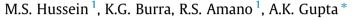
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# Temperature and gasifying media effects on chicken manure pyrolysis and gasification



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#### HIGHLIGHTS

• Syngas from semi-batch gasification of chicken manure is examined.

• Efficiencies of pyrolysis and gasification in steam, CO<sub>2</sub>, and air are compared.

• Steam and CO<sub>2</sub> gasification increased syngas and energy yields.

• Air gasification led to lesser energy yields with high carbon conversion.

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#### ABSTRACT

Continuous increase in chicken meat consumption calls for the chicken industry for unpreceded dense chicken production and associated waste production. The chicken farms produce large amounts of chicken manure that can no longer be directly used as a fertilizer due to concerns of land pollution and water bodies eutrophication. The gasification of chicken manure can convert the negative economic value chicken manure into fuel to help foster energy security and energy sustainability. The pyrolysis and gasification of chicken manure was studied using different gasifying media and temperatures ranging between 600 and 1000 °C in 100 °C temperature steps. The evolved gases were analyzed using gas chromatography and the results are presented in this paper. Gasification with carbon dioxide and steam were found to give the highest energy yield in the form of syngas; air gasification provided highest carbon conversion with low syngas energy yield, at higher temperatures steam and carbon dioxide gasification yielded similar conversion to air gasification but with high syngas energy yield. At higher temperatures, gaseous yields were higher due to the tar cracking and further reformation to provide enhanced carbon conversion. The reduction in tar was more favorable at high temperatures. Tar is known to increase the maintenance time and costs, but its reduction comes at the cost of increased energy input.

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#### 1. Introduction

The average chicken consumption continues to increase annually, and in the USA alone 12 billion pound of dry chicken manure is produced every year [1]. This production exceeds the soil absorption limits if the manure is used as a fertilizer, resulting in environmental issues [2]. In the state of Maryland, chicken manure was attributed to high concentration of phosphorous (60% higher than the levels required for plant growth) found in the soil thus making phosphorous a soil pollutant [2]. The localized traditional fertilizer applications of chicken manure is no longer an option

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as such wastes can be managed by transporting and reforming into usable energy [3]. Thermochemical conversion techniques such as pyrolysis and gasification can convert the chicken manure into syngas, which can be further processed to fuels or directly used for power, and thus help reduce the dependence on fossil fuels. When the waste decomposes in the landfills, it emits methane into the atmosphere which is a greenhouse gas and some environmental activists blame agriculture manure for the global warming that can amount to the extent of fossil fuel burning [4]. Converting the manure will decrease greenhouse gases produced and generate energy in a nearly carbon neutral process [5]. Direct combustion of manure is inefficient compared to pyrolysis and gasification. Due to high moisture and ash content, manure has very low heating value in its solid state compared to gas/liquid products of gasification. The higher heating value of syngas allows a more stable,





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more efficient, and energy denser combustion and thus more efficient energy production. Products of gasification are also easily used in the currently available infrastructure for power generation and transportation. Thermochemical conversion methods such as gasification and pyrolysis are industrially viable options with high throughput compared to bio-chemical conversion methods such as anaerobic digestion due to the high thermochemical reaction rates.

Thermochemical decomposition of solid biowaste starts with the decomposition of the complex and polymeric organic chains, followed by reforming of these products in the presence of the gasifying agent such as steam, air, or CO<sub>2</sub> to produce product gas that is characterized by a higher heating value than the solid biowaste. The major components of product gas are H<sub>2</sub>, CO, CO<sub>2</sub>, CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>2</sub>, and other higher series of hydrocarbons. Undesirable byproducts containing a mixture of heavy aromatic hydrocarbon residues, referred to as tar, are also formed from the escaping of the secondary reforming of cracked polymers which must be further pyrolyzed or reformed to enhance the syngas yield. The fraction of mass converted to tar is highly dependent on the heating rate, gasification media and the reactor temperature. The syngas composition is affected by the gasifying agent, temperature, feedstock composition and other reactor operational parameters under non-catalytic reaction conditions. Compositional homogeneity of the fuel produced from heterogeneous sources including chicken manure, poultry litter, biomass, solid wastes, and coal makes gasification an attractive solution with feed flexibility compared to direct combustion of these low-value heterogeneous feedstocks. Considerable studies have been carried out on biomass gasification on the catalytic effects, and thermochemical parameters such as temperature, heating rate, gasifier type and feedstock [5–20]. Eqs. (1–5) show the major representative governing reactions (considering C to represent the biomass) that occur during gasification.

