PYROLYSIS PROCESSING OF ANIMAL MANURE TO PRODUCE FUEL GASES

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Introduction

Agricultural activities produce large quantities of animal wastes in the form of manures [1,2,3,4]. While some of the manure can be used as fertilizer, not all of it can be consumed in this way and the excess is an environmental liability. Another possibility is to use the manure as a direct or indirect source of fuel for remote power generation [5]. The use of animal manure for fuel has several benefits:

- Inexpensive – cheaper than propane, most natural gas, and electricity
- Avoids the cost of disposal
- Reduces odor and other nuisances associated with large livestock and poultry operations
- The potential applications of the energy-from-manure concept include space heating, steam, and electricity.

The conversion options include combustion, gasification, pyrolysis, and anaerobic digestion. Anaerobic digestion produces a biogas which has a heating value of 600-800 Btu/ft^3, which is 60-80% of the energy value of natural gas. This gas can be used to generate electricity, as a boiler or furnace fuel or to run refrigeration equipment. Gasification can produce a biogas with a heating value of 100-200 Btu/ft^3, only 10-20% of the value of natural gas. This low Btu gas is known as producer gas and can be used in any gas-fired appliance.

Direct combustion is also a possibility, although most fresh manures usually have too high a moisture content to burn and must be dried first. A direct combustion process can be used to produce process or space heat for small scale operations. Large scale operations can be used to produce electricity if the fuel is burned in a boiler and a steam turbine is used.

In the current study, the use of a staged pyrolysis process to produce medium Btu fuel gases (350 – 550 Btu/ft^3) for remote biomass power generation was investigated. This approach has several advantages when compared to more conventional processes:

- It has a higher process throughput than anaerobic digestion.
- It does not consume large quantities of water which must be treated, as in the case of anaerobic digestion.
- It can be used with poultry litter, an abundant resource, which is not as well suited to digestion because of its high lignocellulosic content.
- It can produce a higher Btu gas than conventional gasification processes.
- It can be more easily used with small scale power generation technologies than direct combustion and does not convert as much of the manure nitrogen to NO_x.

While many pyrolysis studies have been done on biomass materials [6-17], most of these have focused on plant biomass instead of animal manures and on the production of liquid fuels, chemicals, or hydrogen, and not fuel gas mixtures (H_2, CO, CH_4).

Animal manures are produced in abundance in the U.S. from several sources (cattle, hogs, pigs, sheep, lambs, layers, broilers, and turkeys). The 1995 estimates of livestock and poultry manures generated in the U.S. were 307x10^6 dry tons/year with an energy potential of 4.6 EJ/year [9]. This compares to total U.S. energy consumption of about 80 EJ/year [9]. Due to the economics of scale, farm animal production has gradually evolved in the direction of larger units, especially in the case of poultry. These concentrated animal populations generate large quantities of manure or litter, but often do not have the ability to use these materials on site for plant nutrients. In fact, manure becomes a liability for the large scale animal production facility instead of a benefit as it was historically on smaller farms. Since manure management has become a lower priority on larger farm operations, this has led to environmental problems such as water pollution and odors.

The fastest growing animal populations in the U.S. are the chickens which are raised for meat production (broilers) with an estimated population of 7018 x 10^6 in 1994 [9]. However, this was a 20% increase from 1990 and a 57% increase from 1985. The manure production averages 0.0403 dry kg/head-dry or 103.2 x 10^6 dry tons per year, equivalent to a human population of 983 million people! These data are summarized in Table 1, adapted from Reference 9, along with data for other types of manures.

Experimental

Samples of 5 manure samples were obtained as candidate materials. These included 2 samples of chicken manure (one broiler, one layer), turkey manure, cow manure, and seabird manure. The ultimate analysis data are provided in Table 2. The chicken manure samples are assumed to be mixed with small amounts of sawdust and should be considered "litters." The turkey manure sample was identified by the supplier as a litter. The seabird manure is believed to be a pure manure. The cow manure sample was dehydrated.

The individual manure samples were subjected to primary pyrolysis studies in a thermogravimetric analyzer with FT-IR analysis of evolved gases (TG-FTIR) at a heating rate of 30 K/min [18,19]. For the chicken #1 sample, additional runs were done at lower (3 K/min) and higher (100 K/min) heating rates for kinetic studies. A summary of the 30 K/min data (average of 3 runs) for all of the samples is given in Table 3.

