are significantly different at $P \leq 0.05$ level and n = 3.

of 14.3 MJ·kg^{-1} for chemically pretreated swine manure solids followed by mechanical separation. The lower heating value in the present study might be due to the collection technique of the manure samples. Increasing the coagulant concentration decreased the samples' heating value. The heating value dropped by 80.4%, 66.x%, and 66.3% corresponding to 2.0X concentration of agricultural lime, hydrated lime, and lime slurry, respectively. **Table 3** also shows that there was a significant effect of adding agricultural lime on the heating value ($P < 0.05$). This decline is attributed to the increase of the inorganic fraction in the manure sample by increasing the coagulant concentration.

The results of the ultimate analysis conducted on the manure samples amended by the three studied coagulants, *i.e.*, agricultural lime, hydrated lime, and lime slurry, and the four levels of coagulant concentrations are shown in **Table 4**. Ultimate analysis of coagulated manure samples provides the weight fraction of its elemental constituents. The weight percentage of these elements was determined in dry basis. The primary elements constituting manure samples are carbon, hydrogen, oxygen, and nitrogen. These major elements are important in assessing the energy value and the suitability of the coagulated samples as biofuel. Low concentrations of sulfur were also found. Carbon concentration varied from 34.46% in raw manure to 17.34% in agricultural lime (2.0X), 12.99% in hydrated lime (2.0X), and 14.68% in lime slurry (2.0X) treatments. Similarly, hydrogen and nitrogen concentrations decreased by increasing the coagulant concentrations. Similar results of carbon and hydrogen concentrations of solid separated manure were reported by Wnetrzak *et al.* [29]. Sulfur also changed negatively by increasing the coagulant concentration. Adding 2.0X of agricultural lime, hydrated lime, and lime slurry to manure samples decreased the sulfur concentration to 0.20%, 0.22%, and 0.25%, respectively. Empirical chemical formulae were determined for the raw and amended manure samples based on their chemical compositions. The molecular weights of the raw manure reached 22.02. Adding 2.0X of agricultural lime, hydrated lime, and lime slurry increased the molecular weight to 32.25, 35.66, and 41.72, respectively.

The composition of the ash of the separated swine manure solids is presented in **Table 5** in the form of percent oxides of the mineral elements. The primary mineral elemental oxides found in the solid manure ash samples were phosphorus, calcium, potassium, and magnesium oxides. These elements provide information on the products during the thermochemical conversion process concerning environmental pollution problems. Phosphorus, calcium, magnesium, and potassium oxides of raw manure ashes reached 37.40%, 21.22%, 13.07%, and 4.65%, respectively. Increasing the coagulant concentration decreased the concentration of P_2O_5, K_2O, and MgO and increased the concentration of CaO. The pronounced rise in the calcium oxide in the present study is due to the addition of a calcium-based amendment to the liquid manure. Small amounts of Na_2O, ZnO, Fe_2O_3, CuO, and MnO were detected in the solid coagulated manure samples.

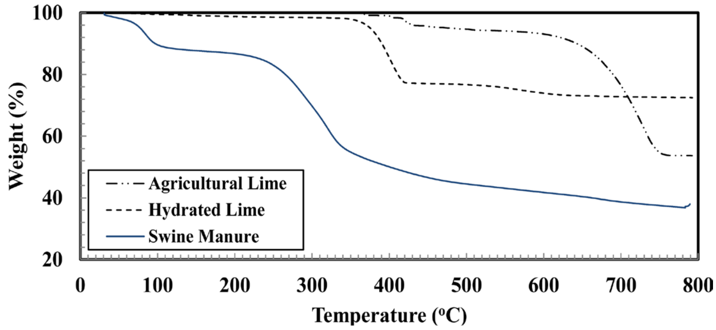
Figure 1(a) shows the pyrolysis weightloss as a function of temperature for the raw separated manure, agricultural lime, and hydrated lime. The weight-loss derivative curves (DTG), illustrated in **Figure 1(b)**, elucidate the various decomposition stages for these feedstocks. In the raw manure, the weight loss proceeded in two consecutive stages: drying and devolatilization. The first stage, *i.e.*, drying, took place between 60˚C and 105˚C as the first weight-loss peak indicates. The volatile matter loss, the second phase, *i.e.*, devolatilization, took

Table 4. Ultimate analysis, empirical formula and molecular weight of raw swine manure solids and amendment samples.

