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I am submitting herewith a thesis written by Bratendu Bagchi entitled “Investigation of nitrogen and phosphorus bearing species in steam gasification of poultry litter”. I have examined the electronic copy of this thesis for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Chemical Engineering.

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(Original signatures are on file with official student records)

INVESTIGATION OF NITROGEN AND PHOSPHORUS BEARING SPECIES IN STEAM GASIFICATION OF POULTRY LITTER

A Thesis Presented for the Master of Science Degree

The University of Tennessee, Knoxville

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Abstract

The production of broiler chickens has become one of the largest sectors in United States agriculture and the growing demand for poultry has led to an annual production growth rate of five percent. Over 70 percent of the production can be traced to the Southeastern United States. With increased demand for poultry, poultry litter management has become a major challenge in the agriculture industry and for the United States Department of Agriculture.

One of the options being considered for chicken litter management is steam gasification of the litter. Detailed study and research of this option has already been carried out at the University of Tennessee Space Institute. Although the steam gasification method has been accepted as a possible and feasible method for litter management, apprehension has been expressed at various forums about the liberation of nitrogen and phosphorus containing species along with the fuel gas and/or the final residue. The possible liberation of phosphorus as phosphine gas with the fuel gas will have an adverse impact on the environment and would pose an unacceptable feature of the steam gasification of litter. Possible liberation of ammonia from the nitrogen containing species is also not acceptable, unless means are developed to capture or control it. Hence, the present study was conducted to study the fate and the environmental impact of the nitrogen and phosphorus containing species released during steam gasification of the poultry litter.

From various preliminary tests carried out with poultry litter, it was concluded that most of the phosphorus remained in the residue and the nitrogen ended up as ammonia in the fuel gas. The effects of temperature and catalyst loading on ammonia liberation were studied in a muffled furnace setup, where the pressure was atmospheric under all the experimental conditions. The ammonia liberated was collected in a scrubbing solution containing dilute hydrochloric acid. The unreacted excess HCl solution was titrated with a caustic solution to indicate the amount of ammonia that had reacted with acid under various experimental conditions.

The amount of ammonia liberation was found to decrease with an increase in temperature during pyrolysis and gasification. It also decreased with an increase in additional catalyst loading. Additional testing was then carried out in a high-pressure fixed bed reactor to determine the preliminary kinetics of the ammonia liberation reaction.

The specific liberation rate measured in the differential fixed bed reactor was then used to design a scrubbing system and to revise (as necessary) the economic feasibility study of chicken litter gasification already performed earlier at UTSI.

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List of Symbols

[N]	Moles of Nitrogen or Molar Concentration of Nitrogen in Litter Sample
X_N	Fractional Nitrogen Conversion on a Molar Basis
k	1^{st} order Rate Constant, Min^{-1}
P_{N2}	Partial Pressure of Nitrogen, Atm
P_{H2}	Partial Pressure of Hydrogen, Atm
P_{NH3}	Partial Pressure of Ammonia, Atm
K_p	Equilibrium Rate Constant, Atm^{-2}
P	Total Pressure, Atm

Chapter I

Introduction

Definition of Problem

The production of broiler chickens has become one of the largest sectors in the United States' agriculture. In 1996, the production of broiler chickens reached approximately 7.6 billion head. The growing demand for poultry has led to an annual growth rate of five percent in production. Over 70 percent of the production can be traced to the Southeastern United States. With the increased demand of poultry and poultry products, waste disposal and management have become major challenges in the agricultural industry. Over five million tons of manure is produced in the Southeastern United States. Although the Southeastern United States produces over 70 percent of the broiler production, the region has fewer than 20 percent of the total farmland available to spread litter as fertilizer.

To take care of the serious problem the poultry litter management poses to the environment, research is going on at UTSI. In past studies, it was demonstrated that steam gasification of the litter is a technically and economically feasible alternative to its disposal. The gasification process generates a fuel gas that can be used as an energy source. However, concern has been raised about the formation of nitrogen and phosphorus bearing compounds in the gasified fuel gas, which may cause environmental hazard if not controlled and left untreated. The gray area now in scientific knowledge is what happens to the nitrogen and phosphorus containing species present in the poultry

litter during gasification. It is a matter of concern particularly because if phosphorus is released as phosphine during steam gasification, then this process will need several modifications to take care of the phosphine before the gas can be used as a source of energy or chemical feed stock. The case is the same with nitrogen. If the nitrogen is released as NO_x or ammonia, it needs to be taken care of to meet existing emission standards.

Hence, an investigation of the fate of nitrogen and phosphorus containing species during poultry litter gasification has become imperative to ensure that the steam gasification process is feasible even if additional cost is incurred in taking care of these undesirable species. The aim of this work and thesis is to investigate these issues and to suggest a suitable solution to any technical problems that may arise.

Gasification of Biomass

The similar carbonaceous character of biomass and coal has allowed processes originally developed for coals to be applied to biomass. Gasification is one such process. Depending on the gasification medium and the reactor flow regime the gasification process generates Low Energy Gas (LEG), Medium Energy Gas (MEG) or High Energy Gas (HEG). Low Energy Gas is a mixture of carbon monoxide, hydrogen and other gases. The heating values of Low Energy Gas range from 150 to 300 Btu/scf. Medium Energy Gas is a mixture of methane, carbon monoxide, hydrogen and other gases with a heating value ranging from 300 to 700 Btu/scf. High Energy Gas is composed predominantly of methane with a heating value ranging from 900 Btu/scf to 1000 Btu/scf.