It can be seen from the results in Table 2 that the ash content decreases in the order cow > turkey > seabird > chicken #2 > chicken #1. The moisture content decreases in the order cow > seabird > chicken #1 > chicken #2 > turkey. Based on considerations of a relatively high volatile matter and low ash and moisture contents, the chicken #1 (broiler) sample was selected as the best sample for more extensive testing. This selection was also based on the large resource potential of chicken manure (see Table 1). Both chicken manure samples were closest in elemental composition to wheat straw, which is a standard plant biomass material. Of course, all of the manure samples have higher nitrogen and sulfur contents than the wheat straw sample, although both of the chicken manure samples were among the lowest.

The TG-FTIR system that was used was subsequently equipped with a post pyrolyzer attachment and run at temperatures of 600, 800, 900 and 1000 °C for the chicken #1 sample and residence times of about 0.5 s. A second two-stage reactor was used to run larger samples with the second stage maintained at temperatures from 1050 to 1150 °C. The latter system was developed for NASA for pyrolysis of mixed waste materials in space [20,21].

The product yields for chicken #1 from the TG-FTIR system with a post pyrolyzer are shown in Table 4. These results indicate a progressive increase in CO, CO_2, CH_4, C_2H_4, NH_3 and HCN and a reduction in tar and oxygenated volatiles (formic acid, acetic acid, CH_3OH, formaldehyde, acetaldehyde, acetone, HNCO) as the temperature increases. H_2O appears to go through a maximum. The H_2 yield is not measured by FT-IR, but normally follows the trend of the CO yield (see below). These changes are the result of secondary

Table 1 - Livestock and Poultry Manures Generated in the United States and their Human Population Equivalents [9]

Livestock/Poultry	Population (10^6)	Manure production (dry kg/head-day)	Manure production (10^6 dry t/year)	Human population equivalent Factor	Human population equivalent (10^6)
Cattle	103.3	4.64	174.9	16.4	1694
Hogs and pigs	59.6	0.564	12.3	1.90	113
Sheep and lambs	8.9	0.756	2.5	2.45	22
Layers	377.5	0.0252	3.5	0.14	53
Commercial broilers	7018	0.0403	103.2	0.14	983
Turkeys	289	0.101	10.7	0.14	40

[a] U.S. Dept. of Agriculture (1995) for population data. Populations of cattle, hogs and pigs, and sheep and lambs are for 1995; remaining populations are for 1994. With the exception of the commercial broiler population, other populations are assumed to be steady-state values because the variations are relatively small for each of the proceeding 10 years.

Table 2 - Elemental Analysis of Manure and Wheat Straw (Reference) Samples*

Sample	Basis	Moisture	Ash	C	H	O	S	N
Chicken I[a]	AR	11.4						
(broiler)	D		22.1	37.0	5.0	30.8	0.8	4.3
	DAF			47.4	6.5	39.5	1.0	5.6
Chicken II[b]	AF	9.6						
(layer)	D		36.3	29.4	3.8	25.2	0.8	4.6
	DAF			46.1	6.0	39.5	1.2	7.2
Turkey[c]	AF	6.0						
	D		52.3	21.5	2.7	14.9	3.3	5.2
	DAF			44.8	5.7	31.8	6.9	10.8
Seabird[d]	AF	13.2						
	D		36.4	18.3	3.4	24.1	2.2	15.6
	DAF			28.8	5.3	37.8	3.4	24.7
Cow[e]	AF	24.5						
	D		74.0	13.2	1.8	8.5	0.6	1.9
	DAF			50.5	7.1	32.8	2.3	7.3
Wheat Straw	AF	7.9						
(NIST)	D		9.0	43.7	5.6	40.9	0.2	0.6
	DAF			48.0	6.2	44.9	0.2	0.7

Notes: AR = As-received; D=Dry; DAF=Dry, Ash Free
*determined by Huffman Laboratories (Golden, CO)

a-Plant Right (Purdy, MO); b-The Real Poop (Chesapeake, VA); c-The Guano Company International (Cleveland, OH); d-Sustane (Cannon Falls, MN); e- Bovung (Assinippi, MA).