Char-Oxidation : 
$$C + O_2 \Rightarrow CO_2$$
 (1)

Boudouard reaction :  $CO_2 + C \rightleftharpoons 2CO$  (2)

Water gas shift reaction :  $CO + H_2O \rightleftharpoons CO_2 + H_2$  (3)

Water gas reaction :  $C + H_2 O \rightleftharpoons CO + H_2$  (4)

Thermal cracking :  $C_n H_m \Rightarrow C^* + C_x H_v + H_2$  (5)

Chicken manure is a heterogeneous mixture of chicken droppings, waste beddings, waste food, and feathers from the coops. Chicken manure is characterized by high nitrogen, phosphorus and ash content which makes it a lower grade feed compared to conventional biomass such as wood. These differences in the constituents of chicken litter from other bio wastes motivates for investigations into the decomposition behavior of chicken litter [21]. Thermogravimetric analysis (TGA) highlighted one of the differences from other bio-wastes and coal. It was found that manure starts decomposition at lower temperatures with maximum weight loss rate observed at 370 °C [22]. TGA also showed a more complicated pyrolysis of chicken manure with three stages of weight loss, unlike woodchips pyrolysis, which occurs in two stages because of lignocellulose content. Cellulose and hemicellulose decomposition, lignin decomposition and residual char devolatilization were found to be the three stages of chicken litter decomposition. Higher manure content in the waste litter assisted in faster decomposition. Higher syngas yields at the expense of decreased liquid and char yields were obtained at higher temperatures [23]. The decarboxylation of minerals carbonates present in chicken manure ash resulted in an increase in CO<sub>2</sub> yields at temperatures above 700 °C and stabilize for temperature above 1000 °C [22]. Decomposition of protein content in chicken litter into hydrocarbons was proposed the reason for highly viscous, acidic bio-oils produced from chicken litter with heating values higher than conventional hardwood derived bio-oils [24].

High ash content constituting one-fifth of the chicken litter by weight conventionally helped in fertilizing applications. But due to large production of chicken litter, the dangers of leaching and eutrophication limits them from being used as fertilizers in traditional methods. So, phosphorous and potassium oxides as ash contents can make it an efficient fertilizer after gasification [25]. However, the issue facing gasification concerns low ash-fusion temperatures experienced due to high Ca, Na, and K components, all of which are present in chicken wastes. Unstable inorganic content interfering with gasification by decarboxylation of carbonates and the low melting points of its constituents makes it essential to consider their kinetic and physical characteristics into gasification models to be operable at high temperatures, unlike the conventional models which consider the ash content to be inert [26].

Co-gasification of chicken litter and coal was successfully demonstrated, but with no change in product gas heat content [27]. Almost equal contents of carbon and oxygen in chicken manure can theoretically make it a self-sufficient feedstock with no need of additional gasifying agent and such method was called " auto-gasification" [28]. But the same investigation also found limited carbon availability for reacting with oxygen due to inhibiting effects from the presence of other hydrocarbon and water gas reaction causing oxidation of evolved CO to form CO<sub>2</sub>. High syngas yields rich in H<sub>2</sub> were also obtained from steam gasification of chicken manure by catalytic enhancement using Ni-Al<sub>2</sub>O<sub>3</sub> as the catalyst in fluidized bed reactors at 600 °C [29]. Other unconventional gasifying techniques such as super-critical gasification were also investigated using chicken litter [30,31]. Investigative techniques used to understand biomass gasification are abundantly available in the literature, which can provide pathway into understanding the kinetics and feasibility of chicken manure as fuel production feedstock as well as the effect of gasifying parameters.

High quality syngas with high hydrogen content can be obtained using steam gasification but with a drawback of high endothermicity and long residence times [32–34]. Use of oxygen/ air is efficient in reducing reaction times and auto-thermal capability, but the need for gas separation for improved quality of syngas is expensive. Use of carbon dioxide as gasifying agent is also feasible which can help in reusing hot exhaust emissions, but the operable temperatures are the highest due to Boudouard reaction equilibrium. Comparative study on the effect of gasifying agent is essential to understand kinetics of litter gasification and help optimize the gasification process according to downstream application for better efficiency and economy. Comparison of steam and CO<sub>2</sub> on woodchips char and grapefruit skin char gasification [35,36], pyrolysis and steam on paper gasification [37] in lab scale and demonstrative studies to examine the effect of gasifying medium were carried out in the past on different types of biomass. Such lab scale studies [37] provide quantified results on the effects of gasifying agent, temperature and feedstock on the product gases that helps in the design and selection of the gasifying conditions necessary for large-scale gasifier operations. However, such studies on the gasification of chicken manure have been limited. Although TGA and STA studies on the decomposition of chicken manure in  $CO_2$ ,  $N_2$ , and air were investigated [38], the need for product gas analysis is essential to provide enhanced understanding of such research.

This present paper investigates isothermal gasification of chicken manure at temperatures ranging from 600 to 1000 °C using different gasifying media (nitrogen, air, carbon dioxide, or steam) in a laboratory scale semi-batch reactor. The evolved gas was analyzed using gas chromatography with specific focus on the evolution of product gas yield and composition. The effects of

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