Gasification medium causes the gasification of coal or biomass to occur. There are four gasification mediums commonly used in gasification. These are air, oxygen, steam and hydrogen. A separate category of gasifiers termed pyrolytic gasifiers utilizes no gasification medium. Air-blown gasification produces a low energy gas because it is diluted by large quantities of nitrogen. Oxygen-blown gasifiers are equivalently simple but produce a medium energy gas. The higher heating value is due to the absence of nitrogen. Gasifiers operating with oxygen can achieve a greater fuel throughput as well. Steam gasification also produces a medium energy gas. Since no combustion can occur in the reactor, heat must be supplied indirectly from an external source. The superheated steam introduced to the reactor provides a portion of the heat and also participates in the gasification reactions. Hydrogasification utilizes a hydrogen-rich atmosphere and fine particulate feedstocks to produce a high energy gas rich in methane. The process requires high pressures and a suitable gasification catalyst. Pyrolytic gasifiers use heat to effect gasification without a gasification medium. The process proceeds by thermal decomposition of the feedstock. The process requires high heating rates and rapid quenching of the product gases to inhibit secondary reactions. The product of steam gasification of biomass is a medium energy gas composed of carbon monoxide, hydrogen, methane, and other hydrocarbons. There are three reactor flow regimes which dominate the area of biomass gasification. They are updraft fixed bed gasifier, the downdraft fixed bed gasifier, and the fluidized bed gasifier. In fixed bed gasifiers, plugs of the raw biomass fuel are usually gravity-fed through the gasifier. Since the reactor operates in this manner, it can contain separate reaction zones for drying, pyrolysis, reduction, and combustion. In updraft gasifiers, the gasification medium flows

countercurrent to the fuel flow. These gasifiers can accommodate fuels with moisture contents as high as 30 to 50 percent, high ash contents, and relatively large fines contents. The product gas exits the reactor with a high tar and condensable aqueous content, but is usually low in particulates. Problems associated with updraft fixed bed gasifiers include channeling and tar condensation in the upper reactor. In downdraft gasifiers, all gases must pass co-current to the fuel flow. A throat or constriction is generally designed into the gasifier. In a combustion zone near the throat, tar and oil components from the upper reactor gasification zone are thermally cracked. The primary contaminants in the product gas generated by downdraft gasifiers are ash and char particulate. Unlike the updraft gasifier, downdraft gasifiers require a relatively low moisture content and fuel of relatively large particle size. The principal problems in downdraft gasifiers are primarily related to fuel quality. They include bridging in the upper reactor, slagging from high ash content, bed plugging from high fines content, and poor gas quality due to excessive fuel moisture. Unlike fixed beds, the flow pattern in a fluidized bed reactor is much less predictable. Most fluidized beds utilize an inert granular bed such as hot silica sand. Upon fluidization, the bed expands and experiences intense bubbling and mixing. Rapid heating provided by the hot silica particles dries, pyrolyzes, and gasifies biomass particles as they circulate. In addition to high heat transfer rates, the fluidization provides a relatively uniform bed temperature. The primary advantage offerred by a fluidized bed gasifier is its compatibility with low quality fuels. A fluidized bed reactor can accommodate a wide range of particle sizes, high ash contents, and high moisture feedstocks. Unfortunately, the automated control systems required to operate a fluidized bed reactor make small units uneconomical.

Catalytic Steam Gasification of Biomass

The application of the catalytic steam gasification concept to biomass is a relatively new area of research. In determining the optimum conditions to handle the broiler litter, the catalytic steam gasification of the broiler litter was carried out using K_2CO_3 and langbeinite as the catalysts by Turner (4). Langbeinite is an inexpensive mineral used in the fertilizer industry. It contains potassium and magnesium sulfate, and it comes in a crystalline form. The chemical formula of langbeinite is $K_2Mg_2(SO_4)_3$. Since, langbeinite is an inexpensive material and readily available, at present all gasification experiments to determine the fate of nitrogen and phosphorus will be done with langbeinite as the catalyst. Catalytic steam gasification has received serious attention because of its potential for high carbon conversion at relatively moderate operating conditions particularly in terms of temperature. The alkali salt or its combination used as a catalyst helps in lowering the reaction temperature. The method of catalytic gasification is explained in chapter IV. The key reactions taking place during this process were explained by Turner (4), and are reproduced as follows:

Steam-carbon reaction	$C + H_2O$	$\longrightarrow$	$CO + H_2$
Steam-carbon reaction	$C + 2H_2O$	$\longrightarrow$	$CO_2 + 2H_2$
Water-gas shift reaction	$CO + H_2O$	$\longrightarrow$	$CO_2 + 2H_2$
Methanation reaction	$CO + 3H_2$	$\longrightarrow$	$CH_4 + H_2O$
Hydrogasification reaction	$C + 2H_2$	$\longrightarrow$	CH_4
Boudouard reaction	$C + CO_2$	$\longrightarrow$	$2CO$

Chapter II

Literature Review

The intensive production of poultry (billions of chickens annually in the United States) has increased the generation of chicken litter and aggravated the waste disposal problem. Currently, the litter is being used either as fertilizer or just being piled up by poultry houses all around the country. These inefficient methods are inadequate to meet environmental standards. So, among the technologies that are being considered for waste management are combustion, gasification, co-firing and anaerobic digestion. For example, catalytic steam gasification of coal is an established and proven technology. Its modification (on a laboratory scale) to apply to poultry litter gasification had been considered by UTSI and MTCI(3). This process has been conceptualized for poultry litter to maximize profit while minimizing environmental impact caused by odor, water pollution, greenhouse gases, antibiotic and pathogen release (4).

Existing shortcomings of the treatment options currently being considered for chicken litter provide a great opportunity for the application of steam gasification to manage and utilize the litter in a more efficient, cost-effective, and environmentally beneficial manner. To make the process of steam gasification of biomass more environmentally feasible, we must know the fate of nitrogen and phosphorus containing species in the biomass (poultry litter in our case). Our basic knowledge of this topic is limited. Considering that most of the thermal coal gasification processes require partially oxidizing environment using air or oxygen. The main concern with coal gasification has

been on controlling NO_x emission. The case is entirely different in the case of steam gasification, which is a reducing environment unlike thermal gasification of coal.

However, the situation is different when pyrolysis of coal is carried out to produce coke. As per "Pollution Prevention and Abatement Handbook" of World Bank Group (1), 0.1 kg of ammonia is produced for every ton of coke produced. Moreover, 1.4 kg of NO_x is also produced with every ton of coke. The oxygen required for the NO_x may be obtained intrinsically from the coal. This suggests that coke manufacturing process yields both ammonia and NO_x.

As per Environmental Protection Agency's compilation (2), ammonium sulphate is produced in many places as a byproduct of coke oven plants. This means that an appreciable quantity of ammonia is released during the process that can be economically recovered as ammonium sulphate.