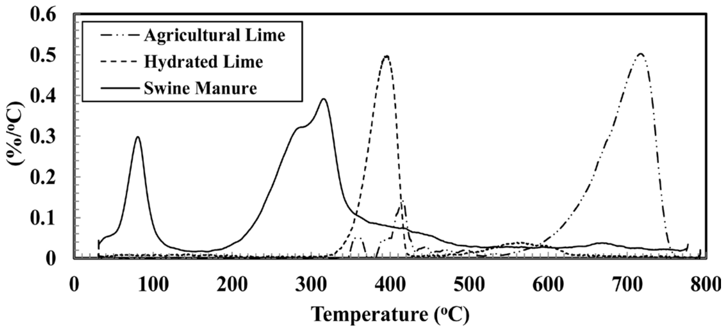
Treatment	Level	C (%)	H (%)	N (%)	O (%)	S (%)	Empirical formula (-)	Molecular weight (g·mol^{-1})
Manure	Raw	34.46	4.60	3.86	23.35	0.83	$CH_{1.602}O_{0.508}N_{0.960}S_{0.009}$	22.02
Agricultural lime	0.5X	22.38	2.21	1.44	26.35	0.39	$CH_{1.185}O_{0.883}N_{0.055}S_{0.007}$	27.52
	1.0X	19.11	1.60	0.97	27.22	0.25	$CH_{1.105}O_{1.068}N_{0.044}S_{0.005}$	30.25
	2.0X	17.34	1.28	0.78	27.78	0.20	$CH_{0.886}O_{1.202}N_{0.390}S_{0.004}$	32.25
Hydrated lime	0.5X	23.23	2.83	1.28	23.64	0.42	$CH_{1.462}O_{0.763}N_{0.047}S_{0.007}$	25.89
	1.0X	15.98	2.68	0.84	23.19	0.30	$CH_{2.013}O_{1.088}N_{0.045}S_{0.007}$	31.65
	2.0X	12.99	2.51	0.67	22.88	0.22	$CH_{2.319}O_{1.321}N_{0.044}S_{0.006}$	35.66
Lime slurry	0.5X	23.79	2.73	1.32	23.48	0.42	$CH_{1.377}O_{0.740}N_{0.048}S_{0.007}$	25.43
	1.0X	20.62	2.53	1.22	23.80	0.37	$CH_{1.147}O_{0.866}N_{0.051}S_{0.007}$	27.54
	2.0X	14.68	2.44	0.83	33.67	0.25	$CH_{1.995}O_{1.720}N_{0.048}S_{0.006}$	41.72

Table 5. Ash metal oxides for raw swine manure solids and amendment samples.

Treatment	Level	P_2O_5 (%)	K_2O (%)	CaO (%)	MgO (%)	Na_2O (%)	ZnO (%)	Fe_2O_3 (%)	CuO (%)	MnO (%)
Manure	Raw	37.40	4.65	21.22	13.07	1.22	NM	2.29	NM[1]	0.32
Agricultural Lime	0.5X	12.35	1.65	66.34	4.61	0.43	0.42	0.82	0.02	0.15
	1.0X	8.27	1.13	72.47	3.10	0.30	0.16	0.61	0.01	0.12
	2.0X	6.42	0.88	75.51	2.55	0.23	0.12	0.52	0.01	0.10
Hydrated Lime	0.5X	16.23	2.30	62.26	5.48	0.64	0.25	0.89	0.02	0.16
	1.0X	9.23	1.33	74.54	3.31	0.38	0.13	0.54	0.01	0.12
	2.0X	6.39	0.98	82.21	2.46	0.27	0.10	0.40	0.01	0.10
Lime Slurry	0.5X	17.52	2.42	61.30	5.64	0.72	0.28	0.90	0.03	0.16
	1.0X	11.70	1.61	69.68	3.98	0.45	0.20	0.70	0.02	0.14
	2.0X	8.48	1.21	97.13	3.18	0.34	0.15	0.55	0.01	0.13



