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Solid fuel production from cattle manure by dewatering using liquefied dimethyl ether

Kazuyuki Oshita [a,b,c,d,*], Satoshi Toda [b], Masaki Takaoka [a,b,d], Hideki Kanda [e,f], Takashi Fujimori [a,b], Kazutsugu Matsukawa [d,g], Taku Fujiwara [d,h]

[a] Graduate School of Global Environmental Studies, Kyoto University, Cluster C, Kyoto daigaku-Katsura, Nishikyo-ku, Kyoto 615-8540, Japan
[b] Department of Environmental Engineering, Graduate School of Engineering, Kyoto University, Cluster C, Kyoto daigaku-Katsura, Nishikyo-ku, Kyoto 615-8540, Japan
[c] Department of Chemical Engineering, KU Leuven, Jan De Nayerlaan 5, 2860, Sint-Katelijne-Waver, Belgium
[d] CREST, Japan Science and Technology Agency, 4-1-8 Honcho, Kawaguchi, Saitama 332-0012, Japan
[e] Department of Chemical Engineering, Nagoya University, Chikusa, Nagoya 464-8603, Japan
[f] PRESTO, Japan Science and Technology Agency, 4-1-8 Honcho, Kawaguchi, Saitama 332-0012, Japan
[g] Multidisciplinary Science Cluster, Kochi University, 200, Monobe-otsu, Nankoku, Kochi 783-8502, Japan
[h] Natural Sciences Cluster, Agriculture Unit, Kochi University, 200, Monobe-otsu, Nankoku, Kochi 783-8502, Japan

HIGHLIGHTS

- Dewatering of cattle manure by liquefied dimethyl ether (DME) was investigated.
- Over 98% of water in manure was removed by DME after 70 min under optimum conditions.
- Crude fat in the manure was also removed by DME.
- An 18.1 times increase in the lower heating value of manure was achieved.
- DME dewatered manure had a lower self-ignition risk than thermally dried manure.

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ABSTRACT

Livestock manure is an animal waste that is generated worldwide, and is one of the most abundant waste materials generated in Japan. Its excess application as a fertilizer can cause negative environmental problems; i.e., groundwater pollution and greenhouse gas emissions. When livestock manure is used as a solid fuel, a significant amount of energy is required to remove the high water content by conventional heating, and the resulting dry material has a self-ignition risk that makes it difficult to treat and store. This study focused on an energy-saving dewatering technology using liquefied dimethyl ether (DME) at room temperature, and investigated the dewatering properties of DME and the resulting mass balance of water in cattle manure. The fuel characteristics and the self-ignition risk of the dewatered cattle manure were also investigated.

Under optimum conditions, over 98% of the water and some of the crude fat content in cattle manure could be removed after 70 min (seven batches) at a total DME/initial water ratio of 28.6. The manure was more efficiently dewatered than some other wet biomass such as sewage sludge and vegetable biomass. Moreover, a similarity in the kinetics between thermal drying and DME dewatering also emerged.

The lower heating value (LHV) of DME dewatered manure under these conditions increased to 13.8 MJ/kg, which was 18.1 times that of original cattle manure. The cattle manure dewatered by DME had a lower self-ignition risk than thermally dried cattle manure because of the extraction of crude fat by DME. Therefore, it could be more efficiently produced and safely used as a biomass fuel following DME dewatering.

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1. Introduction

Livestock manure is a worldwide animal waste, and is one of the most abundant waste materials generated in Japan. Because

* Corresponding author at: Cluster C, Kyoto daigaku-Katsura, Nishikyo-ku, Kyoto 615-8540, Japan. Tel.: +81 75 383 3336; fax: +81 75 383 3338.
E-mail address: oshita@epsehost.env.kyoto-u.ac.jp (K. Oshita).

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it contains not only organics but also large amounts of fertilizing components, such as nitrogen and phosphorus, it is mainly recycled by composting. However, in areas with a high livestock density, excess fertilizer application to agricultural land can cause negative environmental problems, including groundwater pollution by nitrate-nitrogen, pathogens, and the proliferation of bacteria resistant to antibiotics used in animals [1,2].

The global greenhouse gas (GHG) emissions from livestock manure that is stored, treated, used as organic fertilizer on cropland, or deposited on pasture are increasing annually [3]. Most of the emissions in each of these stages involve methane (CH_4) and nitrous oxide (N_2O), which have high global warming potential [4].

Because livestock manure is considered a biomass fuel, similar to sewage sludge, it is used to generate thermal and electrical energy in some countries. In the European Union, it is used to produce electricity because of the 'climate neutrality' of its lifecycle [5]. The methane fermentation of livestock manure can produce biogas [6]. However, this requires a long treatment period, and the digested residue, without much volume reduction, requires proper management. To enhance the heating value of the manure in order to produce a solid fuel, dewatering and drying are required. Dry livestock manure has a high heating value and can be totally combusted by incineration [7]. However, livestock manure has a high water content and required a significant energy for drying by conventional heating. The dry material produced has an odor and self-ignition risk that makes it difficult to treat and store [8].

