Syngas Evolutionary Behavior during Chicken Manure

Pyrolysis and Air Gasification

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Abstract

10 The evolutionary behavior of syngas composition during the pyrolysis and
gasification of chicken manure was examined at different temperatures
and O₂ concentrations. A gas chromatography was used to quantify the
syngas evolved. Pure nitrogen was used for pyrolysis while two different
oxygen concentrations (21% and 10%) in nitrogen were used for
15 gasification. Five specific temperatures examined during pyrolysis and
gasification were from 600-1000 °C in steps of 100 °C. Higher O₂
concentration (21%) produced higher energy yields compared to lower O₂
concentrations. Initial 8-10 minutes' yield produced CO₂ dominant syngas
from decarboxylation after which the compositions changed to

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20 equilibrium. High temperature and low O₂ concentrations yielded higher
CO flow rates and amounts. Equilibrium H₂ content was reduced with an
increase in O₂ concentration due to the rapid oxidation of H₂ in the
presence of oxidative environment. CH₄ was obtained from thermal
cracking with its evolution being similar to that of other higher
25 hydrocarbons evolved, albeit in smaller concentration.

1. Introduction

30 Waste management is amongst the most important global challenges facing the
society for seeking improved healthy environment. The amount of wastes generated
continues to increase so that seeking sustainability requires increased reuse of all waste
materials for further use as feedstock or reformed to usable energy. Global energy
security and energy sustainability requires harvesting clean energy from wastes and low-
35 grade fuels that will help reduce fossil fuel consumption and extend their availability.
This also helps in the mitigation of greenhouse gases as energy produced from wastes and
biomass is nearly carbon neutral. Use of solid organic wastes including municipal solid
wastes, animal wastes along with biomass as an energy source is key to sustainable
energy production and waste disposal. Such energy source has a carbon-neutral effect on
40 greenhouse gas emissions due to their renewable production and disposal [1]. Livestock
manure which includes poultry and other animal litter (excretes, bedding material) was
traditionally land spread for its use as fertilizer and soil amendment. But with increased
amounts of wastes composting due to large volume involved from increased population

causes eutrophication of water bodies including ground water by spreading leachates of
45 nitrates, potassium and phosphorous present in the wastes to pollute both land and water
and spreading into associated pathogens [2]. Environmentally safe disposal techniques
can be equipped with energy production capability. Energy harnessing techniques such as
anaerobic digestion, direct combustion, and gasification are environmentally safe for the
disposal of animal wastes as well as municipal solid wastes. Pyrolysis and Gasification of
50 wastes is an efficient solution over direct combustion, as it can produce liquid/syngas
fuels of medium to high heating value, which can be utilized with the currently available
infrastructure for power generation and transportation. Even though anaerobic digestion
can produce methane its relatively slow production rate makes it less viable strategy
compared to pyrolysis and gasification.

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Gasification is the thermal conversion of solid carbonaceous material at high
temperatures in the presence of gasifying agents, such as air, O₂, steam, CO₂ and their
mixtures to form product gas of high heating value containing H₂, CO, CO₂, CH₄, C₂H₆
and other higher series of hydrocarbons. Tar, containing heavy aromatic hydrocarbon
60 residues, is also formed as an undesired byproduct which can be further thermally or
catalytically cracked or reformed to enhance syngas yield. The composition of syngas
evolved from gasification depends to a large extent on the gasifying agent, temperature,
feedstock chemical properties and other reactor operational parameters. Production of
uniform syngas constituents from versatile sources including chicken manure, poultry
65 litter, biomass, solid wastes, and coal makes it an attractive solution over direct
combustion of these low-value heterogeneous feedstocks. Literature is available on the

investigations of biomass with and without catalysts, using different gasifying agents, temperatures, and gasifiers [1,3–17]. Equations (1–5) show the major reactions that occur during gasification.

