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Behavior of Inorganic Elements in Poultry Manure
during Supercritical Water GasificationTakashi YANAGIDA *¹, Tomoaki MINOWA *¹, Akifumi NAKAMURA *²,
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Poultry manure can be completely gasified in supercritical water. In this paper, the behavior of the seven inorganic elements, N, Ca, K, P, S, Cl and Si in layer poultry manure during supercritical water gasification has been studied to analyze the potential of the by-products of poultry manure gasification for recycling. The inorganic elements in the starting poultry manure, and in the solid and liquid phases after reaction, were quantitatively analyzed. Furthermore, the experimental data were confirmed with thermodynamic equilibrium calculations using computer software. Following gasification the elements N, K and Cl partitioned almost completely into the liquid phase, Ca, P and Si partitioned almost completely into the solid phase, and S partitioned between both phases.

Key Words

Supercritical water gasification, Poultry manure, Waste management, Inorganic element,
By-product utilization

1. Introduction

In recent years, management of livestock manure has been recognized as an important issue in Japan. The livestock manure has previously been converted to compost and used as agricultural fertilizer. However, demand of the compost has been decreased due to the inconvenience of its handling and/or environmental concerns regarding over-use. Many livestock farmers have therefore been facing difficulties in the proper treatment of the surplus livestock manure. The Japanese Government has enforced the law on Promoting Proper Management and Use of Livestock Excreta since November 2004. Thus, an alternative tech-

nology for the utilization of the livestock manure is needed.

There already exist some techniques, such as direct combustion, pyrolysis, gasification, oil production by thermochemical liquefaction and methane fermentation, for an effective utilization of livestock manure¹⁾. Among those techniques, biogas production from methane fermentation of pig and cattle manures, used as a wet material, and power generation from direct combustion of broiler poultry manure, used as a dry material²⁾, are of practical use. However, materials with high nitrogen content cannot be used for methane fermentation since nitrogen inhibits microbial activities during methane fermentation. Furthermore direct combustion cannot be applied to wet materials. Thus, methane fermentation or direct combustion may not be desirable selections for utilization of layer poultry manure which has a high moisture and rich nitrogen content. Supercritical water gasification (SCWG) has been proposed as a new technique for the treatment of layer poultry manure.

Supercritical water is water above its thermodynamic critical point, i.e. 374.2°C and 22.1 MPa³⁾. Organic matter can be decomposed in supercritical water and converted to various useful products, such as gases, saccharides and

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organic acids^{4) ~ 9)}. In a study of SCWG of layer poultry manure using an activated carbon catalyst we have shown that the organic matter in poultry manure can be completely gasified into fuel gases such as H_2 , CO_2 , CH_4 by SCWG¹⁰⁾. Layer poultry manure therefore has the potential to be a desirable energy resource. In practice, however, the layer poultry manure is composed, not only of organic matter, but also of inorganic elements such as N, Ca, P, and thus not only gas, but also solids and liquids, are produced during SCWG. Utilization of the inorganic materials of layer poultry manure is therefore important from the viewpoint of recycling of this material.

To determine the possibility of recycling the by-products of SCWG treatment of layer poultry manure the behavior of seven inorganic elements of N, Ca, K, P, S, Cl and Si that are generated during SCWG of chicken manure was the focus of this study.

2. Experimental

2.1 Materials

Layer poultry manure used for SCWG was collected from a commercial layer poultry farm "SERA FARM" located in Hiroshima, Japan. The properties of the poultry manure are shown in Table 1. Activated carbon (30 μm particle size, coconut shell), was used as the catalyst in SCWG, was obtained from Japan EnviroChemicals, Ltd (Tokyo, Japan).

2.2 Supercritical water gasification of poultry manure

The procedure of the supercritical water gasification of poultry manure is shown in Fig. 1. The reaction was carried out in an autoclave with a capacity of 100 ml. The poultry manure (1.19 g), distilled water (13.26 g), and activated carbon (0.367 g) were charged in the autoclave by adjusting the pressure at 600°C to approximately 30 MPa. This reaction temperature was selected from the literature⁶⁾ as being sufficient for a complete gasification of organic

feedstock. Nitrogen gas, added to 0.5 MPa, was used to purge the residual air in the autoclave. The reaction was then started by heating the autoclave to 600°C using an electric furnace. It took about 60 min to raise the temperature from the room temperature to 600°C. When the temperature reached to 600°C, the heating was stopped. The pressure at 600°C reached to 32 MPa. The autoclave was then immediately cooled down to room temperature using a water bath.