Table 3 – Average Results from Primary Pyrolysis Experiments at 30 °C/min in TG-FTIR System

Sample	Chicken Pellets I	Chicken Pellets II	Turkey Manure	Seabird Pellets	Cow Manure
Moisture	11.2	8.8	5.6	12.7	26.0
Ash	18.3	32.1	46.1	28.4	52.7
Volatile Matter	59.1	52.5	46.6	57.3	17.2
Fixed Carbon	11.4	5.9	2.1	1.8	4.0
Tars	28.55	24.37	31.78	3.31	9.06
CH_4	0.98	0.76	0.72	0.32	0.74
H_2O (pyr)	18.72	15.87	18.01	16.48	19.93
CO_2	14.27	24.77	18.26	18.90	24.87
CO	6.37	8.65	15.11	9.95	15.64
C_2H_4	0.25	0.29	0.25	0.95	0.13
SO_2	0.08	0.06	0.38	2.46	0.49
COS	0.61	0.37	1.77	3.12	0.58
NH_3	1.91	1.92	3.10	10.00	0.93
HCN	1.21	1.66	1.52	5.64	1.46
Formic Acid	0.72	0.39	0.27	1.96	0.00
Acetic Acid	1.63	1.48	0.36	0.00	0.50
CH_3OH	0.10	0.02	0.02	0.00	0.47
Formaldehyde	0.00	0.03	0.00	0.00	0.54
Acetaldehyde	6.31	4.66	4.85	2.95	2.57
Acetone	1.04	1.20	1.33	2.02	0.72
HNCO	1.42	2.58	1.53	16.75	0.86
NO	0.00	0.00	0.00	0.00	1.42

Notes: Yields are given on dry; ash-free wt.% basis except for moisture, ash, volatile matter, and fixed carbon which are given on an as-received basis.

cracking and gasification reactions and the net result is to increase the heating value. These results demonstrate the strong effect of secondary pyrolysis temperature on the gas composition and yield.

The NASA two-stage reactor system could be operated over a relatively narrow range of temperatures for the second stage (1050-1100 °C) in the case of the poultry manure sample, so the results, shown in Table 5, do not show as much variation. At a similar temperature level, the yields of CO_2 and CH_4 appear lower, while the yields of CO and H_2O are similar to the results from the TG-FTIR system (Table 4). The most notable difference was the much lower yields of C_2H_4 and HCN in the NASA two-stage reactor. This is believed to be the result of the catalyst (xerogel) bed in the second stage.

In the NASA reactor, yields for H_2 were reported in the 0.5 – 1.6 wt.% (as-received basis) range. These yields are determined by the difference between the total gas flow rate (minus the N_2 carrier) and the sum of the gases determined by FT-IR analysis, so they are less accurate than the other gas concentration measurements. The yields of H_2 are lower than what is obtained from a plant biomass sample with a similar elemental composition (wheat straw) by a factor of two [20]. This is probably due to the fact that much of the hydrogen in the starting sample ends up as NH_3 in the product gas.

The lower yields of H_2 with respect to wheat straw appear to be compensated for by much higher yields of C_2H_4, which will add to the heating value of the gas. This is especially true in the case of the TG-FTIR experiment with the post-pyrolyzer attachment (see Table 4), i.e., a homogeneous cracking zone.

The as-received char yields are higher (~40 wt.%) in the case of the two-stage reactor, in which the poultry manure pellets were pressed into pellets of approximately 16 g each. This contrasts with the ~30 wt.% yields (fixed carbon plus ash) from the TG-FTIR system, where the sample size is only 30-50 mg. These results suggest that higher fuel gas yields will be achieved by reducing the particle size.

The results of both reactors suggest that the product gas composition (in mole %) will be in the following ranges after condensing out water and NH_3: 15-25% CO, 10-20% CO_2, 25-40%H_2, 5-10% CH_4, 5-15% C_2H_4, <2% HCN, <1% H_2S. Consequently, it appears feasible to produce a medium Btu fuel gas (350-550 Btu/ft^3) from pyrolysis of poultry manure.

The chars collected from both reactor systems were quite reactive, indicating that char combustion to provide process heat should not be difficult. The reactivity is probably enhanced by minerals present in the manure.