While no detailed study has been done on the fate of nitrogen containing species during steam gasification of coal (reducing environment), a study was performed by Manufacturing and Technology Conversion International, Inc. (3), under a grant from the U.S. Department of Energy's Small Business Innovation Program to develop a bio-waste and steam gasification (referred to as steam reforming by MTCI) based power system. The specific objectives of that research were to:

- Perform feedstock characterization tests and optimize the process of gasification of chicken litter

- Conduct market and resource assessment
- Carry out a preliminary integrated system design
- Estimate cost, and
- Perform technical, environmental and economic assessments

As part of the environmental assessments study, they studied the environmental impact of the nitrogen and phosphorus containing species present in poultry litter. A small laboratory-scale steam gasification system was designed, fabricated and assembled. It was comprised of a steam generation subsystem, an electrically heated fluid bed, a screw feed subsystem, particulate filters and a gas analysis subsystem. The objective of the feedstock characterization tests was to evaluate the performance and operability of the steam gasification system for processing poultry manure. The gasification was carried out in a fluidized bed of magnesium oxide. At UTSI, langbeinite was used as a catalyst for fixed bed steam gasification, which was the major difference in the experimental setup between UTSI and MTCI. Detection measurement for phosphine was carried out, since phosphine was the main concern because of the phosphorus content in the litter. Two MTI Model M-200 gas chromatographs (GCs) were used for detailed quantitative analysis of the steam gasification product gases. Representative solid samples and condensate were collected and samples were sent to a commercial laboratory for analyses. The feedstock characterization tests with poultry manure were performed at three different fluidized bed temperatures: 1,100 ^{0}F (593 ^{0}C); 1,300 ^{0}F (704 ^{0}C); and 1,500 ^{0}F (816 ^{0}C). Phosphine was not detected in the product gas during these tests. The carbon conversion improved with bed temperature, which was also demonstrated by

Turner at UTSI in his fixed bed experiments (4). The product gas composition found out by MTCI is shown in Table 2.1.

Apart from the above, MTCI detected Volatile Organic Compounds (VOC) and Semi-Volatile Organic Compounds (SVOC) to the tune of 0.146 mg/g of dry feed and 3.48 mg/g of dry feed respectively. The chief constituents in the VOC were acetone, acrylonitrile, benzene, toluene and that in the SVOC were phenol, naphthalene, fluorine, Acenphthene and phenanthrene. From the results of the gas composition of MTCI, it is clear that the nitrogen in the litter was mainly converted into ammonia. The results of MTCI's experiments indicated that the fluidized bed gasification should operate at about $1,500^0$F (816^0C) for maximum carbon conversion to fuel gas.

According to Alabama Cooperative Extension System (11), ammonia (NH_3) is produced in animal manure by the breakdown of urea and in poultry manure by the breakdown of uric acid. Since ammonia is unchanged, it can be emitted as a gas.

In the final report of Antares Group (5) prepared for Northeast Regional Biomass Program (on the Lower Delmarva Peninsula), the environmental concerns related to the residue and the NO_x are expressed. The concern for NO_x is due to the fact that thermal gasification of biomass usually takes place in the presence of air. The report says, energy conversion offers a means of concentrating phosphorus and potassium in a form that can be removed from the Delmarva ecosystem and transported easily to other locations for use as fertilizer. Table 2.2 shows the concentrations of the major residue constituents in

Table 2.1: Product Gas Composition from MTCI's Experiment (3)

Component	Volume, %
Hydrogen	53.46
Methane	5.96
Carbon Monoxide	5.92
Carbon Dioxide	27.56
Ethylene	3.24
Ethane	0.13
Acetylene	0.15
Hydrogen Sulfide	0.27
Propylene	0
Propane	0
Ammonia	3.15
Hydrogen Chloride	0.16

Table 2.2 : Major Constituents in Chicken Feed and Litter (5)

Constituent	Feed, lb/ton	Feed, wt%	Litter lb/ton	Litter, wt%	lb/ MMBtu	Sources
Nitrogen	75	3.8%	53.4	2.7	4.2	soy, corn, fish, alfalfa
Phosphorus	12	0.6%	33.5	1.7	2.6	soy, corn, phosphate
Potassium	12	0.6%	117.9	5.9	9.2	soy, fish, alfalfa
Sodium	5	0.3%	121.2	6.1	9.5	salt, soy,
Chlorine	6	0.3%	14.0	0.7	1.1	salt, soy, alfalfa
Sulfur	4	0.2%	6.7	0.3	0.5	soy, corn, fish, alfalfa

the feed and litter and their typical sources. Feed modification has been suggested as a means of reducing the nutrient excretion and thereby improving the manure and litter for land application and combustion. The phytase treatment of corn, for example, will change the form of the phosphorus available in the litter for plants but is not likely to improve the impact of phosphorus on combustion equipment. Feed modification will not reduce the concentrations of these elements in the litter or reduce their impact on energy conversion equipment. From the Table 2.2, it is evident that nitrogen and phosphorus are present in a significant proportion. The nitrogen will have the tendency to form oxides (NO_x) during combustion. Oxides of nitrogen are comprised mostly of two compounds, nitric oxide (NO) and nitrogen dioxide (NO_2). Both are formed in the combustion process. Most flue gas contains higher concentrations of NO than NO_2. They react chemically when they are emitted in the atmosphere. Nitrogen can come from the fuel or the combustion air.

A portion of atmospheric nitrogen can oxidize if combustion temperature reaches 2600^0F or higher, as in co-firing. The latter is referred to as thermal NO_x and can be controlled by modifying the combustion process. Nitrogen oxide emissions from poultry litter combustion are very high when compared to fossil fuels because of the higher percentage of nitrogen in the litter. The combustion temperatures for litter firing are typically lower than that for the fossil fuels ($<2600^0$F) and as a result a minimal amount of thermal NO_x is formed from the nitrogen in the air.

According to Antares (5), nitric oxide emissions are strongly dependent on combustion-zone oxygen concentration and the nitrogen content of the biomass fuel. Nitric oxide

emission increases dramatically with increase in excess air and fuel nitrogen. Nitrogen in the litter is very high compared to clean woody biomass fuels. Fuel bound nitrogen must be converted to N_2 or it will convert directly to NO_x emissions. NO_x formation should be highest in co-firing applications where the high nitrogen fuel reacts at high temperatures, forming additional thermal NO_x. Suspension burners can also generate high NO_x levels. Low NO_x suspension burners with staged combustion and flue gas recirculation have not been tested at an industrial scale with poultry litter. Poultry litter characteristics show significant potential for increasing NO_x emissions. Fuels that contain approximately 3% nitrogen, or more than 6 lb fuel N/ million Btu, have significant NO_x potential. Much of this nitrogen exists as free ammonia, which generates NO_x when introduced into an oxidizing environment at temperatures of 2500^0F - 2750^0F, common for utility boilers fired with either coal or oil. Tests of gasification systems, with effectively severe combustion staging, have shown some success in managing NO_x (5). Since the second or higher stage of a combustor will be typically maintained at 1800 ^{0}F, emissions from the thermal gasifier will have NO_x emissions, which will require gas cleaning techniques. The gasification system adopted by UTSI will be at much lower temperature (typically 1300 ^{0}F) than the thermal gasification. Moreover at UTSI, the gasification will take place in absence of air / nitrogen and in a reducing atmosphere. At the given temperature and condition, the possibility of NO_x formation is very low or non-existent. Most of the nitrogen is anticipated to be liberated as ammonia.

