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Oxygen gasification and its syngas upgrading in a fluidized-bed reactor using sand mixed dairy manure

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Abstract. *Low heating value dairy manure, taken directly from a lagoon, was processed using a dryer and a drum sand separator to remove moisture and the sand used for bedding. After the pre-process, the ash content of the dairy manure was reduced from 71% to a minimum of 37%. Oxygen-enhanced gasification was the process chosen to generate high quality synthesis gas. This process limits the nitrogen (N_2) gas composition in the produced synthesis gas compared with the use of normal atmospheric air. Experiments were carried out to investigate the effects of oxygen content and temperature conditions on the syngas composition using a 2-inch diameter fluidized bed reactor. Results showed that the heating value of synthesis gas was increased from 3.9 MJ/kg (104 Btu/ft^3) to 6.1 MJ/kg (164 Btu/ft^3) by using the oxygen-enhanced gasification process. The increased heating value of the synthesis gas was obtained at a temperature of 710^{o}C in an oxygen gasification process. Then, one mole of alkali solution was used to remove the non-combustible gas to enhance the quality of the syngas. Almost twice as much as the lower heating value (LHV) was obtained from the upgraded oxygen gasified syngas. The results of this study will pave the way for the widespread utilization of low quality animal manure for sustainable production of synthesis gas and electrical power via an oxygen-enhanced fluidized bed gasification process.*

Keywords. *Oxygen gasification, dairy manure wastes, thermochemical conversion*

Introduction

Manure has been regarded as an important protein source for crop production for many years (Jokela, 1992). However, large stall cow feedlots and dairies are widely known as major pollution sources of air, soil, and water. One of the consequences of land applications of manure is an increase in the phosphorus concentration (TNRCC, 2001). Also, the demand for manure is much less than the production. Subsequently, a manure storage facility, like a lagoon, needs to be well designed and used to reduce odor and excessive sludge accumulation.

A USDA report (USDA, 2010) listed the types of bedding used for lactating dairy cows in the United States. These include sand, straw or hay, sawdust/wood products, compost manure, rubber mats and tires, corn cobs and stalks, waterbeds, and mattresses. The most frequent materials for bedding were reported to be sand (25.8%) because it is regarded as an ideal choice for a dry and clean environment by preventing bacterial growth. Also, the sand bed material offers a comfortable and uniform bed for cows to lie on. A study (Galvão & Eizenberg, 2013) reported that 91.6% of dairy cows from sand bedding showed no lesions, while cows from water beds showed only 26.1% with no lesions.

Gasification, as one of the thermochemical conversion processes, was recognized as having a bright future since it can process low heating valued biomass wastes (Sipilä, 2013). The gasification process takes place in a smaller amount of oxygen than is needed for complete combustion, resulting in the production of flammable gases of H_2, CO, CH_4, and other hydrocarbons. The synthesis gases produced from the gasification process can generate electricity through an engine generator, and produce usable chemicals of methanol through the Ficher-Trosch process. However, the sand mixed dairy waste can hardly be used for the thermal conversion process as it includes a very high ash content resulting a low heating value.

In this study,

1) The characteristics of sand mixed dairy manure were examined for dairy manure processing.
2) Oxygen and air gasification were conducted using the processed dairy manure, and the syngas at different conditions were compared.
3) The produced syngas was upgraded using an alkali solution to obtain a better syngas quality.

It is expected that the processing conditions for the sand mixed manure will be an important reference for the further utilization of dairy manure wastes. Also, the unique gasification conditions of oxygen gasification and syngas upgrading, in addition to air gasification, will help in selecting the process technologies for the utilization of low quality biomass wastes.

Materials and Methods

Dairy Manure Sample and Drying System

Dairy manure was collected from pit at the Sierra Dairy in Texas. The manure was first dried on the field for 30 days. The as-received dairy manure with 30% moisture content (MC) was further dried using a 3ft x 3ft x 6ft box type dryer with a heated air inlet. Manure samples with an initial MC of 30% were dried to 0, 10, and 20% MC. Then, the manure was ground through a 2 mm-screen using Wilely Laboratory Mill for the gasification experiment in a bench scale gasifier.

