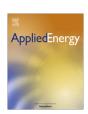


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# Compositional characteristics and energy potential of Chinese animal manure by type and as a whole



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#### HIGHLIGHTS

- Different types of animal manure presented a wide variation in their composition.
- Pig and beef manure had higher heating value than the other types of animal manure.
- Dairy and beef manure had the most similar energy properties.
- Several significant correlations between 18 parameters were identified.
- The thermal energy, syngas and methane of animal manure in China were calculated.

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#### ABSTRACT

In this study, 838 representative animal manure samples were collected from 552 sites across China. Chemical analyses of 19 parameters, including the proximate analysis, ultimate analysis, heating values and some essential mineral elements, were conducted on the samples. The energy potential of animal manure in China was quantified based on the chemical analysis. The results showed that the chemical characteristics of the different types of animal manure were highly variable. Principal component analysis results demonstrated that the closest compositional characteristics were between dairy manure and beef manure. Several strong and important associations, namely phosphorus–magnesium, phosphorus–copper, phosphorus–zinc, copper–zinc, calcium–potassium, fixed carbon–calcium, volatile matter–ron and ash–volatile matter–fixed carbon–carbon–hydrogen–higher heating value–lower heating value, were identified. The calculated outputs of total potential annual thermal energy, syngas and methane yields from the five types of animal manure in China were 4400.63 TJ, 983.40 × 10<sup>9</sup> m³ and 188.89 × 10<sup>9</sup> m³, respectively. The air gasifier energy conversion efficiency (*t* = 850 °C, equivalence ratio (ER) = 0.3) for different animal manures was in the range of 66.80–83.22%.

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#### 1. Introduction

China has been the largest producer of animal manure in the world as its intensive farming produces approximately 4 billion tons of animal manure annually [1]. The considerable amount of animal manure has presented an increasing number of environmental challenges [2]. As it is well known that animal manure is an important source of bioenergy; the effective utilization of animal manure as bioenergy feedstock for waste-to-bioenergy conversion processes has attracted much attention at the global and national scales, as it could not only reduce the waste disposal costs,

but also alleviate pressures on the environment and provide clean energy [3–6].

The main methods available for renewable energy extraction from animal manure include thermochemical and biochemical conversion processes [7–11]. The conversion process, conversion efficiency and the bio-fuel and chemical production of the two conversion processes are related to the animal manure properties, including proximate analysis, ultimate analysis, mineral elements and heating values [12–15]. Some studies have shown that the composition of animal manure may vary considerably depending on the type, growth stage, animal diet and housing system [16–19]. In addition, animal manure generally consists of bedding material, excreta, waste feed, feathers and minerals of different origins, which increase the variability of the animal manure composition [20,21]. As a major country for animal husbandry, the breeding scale, animal diet and management systems in China

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are different than other countries. Therefore, the goals of this study were to characterize the basic composition of Chinese animal manure and evaluate its energy potential based on the chemical characterization. The results of this study will provide a basis for the alternative use and suitability of animal manure for thermochemical and biochemical conversion.

#### 2. Materials and methods

#### 2.1. Sample collection

A total of 838 representative animal manure samples, including 209 pig manure samples, 217 dairy manure samples, 139 beef manure samples, 162 layer manure samples and 111 broiler manure samples, were collected from 552 sites across China from 2011 to 2013. The distribution of the different animal manure samples collected in China is shown in Fig. 1. All of the samples studied were obtained from a variety of sources: large-scale farms, rising areas and households specializing in animal breeding. The number of samples selected from each province was proportional to the local livestock production. To obtain representative samples, we collected the animal manure samples from different locations, under different weather conditions, from different breeding systems, at different growth stages, and at different elimination times and subjected them to different storage methods and durations.

Each sample was collected from different positions on the unit floor in each barn and thoroughly mixed to obtain a representative batch of approximately 2 kg. All of the collected samples were placed into a  $70\pm5$  °C forced-air drying oven and were dried for 18–24 h until there was no significant loss of moisture according to TMECC 03.09-A [22]. After cooling, the samples were ground and passed through a 0.5 mm sieve (Retsch Gmbh, Haan, Germany). The samples were stored in plastic containers before analysis.