According to the report on Delmarva Peninsula (5), gasifiers can reduce NO_x formation through staged combustion to convert a high percentage of the fuel (litter) nitrogen to N_2

in reducing conditions. A rotary kiln gasifier (5) achieves 0.18 lb NO_x / MMBTU in a staged combustor, much less than the typical control levels of 0.6 lb NO_x / MMBTU. These levels were also achieved with high (8 wt%) nitrogen sewage sludge in a fluidized bed gasifier in California (5). Small scale gasification and pyrolysis system manufacturers like Thermogenics and Brightstar, intend to cool and quench combustible gases so that particulate chemicals can be recovered in an electrostatic precipitator, which is being tested in detail (5). Phosphorus in the form of P_2O_5 typically makes up 4 wt% of the litter as fired (5). In combustion it reacts to form other phosphates that adhere to boiler walls. In gasification and combustion it forms phosphoric acid that will condense in the cold economizers, causing corrosion (5). Phosphates are hard deposits that are difficult to remove. The first plant in England to fire poultry litter reported severe problems with phosphate deposits that were similar to the experience of almond processors in California (5). In England, the Fibrowatt built power plants depend on collecting large quantities of phosphorus and potassium as deposits on waterwalls for recovery and sale as a major constituent in their "fiberphos" fertilizer product (N-P_2O_5-K_2O of 0-24-14) (5).

So, from the above it is clear that some of the phosphorus in the residue may end up as phosphate deposits if it gets adequate moisture from the steam when the system cools down to near ambient temperature. At the gasification temperature (1300^0F), the phosphorus will remain as P_2O_5 in the residue. The residue should not be allowed to collect on any equipment at lower temperature. As far as nitrogen is concerned, it will be liberated as gas.

Chapter III

Theoretical Discussion

Reaction Mechanisms for Nitrogen and Phosphorus Liberation from Carbon, Hydrogen Containing Material

Nitrogen makes up about 2 to 3% of the litter composition. The steam gasification of poultry litter is carried out in the absence of air. The gasification is usually carried out at temperature between 1100 – 1400 ^{0}F. At these conditions the possibility of NO_x formation is nil. Hence, it is assumed by us based on the literature review that the nitrogen released will be mostly in the form of ammonia. This has also been confirmed by MTCI's report (3). Also the pollution prevention handbook of World Bank Group (1) indicates that the process of pyrolysis of coal produces ammonia. The EPA compilation (2) indicates that one of the viable method of producing ammonium sulphate is by absorbing ammonia from coke oven gas. Coke oven gas is produced when pyrolysis of coal is carried out in the coke oven. The conditions for steam gasification of poultry litter are similar to the pyrolysis of coal in the sense that both processes are carried out in an oxygen starved atmosphere. As shown later on in chapter V, a considerable amount of nitrogen is released during pyrolysis / gasification of the chicken litter. It can be argued that it is released as nitric acid or potassium nitrate. To prove that no nitrogen is released as nitric acid, one experiment was carried out with just water as the absorbing solution and the pH was observed to go up due to the formation of aqua ammonia. If nitric acid had formed, then the pH would have gone down. Secondly, most of the potassium remained in the solid residue formed after gasification ruling out the formation of

potassium nitrate. All of the above and the literature review indicate that the nitrogen in the litter is released most likely as ammonia.

Before going into the details of ammonia liberation and fate of phosphorus in the litter, it is necessary to present the composition of poultry litter. Table 3.1 indicates the typical composition of the chicken litter obtained from various sources.

Phosphorous (as P_2O_5) makes up 2 – 4 % of the litter. The vapor pressure of P_2O_5 is extremely low, even at high temperature. As per Figure 3.1 (vapor – liquid phase diagram for H_2O - P_2O_5 system (6)), at P_2O_5 concentration below 30% in the phosphoric acid solution, there will not be any P_2O_5 vapor in the gas. This explains why the phosphorus (as P_2O_5) in MTCI's experiments remains mostly in the residue or gets deposited as solid deposits in the downstream equipments.

At various levels, concern has been raised about the possibility of release of phosphine gas (PH_3). Glindemann (10) explained that the elemental metals present in the crust of the earth indicate strong reduction conditions and are capable of reducing phosphate to phosphides and that most of the phosphorus naturally exist as phosphides. These phosphides in the presence of mineral acid like sulphuric acid releases phosphine. In the case of steam gasification, these phosphides will not come in contact with mineral acid. MTCI (3) had confirmed that there was no phosphine or phosphorus containing species in the gas from the steam gasification of poultry litter. MTCI had procured safety equipments and detection systems to detect even traces of phosphine. According to them,

Table 3.1: Composition of Chicken Litter (as received), Weight %

Constituent	MTCI (3)	Antares group (5)	UTSI (9)
Moisture	17.7	27.4	28.5
Carbon	25.93	27.22	NM
Hydrogen	3.62	3.72	NM
Nitrogen	2.59	2.69	2.72**
Sulfur	0.48	0.33	0.1
Potassium	NM	NM	2.37**
Phosphorus	NM	NM	1.87**
Ash	30.06	15.7	14.5
Oxygen	19.62	23.10	NM
Chlorine	0.88	0.71	0.74**