Drum Sand Separation

A drum sand separator was designed and developed based on the results in the section “Dairy Manure Characteristics.” A one foot diameter drum filter was placed in a square 16 x 16 x 44 inch box. Iron poles were used as support for the steel woven wire mesh-20 cloth inside and mesh-40 outside the drum. Once the sand mixed dairy manure was inserted into the center part of the drum, particles smaller than mesh-20 were filtered out first, and then particles smaller than mesh-40 were removed. The sand removed from the drum fell directly into the collecting box. At the outlet of the sand separator, the processed dairy manure was obtained for the gasification process. The adjustable angle for the sand separator was manipulated to find the best inclined angle for transferring the manure to the outlet. A DC motor was used to control the speed of the drum rotation.

Fluidized Bed Gasification System and Syngas Upgrading

The gasification experiments were conducted using a bench-scale fluidized-bed gasifier. A single zone tube furnace heated the main reactor of 2 inch diameter x 33 inch length. The processed dairy manure was inserted into the main reactor using a 4 cm diameter screw auger. Two K-type thermocouples and pressure tubes were placed to monitor the reactor conditions. Mulgrain 47-10 x18 (CE Minerals, Andersonville, GA) as bed materials (-20 and +40 mesh) were used. The mean diameter was about 630 µm and the density was reported as 1.45 g/mL. Air and oxygen flows were connected to the gasification reactor with flow controllers. A TAMU designed cyclone was used to remove the solid particles, and a scrubber was used to remove light particle matter and reduce the gas temperature. Also, a scrubber with alkali solution was utilized to improve the syngas by removing non-combustible CO_2 gas. Then, an orifice meter was located next to the scrubber to measure the flow rate of the synthesis gas.

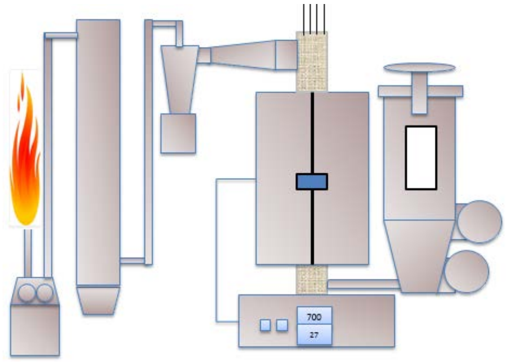


Figure1. Schematic diagram of a bench scale fluidized bed gasifier.

Analytical Methods and Data Analysis

The proximate data and moisture content of the dairy manure were secured based on the methods of ASTM E1755 and D3172. The heating value (HHV) and elemental data were obtained using a Parr bomb calorimeter and a Vario MICRO Elemental analyzer. The particle size diameter of the manure and sand were determined using USA Standard Sieve Nos. 12, 16, 20, 30, 40, 45, 50, 60, 70, 80, and 100 (ASTM E-1 specification, Fisher Scientific Company, USA). The volumetric gas composition was determined using a gas chromatograph (TCD-GC), which can detect gas mixtures of H_2, N_2, O_2, CO, CH_4, CO_2, C_2H_4, C_2H_6, C_3H_6, and C_3H_8.

The following equation was used to understand the lower heating value of syngas.

Heating value (HV) of syngas:

$$HV\left(\frac{MJ}{Nm^3}\right) = \frac{1}{100}\begin{pmatrix} 10.78 \cdot Y_{H2} + 12.63 \cdot Y_{CO} + 35.88 \cdot Y_{CH4} + 56.07 \cdot Y_{C2H2} + 59.45 \cdot Y_{C2H4} \\ +64.34 \cdot Y_{C2H6} + 81.41 \cdot Y_{C3H6} + 87.57 \cdot Y_{C3H8} \end{pmatrix} \tag{1}$$

where Y_i = %mole (v/v) of syngas of each gas component

Experimental Design

- The characteristics of sand mixed dairy manure were examined using standard sieving pans to find the effects of different moisture content (MC) conditions and the ground/non-ground conditions on the efficiency of sand separation as shown in Table 1.