2.3 Separation of the products

The procedure for separation of the products of SCWG treatment of poultry manure is also shown in Fig. 1. After cooling to room temperature, the product gas was removed to a sampling bag. The autoclave was then opened and the reaction mixture was removed for separation. The reaction mixture was separated into solid and liquid phases by vacuum filtration using a 0.10 μm pore size membrane filter (Advantec Toyo Kaisha Ltd., Tokyo, Japan). The liquid phase was collected in a sampling tube. The solid phase remaining on the filter was rinsed with distilled water, dried at 105°C for 24 hours and then collected in a sampling tube for analysis.

2.4 Analysis of inorganic elements

Analysis of the inorganic elements in the both the raw materials and the products of SCWG was conducted by Sumika Chemical Analysis Service, Ltd (Tokyo, Japan). The N in the solid phase was measured in an NCH determination apparatus equipped with an oxygen cycle combustor and a TCD detector. The N in the liquid phase was determined by an ultraviolet (UV) spectrophotometric method based on Japanese Industrial Standards, JIS K 0102.45.2. For both liquid and solid phases quantitative analysis of Ca, P, S and Si was carried out by inductively coupled plasma atomic emission spectrometry (ICP-AES: IRIS Advantage, Nippon Jarrell-Ash Co. Ltd., Tokyo, Japan); K was determined by atomic absorption spectroscopy (AAS: Z6100, Hitachi, Ltd., Tokyo, Japan) and Cl was determined by ion chromatography (IC: DX320J, Dionex Corporation, Osaka, Japan).

The recovery of the inorganic elements of the raw material in the products was calculated as the recovery ratio as follows:

$$\text{Recovery ratio (\%)} = 100 \times (E_{\text{sol or liq}} - E_{\text{ac}}) / (E_{\text{man}}) \quad (1)$$

E_{man} = the initial amount of poultry manure used for the experiment $\times$ the inorganic element content of the poultry manure (2)

E_{ac} = the amount of activated carbon in the sample

$\times$ the inorganic element content of the activated car-

Fig. 1 Scheme of SCWG and separation of poultry manure

bon (3)

$E_{\text{sol or liq}}$ = the amount of the solid or liquid phase after SCWG $\times$ the inorganic element content of the solid or the liquid phase (4)

where $E_{\text{sol or liq}}$ is the amount of the inorganic element in the solid or liquid phase after SCWG, E_{man} is the amount of the inorganic element in the poultry manure and E_{ac} is the amount of the inorganic element in the activated carbon.

2.5 Thermodynamic equilibrium calculation

The behavior of inorganic elements during SCWG treatment of poultry manure was simulated with the thermodynamic equilibrium calculation software, HSC Chemistry version 6.12 (Outokumpu Research Oy, Pori, Finland) that is the most widely used computational thermochemistry application in the world.

In the first step, 142 chemical compounds which consisting of H, C, N, O, Si, P, Cl, K and Ca were selected. Initial input data of the relative amount of each element in one kg of poultry manure was calculated based on the data in Tables 1, 2 and temperature conditions of 25°C. Initial input data for calculation of the thermodynamic equilibrium is shown in Table 3. The thermodynamic equilibrium for the initial data was calculated from this input data based on a temperature of 25°C. Subsequently, using a thermodynamic equilibrium calculation based on a temperature of 600°C and a pressure of 32 MPa, the mole amount of the 142 selected chemical compounds was obtained. The mole amount of gases such as H_2 , CH_4 and CO_2 , generated from organic matter was subtracted from the data in order to simulate the irreversibility of this process. The thermodynamic equilibrium

was then recalculated to simulate conditions under which the pressure and the temperature of the reaction were decreased. Finally, the mole amount of the selected 142 chemical compounds under conditions of 25°C and 0.1013 MPa was obtained. These data were reflected the equilibrium conditions after SCWG treatment of poultry manure. The recovery ratio was calculated as follows:

$$\text{Recovery ratio (\%)} = 100 \times C_{\text{sol, liq, or gas}} / C_{\text{man}} \quad (5)$$

where $C_{\text{sol, liq, or gas}}$ is the mole amount of inorganic element in the solid, liquid or gas phase after SCWG, C_{man} is the mole amount of element in the poultry manure and is the initial input data used for the thermodynamic equilibrium calculation.