DME has been used commercially as an aerosol propellant, as a sustainable replacement for chlorofluorohydrocarbons (CFHCs), and as a fuel in vehicle engines. China has established the industrial production of coal-based DME that is competitive in price with petroleum-based fuels [9–10]. In Europe, DME has been produced via black liquor gasification, and was successfully used as a fuel in different Volvo DME trucks in the European BioDME project [11]. New dewatering processes have been developed using liquefied dimethyl ether (DME) as a water extractant.

The advantages of DME dewatering processes are based on the following characteristics: (1) DME exists as a gas at room temperature and ambient pressure. Its standard boiling point is −25 °C, and it easily liquefies at 0.51–0.59 MPa at room temperature (20–25 °C). (2) DME has a partial miscibility with water and a high affinity to organic compounds. At room temperature, water is soluble in DME in the range of 7–8 wt.% [12]. After extraction, liquid DME is evaporated by depressurization, and the extracted water is separated. Because of its low boiling point, the recycling processes of DME, including its evaporation and liquefaction, permit the efficient use of unharnessed low-level heat sources. The dewatering energy is almost half of that required by existing thermal drying techniques [13].

This technology can operate at room temperature, and some of the applications [14–23] are presented in Table 1.

In previous studies, most of the contact methods used for extraction were of the fixed-bed extraction type. Regardless of the nature of the sample, the extraction efficiency of water is over 78% under optimized conditions. The extraction efficiency is influenced by extraction time, the DME/initial water ratio and the particle size of the samples. Although it is favorable in terms of energy and cost to extract a greater amount of water at a lower DME/initial water ratio (as close to the theoretical value (12.5–14.3) as possible) and a shorter dewatering time, the process is still influenced by the particle size of samples. The range of extraction times and DME/initial water ratios that have been used are widely distributed in the ranges of 7.3 min–2.0 h, and 14–89, respectively. Coal was considered to be dewatered more easily than a biomass sample; i.e., sewage sludge. This technology has not yet been applied to livestock manure. The livestock manure dewatering properties by DME and the characteristics of the dewatered manure as a fuel remain unknown.

This study investigated solid fuel production from livestock manure following dewatering using liquefied dimethyl ether. This study focused on manure produced by dairy cattle, one of the largest livestock herds in the world. The dewatering efficiency, the water and solid mass balances of dairy cattle manure treated with liquefied DME, the characteristics of the dewatered cattle manure as a fuel, and the self-ignition risk of the dewatered cattle manure were investigated.

2. Materials and methods

2.1. Cattle manure

Dairy cattle manure was collected as a mixture of dung, urine, and bedding straw from the Kyoto Prefectural Agriculture, Forestry and Fisheries Technology Centre in December 2012. The sample manure was a cake-like substance with high water content and containing bedding straw, and was preserved in polypropylene bottles and cooled at 4 °C. Before the DME dewatering experiment, sample manure was homogenized.

The characteristics of the cattle manure samples before DME dewatering are shown in Table 2. The details of the analytical method are shown in Section 2.3. The water and crude fat contents of this sample were 81.8% and 1.5% dry base (D.B.), respectively. The volatile total solid (VTS) and CHN contents and the HHV were 83.4%, 42.7%, 5.7%, and 2.3% D.B. and 16.7 MJ/kg-D.B., respectively. The HHV was approximately 87% that of wood [24]; however, the calculated lower heating value (LHV) was extremely low because of the high water content; therefore, it was not suitable for use as a fuel.

2.2. Experimental setup and conditions

Fig. 1 is a schematic diagram of the DME dewatering experimental setup. The experimental setup was based on a batch mixing type extraction, which differed from the fixed bed extraction systems used in earlier studies (Table 1). However, batch-mixing extraction is important and can easily determine the dewatering properties of samples and predict the dewatering kinetics in fixed bed extraction using a tank-in-series model during the next stage. This experimental setup consisted of four main parts: (1) a vessel for storing liquefied DME (Vessel 1, TVS-1-100, 500 cm^3, Taiatsu Techno Corp., Saitama, Japan); (2) a vessel for dewatering (Vessel 2, HPG-96-3, 26.5 mmφ × 238 mm, Taiatsu Techno Corp.) with an impeller (H:50 mm × L:15 mm × D:2.0 mm), a stirring motor (VP motor, Taiatsu Techno Corp.), and a stirring speed controller (Taiatsu Techno Corp.); (3) a vessel for storing the separated liquid (Vessel 3, HPG-96-3, 100 cm^3, Taiatsu Techno Corp.); and (4) a trap column (HPG-10-5, 11.6 mmφ × 190 mm, Taiatsu Techno Corp.).

Since it was necessary to bring the cattle manure into contact with liquefied DME under ideal conditions, a 10.0 g spherical sample (diameter approximately 26.5 mm) was packed into vessel 2. Liquefied DME was produced by cooling pure gaseous DME (Sumitomo Seika Chemicals Co., Ltd., Osaka, Japan) to −12 °C with ethanol and ice, and was then pressurized at 0.2 MPa and stored in vessel 1. Vessel 1, containing the liquefied DME, was then placed into a bucket of water and its temperature was maintained at 25 °C. Vessels 2 and 3 were preliminarily purged with 0.3 MPa DME gas. Under pressurization at 0.7 MPa using nitrogen gas, liquefied DME was transferred to vessel 2.