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Poultry litter is one of the major waste sources from the poultry industry that has only increased with time due to our quest for increased production. Manure, waste beddings, waste food, and feathers constitute poultry litter that has high ash content. 80 Manure contains a considerable amount of organic nitrogen from proteins and amino acids. Abundant literature is available on pyrolysis and gasification of biomass, but differences exist in the amounts of various elements present in chicken litter than biomass. These include low heating value, high ash content, and high nitrogen content. These differences cause many challenges that have motivated many researchers to study 85 the pyrolytic behavior of chicken litter [18]. Thermogravimetric analysis of poultry litter and comparison with coal revealed that decomposition of poultry litter starts at lower temperatures than that of coal and has a maximum weight loss rate at around 370 °C [19]. TGA results on the pyrolysis of chicken litter showed three stages of weight loss, unlike woodchips pyrolysis which occurs in two stages because of lignocellulose content [18].

90 Chicken litter pyrolysis involves three stages of decomposition of cellulose and hemicellulose with a peak at a temperature less than that of wood chips, followed by manure and lignin decomposition and the last stage of residual char devolatilization. Higher manure content assists in faster decomposition of waste litter. Increase in temperature increases syngas yields, and decreases liquid and char yields [20]. At 95 temperatures above 700 °C, CO₂ yields increased and it was attributed to decarboxylation of minerals carbonates in the ash and reached a stable value above 1000 °C [19]. Highly viscous bio-oils were produced from chicken litter by fast pyrolysis. The results showed that bio-oil from chicken litter was relatively less acidic than that obtained from hardwood [21]. These pyrolysis results also showed that higher heating value (HHV) of 100 bio-crude oil from chicken litter to be higher than that produced by hardwood due to the conversion of its protein content into higher hydrocarbons from the absence of CO₂ and N₂.

The high inorganic content in poultry litter (>20%) aids in fertilizing capabilities. 105 For syngas production, the inorganic components can provide catalytic activity. However, a major drawback of dealing with chicken litter lies in the handling difficulty due to the low fusion temperature of inorganics present since the chicken litter ash contains high amounts of Ca, Na, and K. Such high amounts of ash content in chicken litter with phosphorous and potassium oxides makes it an efficient fertilizer even after 110 gasification [22]. While the effect of other alkali and alkaline earth metal compounds on product gas is not known, decarboxylation of CaCO₃ was observed at temperatures above 700 °C [19]. The presence of gas evolution from inorganic matter in manure and the low

melting points of its constituents calls for the inclusion of ash chemistry into the modeling of high-temperature gasification and pyrolysis models [23]. Presently ash is usually considered inert in biomass gasification models.

Chicken litter is characterized by high nitrogen content due to the presence of protein and amino-acids compared to woodchips or other biomass feedstock [19]. The amine and carboxylic groups in the amino acids increase the complexity of gasification reaction with releasing CO_2 by decarboxylation and nitrogen compounds (such as NH_3 , HCN, and HCNO as gases) which are NO_x precursors and N-bound char and tar compounds. Studies on the evolution of nitrogenous species revealed NH_3 as the dominant nitrogenous gas species and rest of N contained in char at low temperatures (<600 °C) while at higher temperatures, HCN was the main nitrogenous gas product and high yields of tar containing nitrogen [19]. Nitrogenous gas species yield was found to reduce with increase in heating rate which may be due to an increase in N-bound tar yields. It is suggested that the presence of volatile nitrogen makes such feedstock a viable option for NO_x control since pyrolysis of chicken litter releases nitrogenous gaseous species which separates most of the nitrogen bound in the feedstock, unlike coal.