Table 1. Dairy manure treated conditions for sieving test

	Ground	Non- Ground
0% MC	x	x
10% MC	x	
20% MC		x

- A drum sand separator was tested at different angles of 3, 7, and 10°. The drum rotation speeds were varied as well.
- Air and oxygen gasification was completed using the processed dairy manure.
- The syngas upgrading was done using an alkali solution through a scrubber to improve the syngas quality.

Results and Discussion

Sand-mixed Dairy Manure Characteristics

Table 2 shows the properties of sand-mixed dairy manure compared to fresh manure obtained directly from the dairy cattle. The as-received sand-mixed manure contained almost 71% ash resulting in a very low heating value of 5.5 MJ/kg, while the fresh manure showed 18 MJ/kg with a 16% ash content. The biomass waste with a high ash content can cause fouling and slagging problems in a high temperature oxygen present reactor (Maglinao & Capareda, 2010).

Table 2. Characteristics of dairy manure directly from lagoon, and fresh manure

Dry basis	HV (MJ/kg)	VCM (%)	ASH (%)	FC (%)	MC (%)
As received	5.5±0.1	25.5 ±0.7	70.6±0.6	3.9±0.3	32.1±0.3
Fresh manure	17.8+0.4	70.8+1.6	15.7+0.6	13.5+1.0	-

Eleven USA Standard mesh sieves were used to separate the previously conditioned dairy manure (dried ground, dried non-ground, 10%MC ground, and 22% non-ground manure samples) as shown in Figure 2. In all conditions, each separated manure below mesh-30 showed an ash content less than 40 - 50% except for the condition of the non-ground manure samples below mesh-16. As the manure sample was not ground, some big lumps containing sand below mesh-16 had a high ash content. On the other hand, the ground samples below mesh-20 showed a constant ash content of about 40%. The fully dried manure obtained an almost close to 40% ash content below mesh-20 as well, while the moist dairy samples remained near 50% below mesh-40 or 50. The lowest ash content in the processed manure was obtained as 39% ash content from the fully dried ground dairy manure sample below mesh-30. Above mesh-45 or 50, the separated samples showed an abrupt increase in ash content, which can be regarded as coming from the sand.

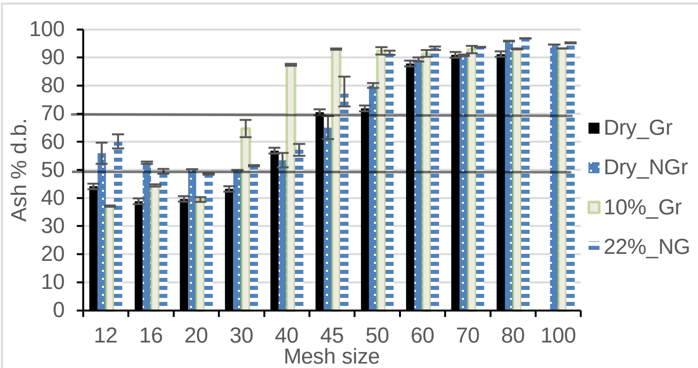


Figure 2. Ash contents in each separated sand mixed dairy manure using different sieves.

Figure 3 shows the cumulative distribution mass fractions of the separated dairy manure based on ash content. The effect of ground/non-ground conditions varied the amount of manure recovered at a certain size of mesh. If the processed manure is targeted to have less than 50% ash, the ground sample recovered only 20 wt.% with about 40% ash content, while the non-ground manure recovered up to 50wt.% with about 50% ash content. The different ash content in the different ground/non-ground manures above mesh-40 also varied the heating values and the elemental data as shown in Figure 4. The heating value (HV) of the dried ground manure sample was determined as 11.4 MJ/kg, while the HV of the unground sample showed 9.3 MJ/kg, which were highly improved from the as-received dairy manure of 5.5 MJ/kg. The lowest ash content in the manure samples, was found for ground manure with a 10% MC below mesh-12. However, the manure below mesh-40 for all the conditions was the optimum condition for separating sand from the dairy manure as the average ash content showed below 50% with high mass recovery of 40 wt.%.

