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# Effects of organic waste co-digestion on CH<sub>4</sub> generation rate and total CH<sub>4</sub> yield.

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#### ABSTRACT

 $CH_4$  yield during separate anaerobic digestion of pig manure, cow manure, food waste, and during codigestion of 13 mixtures with different relative proportions of these three biomass materials under mesophilic conditions over a 36 day period was measured. Biomass materials were collected from local farms and households near Aalborg, Denmark (an area with dense animal production), and measurements were conducted via batch experiments under bench-scale conditions.

The results showed that co-digestion can significantly increase ultimate  $CH_4$  yield compared to separate digestion. For the biomass materials considered here 12 out of the 13 co-digested mixtures yielded increased  $CH_4$  production compared to separate digestion. Results further indicated that  $CH_4$  production is initiated faster during co-digestion compared to separate digestion. For the materials investigated here relative cumulative  $CH_4$  production (cumulative  $CH_4$  yield at any given time divided by ultimate  $CH_4$  yield) was significantly higher during co-digestion compared to separate digestion during the first 10 days of the digestion process.

Keywords: Anaerobic digestion, cumulative CH4 yield, animal manure, food waste, batch experiments .

#### **1. INTRODUCTION**

The realization that human-made emissions of greenhouse gases (primarily from fuel combustion) is a significant threat to our future environment has resulted in a growing interest in carbon neutral fuels such biomass.

At present biomass (both from energy crops and from biomass wastes) constitutes about 13% of the global energy consumption [1]. Despite this, the energy in biomass wastes, especially in animal manure is currently under-utilized. Energy contained in animal manure (mainly from agricultural meat and dairy production) corresponds to about 14% of the current global energy consumption but less than 1% of this energy is currently being utilized. Animal manure therefore, represents a large, currently unused energy source. Anaerobic digestion has been widely used to treat wet wastes such as animal manure and food waste etc. with the aim of energy extraction. After digestion such wastes are also more suitable for soil application as nutrients are more readily available [2] and odor emissions are reduced compared to undigested materials..

Several physical, chemical and thermal methods have been applied prior to digestion to improve biomass  $CH_4$  yield [3 - 7]. Examples of pre-treatment methods are crushing, addition of strong acids or bases, exposure to elevated temperature and pressure or combinations thereof. Such methods are especially effective with respect to materials such as straw which are difficult to degrade under anaerobic conditions.

An alternative approach is to co-digest different biomasses in appropriate proportions. Co-digestion has been shown to increase  $CH_4$  potential over that of separate digestion [8 - 20].

Although co-digestion has been shown to improve biomass  $CH_4$  yield compared to separate digestion, knowledge about how improvement in  $CH_4$  yield depends on biomass material composition (the types of biomass that are co-digested) is very limited. Such knowledge, however, is valuable as it allows for optimization of biomass mixture composition for a given co-digestion plant based on the types of biomass available in the region. Whether effects of co-digestion on  $CH_4$  yield depend on digestion process time is also not known. The objective of this study was therefore to assess the impact of co-digestion on  $CH_4$  yield across a set of biomass mixtures with different compositions based on the same three raw biomass materials (cow manure, pig manure and food waste) and to evaluate the dependency of  $CH_4$  yield improvement on digestion time under mesophilic conditions.

#### 2. MATERIALS AND MATHODS

Evaluation of co-digestion impact on CH<sub>4</sub> vield in response to variations in biomass composition and as a function of digestion time was carried out based on cow manure, pig manure, and food Animal waste. manures were collected at local farms in the vicinity of Aalborg city, Denmark, while food waste (about 30% bread, 30 % vegetables, 30% rice/pasta, and 10% meat/fish, wet weight) was collected from selected residential homes in Aalborg. The three biomasses were stored at 4°C until needed. Inoculum (digested sewage sludge from a wastewater treatment plant in Aalborg) was collected a few days before use and starved until use, to reduce its gas production.