Investigations on fixed-bed air gasification of chicken litter and coal blends found no significant effect on the produced syngas heating value and demonstrated the feasibility of chicken litter usage as gasification feedstock [24]. Kinetics of 'auto-gasification' based on using the ultimate analysis of the sample to conjecture that the amount of carbon can be gasified by the amount of feed bound O_2 in the sample in O_2

gasification [25]. They also indicated that a share of carbon reacts to hydrocarbons while another share participates in water gas reaction which leads to scarcity of carbon to react with fuel bound O_2 causing further oxidation to form CO_2 . Catalytic steam gasification of chicken manure in a fluidized bed at temperatures around 600 °C revealed an increase in H_2 content and total gas yields with the addition of $Ni-Al_2O_3$ catalyst [26]. Super-critical gasification of chicken manure was also investigated [27,28]. Literature regarding the parametric effects in gasification of poultry manure is limited although, abundant literature is available on such studies using biomass.

The present paper investigates the pyrolysis and O_2 gasification of chicken manure at temperatures ranging from 600 °C to 1000 °C in steps of 100 °C with a specific focus on the evolution of product gas yield and composition. Product gas parameters such as gas composition, yield of H_2 , gaseous C_nH_m , and heating value are evaluated to reveal the effects of temperature and O_2 content in the gasifying agent. The data obtained augments to the fundamental knowledge of syngas evolution from chicken manure gasification which assists in the design of gasifiers as well as validation of computational models and model development for high-ash, low-energy content feedstocks containing significant amounts of fuel bound nitrogen.

2. Experimental

2.1. Reactor Facility

A schematic diagram of the laboratory scale semi-batch reactor facility used for investigating the pyrolysis and gasification behavior of chicken manure is given in Fig. 1.

N₂ of known flow rate was used as a tracer gas for all the experiments that helped to
160 quantify the amounts of various gas species evolved. Pyrolysis was investigated by
flowing only N₂, while two different flow rates of O₂ in N₂ were used to examine O₂
gasification. The gasifying medium along with N₂ was passed through a preheating zone
consisting of a furnace that was set to a temperature equal to that of the main reactor.
Preheated mixture of different gasification agent gases was then allowed to enter the
165 main reactor furnace located immediately downstream of the preheating furnace where it
reacted with the chicken manure sample in quasi-isothermal conditions. The sample was
filled in a quartz sample holder and inserted through the quick disconnect coupling after
the reactor reached the set-point temperature. Time was counted starting from the time of
sample insertion into the reactor.

170 Evolved syngas mixture from the reactor was first condensed in an ice followed by
a water bath to remove tar and moisture. A portion of the tar-free syngas was sent
through sampling line while the remaining (excess) gases were vented out through the
exhaust duct after dilution. Moisture was removed using anhydrous calcium chloride in a
175 desiccant. A majority of the syngas yield was evolved during first 5 minutes so that the
product gas mixture samples were collected in sampling bottles for each minute to
determine the evolutionary behavior of syngas yield. After the first 5 minutes, sampling
time was at longer time duration so that gas sample was directly introduced into the gas
chromatograph for the remaining duration of the reaction. Micro gas chromatograph was
180 used to determine mole fractions of evolved gas species which can analyze samples at a
sample rate of approximately three minutes during continuous acquisition. Micro GC was

calibrated to quantify H₂, CO, CO₂, CH₄, C₂H₆, C₂H₄, C₂H₂, N₂ and O₂ to an accuracy to $\pm 0.1\%$.

185 *2.2. Operating conditions*

Chicken manure used for the present investigation was a dried chicken manure fertilizer sample in granular form. The ultimate and proximate analysis along with the higher heating value (HHV) [29] of the sample is given in Table 1. Tracer gas flow of 2.1 slpm of N₂ was used for all the experiments reported here at temperatures of 600 °C to 190 1000 °C. Three different O₂ gasification tests were analyzed having 0, 10, and 21% of O₂ concentration at fixed N₂ flow rate (2.1 slpm).

3. Results and discussion

195 This work focuses on examining syngas yield at different concentrations of O₂ in the gasifying medium, including the pyrolysis case. Product syngas is characterized by composition and yield of defined major gas species. The evolutionary behavior of syngas yield and its composition for different pyrolysis and gasifying conditions was studied. CO and CO₂ compositions were analyzed to determine the dominating reaction for 200 different O₂ concentrations in the gasifying medium. Hydrocarbon evolution (CH₄ and C₂) was compared to investigate the effect of O₂ and reaction temperature on the thermal cracking reactions.