After the cattle manure sample was immersed in the liquefied DME in vessel 2, the dewatering time per batch, stirring speed, and the number of batch treatments (DME/initial water ratio was

Table 1
Summary of a literature review regarding the extraction of water (or other substances) using liquefied dimethyl ether.

Samples				Optimized conditions and results						Refs.
Target	Water content (%)	Particle size (mmφ)	Amount (g)	Scale	Contacting method	DME flow rate (L h^{-1})	DME/initial water ratio[b] (g-DME g $water^{-1}$)	Extraction time [b]	Extraction efficiency (%)	
Sub-bituminous coal (Warra coal)	40.6	0.85–2.80	6.11	Lab scale	Fixed bed	0.6	20.6	7.3 min	78.2	[14]
Sub-bituminous coal (Warra coal)	40.6	0.85–2.80	5019	Bench scale	Fixed bed	100	34.3	1.0 h	98.3	
Sewage sludge (Six types)	77.0–82.2	4.5	1.0	Lab scale	Fixed bed	0.04	65.0–70.0	2.0 h	93.5–98.1	[15]
Sewage sludge	78.9	Rod shape: 4 mm × 20–50 mm	3200	Bench scale	Fixed bed	105.2	14.0	30 min	97.7	[16]
Superabsorbent polymer (SAP)	75.0	1.0	1.0	Lab scale	Fixed bed	0.04	71.0	2.0 h	93.3	[17]
Wet woodchip	56.0	1.0–5.0[a]	7.0	Lab scale	Fixed bed	N.D.	20.4	N.D.	87.0	[18]
Vegetal biomasses (4 kinds)	42.0–79.0	i.e. Coffee grounds: 2.5	4.84–6.85	Lab scale	Fixed bed	0.6	60.0–80.0	25–48 min	81.3–88.7	[19]
Sediment contaminated by PCBs	Water: 60.0 PCBs: 8.7 mg/kg-dry	4.0	1.0	Lab scale	Fixed bed	0.05	67.0	1.2 h	Water: 96.3 PCBs: 99.1	[20]
Wet soil with heavy oil	Water: 15.7 Oil: 24.0	N.D.	4780	Bench scale	Fixed bed	100	89.0	1.0 h	Water: >99 Oil: >99	[21]
Pure water dissolved phenol	Phenol: 5.5	N.D.	4.00	Lab scale	Batch extraction	–	1.07	1.0 min	Phenol: 79.0	[22]
Microalgae (7 kinds)	Water: 78–93 Crude 9.9–40.1 (dry base)	N.D.	N.D.	Lab scale	Fixed bed	0.6	70.0	–	Water: 80–90 Lipid: >97.5	[23]

N.D.: Not described.
[a] Estimated value from the figure in the reference [18].
[b] A part of the DME/initial water ratio and extraction time were calculated from the data in each reference.

Table 2
Characteristics of cattle manure samples.

Item	Unit	Mean	S.D.
Water content	%	81.8	1.4
VTS	%-D.B.	83.4	1.7
C	%-D.B.	42.7	0.2
H	%-D.B.	5.7	0.3
N	%-D.B.	2.3	0.2
Crude fat	%-D.B.	1.5	–
HHV	MJ kg-$D.B.^{-1}$	16.7	0.4
LHV	MJ kg^{-1}	0.76	–

VTS: Volatile total solid, HHV: Higher heating value,
LHV: Lower heating value (Calculated).
D.B.: Dry base, S.D.: Standard deviation.

constant at 4.1 per batch) were controlled at 1–60 min, 0–600 rpm, and 1–8 times, respectively.

The separated liquid, which contained mainly DME and water, was transferred to vessel 3 by pressurization at 0.7 MPa using nitrogen gas from the upper part of vessel 2. To separate DME from water, it was gasified by reducing the pressure to the ambient level in vessel 3. Gaseous DME was passed through the trap column containing 7.5 g of $CaCl_2$ (EP, U-tube No.1, 1.5–2.5 mmφ; Nakalai Tesque Inc., Kyoto, Japan) for 1 h to trap trace levels of gaseous moisture. All dewatering experiments were conducted in duplicates and the results were reported as mean values. The mass balance for DME dewatering was determined by measuring the weight variations of vessel 1 (liquefied DME), vessel 2 (cattle manure), vessel 3, and the trap column before and after the dewatering experiments using electronic balances.

2.3. Characterization of the cattle manure and its dewatered products

The cattle manure characteristics before and after dewatering were evaluated in terms of water, organic, CHN, crude fat contents, and the heating value. The water and organic contents were analyzed in triplicates using standard methods [25]. The CHN content and the higher heating value (HHV) were analyzed in triplicates using a CHN monitor (MT-6; Yanako Technical Science Co. Ltd., Tokyo, Japan) and a bomb calorimeter (CA-4AJ: Shimadzu Corp. Kyoto, Japan) according to the respective Japanese Industrial Standards [26,27]. The crude fat content of the original cattle manure sample was determined in duplicates using by a simple shake extraction method for 1 h using diethyl ether [28]. To determine the amount of crude fat extracted with water by DME, the water sample after the separation of DME were first decanted from vessel 3 to another glass bottle, and the adhered crude fat in vessel 3 was then dissolved in ethanol and decanted into the same bottle. This mixed liquid was dried in an oven at 105 °C for 24 h, and the weight of the remaining crude fat was measured.