(a)



(b)

Figure 1. Agricultural lime, hydrated lime and swine manure (a) weight loss, (b) weight loss derivative.

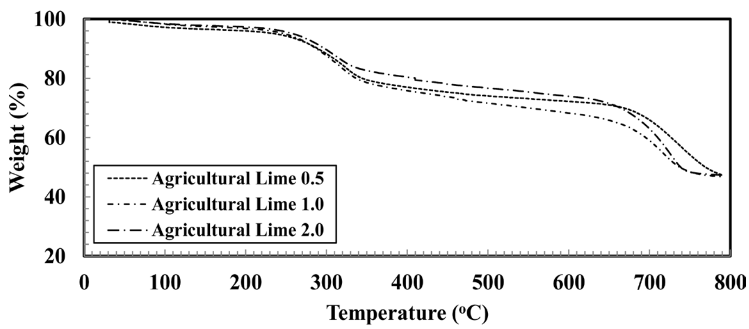
place between 220˚C and 350˚C. Devolatilization of raw manure reached its peak value of 0.392 %·˚C^{-1} at the temperature level of 315.9˚C (**Table 6**). Park *et al*. [33] used a TGA to determine the thermal decomposition of swine manure under nitrogen environment. They reported that the mass change in the first stage reached 1.2%·˚C^{-1}. Additionally, they reported 40.9% and 37.5% mass changes between 200˚C to 400˚C and 400˚C to 600˚C, respectively. Fresh agricultural lime showed a small peak as compared with raw manure and hydrated lime. However, hydrated lime showed a clear decomposition stage between 340˚C and 430˚C. At the temperature levels of 415.4˚C and 395.2˚C, the devolatilization peak reached 0.144˚C·min^{-1} and 0.500˚C·min^{-1} for agricultural lime and hydrated lime, respectively. Accordingly, the agricultural lime could be considered a thermally stable feedstock. Its major decomposition stage was delayed to higher than 600˚C and ended at 750˚C. Zhang *et al*. [34] also reported two distinctive stages of thermal decomposition of calcium compounds. They reported that the first phase took place between 400˚C and 600˚C and the second phase took place above 700˚C.

Amended manure samples using agricultural lime, hydrated lime, and lime slurry showed various levels of decomposition stages. **Figures 2-4** show the weight loss and the weight-loss derivative curves of the manure samples amended by the three coagulants, *i.e.*, agricultural lime, hydrated lime, and lime slurry. Two weight-loss peaks were detected during the pyrolysis of the manure samples amended with agricultural lime. The temperatures, corresponding to the decomposition peaks in the first stage as compared to those for raw manure, are listed in Table 6.

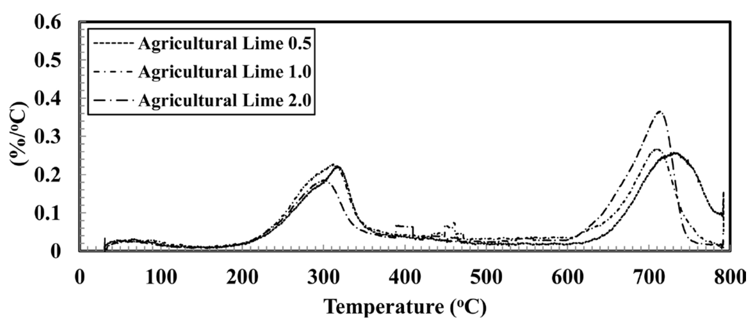
Manure samples amended with hydrated lime and lime slurry showed three decomposition stages: two small peaks (220˚C - 420˚C) and a larger one that took place under the temperature range of 600˚C to 715˚C. These observations indicate that under extremely high temperature levels (650˚C - 750˚C) full decomposition of the coagulant is achievable. It is worth noting that, in the current study, the decomposition peaks did not follow a clear trend by increasing the coagulant concentration. This observation could be attributed to the fact that under pyrolysis conditions or any thermal treatment, the original feedstock matrix is transformed into a new structure biochar that might have its thermal properties.