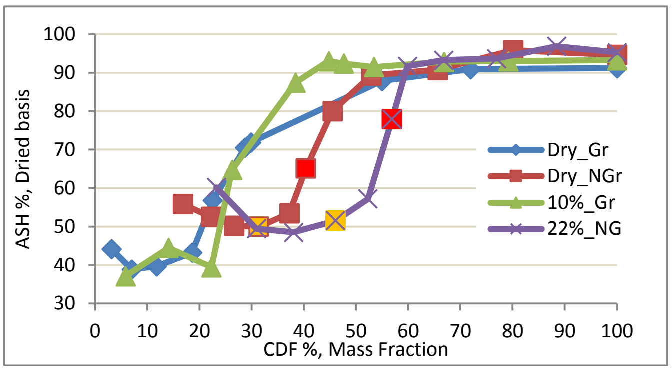


Figure 3. Cumulative distribution of mass fractions vs. ash content

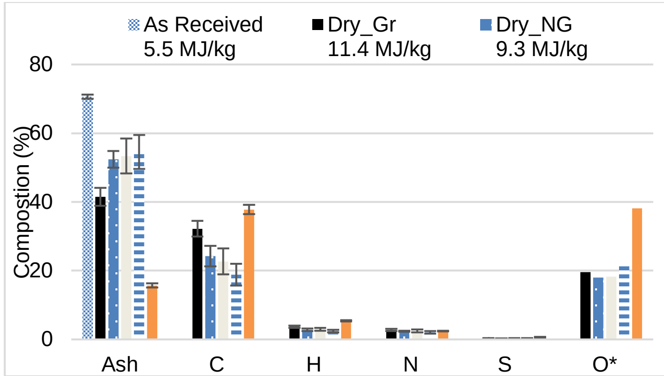


Figure 4. Elemental data and heating value of dried ground/non-ground conditions

Drum Separation

With the selected mesh size based on the previous section, a developed and fabricated drum sand separator was used to continuously process the sand mixed manure. Also, the separator was studied to understand the effect of the angle and the speed of the drum separator on the ash content with the fully dried non-ground manure sample. Figure 5 shows that the drum separator at an angle of 10° needed more than 3 cycles of the sand mixed dairy manure to obtain the minimum ash content, while a one-time process with the angle at less than 7° was enough. When the drum separator had a high angle, the manure samples went through the separator too fast to be separated. Also, the effect of the rotating speed of the drum separator on the ash content was tested with an rpm of 30, 50, and 70 at an angle of 7°, which resulted a minimal variation of the ash content.