*NM – not measured

** - Constituents were analysed by Galbraith (13) as part of this study (thesis)

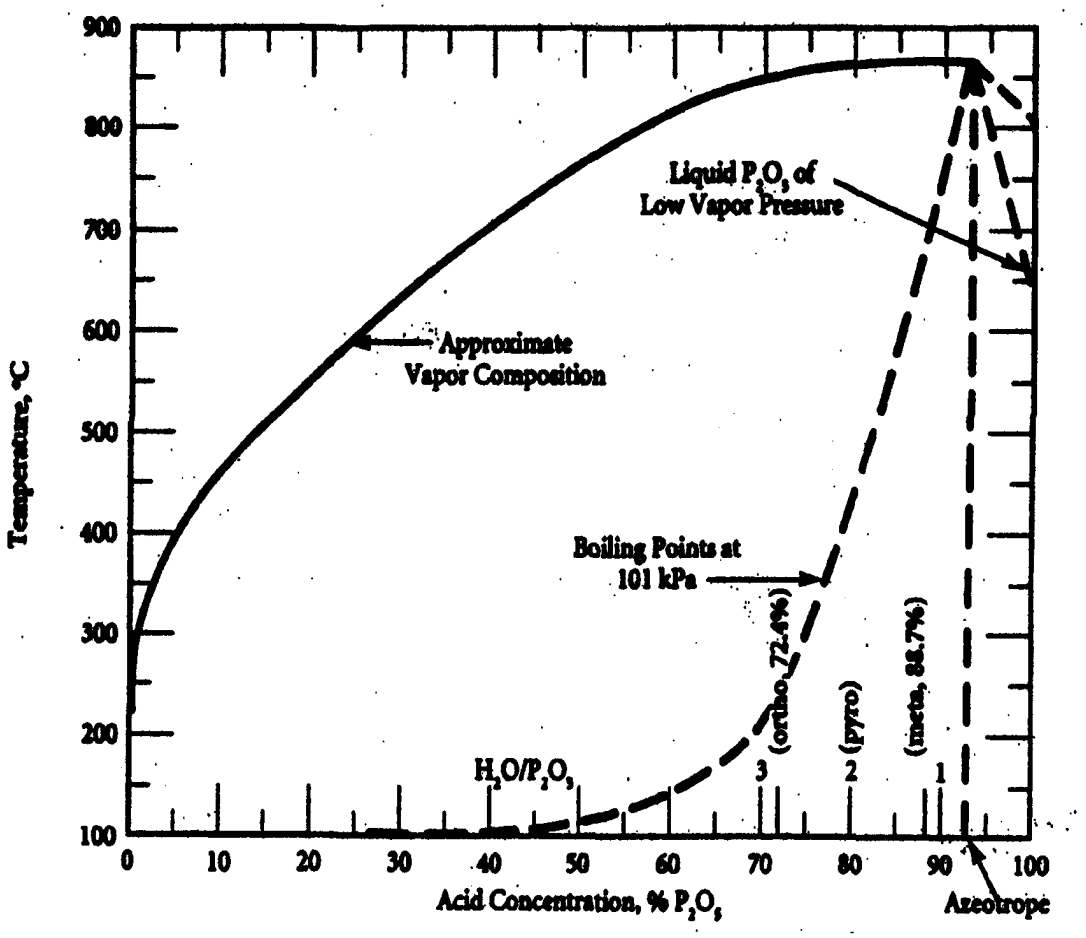

Figure 3.1: Vapor-Liquid Phase Diagram for H_2O-P_2O_5 System (6)

Based on information in Brown and Whitt, Ind. and Engr. Chem, Vol. 44, (1952), p. 615.

only faint stains of phosphine were found at temperature of less than 1100^0F. At temperature above 1100^0F, the detector tubes were clean with no trace of phosphine.

Based on the above, it was assumed that under our steam gasification conditions no phosphorus component will be present in the gas liberated during gasification.

Thermodynamics of Ammonia Liberation

As mentioned earlier, phosphorus will remain in the litter residue or will be recovered as phosphate deposit. So, nitrogen only will be considered in thermodynamic and kinetic study.

The two factors that will have a pronounced effect on the release of ammonia are temperature and percent additional catalyst in the litter. The catalyst which was used in our experiments was langbeinite ($K_2Mg_2(SO_4)_3$). Both langbeinite and potassium carbonate as a catalyst were studied in the past by UTSI. Since langbeinite is a cheap and readily available material, we selected it currently for the study of the fate of nitrogen and phosphorus. The amount and method of catalyst feeding is discussed in the Chapter IV. The effect of gasification pressure on the carbon conversion and the specific rate of gasification were studied earlier and found to have little or no effect in the 50 – 300 psig range studied (4). Hence, going by that result the effect of pressure was not considered to be a major factor on the release of ammonia during steam gasification.

The basic reaction for the manufacture of ammonia commercially is as denoted below;

$$N_2\,(g) + 3H_2\,(g) \underset{100 \text{ atmosphere, } 500^0C}{\overset{\text{Iron catalyst}}{\rightleftharpoons}} 2NH_3\,(g)$$

The above reaction takes place in a bed of catalyst through which the stoichiometric amount of nitrogen and hydrogen is circulated. The temperature and pressure conditions shown above for ammonia manufacture are typical and may vary depending on the technology used. As denoted above, the reaction is reversible. Table 3.2 lists the values of equilibrium constant K_p for ammonia synthesis with the corresponding temperature (7). The values of K_p are derived from the JANAF tables (7). The values listed in the JANAF table are at 1 atmosphere total pressure. We know for the above reaction,

$$K_P = \frac{P^2_{NH3}}{P_{N2} * P^3_{H2}}$$

As indicated in the Table 3.2, the equilibrium constant (K_P) decreases as the temperature increases. This means that as the temperature increases the amount of ammonia liberation will keep on decreasing and the amount of nitrogen and hydrogen liberation will keep increasing, i.e., the equilibrium shifts towards left following the backward reaction. The ammonia liberation from litter gasification versus temperature was studied in detail and is discussed in the chapter 5. Gasification data show that gasification rate and the composition of the gasified product are greatly influenced by the catalyst loading on the litter during gasification (4). So, it is considered that the rate of reaction of the fuel bound nitrogen with the available hydrogen (from the litter or externally from steam gasification) and the amount of ammonia released will also depend on the loading of the additional catalyst. The catalyst itself is in powdered form and is physically mixed with the chicken litter before pyrolysis / gasification.