2.4. Self-ignition risk of DME dewatered manure

It is important to understand the self-ignition and explosive properties of coals and biomass fuels for the safe operation of plants that handle, store, or process these materials [8]. This study also focused on the exothermic oxidation reaction that occurs during the storage of dewatered cattle manure, and the influence that DME dewatering has on the relationship between the critical self-ignition temperature T_f (K) and the dewatered sample volume obtained from r (m) (the characteristic linear dimension of the sample or the shortest distance from the center of the sample to its surface). It was determined using the Frank-Kamenetskii (FK) Eq. (1) [29]:

$$\frac{Q}{\lambda}\frac{E}{RT_f^2}r^2\rho z e^{\left(-\frac{E}{RT_f}\right)} = \delta \quad (1)$$

where δ is FK parameter (−), Q is the heat of reaction (J g^{-1}), λ is the thermal conductivity (J s^{-1} m^{-1} K^{-1}), E is the apparent activation

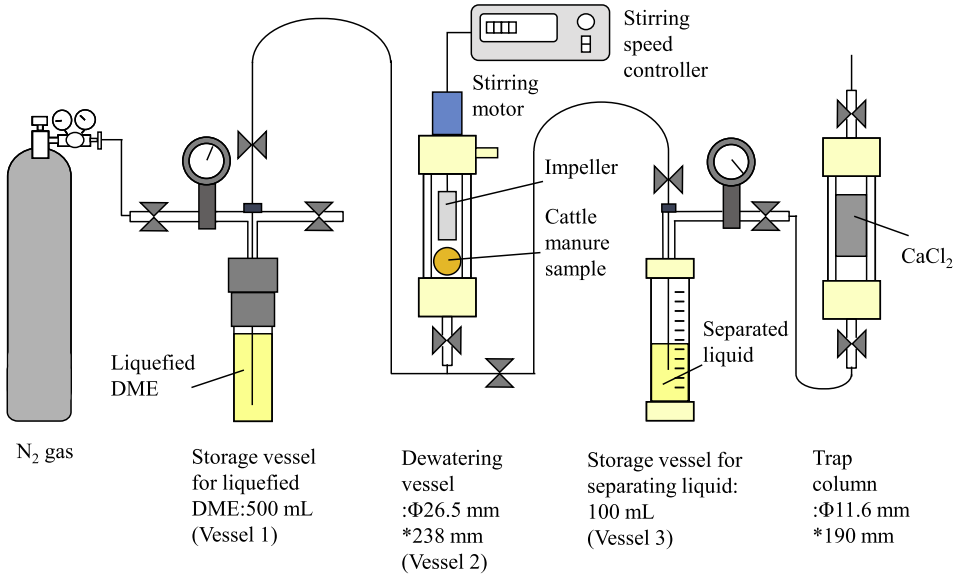


Fig. 1. Schematic diagram of the DME dewatering experimental setup.

energy (J mol^{-1}), R is the universal gas constant (8.314 J K^{-1} mol^{-1}), z is the frequency factor (s^{-1}), and ρ is the bulk density (g m^{-3}).

The DME dewatered cattle manure was prepared under the optimized conditions described in the Results and Discussion. As a reference sample, thermally dried cattle manure was prepared by heating at 383 K for 24 h in a temperature-controlled chamber. The Q, E, and z of each sample were estimated by thermogravimetric (TG) and differential thermal analysis (DTA), as well as the Coats–Redfern (CR) equation [30]. The ρ of each sample was directly analyzed using a Vernier micrometer and an electronic balance, with measurements performed in triplicates. The details of these analyses are given in the Supporting Information.

3. Results and discussion

3.1. Mass balances of cattle manure in DME dewatering

Fig. 2 shows the mass balance before and after the DME dewatering of cattle manure under the conditions of 600 rpm and 10 min per batch (first, second, fourth, and seventh batch treatments). As the number of batch treatments increased, the mass of dewatered water increased. The amounts of extracted crude fat were small (maximum of 0.85%). The amount of solid material in the manure samples was almost unchanged following the DME treatment. In each batch treatment, the mass balances were consistent.