3.1. Evolution of Product gas flow-rate

205 Figures 2–4 **Error! Reference source not found.** show the evolution of various components in the total syngas yield which includes H_2 , CO , CH_4 , CO_2 , C_2H_6 , C_2H_4 , and C_2H_2 . Temperature has a positive and dominating effect on the net yield of syngas. An increase in temperature enhanced the conversion to gas over char/liquid products, which supports the findings given in the literature on different feedstocks. The peaks are caused
210 due to de-volatilization of the chicken manure sample. With the increase in temperature, the peaks of the flow rates shift towards lower residence times due to increased heating rates that enhance reaction kinetics of decomposition. The dependence of total gaseous flow rates on O_2 concentration in gasifying medium is more complex as it also depends on the reaction temperature. Pyrolytic yield corresponds to first 8-10 minutes during
215 which the sample is converted into char and the duration of pyrolysis has low a dependence upon reaction temperature. The yield after 10 minutes corresponds to the char-gasification reactions which includes oxidation with composition dependent on Boudouard reaction equilibrium. While for the case of 10% O_2 , the char gasification yield is less relative to 21% O_2 ; the char gasification is negligible in 0% O_2 case. This shows
220 that the yield is from enhanced char gasification as also observed from the literature [30]. The char gasification reaction is relatively slow as observed from Fig. 3. The results show that while the de-volatilization took around 10 minutes, the gasification took around three times of that for pyrolysis time. This reaction was not observed for temperatures below 800 °C meaning that gasification reactions are important at higher temperatures (above
225 700 °C). Although the manure gasification can be broadly separated into regimes of de-volatilization and char-gasification, there exists an intermediate zone between these two phases, during which both the phases co-exist which can be observed by the difference

between 0% and 21% cases as seen from a partial overlap of de-volatilization and char-gasification, compare Fig. 2 with Fig. 4.

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3.2. Product gas composition

The evolution of dry gas composition in the syngas without the tracer gas is presented in Figs. 5–7. During the first 8-10 minutes, which is a thermally transient period until the sample reaches thermal equilibrium with the reactor, the evolution of CO₂ is the dominant constituent, see Fig. 5. From Figs. 5 and 6, the dominance of CO₂ during early period is consistent and it can be attributed to both the decarboxylation of amino acids, acetic acid and other carboxylic groups generated during lignocellulose decomposition. After the decarboxylation and when the temperature of the sample exceeds 500 °C, the sample starts breaking other CH, CO, and C=O groups to generate CH₄, CO₂, CO, and other gases [31]. Pyrolytic water [19], which is released during this process, also accounts for H₂ production through reforming of hydrocarbons apart from thermal cracking. The evolution of C₂ hydrocarbon gases is similar to CH₄, through pyrolysis of higher hydrocarbons and other alkyl groups. Results shown in Fig. 7 for 0% O₂ at 1000 °C case shows that the initial period is dominated by syngas (H₂ and CO) as opposed to CO₂ unlike the other cases examined here. This can be attributed to a very high heating rate of the sample and cracking hydrocarbons groups to be faster than carboxylation. After the initial pyrolysis, the gases evolve according to the slow char gasification. Examination of Fig. 5 reveals that amount of H₂ produced for the 0% O₂ case is considerably higher than the evolved CO₂, although the total yield is almost negligible after the pyrolytic stage. Comparing Figs. 5–7, such behavior is observed at all

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the investigated temperatures. Low CO_2 content in the syngas can be attributed to the absence of sufficient amounts of O_2 to result in high H_2 yield. The presence of O_2 at 1000 °C, the high concentration of CO_2 can be due to the oxidation of some of the hydrocarbons evolving during this early period.