Table 6. Pyrolysis characteristics for raw manure, coagulants, and coagulated solids.

Treatment	Level	T_{p1} (˚C)	$(dW/dt)_{p1}$ ($mg \cdot s^{-1}$)	Energy required for pyrolysis ($MJ \cdot kg^{-1}$)
Manure	Raw	315.9	0.392	6.37
Agricultural lime	Raw	415.4	0.144	-
Hydrated lime	Raw	395.2	0.500	-
Agricultural lime	0.5X	316.0	0.222	3.16
	1.0X	311.8	0.277	2.56
	2.0X	299.9	0.186	2.47
Hydrated lime	0.5X	294.4	0.144	5.63
	1.0X	391.6	0.141	5.02
	2.0X	396.7	0.158	4.80
Lime slurry	0.5X	297.9	0.195	6.15
	1.0X	288.3	0.114	5.65
	2.0X	293.6	0.0.06	5.05



(a)



(b)

Figure 2. Samples amendment with agricultural lime (a) weight loss, (b) weight loss derivative.

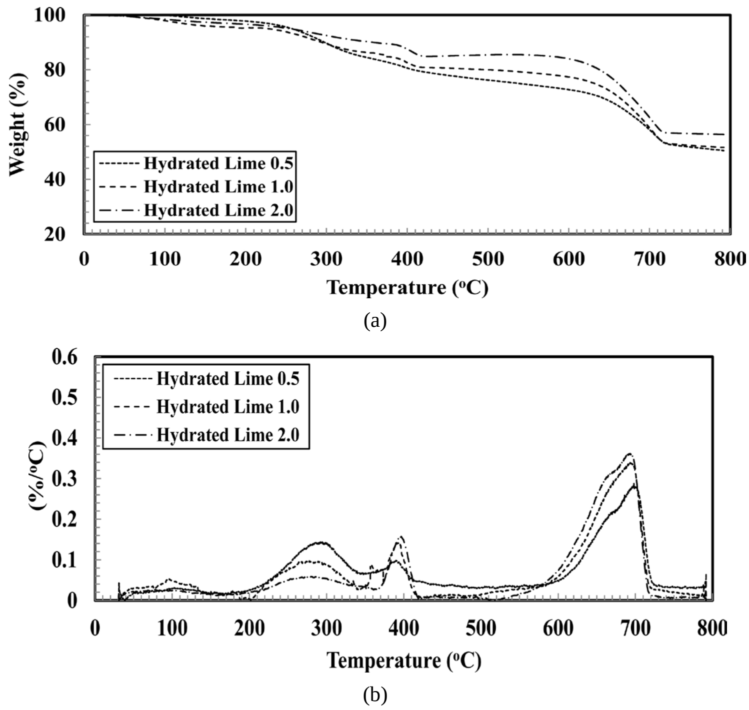


Figure 3. Samples amendment with hydrated lime (a) weight loss, (b) weight loss derivative.