#### 2.2. Chemical analysis

All of the chemical analyses were performed in duplicate, and the results, except for the moisture (MC), were expressed on dry basis.

#### 2.2.1. Proximate analysis

MC was determined according to TMECC 03.09-A [22]. The ash content was determined according to TMECC 05.07-A [23]. The volatile matter (VM) in the animal manure was determined

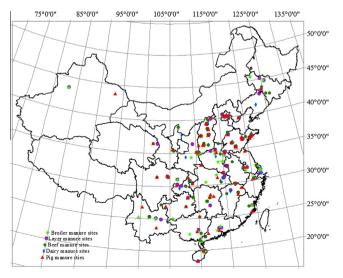


Fig. 1. Distribution of the different animal manure samples in this study.

according to ASTM E872-82 [24]. The fixed carbon (FC) content was obtained by Eq. (1) [25]:

$$FC (\%) = 100 - VM (\%) - Ash (\%)$$
 (1)

A van Krevelen diagram is a useful mean of comparing biomasses and fossil fuels in terms of their O/C and H/C ratios. It can illustrate the energy contents of the biomass based on the oxygen–carbon and hydrogen–carbon bonds contained in the materials and summarize the specific groups for selection in a thermal conversion system [26–31].

#### 2.2.2. Ultimate analysis

This analysis was performed to determine the carbon (*C*), hydrogen (H), nitrogen (N), and sulfur (*S*) contents of the animal manure samples using a CHNS elemental analyzer (Vario EL II, Hanau, Germany). The O content was obtained by Eq. (2) [32]:

$$O~(\%) = 100 - (C~(\%) + N~(\%) + H~(\%) + S~(\%) + Ash~(\%)) \eqno(2)$$

#### 2.2.3. Mineral elemental analysis

The mineral elements in biomass are a particularly important consideration for the selection of thermochemical conversion process. Alkali metals are generally the main cause of slagging, fouling and sintering [12–15]. Phosphorus can increase the slagging potential of deposits [33]. Copper and zinc can also cause corrosion by sulfate reaction and are related to particulate emissions and subsequent utilization of ashes [16,34]. Therefore, the concentrations of phosphorus (P), potassium (K), sodium (Na), calcium (Ca), magnesium (Mg), iron (Fe), copper (Cu) and zinc (Zn) were carried out according to the Test Methods for the Examination of Composting and Compost (TMECC, 2002) [35]. As alkali metals are very sensitive, the determination of these metals would be repeated by adding the parallel samples if the coefficient of variation of their concentration is higher than 10%.

#### 2.3. Energy potential estimation

#### 2.3.1. Thermal energy potential by combustion

Calorimetry is an experimental procedure that is used to determine the heating value. In this study, the gross caloric value (GCV) of animal manure was determined by bomb calorimetry according to ASTM E711 [36]. The higher heating value (HHV) and lower heating value (LHV) were calculated using Eqs. (3) and (4) as follows:

$$HHV = GCV - 0.094283 \times S \tag{3}$$

$$LHV = HHV - 0.21564 \times H \tag{4}$$

where HHV (MJ/kg) is the high heating value of animal manure per kg, GCV (MJ/kg) is the gross caloric value of animal manure per kg, S(%) is the total sulfur content of animal manure per kg. LHV (MJ/kg) is the lower heating value of animal manure per kg, and H(%) is the total hydrogen content of animal manure per kg.

The theoretical thermal energy potential of animal manure by combustion can be calculated based on the amount of animal manure referenced from the China Animal Husbandry Yearbook [37]. Eq. (5), modified from the equation used by Singh et al. [38], was used to calculate the energy potential of animal manure. The LHV in the equation used by Singh et al. was replaced by the HHV analyzed in this study.

$$Y = \sum_{i}^{n} M_{i} RF_{i} D_{i} HHV_{i}$$
 (5)

where Y (TJ/year) is the energy potential of animal manure excreted by livestock in tons per year,  $M_i$  (tons/year) is the mount of animal

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