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Comparing the syngas composition during char gasification for different O_2 concentrations show significant differences in the mole fractions of H_2 , CO , and CO_2 . From Figs. 8–10, at increased temperatures, the observed increase in CO concentration is attributed to the Boudouard reaction that is driven towards dry gasification portion of
260 char. This dependence is significant only for 10% and 21% O_2 cases, compare Figs. 5, 8, and 11. The H_2 content in syngas decays to zero during char gasification for these two cases, unlike for 0% cases in which H_2 concentration only stabilized (i.e., no increase). This absence of H_2 corresponds to the presence of excess O_2 to oxidize H_2 and thus a decrease in H_2 content. Figures 9 and 12 reveals that the trend of H_2 evolution is similar
265 to the evolution of CH_4 and C_2H_m , which means that the H_2 released for the O_2 content of 10% and 21% is mostly from cracking of hydrocarbons. Hydrocarbons formed thermally crack to give lighter hydrocarbons which decompose to generate H_2 as seen from Eq. (5). Comparing the results from Figs. 10 and 13, increase in O_2 content in the gasifying medium reduced the CO content in syngas during char gasification implying more char
270 oxidation than char gasification that leads to more CO_2 . Temperature and O_2 concentrations play a major role in the CO and CO_2 evolution during gasification. For low temperatures and high O_2 content, CO_2 is favored over CO .

3.3. Cumulative energy yield

275 The energy yield (total heating value of evolved gas) was calculated to investigate the effect of gasifying conditions. As seen from the Fig. 13, the effect of an increase in temperature was to increase the heating rate for an effective breakdown of hydrocarbons into gases which increased the gaseous hydrocarbon content and gasification kinetics to increase the energy yield. At lower temperatures, more tar was formed which cannot be
280 quantified by microGC. A notable feature from the comparison between different O₂ content in gasifying medium is the differences in energy yield with an increase in temperature between 0% case (pyrolysis case) and the other gasification cases. For 0% case, the total energy yield for temperatures lower than 1000 °C is lower compared to the 21% O₂ case. This is due to the dependence of effective pyrolysis of the sample (majorly
285 thermal decomposition for 0% case), while for the 10%, and 21% O₂ gasification cases, the presence of excess O₂ provided improved char gasification even at lower temperatures. The release of more CO compared to CO₂ at higher temperatures increased the energy yield, but the increase in energy yield with temperature is highest for 0% case. At 1000 °C, it can be seen that the energy yield of 10% case is the lowest as compared to
290 other temperatures. This observation reveals that the dependence of O₂ content on total energy is not simple because for pyrolysis (0%) case, the high energy yields due to efficient gaseous hydrocarbon yield and thermal cracking of hydrocarbons to H₂ which has high heating value, while for 21% case the increase is due to increase in CO content. For the 10% case, the energy yield is lower because the O₂ content is relatively high to
295 oxidize the tar content and the increase in CO yield is lower for this case compared to 21% O₂ because of low O₂ content. This infers that partial oxidation of sample to produce

CO is efficient at lower temperatures, and if higher temperatures are used, O₂ content in the gasifying medium must be controlled to make it comparable to pyrolysis condition.

300 *3.4. Residue from gasification*

Figure 15 shows a comparison between the chicken manure sample before and after gasification with non-zero O₂ (gasification cases). An important parameter that needs to be considered here is very high ash content in chicken manure compared to any major biomass sources. This high ash content with low fusion temperatures calls for
305 better gasifier coatings with corrosion resistance. This ash produced can be utilized as a fertilizer, which means the gasifiers built for chicken manure gasification should account for the collection of high volumes of ash in their design with due consideration to corrosion and deposition resistance. This also reveals better material destruction capabilities from gasification to reduce the waste products into 80% gaseous fuels and
310 20% fertilizers by wt. neglecting the CO₂ production compared to composting which is used for only as fertilizer and its over-usage can cause eutrophication of groundwater.

3.5. Error Analysis

The accuracy of the calibrated gas compositions from the microGC was estimated
315 be 0.1%. The data uncertainty of flow rates and composition of product gas species lies within the bounds of the symbol sizes used in the figures.