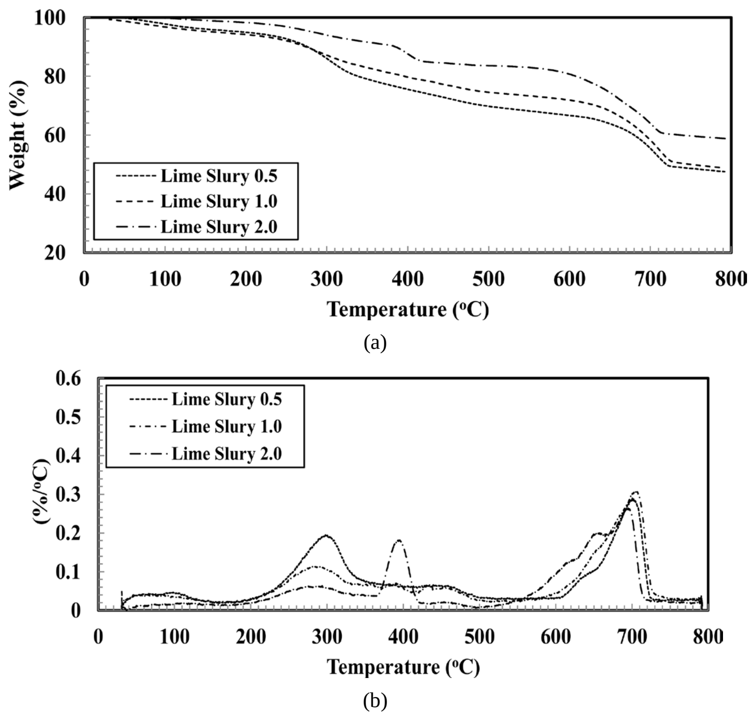


Figure 4. Samples amendment with lime slurry (a) weight loss, (b) weight loss derivative.

3.2. Assessment of Coagulated Swine Manure Solids as a Biofuel Feedstock

In addition to the energy content of the solid separated swine manure and its thermal degradation, which were mentioned earlier, it was essential to compare the carbon, hydrogen and oxygen relationships of these feed stocks. Figure 5 illustrates the effects of the coagulant addition on the O/C versus H/C atomic ratios along with

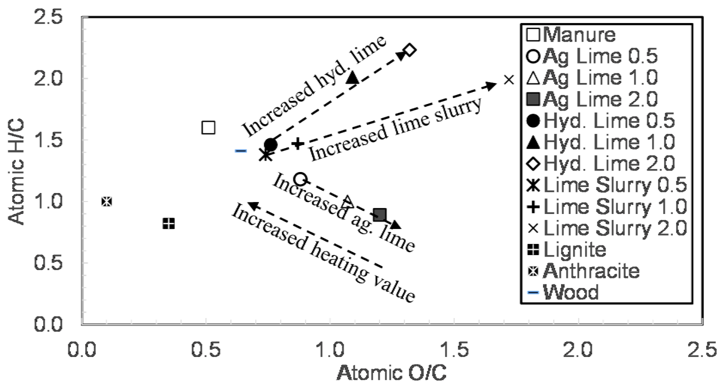


Figure 5. Van Krevelen diagram for raw swine manure and amendment samples as compared with coal and cottonwood.

two types of coal and cottonwood for comparison. A similar diagram was developed by Van Krevelen [35] to study the quality of coal. The graph shows that decreasing the O/C and increasing the H/C atomic ratios increases the energy content of the fuel source. This figure depicts that dry swine manure has O/C and H/C values of 0.5 and 1.6, respectively. These values placed dried manure in a location higher than that of cottonwood, as reported by Sadaka *et al*. [36]. These results revealed that raw manure solids could be co-fired with biomass. An interesting trend was observed by adding agricultural lime to coagulate swine manure solids. Increasing the agricultural lime concentration increased the O/C and decreased the H/C atomic ratios. A noticeable reduction in the heating values was observed, as depicted in the graph. In contrast, increasing hydrated lime or lime slurry concentrations increased the H/C atomic ratios and it decreased the O/C atomic ratio, which led to an overall reduction in the feedsrock heating value. The increase in oxygen concentration and the decrease in carbon concentration (**Table 4**) resulted in a noticeable rise in the O/C ratio for amended manure samples. On the other hand, the hydrogen concentration reduction corresponding to the increase in coagulant addition increased the H/C ratio. These two factors negatively affected the heating value of the produced feedstock. These results revealed that the lower the amendment addition, the higher the energy content of the coagulated swine manure samples. Nevertheless, these findings should be taken into consideration along with the outcome of the manure coagulation effectiveness.