3.2. Dewatering properties

The dewatering properties of DME for cattle manure were evaluated using the dewatering ratio and DME saturation ratio. The dewatering ratio Ew (%) and DME saturation ratio DSw (%) were defined by Eqs. (2) and (3), respectively:

$$Ew = \frac{w_t}{w_0} \cdot 100 \quad (2)$$

$$DSw = \frac{w_{n,t}}{w_D} \cdot 100 \quad (3)$$

where w_t is water mass dewatered by DME (g) at t of dewatering time and w_0 is the initial water mass in the cattle manure (g). $w_{n,t}$ is water mass dewatered by DME per batch and w_D is maximum

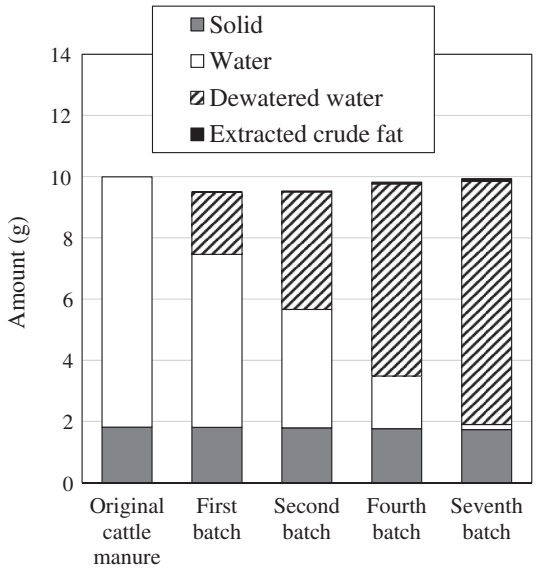


Fig. 2. The mass balance before and after the DME dewatering of cattle manure at 600 rpm and 10 min per batch (first, second, fourth, and seventh batch treatments).

extractable amount of water based on the amount of DME per batch treatment, with a water solubility in DME of 7.2 wt%.

Fig. 3(a) shows the relationship between dewatering time and dewatering ratio in the first batch treatment (DME/initial water ratio 4.1). Although there was little difference in the final dewatering ratios according to stirring speed, the dewatering ratio was higher at greater stirring speeds after a dewatering time of 5–10 min. This suggests that the transfer of water from manure to DME is more effective with stirring than by convection over short dewatering periods. After 20 min, the dewatering ratios were saturated at 25–30% and the DME saturation ratios were 90–100%, which indicates that the water solubility of the DME was most effective over short dewatering periods.

Fig. 3(b) shows the relationship between dewatering time and dewatering ratio for the multi-batch treatment. Multi-batch treatment indicates that the same manure sample is repeatedly dewatered by fresh-DME. The dewatering time of each batch treatment

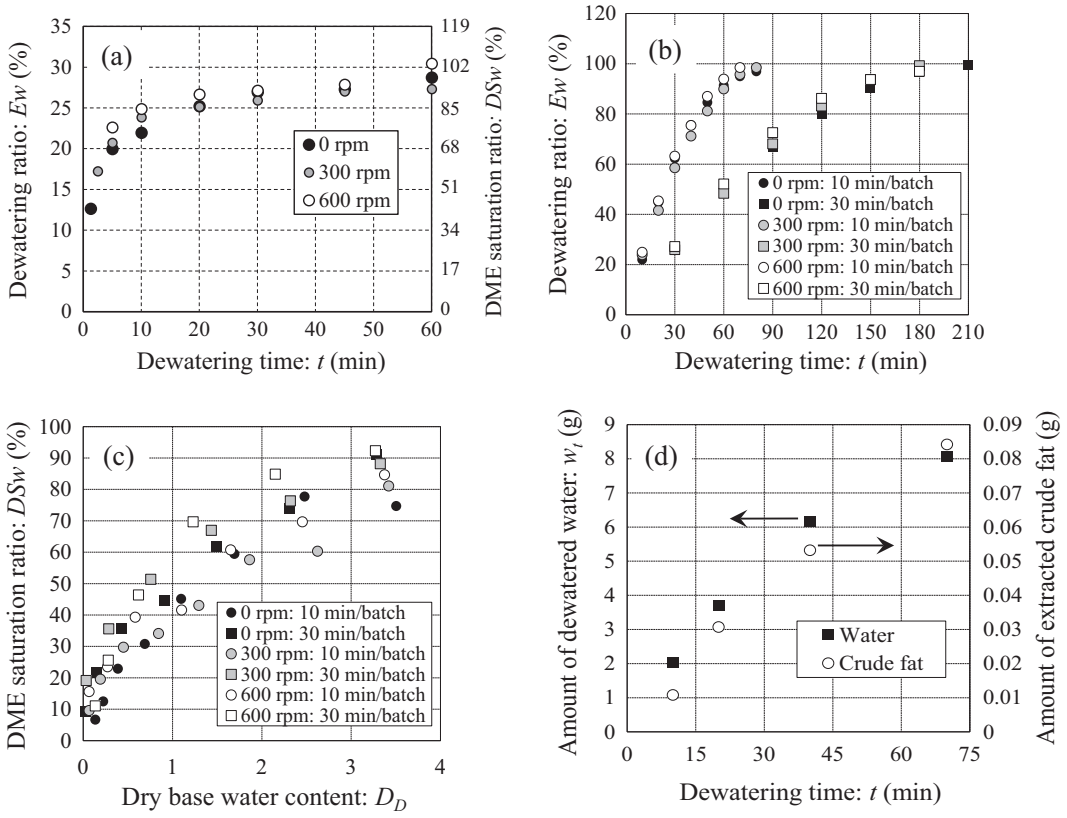


Fig. 3. The cattle manure dewatering properties of DME. (a) Relationship between the dewatering time and dewatering ratio in the first batch treatment (DME/initial water ratio 4.1). (b) Relationship between dewatering time and dewatering ratio for multi-batch treatment, (c) Relationship between dry base water content and DME saturation ratio. (d) Temporal trends in the amount of water and crude fat extracted.