3. Results and discussion

During SCWG, not only the gases, but also solids and liquids, are produced. In our previous work¹⁰⁾ we have shown that poultry manure can be completely gasified at reaction conditions of 600°C and 32 MPa as described in the experimental section. Fig. 2 shows the features of the solid and liquid phases generated by SCWG treatment of poultry manure. The solid phase was a mixture of the ash in the poultry manure and the activated carbon catalyst. The liquid was clear and colorless. The content (wt%) of inorganic elements in the raw materials and the solid and liquid phase products is shown in Table 2. Quantitative analysis of N,

Table 1 Properties of poultry manure

Component	[wt%]
C	34.7 (dry basis)
H	4.4 (dry basis)
O	47.2 (dry basis) ^{a)}
Ash	13.7 (dry basis) ^{b)}
Moisture content	62.8

a) Calculated as the difference between C, H and ash

b) Sum of minor elements

Table 3 Initial input data for thermodynamic equilibrium calculations

	[kmol] ^{a)}	remarks
H_2O	6.534E+02	Sum of the moisture in the poultry manure and added distilled water
H	1.624E+01	Divided into H_2 and H of NH_3
C	1.075E+01	Input as C
N	1.381E+00	Input as NH_3
O	1.097E+01	Input as O_2
Si	3.311E-02	Input as Si
P	1.922E-01	Input as P
Cl	3.463E-02	Input as Cl_2
K	2.093E-01	Input as K
Ca	3.434E-01	Input as Ca

a) On a basis of one kg poultry manure

Table 2 Content of inorganic elements (wt%) in the raw materials and products of SCWG of poultry manure

		N	Ca	K	P	S	Cl	Si
Raw materials	poultry manure ^{a)}	0.52	3.7	2.2	1.6	0.44	0.33	0.25
	activated carbon ^{a)}	0.25	0.11	— ^{b)}	0.016	0.034	0.01	0.069
Products	solid phase ^{a)}	— ^{b)}	4.8	— ^{b)}	1.4	0.1	— ^{b)}	0.33
	liquid phase	0.21	0.0007	0.0078	0.0001	0.0056	0.011	0.0013

a) Dry basis, b) No data, *1.190g of poultry manure, 0.367g of activated carbon and 13.260g of distilled water were used for the experiment.

Fig. 2 Appearance of solid phase (a) and liquid phase (b) following SCWG treatment of poultry manure

K and Cl in the solid phase of the product was not possible because the amount of those elements was too low. Fig. 3 shows the recovery of inorganic elements in the solid and liquid phases of the products of SCWG. These inorganic elements were not moved to gas phase following SCWG treatment of poultry manure. Recovery was calculated as a recovery ratio that is defined by Eq. (1) and (5) described in the experimental section. For calculation of Eq. (1) it was assumed that the activated carbon catalyst was not gasified¹¹⁾. Table 4 shows the chemical form of each element and its mole fraction based on the thermodynamic equilibrium calculations.

Based on the results shown in Fig. 3, the behavior of the seven inorganic elements analyzed can be classified into

three groups; N, K and Cl almost completely partitioned into the liquid phase; Ca, P and Si almost completely partitioned into the solid phase and S partitioned into both phases. In these experiments the inorganic elements in the gas phase were calculated by thermodynamic equilibrium calculations (Fig. 3). The result of these calculations supported the idea that inorganic component gases such as H_2S or NH_3 are not produced after SCWG treatment of poultry manure (Table 4). The total recovery ratios calculated for each element based on the experiment data were not exactly equal to 100% due to a hundering of minor elements (Fig. 3). However this discrepancy may not have a significant effect on the behavior of the minor elements since the behavioral tendencies of the elements was very clear and, furthermore, the experimental results were in good agreement with the thermodynamic equilibrium calculation data.

3.1 Behavior of Nitrogen, Potassium and Chlorine

The elements N, K and Cl were almost exclusively in the liquid phase following SCWG treatment. This conclusion was reached from the results of the experimental data as well as from equilibrium calculations that corresponded well to the experimental data. According the thermodynamic equilibrium calculations predominant chemical forms of N, K and Cl in the liquid phase were, NH_4^+ , K^+ and Cl^- (Table 4). This result indicates that these ions in the liquid phase, in particular, NH_4^+ are important from the point of view of environmental issue. Waste water quality standards

Fig. 3 The recovery ratio of N, Ca, K, P, S, Cl and Si following SCWG treatment of poultry manure a): Experimental data estimated by eq.(1), b): Thermodynamic equilibrium calculation data estimated by eq.(5). These inorganic elements were not moved to gas phase after SCWG treatment