It was essential to identify a unit function for the standardization of comparison. As a result, the unit function selected was 1 kg of the dried feedstock. It should be mentioned that this dry amount of feedstock started at different levels of the "as received" feedstock due to the variation in the initial moisture content levels. The total energy required to pyrolyze the wet feedstock could be obtained from the following equation:

$$Q_{total} = Q_{heating1} + Q_{drying} + Q_{heating2} + Q_{pyrolysis} \tag{1}$$

where

Q_{total}: is the total energy required for pyrolysis (MJ·kg^{-1}).

$Q_{heating1}$: is the energy needed to heat the wet feedstock from 25˚C to 100˚C (MJ·kg^{-1}).

Q_{drying}: is the energy required to dry the feedstock (MJ·kg^{-1}).

$Q_{heating2}$: is the energy needed to heat the dried feedstock from 100˚C to 550˚C (MJ·kg^{-1}).

$Q_{pyrolysis}$: is the energy required to pyrolyze the dried feedstock (MJ·kg^{-1}).

The energy needed to heat the feedstock ($Q_{heating1}$) was determined by adding the required energy to heat its two components, *i.e.*, manure and coagulant solids and moisture. Each constituent of the energy was determined by multiplying its mass, specific heat, and the difference in the temperature between 100˚C and 25˚C. Specific heat capacity was assumed to be between 2.1 - 2.5 kJ·kg^{-1}·˚C^{-1} for general organic materials [37]. The energy required to dry the feedstock was calculated by multiplying the water content and the latent heat of vaporization of water, 2090 kJ·kg^{-1} [38]. The energy required to heat the dried feedstock ($Q_{heating2}$) was calculated in a similar manner to $Q_{drying1}$ with the exception that no water exists as well as the temperature rise between 550˚C - 100˚C. The energy required to pyrolyze the dried feedstock, $Q_{pyrolysis}$, was estimated to be 300.00 kJ·kg^{-1} according to the literature [39].

The total energy required to pyrolyze raw manure reached 6.37 MJ·kg^{-1}, as shown in **Figure 6**. Increasing the

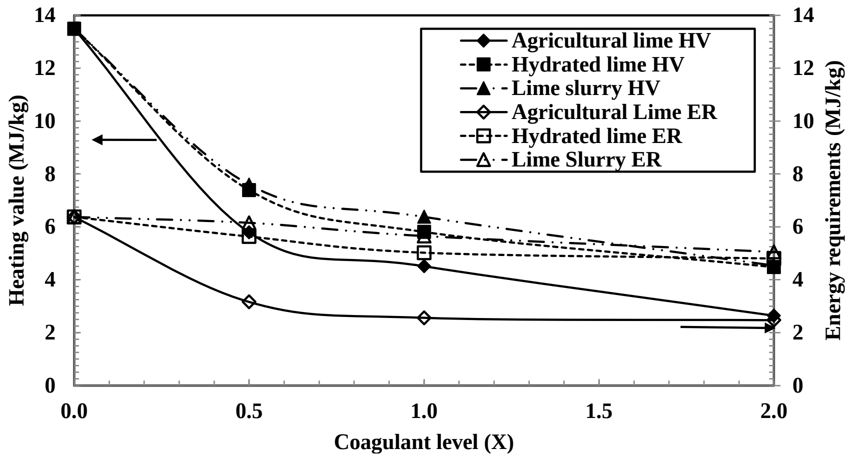


Figure 6. A comparison between the heating value (HV) and the energy required (ER) for pyrolysis for samples amendment with agricultural lime, hydrated lime, and lime slurry.