was set to 10 or 30 min. Under all conditions, the dewatering ratio increased as the dewatering time increased. However, when the dewatering time per batch was 10 min, the total dewatering time was one third to one half of that when the dewatering time per batch was 30 min, because the amount of extracted water did not differ markedly between the 10 and 30 min batch treatments for the same number of batch treatment. Although the influence of stirring speed on the dewatering ratio was not large, the most effective dewatering ratio was achieved at 600 rpm and a dewatering time of 10 min per batch. Under these conditions, over 98% of the water content in cattle manure could be removed after 70 min (seven batches) at a total DME/initial water ratio of 28.6. When these optimized conditions were compared with literature values for laboratory-scale experiments (Table 1), it was clear that higher dewatering ratios could be achieved for the DME dewatering of cattle manure with shorter extraction times or lower DME/initial water ratios than for sewage sludge, superabsorbent polymers, vegetable biomass, and contaminated sediments, despite the use of different contact methods and sample diameters. The cattle manure used in this study could have been easily dewatered by DME because it contained bedding straw, which maintained a contact area between the sample and DME even during the dewatering process.

Fig. 3(c) shows the relationship between the dry base water content D_D (–) and the DME saturation ratio. The dry base water content of a sample was defined by Eq. (4):

$$D_D = \frac{w_t}{S_t} \tag{4}$$

where S_t (g) is the mass of solid content in the sample at dewatering time t.

From this figure, it can be seen that the DME saturation ratio decreased as the dry base water content decreased. Moreover, the DME saturation ratio was higher under conditions with a longer dewatering time per batch and higher stirring speed. The dry base water content is sometimes used in relation to the drying rate in the heat drying characteristic curve, which generally has a pre-heating, constant and falling rate period [31]. The DME saturation ratio indicates the degree of water saturation of liquefied DME in each batch treatment, and can be considered the dewatering rate in this experimental system. Although heat drying and DME dewatering are two different processes, they have similarities since dewatering rates strongly depend on the difference in water concentration between air or DME and sample manure. The curves in Fig. 3(c) are similar to drying characteristic curves, and almost always consist of a decreasing dewatering rate period. The phenomenon indicated in Fig. 3(c) is likely to have been caused by the decreasing amount of water on the surface on the cattle manure sample and the limitation of internal water transfer to the DME phase. When the dry base water content was below 1.0, the DME saturation ratios were no more than 50%. Because the water extractability of DME could not be fully utilized within this range, the introduction of a counter current flow contact extraction between cattle manure and DME would result in more effective dewatering.

Fig. 3(d) shows the time trend of the extracted water and crude fat. These results were obtained under the conditions of 600 rpm and 10 min per batch (first, second, fourth, and seventh batch treatments). Because the extraction trends of crude fat were similar to the dewatering trends and the ratio of the extracted crude fat to the extracted water was almost constantly 1.2%, it was concluded that crude fat and water were simultaneously removed

Table 3
Characteristics of the cattle manure and the extracted crude fat after the DME treatment of cattle manure at 600 rpm and 10 min per batch (first, second, fourth, and seventh batch treatments).

Item	Unit	First batch		Second batch		Fourth batch		Seventh batch		Crude fat[a]	
		Mean	S.D.	Mean	S.D.	Mean	S.D.	Mean	S.D.	Mean	S.D.
Water content	%	75.8	1.7	68.4	0.9	49.3	0.61	8.74	0.78	–	–
VTS	%-D.B.	85.5	0.06	86.7	0.29	87.4	1.48	86.0	0.63	>99	–
C	%-D.B.	41.1	0.77	41.0	0.37	39.7	1.11	40.5	0.48	75.40	0.45
H	%-D.B.	5.9	0.05	5.7	0.09	5.6	0.12	5.6	0.08	11.81	0.24
N	%-D.B.	2.6	0.09	2.5	0.22	2.6	0.06	2.6	0.11	0.87	0.09
HHV	MJ kg-D.B.$^{-1}$	17.0	0.004	16.9	0.09	16.7	0.28	16.6	0.08	40.1[b]	–
LHV	MJ kg^{-1}	1.90	–	3.22	–	6.58	–	13.81	–	37.1–37.5	–

VTS: Volatile total solid, HHV: Higher heating value, LHV: Lower heating value (Calculated).
D.B.: Dry base, S.D.: Standard deviation, N.A.: Not analyzed.
[a] Crude fat is after the seventh batch treatment.
[b] Calculated from the elemental composition using the prediction formula [32].

from the cattle manure using DME. While the crude fat content was 1.5% D.B. in the original cattle manure, approximately 4.0% D.B. crude fat was extracted using DME. This extracted crude fat could contain not only crude fat but also some organic materials; i.e., odorous compounds [16].