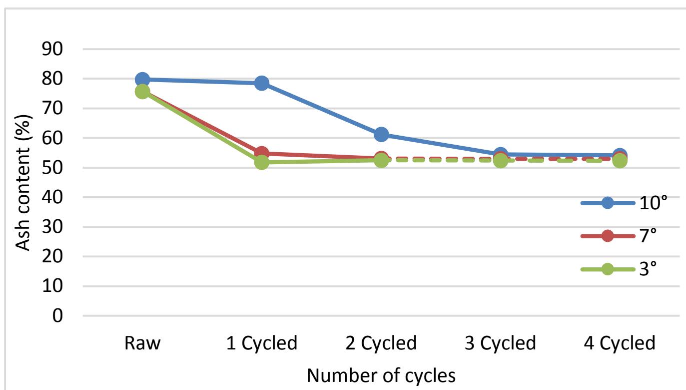


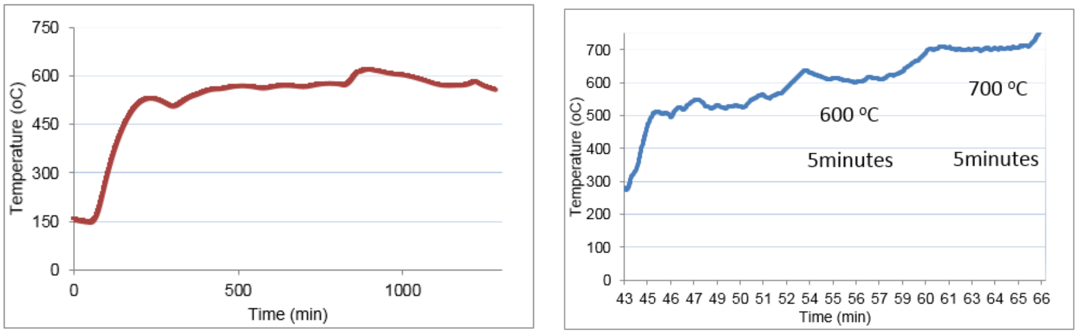
Figure 5. Ash contents depending on the different angles of the drum separator

Air and Oxygen Gasification Process

The processed dairy manure from the drum sand separator was analyzed and compared with the as-received data illustrated in Table 3. First, the as-received manure was used for heating the pilot scale TAMU gasifier as shown in Figure 6 (a). However, the temperature with the unprocessed dairy manure cannot increase the lower bed temperature above 600°C, and it rather decreases the temperature of the reactor. Once the processed manure was used, the temperature was easily controllable as shown in Figure 6 (b).

Table 3. Characteristics of the processed dairy manure using dryer and sand saperator. *by difference

	HV (MJ/kg)	VCM (%)	ASH (%)	FC (%)	MC (%)	C	H	N	S	O*
As-received manure	5.5±0.1	25.5 ±0.7	70.6±0.6	3.9±0.3	32.1±0.3	*Not applicable*				
Processed manure	9.1±0.2	42.5±0.1	14±1.2	43.5±0.4	1.3±0.2	24.3	2.8	2.4	0.27	26.8



(a) (b)

Figure 6. Gasification reactor temperature profile with (a) as-received dairy manure and (b) processed dairy manure

Air and oxygen gasification using the processed manure was conducted in a bench scale fluidized bed reactor and the result is shown in Figure 7. The condition of the equivalence ratio (ER) was ignored, and the syngas sample was collected when the syngas was flamed. The 60 – 70% of oxygen mixed with N_2 gas for the oxygen gasification was used. As the temperature rose, the non-combustible N_2 and CO_2 gasses decreased in both the air and oxygen gasification processes. On the other hand, the combustible H_2, CO, CH_4 gasses and other hydrocarbons (HC) increased. It was reported that the H_2 and CO compositions rose at a higher temperature, while the non-combustible gases decreased (Karmakar & Datta, 2011; Maglinao Jr, 2013). The variation of gas composition depending on the temperature changes resulted from the combination reactions of the water-gas shift and dry reforming reaction (Pinto et al., 2003). More oxygen in the gasification process led to the production of more CO and CO_2 gases than with the air gasification, while the production of N_2 gas in oxygen gasification was reduced. The varied gas composition depending on the conditions affected the LHV (lower heating value) of each experiment. The LHV of the air gasification was 3.9 MJ/m^3 at 680ºC and 4.3 MJ/m^3 at 710ºC, while the LHV of the oxygen gasification was 4.8 MJ/m^3 at 670ºC and 6.1 MJ/m^3 at 710ºC.