4. Conclusions

320 The pyrolysis and gasification of chicken manure at two different O₂
concentration in air at different isothermal temperature conditions have been examined.
The results provided detailed information on the evolutionary behavior of syngas
composition and yield, energy yield and residual material. The evolution of syngas flow
rates suggests increased gaseous products yield with the increase in temperature and O₂
325 content in the gasifying agent. The quality of gases produced was determined from the
chemical composition of the gases evolved. Higher O₂ content in gasifying medium
produced higher CO₂ content in the syngas at low gasification temperatures. However, at
higher temperatures (more than 800 °C) CO₂ decomposed into CO by reaction with the
char residuals. The gaseous evolution occurred in approximately two stages. They
330 included rapid decarboxylation and cracking of hydrocarbons followed by gasification of
residue char formed after de-volatilization. The cumulative energy yields showed that
gasification by partial oxidation produces more energy compared to pyrolysis and very
high temperatures are required for pyrolysis to match the energy yield from air
gasification. The results also showed that at higher temperatures, due to better conversion
335 kinetics, higher O₂ content in gasifying medium assists to enhance carbon oxidation. At
higher temperatures, due to Boudouard reaction equilibrium, higher CO is favored – more
O₂ content produces more CO₂ which then reacts with char to enhance CO yield.
Residues after gasification were ash (mineral matter) that is high in chicken manure
compared to other biomass feedstocks so that better and corrosive resistant hardware will
340 be required to handle high ash amounts that also has low melting points to provide issues
of fouling and deposition on heat exchange equipment in chicken-manure-fired feedstock
systems.

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Figure captions:

Fig. 1. A schematic diagram of the semi-batch reactor

Fig. 2. Product gas evolution for pyrolysis case (0% oxygen gasifying medium)

Fig. 3. Product gas evolution for 10% oxygen in gasifying medium

Fig. 4. Product gas evolution for 21% oxygen in gasifying medium

Fig. 5. Evolutionary behavior of gas species mole fraction at 800 °C for 0% O₂ concentration (pyrolysis case)

Fig. 6. Evolutionary behavior of gas species mole fraction at 900 °C for 0% O₂ concentration (pyrolysis case)

Fig. 7. Evolutionary behavior of gas species mole fraction at 1000 °C for 0% O₂ concentration (pyrolysis case)

Fig. 8. Evolutionary behavior of gas species mole fraction at 800 °C for 10% O₂ concentration in air gasification case

Fig. 9. Evolutionary behavior of gas species mole fraction at 900 °C for 10% O₂ concentration in air gasification case

Fig. 10. Evolutionary behavior of gas species mole fraction at 1000 °C for 10% O₂ concentration in air gasification case

Fig. 11. Evolutionary behavior of gas species mole fraction at 800 °C for 21% O₂ concentration in air gasification case

Fig. 12. Evolutionary behavior of gas species mole fraction at 900 °C for 21% O₂ concentration in air gasification case

Fig. 13. Evolutionary behavior of gas species mole fraction at 1000 °C for 21% O₂ concentration in air gasification case

Fig. 14. Cumulative energy yield from the syngas at different temperature and O₂ content

Fig. 15. Original chicken manure sample (left) and gasified residue sample (right)

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

Figure 10

Figure 11

Figure 12

Figure 13

Figure 14

Figure 15

Chicken Manure - Fresh Sample

Chicken Manure - Gasified residue (Ash)

Table 1

<i>Proximate Analysis (wt. % dry)</i>	
Volatile content	65.56
Ash content at 550 °C	21.65
Fixed carbon	12.8
<i>Ultimate Analysis (wt. % dry)</i>	
Carbon	35.59
Hydrogen	4.57
Nitrogen	4.98
Sulfur	1.45
Oxygen	35.52
HHV (in MJ/kg)	13.15

Table 1. Proximate and Ultimate analysis of chicken manure [33]