3.3. Characteristics of cattle manure dewatered by DME

Table 3 shows the characteristics of the cattle manure and the extracted crude fat after the DME treatment of cattle manure at 600 rpm and 10 min per batch (first, second, fourth, and seventh batch treatments). The extracted crude fat was characterized by a low N and high C and H organic content, with a HHV of 40.1 MJ/kg-D.B. (calculated from the elemental composition using the prediction formula [32]). DME can also extract the crude oil accumulated in microalgae [23], with literature values for the CHN composition and HHV of extracted crude oil being similar to the results of this study. The results shown in Tables 2 and 3 indicate that the VTS and N contents in dewatered cattle manure were unchanged from the original manure samples following DME dewatering, but the C and H contents and the HHV decreased slightly. The reason that the C and H content, and the HHV in cattle manure decreased following DME dewatering was due to the extracted crude fat, which was composed mainly of C and H, and

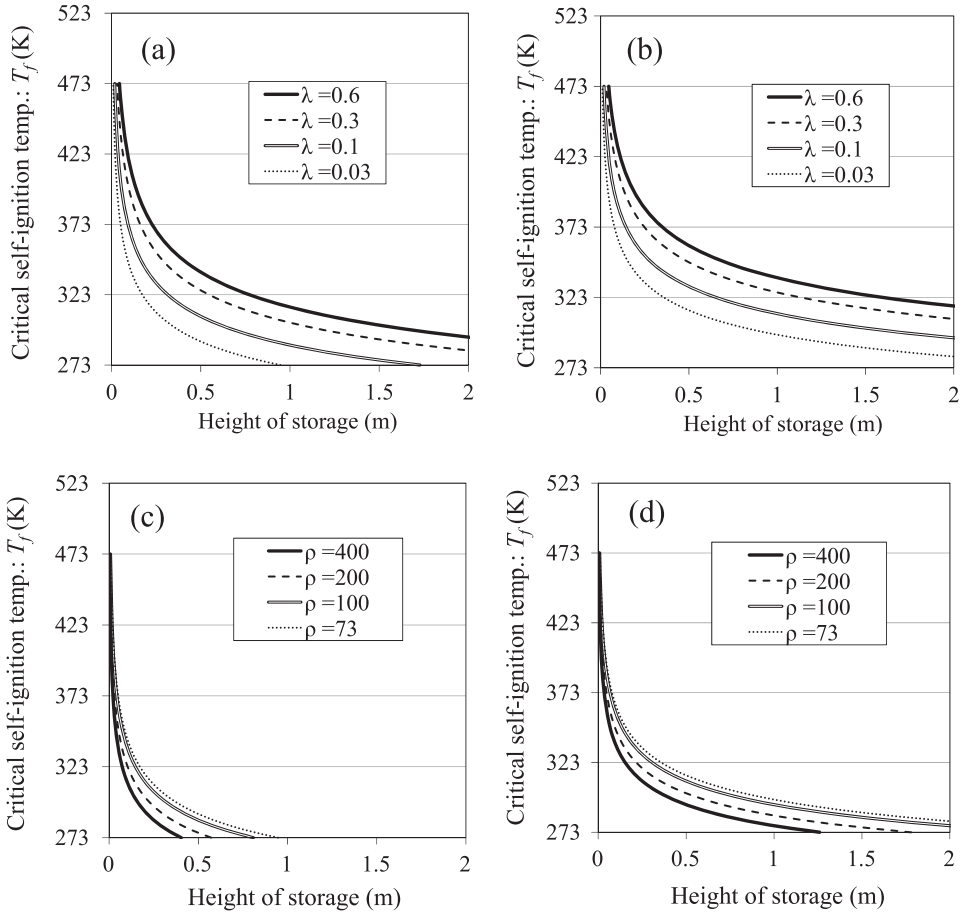


Fig. 4. The FK simulation results of (a) thermal dried manure and (b) DME dewatered manure with fixed ρ (73 kg m^{-3}) and (c) thermally dried manure and (d) DME dewatered manure with fixed λ (0.03 J s^{-1} m^{-1} K^{-1}).

Table 4
Characteristics of wood, coal, lignite, refuse derived fuel (RDF), and biomass [33].

Item	Unit	Untreated wood		Treated wood		Bituminous coal		Lignite		RDF		Sewage sludge [a]	
		Mean	S.D.	Mean	S.D.	Mean	S.D.	Mean	S.D.	Mean	S.D.	Mean	S.D.
Water content	%	17.3	16.7	15.2	10.2	3.69	0.45	13.4	0	10.1	9.70	6.53	3.92
VTS	%-D.B.	80.2	4.75	76.0	5.91	29.9	3.18	45.7	2.12	73.4	4.31	50.4	3.44
C	%-D.B.	49.6	2.06	48.4	2.57	74.5	2.45	58.8	3.08	45.5	5.34	33.2	6.56
H	%-D.B.	5.94	0.38	5.76	0.44	4.65	0.14	4.09	0.37	6.93	1.95	4.55	0.53
N	%-D.B.	0.37	0.49	1.00	1.11	1.32	0.01	0.81	0.26	0.80	0.46	4.05	1.13
HHV	MJ kg-D.B.$^{-1}$	19.6	1.32	19.0	0.90	30.2	0.51	23.5	0.15	20.2	2.83	14.5	2.49
LHV	MJ kg^{-1}	14.6	–	14.6	–	27.9	–	19.1	–	16.2	–	11.8	–

VTS: Volatile total solid, HHV: Higher heating value, LHV: Lower heating value (Calculated).
D.B.: Dry base, S.D.: Standard deviation.
[a] Thermally dried sample.