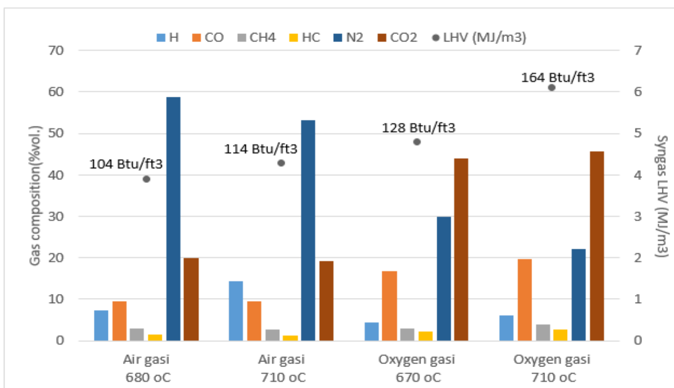
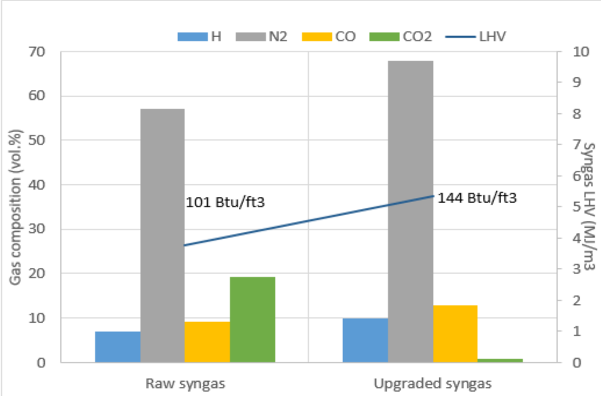


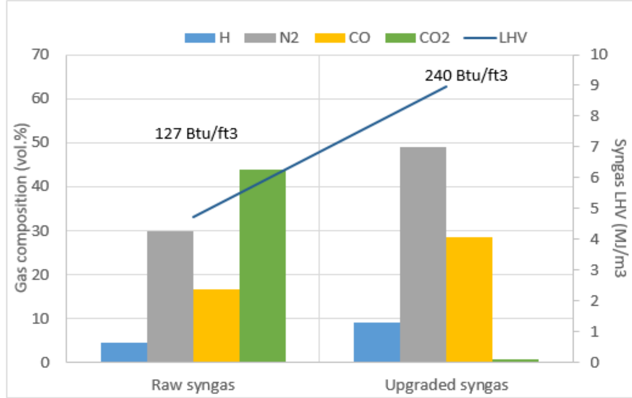
Figure 7. Syngas composition from air and oxygen gasification of the processed dairy manure.

Syngas Upgrading

The produced syngas was put through a scrubber containing four spray nozzles for gas cleanup and upgrading. The syngas at a temperature of 680ºC for air gasification and 670ºC for oxygen gasification was upgraded using 1M of alkali solution. The CO_2 composition in the syngas was almost removed from both the air and oxygen gasification process, which resulted in a relative increase in the other gasses as shown in Figure 8. This helped to enhance the quality of the syngas by about 40% from air gasification and 89% from oxygen gasification. As more CO_2 was included in the syngas from the oxygen gasification, a much higher increase in syngas energy content was achieved. The LHV of the produced syngas was recommended to be greater than 4.2 MJ/m^3 for engine use according to Shah et al. (Shah, Srinivasan, D Filip To, & Columbus, 2010). The syngas upgrading process helped a low quality syngas to be useful for power generation.



(a) Air gasification



(b) Oxygen gasification

Figure 8. Syngas upgrading using 1M alkali solution

Conclusion

Air and oxygen gasification experiments were conducted using processed dairy manure. First, the characteristics of sand mixed dairy manures were studied by separating them with different sieves in a drum sand separator. The lowest ash content was obtained when the sample was fully dried and ground with a 10% MC below the size of mesh 20, while the optimal condition for lowest ash content and high mass recovery was determined to be the separated manure below mesh-40 with all the processing conditions (fully ground/unground, and 10% and 20% MC sample). The processed manure was then used for the gasification process. The highest LHV of syngas was obtained as 4.3 MJ/m^3 for air gasification and 6.1 MJ/m^3 for oxygen gasification at a temperature of 710ºC. The produced syngas was further upgraded using an alkali solution by removing the non-combustible CO_2 gas to increase the heating value of the syngas. The quality of the syngas after the upgrading was improved to 5.4 MJ/m^3 (air gasification) and 8.9 MJ/m^3 (oxygen gasification). This study could be a basis for conducting a gasification experiment using a pilot scale reactor for engine power generation as the required syngas heating value was reported as 4.2 MJ/m^3.

Acknowlegement

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