Table 4 Chemical forms of each inorganic elements and, mole amount and mole fraction of each chemical form, determined by thermodynamic equilibrium calculations

element	chemical forms	mole amount [kmol] ^{a)}	mole fractions ^{b)}
N	NH ₄ ⁺	1.38E+00	1.00
	(NH ₄) ₂ SO ₄	9.36E-07	0.00
	NH ₄ HCO ₃	4.97E-07	0.00
Ca	Ca ₅ (PO ₄) ₃ OH	6.33E-02	0.93
	Ca ²⁺	1.22E-02	0.04
	CaSO ₄	1.05E-02	0.03
	CaCO ₃	6.93E-04	0.00
	CaHPO ₄	2.58E-06	0.00
K	K ⁺	2.10E-01	1.00
	KHCO ₃	1.01E-08	0.00
P	Ca ₅ (PO ₄) ₃ OH	6.33E-02	1.00
	CaHPO ₄	2.05E-08	0.00
	K ₃ PO ₄	1.30E-10	0.00
S	SO ₄ ²⁻	1.44E-02	0.29
	CaSO ₄	1.05E-02	0.21
	S ₄ O ₃ ²⁻	5.57E-03	0.45
	S ₃ O ₃ ²⁻	9.40E-04	0.06
	(NH ₄) ₂ SO ₄	9.36E-07	0.00
	HS ₂ O ₇ ⁻	2.28E-07	0.00
	HSO ₄ ⁻	2.40E-08	0.00
Cl	Cl ⁻	4.00E-02	1.00
Si	SiO ₂	3.00E-02	1.00

a) Chemical forms, with the mole amount over 1.00E-10, are listed. The total mole amount of each element corresponded to the initial mole amount

b) Mole fraction = Mole amount of the specific chemical form of the element / Total mole amount of the element

in Japan define that N concentration in waste water must be less than 120 mg/l^[12]. The N concentration of the liquid phase following SCWG treatment of poultry manure was in the region of 2,000 mg/l. Thus waste water treatment will be required after SCWG treatment of poultry manure. Alternatively NH₄⁺ might be recovered as ammonia or an ammonium compound. Methane fermentation has often been employed in the treatment of livestock manure. In this process the fermentation sludge is produced as a by-product. This fermentation sludge can be used as a liquid fertilizer. However the demand for fermentation sludge as a liquid fertilizer is decreasing. Additionally, the sludge recovered from methane fermentation is not an ideal fertilizer since this sludge is a mixture of organic and inorganic matter. In contrast the liquid phase of SCWG is a desirable resource for the recovery of material that can be recycled since, compared with the methane fermentation sludge, it has a low level of impurities.

3.2 Behavior of Phosphorus, Calcium and Silicon

The inorganic elements Ca, P and Si were almost exclusively in the solid phase following SCWG treatment of poultry manure. The tendency of Ca, P and Si to distribute to the solid phase as judged from the experimental data corresponded well with the results of the equilibrium calculations. The element P existed completely as hydroxyapatite, Ca₅(PO₄)₃OH (Table 4). The mole ratio of Ca to P in hydroxyapatite and chicken manure are 1.67 and 1.79 (Table 3), respectively. Surplus Ca could become Ca²⁺, CaSO₄ and CaCO₃ (Table 4). The main component of the solid phase (with the exception of the activated carbon catalyst) of poultry manure following SCWG was apparently hydroxyapatite as shown in Tables 2, 4. The inorganic element P is an important element for the production of chemicals or fertilizers. Hydroxyapatite, which is a calcium phosphate, is also an important material for medical, cosmetic and dental usage. Recovery of both the by-product P, and the activated carbon catalyst, from the solid phase of the SCWG-treated poultry manure is expected and utilization of these recovered materials will be important from the standpoint of recycling the low material.

3.3 Behavior of Sulfur

According to the equilibrium calculations 79% of S moved to the liquid phase while the remainder moved to the solid phase following SCWG treatment of poultry manure. The tendency of S to distribute in both the solid and liquid phase as assessed by the experimental data corresponded with the result obtained by equilibrium calculation. Sulfur existed predominantly in the forms SO₄²⁻ and S₄O₃²⁻ in the liquid phase (Table 4). In contrast, CaSO₄ predominated in the solid phase.

4. Conclusions

The behavior of the inorganic elements, N, Ca, K, P, S, Cl and Si during SCWG treatment of poultry manure in the presence of an activated carbon catalyst was studied. The experimental corresponded well with the data obtained by thermodynamic equilibrium calculations. Almost all of the N, K and Cl moved to the liquid phase whereas all of the Ca, P and Si moved to the solid phase following treatment. Sulfur distributed in both the liquid and the solid phases. Thermodynamic equilibrium calculations indicated that inorganic derived-gas was not produced after SCWG treatment of poultry manure. Therefore the gases obtained from SCWG treatment of poultry manure may be composed of C, H and O. The data indicates that the liquid phase following SCWG treatment of poultry manure has concentration of ammonium in water and that the solid phase, with the

exception of activated carbon catalyst, is mainly composed of a calcium phosphate, hydroxyapatite. The results suggested that SCWG treatment of poultry manure will produce by-products that can be recycled for other uses. For example ammonium and calcium phosphate can be recovered from the liquid and the solid phase, respectively and could be recycled for a number of applications in both agriculture and medicine.

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