Table 5
Parameters of the FK simulation of thermally dried and DME dewatered cattle manure.

Parameter	Symbol	Unit	Thermal drying	DME dewatering
FK parameter	δ	–	2.52	
Universal gas constant	R	J K^{-1} mol^{-1}	8.314	
Apparent activation energy	E	J mol^{-1}	54,840	66,760
Frequency factor	z	s^{-1}	193.6	3054
Heat of reaction	Q	J g^{-1}	8390	8601
Thermal conductivity	λ	J s^{-1} m^{-1} K^{-1}	0.03–0.6	
Bulk density	ρ	kg m^{-3}	73–400	
Critical self-ignition temperature	T_f	K	273–473	

had a large HHV. The LHV of dewatered manure increased to 13.8 MJ/kg following DME dewatering, which was 18.1 times that of original cattle manure. Table 4 shows the characteristics of wood, coal, lignite, refuse derived fuel (RDF), and thermally dried biomass [33]compared dewatered manure after the seventh DME treatment (Table 3). Water contents of all samples were sufficiently low. Although the value as a fuel of DME-dewatered manure was lower than that of bituminous coal and lignite, the C and H contents and HHV of dewatered manure were between those of RDF and sewage sludge. LHV of dewatered manure was lower than that of RDF, but slightly lower than that of wood. DME-dewatered manure can be used as a fuel to generate electric power and heat using a boiler, such as wood [34].

Kanda et al. (2010) estimated that the primary energy required to remove 1 kg water using DME was 1109 kJ/kg H_2O, which is less than half of the latent heat of water vaporization [14]. Therefore, cattle manure dewatering by DME could be more energy efficient than the thermal drying process.

3.4. Estimation of the self-ignition risk

Table 5 shows the parameters of this simulation for both thermal drying and DME dewatering. δ was set to 2.52, as the cube shape of a cattle manure storage facility [35]. Q, E, and z of each sample were calculated from the result of TG–DTA and the CR equation. These results are shown in Figs. S-1 and S-2 in the Supplementary Information. λ of each sample was within the range of 0.03–0.6 J s^{-1} m^{-1} K^{-1}, as reported by Iwabuchi et al. (1993 and 1999) and Ahn et al. (2009) [36–38]. Because the ρ of each sample could vary according to the storage conditions, it was set to be within the range 73–400 kg m^{-3}, which reflected the values directly analyzed (Table S-1) and reported by Ahn et al. (2009) [38]. These parameters were applied to the FK Eq. (1) and the relationship between T_f and r of both cases was calculated with varying λ and ρ.

First, the relationship of the storage height and T_f with a fixed ρ (73 kg m^{-3}) and a varied λ for both thermal drying and DME dewatering are shown in Fig. 4(a) and (b), respectively. When the storage height increased or λ decreased, T_f decreased and the self-ignition risk was higher in both figures. The reason for this could be the difficulty in heat radiation from the treated cattle manure storage. The T_f of DME dewatering was higher than the T_f of thermal drying under identical conditions. For example, the former was 335 K and the latter was 313 K under conditions of λ = 0.6 J s^{-1} m^{-1} K^{-1} and storage height = 1.0 m. Next, the relationships of the storage height and T_f with a fixed λ (0.03 J s^{-1} m^{-1} K^{-1}) and varied ρ were considered in the case of thermal drying and DME dewatering, and the results are shown in Fig. 4(c) and (d), respectively. When the ρ increased, T_f decreased, as can be seen in both figures. The T_f of DME dewatering was also higher than the T_f of thermal drying under identical conditions. Therefore, the manure dewatered by DME would have a lower self-ignition risk. This tendency has also been reported in the oxygen reactivity of DME dewatered sub-bituminous coal following spontaneous ignition tests [14]. The main reason for this tendency was the increasing E of the DME dewatered manure following the extraction and removal of crude fat with a large HHV and low boiling point.

4. Conclusions

This study investigated the dairy cattle manure dewatering properties of DME, and the characteristics and self-ignition risk of the dewatered cattle manure when used as a fuel.

Under optimum conditions, over 98% of the water and some of the crude fat content in cattle manure could be removed after 70 min (seven batches). At a total DME/initial water ratio of 28.6, the manure was dewatered more effectively than some other wet biomass such as sewage sludge and vegetable biomass. Moreover, a similarity in the kinetics between thermal drying and DME dewatering was also observed.

The LHV of DME dewatered manure under these conditions increased to 13.8 MJ/kg, which was 18.1 times that of the original cattle manure. The cattle manure dewatered by DME had a lower self-ignition risk than thermally dried cattle manure because of the extraction of crude fat by DME. Therefore, it could be produced more efficiently and used safely as a biomass fuel using DME dewatering.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.fuel.2015.06.063.

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