Table 3.2 : Equilibrium Constant (K_p) versus Temperature (K) at 1 Atm Pressure

Sl No.	Temperature (K)	Equilibrium Constant (K_p), atm^{-2}
1	500	0.606
2	600	0.251
3	700	0.132
4	800	0.08
5	900	0.054
6	1000	0.04

Kinetics of Ammonia Liberation

The established process of ammonia manufacturing is by reacting nitrogen with hydrogen as shown previously. The temperature and pressure for the reaction in our case were 700^0C and 100 psig respectively. The catalyst in our case was langbeinite, which is the catalyst for the steam gasification. The net rate of ammonia liberation in our case will depend on :

a) The rate at which nitrogen is released from the solid phase in the litter to the gaseous phase as nitrogen gas, i.e.,

   $2\,(N\text{-}X)_{solid} \longrightarrow N_2\,(g) + X_2\,(s)$

   Where, N-X is the solid compound of nitrogen present in the litter. The solid compound may be acrylonitrile, potassium nitrate, potassium or hydrogen cyanide, uric acid, etc. These compounds of nitrogen are generally found in wood, saw dust and poultry litter.

b) The rate at which the ammonia liberation proceeds in the forward direction , i.e.,

N_2 (g) + $3H_2$ (g) $\longrightarrow$ $2NH_3$ (g)

c) The rate at which it disintegrates back into nitrogen and hydrogen, i.e.,

$2NH_3$ (g) $\longrightarrow$ N_2 (g) + $3H_2$ (g)

d) The rate at which the liberated ammonia diffuses into the aqueous phase of dilute hydrochloric acid solution used as absorbing medium.

e) Finally the rate at which the diffused ammonia is chemically absorbed in dilute hydrochloric acid solution, i.e.,

NH_3 (g) + HCl (aq.) $\longrightarrow$ NH_4Cl (aq.)

The nitrogen consumption in the chicken litter with time is discussed in Chapter V. The overall or net rate of ammonia liberation was first modeled as a first order expression in order to have a simplified approach. The applicability of this simple model is discussed in Chapter V.

So, assuming the net rate is dependant on the concentration of the nitrogen containing species in the litter at a given reaction temperature.

i.e.,

$-r_N$ (rate of consumption of nitrogen)= k * [N-X]

where,

$-r_N$ = d[N-X]/dt

[N-X] = concentration of nitrogen containing species at any given time in litter

k = 1^{st} order rate constant

Now, concentration of nitrogen containing species is effectively the concentration of the nitrogen (as atomic nitrogen) in the litter.

Hence, [N-X] = [N]

The nitrogen present in litter at any time t is computed by integrating the above equation.

$$-r_N = d[N]/dt = k * [N]$$

on integration gives,

$$\ln([N] / [N_0] = - k * t$$

where, $[N_0]$ is initial concentration of nitrogen in litter

Now, $X_N = \dfrac{[N_0] - [N]}{[N_0]}$, which gives

$$1 - X_N = [N] / [N_0]$$

Therefore,

$$-\ln(1-X_N) = k * t \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (3.1)$$

where,

X_N = conversion

= (Number of moles of nitrogen initially present in the litter - Number of moles of nitrogen at time t) / Number of moles of nitrogen initially present in the litter

If the overall rate is first order then on plotting , $-\ln(1-X_N)$ versus t, we will get a straight line. The slope of the line would then give the rate constant k for the overall ammonia release. The validity of this model will be tested in chapter V.

Chapter IV

Experimental Procedure

Analysis of Broiler Litter, Residue and Absorbing Solution

The first stage in the experimental program was the determination of the various constituent elements present in the broiler litter and residue. The residue henceforth is referred to as the solid mass left over after pyrolysis / gasification of the litter. The nitrogen, phosphorus and total chlorides in the absorbing solution were also analyzed and determined.

Galbraith Laboratories (13) determined the nitrogen, phosphorus, total chlorides and potassium in the litter and two particular samples of the residue. They also determined nitrogen, phosphorus and total chlorides present in two particular samples of absorbing solution of hydrochloric acid, described below. The material balance was performed on nitrogen, phosphorus, and chlorides to see how much of each element was released during pyrolysis and gasification of the litter. The residue samples were analyzed for all the above elements both after pyrolysis and gasification (one sample in each case).

The absorbing solution, which was dilute hydrochloric acid solution of known strength, was titrated against dilute caustic soda solution both before starting the experiment and after the experiment was terminated. The sample volume of the absorbing solution used for titration in each case was 10 ml. However, the volume of the absorbing solution was typically 200ml to start with but it increases during gasification due to condensation of

unreacted steam. This increase in volume of the absorbing solution was accounted for while calculating ammonia absorbed in the solution. The difference in the caustic soda requirement for titration in the two cases gave the amount of hydrochloric acid that would have reacted with the ammonia released during pyrolysis / gasification experiment. It should be noted here that chloride is released from the chicken litter as hydrogen chloride gas and then absorbed as hydrochloric acid. However, the amount of hydrogen chloride liberated is too low and hence neglected in the titration calculation.

The calculation procedure is as follows;

The titration reaction is;

$$NaOH + HCl \longrightarrow NaCl + H_2O$$

Since, N(normality of solution) * V (volume of solution) = constant

But, for the above chemical reaction, normality of the solution will be same as the molarity of the solution.

Hence, M(molarity of solution) * V (volume of solution) = constant

M_1 = Molarity of the starting solution of hydrochloric acid (known)

Then, if v_2 (ml) = volume of NaOH required to neutralize volume v_1 (ml, typically 5 or 10 ml) of starting solution of hydrochloric acid of known strength (molarity M_1)

Then,

M_2 = Molarity of the given caustic solution = $\dfrac{M_1 * v_1}{v_2}$ ……(3.1)

From the above, m_1 = Gram-Moles of HCl in the starting scrubbing solution = $M_1 * V_1$. ……(3.2)

where, V_1 = Volume of starting scrubbing solution of HCl (typically 200ml)

If, v_3 (ml) = volume of NaOH of Molarity M_2, calculated before, is required to neutralize known volume v_4 (ml, typically 5 or 10 ml) of final scrubbing liquor solution of hydrochloric acid,

Then,

M_4 = Molarity of the final scrubbing solution = $\dfrac{M_2 * v_3}{v_4}$

m_2 = Gram-Moles of HCl in the final scrubbing solution

$= M_4 * V_2$ ……(3.3)

where, V_2 = Volume of the final scrubbing solution (typically 250 ml)

Final volume of the absorbing solution may vary and depends on the amount of unreacted steam that condenses in each case.

Since, as per the reaction of ammonia with hydrochloric acid, 1 mole of ammonia reacts with 1 mole of hydrochloric acid as follows;

NH_3 (g) + HCl (aq.) $\longrightarrow$ NH_4Cl (aq.)