Conclusions

Pyrolysis is an interesting alternative to land application or incineration of animal manures. Chicken manure appears to be well suited to this approach because of its relatively low ash and moisture contents and its availability in significant quantities at many locations in the United States. A combination of primary and secondary pyrolysis processing is able to produce a medium Btu fuel gas.

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Table 4 - Results from TG-FTIR Experiments with Post Pyrolyzer Attachment for Chicken #1 Sample.

Post Pyrolyzer Temperature Run Number	**600 C AFR3811**		**800 C AFR3810**		**900 C AFR3809**		**1000 C AFR3808**	
	Product Yields (wt.%)							
	a.r.	daf	a.r.	daf	a.r.	daf	a.r.	daf
Moisture	7.7		7.9		9.1		11.4	
Ash (a.r.)	20.6		18.8		20.1		18.9	
Ash (dry)	22.3		20.4		22.1		21.3	
VM	60.7	82.81	60.0	81.86	58.3	82.3	58.1	83.36
Fixed Carbon	11.0	15.01	13.3	18.14	12.5	17.7	11.6	16.64
Tar	20.00	27.29	1.79	2.44	0.00	0.00	0.00	0.00
CH_4	0.67	0.91	1.70	2.32	2.15	3.04	2.42	3.47
H_2O (pyr.)	13.90	18.96	17.20	23.47	14.70	20.76	12.10	17.36
CO_2	11.10	15.14	14.51	19.80	15.36	21.69	17.29	24.81
CO	4.96	6.77	9.51	12.97	10.22	14.44	12.89	18.49
C_2H_4	0.23	0.31	1.70	2.32	6.02	8.50	6.39	9.17
SO_2	0.00	0.00	0.04	0.05	0.05	0.07	0.07	0.10
COS	0.33	0.45	0.14	0.19	0.00	0.00	0.00	0.00
NH_3	1.17	1.60	1.10	1.50	1.15	1.62	1.21	1.74
HCN	0.75	1.02	0.85	1.16	1.20	1.69	1.54	2.21
Formic Acid	0.24	0.33	0.00	0.00	0.00	0.00	0.00	0.00
Acetic Acid	1.10	1.50	0.00	0.00	0.00	0.00	0.00	0.00
CH_3OH	0.07	0.10	0.12	0.16	0.00	0.00	0.00	0.00
Formaldehyde	0.30	0.41	0.40	0.55	0.11	0.16	0.00	0.00
Acetaldehyde	4.57	6.23	0.58	0.79	0.00	0.00	0.00	0.00
Acetone	1.32	1.80	0.23	0.31	0.17	0.24	0.05	0.07
HNCO	1.11	1.51	0.82	1.12	0.81	1.14	0.62	0.89
NO	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
sum of volatiles	61.82	84.34	50.69	69.15	51.94	73.36	54.58	78.31
difference between balance and gasses	-1.12	-1.53	9.31	12.70	6.36	8.98	3.52	5.05

Notes: All yields are expressed in grams of a given product per gram of initial sample * 100% on as-received (a.r.), dry (dry), and dry, ash-free (daf) bases.

Table 5 - Results from NASA Two-Stage Pyrolyzer Experiments with Chicken #1 Samples*

Post Pyrolyzer Temperature	**1100 °C**	**1100 °C**	**1100 °C**	**1100 °C**	**1100 °C**	**1050 °C**
Run Number	22	23	24	25	26	27
Char	41.1	40.7	40.8	40.8	40.7	41.1
H_2O	12.3	14.6	13.1	15.3	15.2	12.4
Carbon	0.8	2.6	9.2	2.8	4.1	9.1
Trap & Filter	4.7	4.5	2.9	2.8	3.9	14.1
Gases	41.0	38.2	37.8	38.6	36.3	23.4
H_2	1.6	0.6	0.5	1.2	0.7	1.1
C_2H_4	0.4	0.3	0.4	0.3	0.3	0.3
CH_4	3.0	3.0	3.3	3.6	3.0	1.7
CO_2	23.0	21.0	20.2	19.7	19.0	15.1
CO	13.0	13.3	13.4	13.8	13.3	5.2
NH_3	1.5	1.3	<0.1	1.2	2.4	1.2
HCN	0.3	<0.1	<0.1	0.3	<0.1	0.5

*results are given on an as-received basis; char = fixed carbon plus ash

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