Food waste and cow manure (which contained dry clumps) were initially homogenized (blended) to < 2mm particle size. Dry matter (DM) and volatile solids (VS) contents of the three biomass materials and the inoculum were measured in duplicate on 10 g samples, by weighing, drying at 105°C for 24 hours, weighing, and ignition for two hours at 550 °C, followed by

Table 1. Properties of the three biomass materials (cow manure, pig manure, food waste), inoculum and 13 biomass mixtures used. DM, VS,  $B_{CH4,ult}$  are dry matter, volatile solids contents and, cumulative (ultimate) CH<sub>4</sub> yield after 36 days of digestion, respectively.

			VO	
Material	DM		VS	$\mathbf{B}_{\mathrm{CH4,36}}$
	%		% of DM	L kg VS <sup>-1</sup>
Pig manure	0.9		57.1	594
Cow manure	25.4		60.3	240
Food waste	34.7		91.6	344
Inoculum	4.6		50.1	40
	Cow manure	Pig manure	Food waste	_
Percentage of wet mass				
Mixture 1	70	28	2	261
Mixture 2	70	24	6	260
Mixture 3	70	20	10	264
Mixture 4	58.5	37.5	4	284
Mixture 5	58.5	33.5	8	270
Mixture 6	49	49	2	310
Mixture 7	47	47	6	285
Mixture 8	45	45	10	306
Mixture 9	37.5	58.5	4	292
Mixture 10	33.5	58.5	8	330
Mixture 11	28	70	2	363
Mixture 12	24	70	6	349
Mixture 13	20	70	10	398

weighing. Resulting values are given in Table 1.

13 mixtures with different composition were prepared by mixing cow manure, pig manure and food waste in appropriate proportions. The relative amounts (in terms of wet mass) of cow and pig manure in the mixtures were 0 - 70%, while the amount of food waste was 0 - 10%. These ranges were selected to represent the approximate biomass availability in regions with intensive animal and dairy production. The properties of the 13 biomass mixtures in terms of relative mixture composition are given in Table 1.

### 8<sup>th</sup> i – CIPEC October 15 – 18, 2014, HangZhou, China

Batch digestion experiments using 250 mL serum bottles were carried out for all materials, material mixtures and inoculum (control) in duplicate. Samples were prepared by adding 10 g of each material or material mixture (wet weight) and 100 g inoculum to each bottle (control samples, contained 110 g inoculum). Mean VS concentration across all 34 samples was 30 g L<sup>-1</sup> with a relatively small standard deviation of 3g L<sup>-1</sup>. Therefore effects of variations in overall VS concentration on CH<sub>4</sub> yield (dilution effects) are expected to be negligible. Bottles were initially flushed with N<sub>2</sub> to expel O<sub>2</sub> and subsequently sealed and incubated at 37°C for 36 days. Gas production was measured daily during the first part of the experiment and semi-daily during the remaining part in response to the variation in gas production, using a low friction glass syringe At regular intervals duplicate gas samples for analysis of CH<sub>4</sub> and CO<sub>2</sub> content on a gas chromatograph (Agilent 7890) were collected. Cumulative CH<sub>4</sub> production (B<sub>CH4</sub>) as a function of digestion time, corrected for production by the inoculum and normalized to 0 °C and 1 atm, was then calculated assuming that produced gas consisted only of CO<sub>2</sub> and CH<sub>4</sub>.

#### 3. RESULTS AND DISCUSSION

B<sub>CH4</sub> for cow manure, pig manure, food waste and the 13 mixtures are shown in Fig. 1 as a function of digestion time. Corresponding values of ultimate CH<sub>4</sub> yield (B<sub>CH4,ult</sub>) taken as the cumulative CH<sub>4</sub> potential after 36 days of digestion are shown in Table 1. Per mass of VS, pig manure had the highest CH<sub>4</sub> yield, followed by food waste and cow manure. Approximately 90% of  $B_{CH4,ult}$  of pig manure is exhausted after about 14 days of digestion. In comparison less than 50% of  $B_{CH4,ult}$  of cow manure and food waste are exhausted within that time period.