Therefore, gram moles of ammonia reacting with HCl = gram moles of HCl reacting = $(m_1 - m_2)$

From equations 3.1,3.2 and 3.3,

Gram moles of ammonia reacting = $M_1 [V_1 – \{V_2 * (v_1 * v_3)/ (v_2 * v_4)\}]$

In case of pyrolysis, when $V_1 = V_2$,

Gram moles of ammonia reacting = $M_1 * V_1 [1 - (v_1 * v_3)/ (v_2 * v_4)]$

The above-described procedure will give the total amount of ammonia liberated from the given amount of chicken litter taken for pyrolysis or gasification as the case may be. The

amount of chicken litter taken for each experimental run was typically 10.5 g. The actual amount of ammonia released for a particular case can be calculated by doing material balance from the result of the analysis of the litter and the residue furnished by Galbraith Laboratories (Table 5.1). On comparing the actual amount of ammonia or nitrogen released with the experimental amount calculated by the above method, the results were found to be close. Some typical calculations are enclosed in the following chapter.

No calculation procedure for phosphorus evolution was necessary, as the result from the Galbraith analysis suggested that most of the phosphorus was still remaining in the residue.

Pyrolysis of Broiler Litter

The primary gasification of carbonaceous compounds generates both char and volatiles. In a bench-scale fixed-bed apparatus, products from this pyrolysis process may interfere with the subsequent secondary gasification of fixed carbon. For example, tars and oils, which come out as volatiles at pyrolysis temperatures, may condense at lower temperatures. These compounds may then foul the apparatus or even interfere with operating procedures. For this reason, the production of char was performed in a Barnstead Thermolyne - Model F48015 muffle furnace at atmospheric pressure. A few gasification experiments (explained in next chapter) were also performed in this muffle furnace setup. The schematic of the muffle furnace is enclosed as Figure 4.1. The muffle furnace housed a cylindrical stainless steel container to maintain a completely inert atmosphere during pyrolysis. The container had a heavy lid, which had an inlet for the

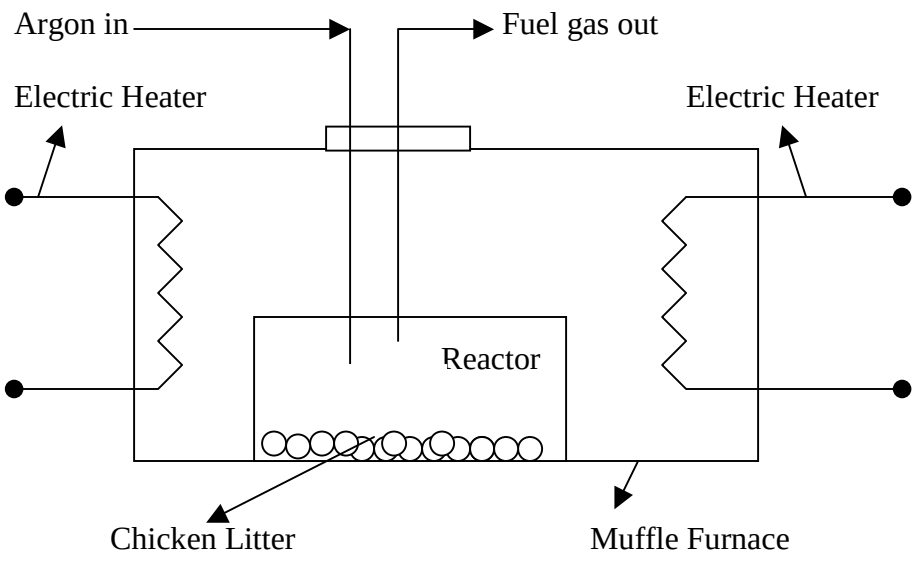

Figure 4.1: Schematic of Muffle Furnace

inert gas (argon) and an outlet for the volatiles and tar to escape. The reactor meant for pyrolysing or gasifying the litter is placed in the furnace and is heated electrically by means of electric coils on the side of the furnace. Tests were performed before the commencement of each experiment to ensure that there were no leaks in or around the reactor. These leak tests were performed before any pyrolysis or gasification experiment to ensure the results were as accurate as possible under the most ideal conditions. To make it leak proof the reactor was sealed with glass wool. Equipment was also regularly maintained and cleaned to make sure that the most accurate results were obtained for each run. A schematic of the muffle furnace and the associated equipments is shown in Figure 4.2. Approximately 10 gram sample of the litter was used for every pyrolysis run and the reactor volume was purged with argon during the run. The muffle furnace was then set to the desired temperature. The reactor was continuously purged with the inert gas to help remove the volatiles from the container. The outgoing gases were sent into a

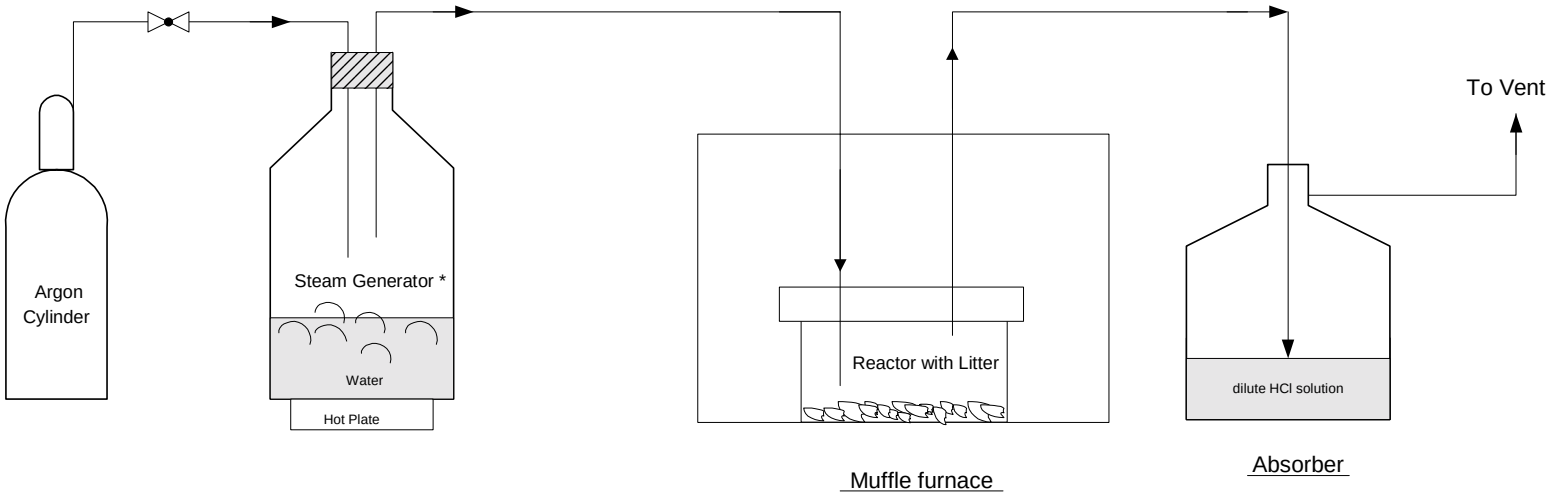

Figure 4.2: Arrangement of Muffle Furnace , Absorber system

*Steam generator will be online only when gasification is carried out in Muffle Furnace