coagulant concentration decreased the energy needed for pyrolysis. The maximum energy required for pyrolysis of 6.15 MJ/kg was achieved with manure sample coagulated by lime slurry of 0.5X, whereas the lowest energy needed for pyrolysis of 2.47 $MJ \cdot kg^{-1}$ was achieved with manure sample coagulated by agricultural lime of 2.0X. The reduction of the energy required for pyrolysis can be attributed to the significant reduction of the energy required for drying. The net energy, as designated by the difference between the energy content of the feedstock and the energy needed for pyrolysis, could be also perceived from **Figure 6**. The net energy showed positive values for the three coagulant types and concentrations with the two exceptions of hydrated lime and lime slurry of 2.0X. This figure depicts that the higher concentrations of chemical coagulant decreased the heating value of the coagulated sample to the extent that the energy content would not be sufficient to pyrolyze the feedstock.

3.3. Assessment of Coagulated Swine Manure Solids as a Soil Amendment

As mentioned earlier, **Table 3** revealed that adding coagulants to separate swine manure solids affected its pH values. Five cases out of the nine studied cases showed that the pH values were far from optimal levels for composting. Velis *et al*. [40] reported that the optimum pH value for the composting process was in the range of 5.0 to 9.0. Adding agricultural lime (0.5X, 1.0X, and 2.0X) as well as adding lime slurry (0.5X) were the only acceptable cases for the composting process in terms of pH value. In addition to manure pH value and nutrient content described earlier, carbon to nitrogen ratio (C/N) is a crucial parameter governing the decision of composting the feedstock. C/N ratio is an important value that helps to evaluate the suitability of the feedstock as a soil amendment. C/N ratio of raw manure reached 8.93, as shown in **Table 7**. Although, the carbon concentration for the fresh manure was higher than that of any other sample (**Table 4**), its nitrogen concentration also was the highest. Accordingly, lower C/N ratios were obtained. C/N ratio of all the tested samples ranged between 15.54 and 22.23, indicating that these feedstocks could potentially be composted. Carbon concentration requires enhancement by adding a carbon source feedstock to reach the optimum C/N ratio of 30, as reported by Zhu [41]. Increasing the coagulant concentration increased the C/N ratio for the two coagulants, *i.e.*, agricultural lime and hydrated lime. The maximum C/N ratio of 22.23 was observed with agricultural lime of 2.0X. Increasing the concentration of lime slurry did not show a similar trend as was found with agricultural lime and hydrated lime. Increasing the concentration of lime slurry from 0.5X to 1.0X decreased the C/N ratio from 18.02 to 16.90. Further increase in the lime slurry concentration to 2.0X increased the C/N ratio once again to 17.69. Jørgensen and Jensen [28] reported a narrowing range of C/N ratios (7 - 14) for chemically separate swine manure. It might be due to the characteristics of the chemicals themselves. Another reason they mentioned was that manure was anaerobically digested before solid separation.

An important step in the preparation process of composting the produced feedstock is to determine the amount of bulking material required to adjust the C/N ratio to reach the optimum range, *i.e.*, 30. Bulking agents have low moisture content and high C contents [42]. When added to manure before composting, they increase the C/N ratio, decrease overall moisture content, and improve the structure and porosity of the composting mixture. The composting of manure with a bulking agent results in an accelerated and odor-free process. The bulking agent absorbs excess moisture. The C/N ratio of a mixture of two feedstocks could be obtained as follows:

$$C/N = \left(\frac{Q1 \times (100 - M1) \times C1 + Q2 \times (100 - M2) * C2}{Q1 \times (100 - M1) \times N1 + Q2 \times (100 - M2) * N2} \right) \tag{2}$$

where:

C/N: is the carbon to nitrogen ratio.

Q1: is the manure weight, kg.

Q2: is the bulking material weight, kg.

M1: is the manure moisture content, %.

C1: is the manure carbon concentration, $g \cdot kg^{-1}$.

N1: is the manure nitrogen concentration, $g \cdot kg^{-1}$.

M2: is the bulking agent moisture content, %.

C2: is the bulking agent carbon concentration, $g \cdot kg^{-1}$.