While  $B_{CH4,ult}$  of cow manure, pig manure and food waste cover a relatively wide range (240 – 594 L kgVS<sup>-1</sup>),  $B_{CH4,ult}$  for the 13 mixtures only ranged between 260 and 398 L

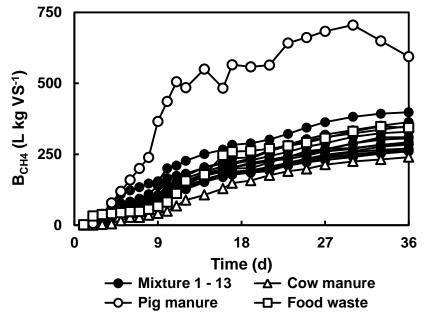


Figure 1. Cumulative  $CH_4$  production as a function of time for cow manure, pig manure, food waste and 13 mixtures of these materials (averages of two replicates).

kgVS<sup>-1</sup>. Thus, mixing of different materials averages variations in  $B_{CH4}$  for the individual materials. As cow manure has the lowest  $B_{CH4,ult}$ , the  $B_{CH4,ult}$  of the 13 mixtures generally increases with increasing fractions of pig manure and food waste and decreasing fraction of cow manure (Table 1). If there are no effects of codigestion on  $B_{CH4}$  for the 13 mixtures,  $B_{CH4}$  for each mixture at any given digestion time, t, can be calculated as a sum of the contributions to  $B_{CH4}$  by cow manure, pig manure and food waste obtained during separate digestion, respectively.

$$B_{CH_4}(t) = \sum_{i=1}^{n} B_{CH_4,i}(t) x_i$$
(1)

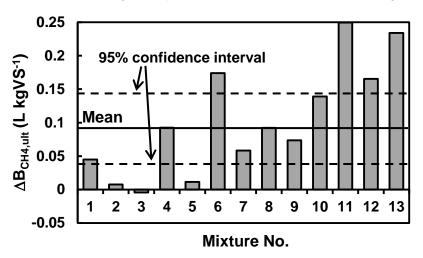
Where  $B_{CH4}(t)$  is  $B_{CH4}$  for the mixture at digestion time t, and  $x_i$  is the fraction of VS mass originating from cow manure (i = 1), pig manure (i = 2), and food waste (i = 3), respectively (inoculum is disregarded when calculating the relative fractions). The relative change in  $B_{CH4}$  using co-digestion instead of separate digestion can then be calculated using:

(2)

$$\Delta B_{CH_4}(t) = \frac{B_{CH_4}(t)}{\sum_{i=1}^{n} (B_{CH_4,i}(t) \ x_i)} - 1$$

Where  $\Delta B_{CH4}(t)$  is the relative change in  $B_{CH4}$  at digestion time, t, and  $B_{CH4}(t)$  is the measured cumulative CH<sub>4</sub> yield at time t, for the mixture in question.

Values of  $x_i$  corresponding to each of the 13 biomass mixtures were determined based on the VS contents of cow manure, pig manure and food waste in combination with the relative mass fractions of these three materials in each mixture (Table 1). Values of  $\Delta B_{CH4}(t)$  were then calculated for each of the 13 biomass mixtures. Resulting  $\Delta B_{CH4,ult}$  for the 13 mixtures are shown in Fig. 2.



# Figure 2. Relative change in ultimate CH<sub>4</sub> potential $(\Delta B_{CH4,ult})$ by co-digestion vs. separate digestion for the 13 mixtures. Horizontal solid and dashed lines are mean $\Delta B_{CH4,ult}$ and 95% confidence interval, respectively.

Figure 2 shows that for 12 out of the 13 mixtures, there is a positive effect on ultimate CH<sub>4</sub> yield ( $\Delta B_{CH4,ult} > 0$ ). This means that for these mixtures, co-digestion yields more CH<sub>4</sub> than if they were digested separately.

The data in Fig 2 shows that it is possible to achieve an increase in  $CH_4$ yield of up to 24% by-co digestion and further indicate that there may be an optimal mixture composition for which  $(\Delta B_{CH4.ult}$  is at a maximum. On average, across all 13 mixtures, codigestion results in an increase in ultimate CH<sub>4</sub> yield of about 10% which based on the 95% confidence intervals shown in Fig. 2 is significant. A possible explanation for the positive effects of co-digestion is that especially pig manure provides pH

control and nutrients to the mixtures, This is especially relevant during digestion of the food waste where production of volatile fatty acids (VFA) early in the process can result in inhibition problems. Similar effects of pig manure have been documented earlier [8, 13 - 15, 21]. Co-digestion is often regarded as having a positive impact on digestion process performance. This is in agreement with the data in Fig. 2 that shows that co-digestion generally improves CH<sub>4</sub> yield, however, the data also indicate that positive impacts of co-digestion on CH<sub>4</sub> yield cannot always be guaranteed.

The relative fraction of  $B_{CH4,ult}$  produced by a given biomass mixture at any given time t  $\leq$  36 days can be determined as:

$$B_{CH_4,rel}(t) = \frac{B_{CH_4}(t)}{B_{CH_4,ult}(t)}$$
(3)

Where  $B_{CH4,rel}(t)$  is the relative fraction of  $B_{CH4,ult}$  produced at time t. Values of  $B_{CH4,rel}(t)$  were calculated for each of the 13 mixtures based on Eq.(3) using both the measured  $B_{CH4}(t)$  values (corresponding to codigestion) and estimates of  $B_{CH4}(t)$  from Eq.(1) (corresponding to separate digestion). The results are shown in Fig. 3. From day 3 to day 17,  $B_{CH4,rel}$  for co-digestion (in Fig. 3 labeled  $B_{CH4,rel,mix}$ ) is significantly higher (as based on the 95% confidence intervals) than  $B_{CH4,rel}$  for separate digestion ( $B_{CH4,rel,sep}$ ). Defining the rate of change in  $B_{CH4,rel}$  with time as r:

$$r = \frac{d(B_{CH_4, rel})}{dt}$$

Figure 3 shows that during the first approximately10 days of digestion. r for co-digestion  $(r_{mix})$ is generally higher than r for separate digestion  $(r_{sep})$ , while the opposite is the case between day 10 and 17. During the initial 10 days, biomass conversion into CH<sub>4</sub> proceeds faster during codigestion compared to separate digestion on a relative basis, while between days 10 and 17, the separate digestion process 'catches up' with co-digestion and relative biomass conversion into CH<sub>4</sub> becomes similar for the two processes. Thus, in addition to generally improving ultimate CH<sub>4</sub> yield, co-digestion also seems to initiate CH<sub>4</sub> production earlier and more rapid than separate digestion.

#### 4. CONCLUSIONS

Impact of separate digestion of cow manure, pig manure and food waste, as well as co-digestion of these materials in different proportion in 13 biomass mixtures, on  $CH_4$  yield was investigated. Results showed that co-digestion generally increased ultimate  $CH_4$  yield in comparison with separate digestion. On average co-digestion increased ultimate  $CH_4$  yield by about 10 % across the 13 mixtures and improvements in ultimate  $CH_4$  yield as high as 24% for individual mixtures as compared to separate digestion was observed. Results further indicated that  $CH_4$  production starts earlier and proceeds at a higher rate early in the digestion process during co-digestion as compared to separate digestion. As the results presented here were obtained based on bench-scale batch experiments, the results are likely not directly transferable to full-scale continuous anaerobic digestion plants. However as the results observed in this study are statistically significant, it is very likely that the tendencies discussed above are valid also under full-scale and continuous conditions.

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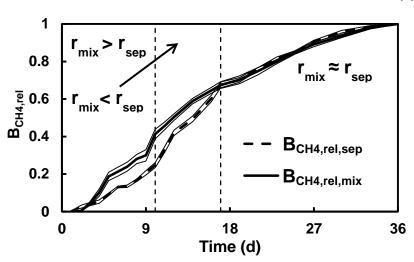


Figure 3. Fraction of ultimate CH<sub>4</sub> potential produced ( $B_{CH4,rel}$ ) as a function of time (Eq.(3)) for co-digestion (based on measured values) and separate digestion (based on estimates by Eq.(1)). Curves are averages across all 13 mixtures and thin lines are 95% confidence intervals.  $r = d(B_{CH4,rel})/dt$  and subscripts 'sep' and 'mix' indicate separate and co-digestion, respectively

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