N2: is the bulking agent nitrogen concentration, $g \cdot kg^{-1}$.

As a result, by rearranging the previous equation, the amount of the bulking agent could be determined using the following equation.

$$Q2 = Q1 * = \left(\frac{(C/N \times (100 - M1) \times N1 - (100 - M1) \times C1)}{((100 - M1) \times C2 + C/N \times (100 - M2) \times N2)} \right) \tag{3}$$

Corn stalks were selected as a candidate feedstock with the assumption that its initial moisture, carbon and nitrogen contents are 11.00%, 41.18%, and 0.78%, respectively [43]. **Table 7** shows the required amount of corn stalks to bring the C/N ratio to 30 based on 1000 kg of the feedstock. The results showed that raw manure requires 1.65 ton/ton of corn stalks to reach the same C/N level. Sadaka and Ahn [43] biodried (partially compost) solid separated swine manure. They reported that adding crop residues to the manure enhanced the process performance and added more profit to producers since no external heat was supplied to dry the feedstock. They also mentioned that the biodrying process is a valid method for reducing manure corn stover moisture content and producing a feedstock suitable for thermochemical gasification technology.

It was observable from **Table 7** that increasing the agricultural lime, hydrated lime, and lime slurry concentrations from 0.5X to 2.0X reduced the required amounts of corn stalks by 65.1% (from 0.75 to 0.26 ton/ton), 46.6% (from 0.26 to 0.18 ton/ton), and 23.6% (from 0.33 to 0.25 ton/ton), respectively. As mentioned earlier, a significant decrease in the carbon concentration was observed with the increase in coagulant concentration. Once again, from crop residues composting perspective, adding less bulking agent would be more desirable as less biomass would be transported.

Table 7. Carbon to nitrogen ratio, bulking agent requirements, hydrogen to carbon atomic and oxygen to carbon atomic ratios.

Treatment	Level	C/N[1] (-)	CS[2] (ton)	H/C[1] (-)	O/C[1] (-)
Manure	Raw	8.93	1.65	1.60	0.51
Agricultural Lime	0.5X	15.54	0.75	1.18	0.88
	1.0X	19.70	0.42	1.00	1.07
	2.0X	22.23	0.26	0.89	1.20
Hydrated Lime	0.5X	18.15	0.34	1.46	0.76
	1.0X	19.02	0.23	2.01	1.09
	2.0X	19.39	0.18	2.32	1.32
Lime Slurry	0.5X	18.02	0.33	1.38	0.74
	1.0X	16.90	0.36	1.47	0.87
	2.0X	17.69	0.25	1.99	1.72

[1]Atomic ratio (-); [2]Corn stalks (ton).

4. Conclusions

From the experimental work described in this article, several important conclusions can be drawn:

- Increasing the coagulant treatment level increased the total solids, ash content, and pH of manure samples, whereas it decreased their volatile solids and heating value.
- The heating value of raw manure was 13.49 MJ·kg^{-1}, whereas it was 2.64 MJ·kg^{-1} for agricultural lime, 4.48 MJ·kg^{-1} for hydrated lime, and 4.54 MJ·kg^{-1} for lime slurry at the coagulant 36.13 gm·liter^{-1} rate.
- Increasing the coagulant concentration decreased the acceptability of the solid separated swine manure as a biofuel source.
- Based on the net energy, the maximum acceptable coagulant concentrations that allow pyrolyzing the final product were 48.80 (2.0X), 18.06 (1.0X), and 18.06 (1.0X) gm/liter for agricultural lime, hydrated lime, and lime slurry, respectively.
- Considering only the C/N ratio increasing the coagulant concentration tended to increase the acceptability of the solid separated swine manure as a composting source.
- Based on the pH values, the maximum acceptable coagulant concentrations that allow composting the final product were 48.80 (2.0X), 0.00 (0.0X), and 9.03 (0.5X) gm/liter for agricultural lime, hydrated lime, and lime slurry, respectively.

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