flask partially filled with dilute hydrochloric acid solution and bubbled through the solution to allow the tars and other heavy volatile compounds to condense and the ammonia to react before the gases were released into the atmosphere through the exhaust hood's vent. The pyrolysis was carried out for three hours from the time the desired temperature of 300 – 700^0C was reached in the muffle furnace. The desired temperature would reach within approximately 30 minutes. At the end of the pyrolysis, the furnace was cooled to room temperature while maintaining continuous purge with the inert gas (argon). This process took six to seven hours since the furnace was always closed during this stage. This was done to prevent the hot residue to come in contact with air and oxidize. In all the experiments in which catalytic gasification was performed in the muffle furnace, the catalyst (langbeinite) was added in the beginning of the experiments and physically mixed in the reactor with the chicken litter using a spoon or spatula.

In the cases where catalytic gasification was carried out in the differential fixed bed reactor, the catalyzed pyrolyzed broiler litter (containing catalyst prior to pyrolysis) was taken out of the muffle furnace after cooling and then crushed in an agate mortar and sieved. The particle size of the char used in the gasifier was usually between 30 to 100 mesh. After sieving, the char was transferred to the fixed bed reactor for gasification experiments, the procedure for which is in the following section. A few gasification experiments were also carried out in the muffle furnace setup. The only change in the setup was that the argon was passed through a flask containing steam / water. The flask was filled with water and placed on a hot plate, so that an unknown quantity of steam was

constantly produced. When the argon was passed through this flask, it picked up steam due to its pressure and then entered the steel reactor, as shown in Figure 4.2. The reactor outlet contained gasified fuel gas containing ammonia. The ammonia was then absorbed in a dilute hydrochloric acid solution, as it was done during pyrolysis experiments.

Steam Gasification of Pyrolyzed Char

The catalytic steam gasification experiments were carried out both in the muffle furnace at atmospheric pressure as well as in the bench scale high-pressure, high-temperature fixed-bed gasifier system. A schematic of the differential fixed-bed reactor is shown in Figure 4.3. The gasifier in the fixed bed system was typically operated with a downdraft gas flow regime and in a differential fixed bed mode. The gasifier was designed to operate at the desired temperature, pressure and steam/water flow conditions.

Here is an excellent description of the fixed bed gasification unit as given by Turner(4). "The core part of this bench scale gasification unit was the gasifier reactor. The reactor body was constructed of a 3/4-inch Type 304 stainless steel tubing, with a wall thickness of 0.0065-inch. This allowed a working pressure as high as 1500 psi at 1400^0F. The reactor was sealed with an end cap on one end and filled with ceramic beads on a 200-mesh stainless steel screen. This provided support for the char sample. The char sample to be gasified was supported by two 200-mesh stainless steel screen baskets placed above the ceramic packing, closer to the center of the reactor. A Type K thermocouple was introduced from the other end cap and was placed close to the top of the char bed. The

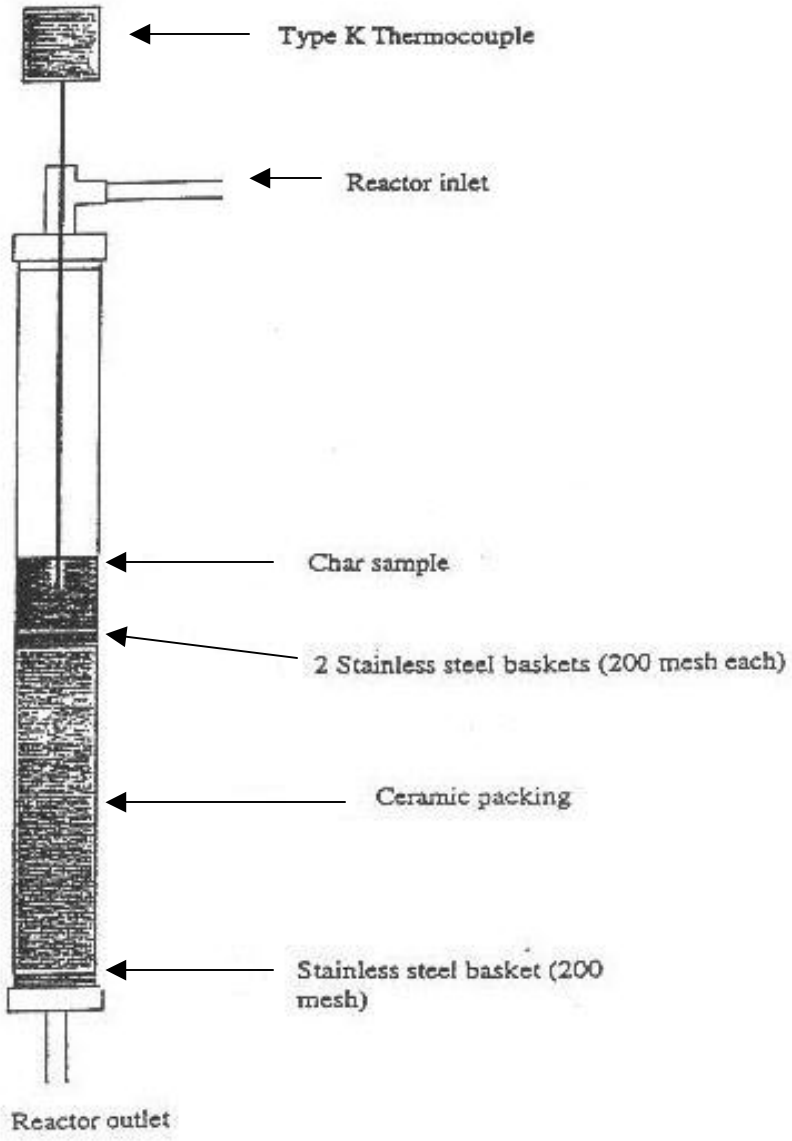

Figure 4.3: Schematic of Differential Fixed-Bed Reactor

thermocouple was used to monitor the bed temperature throughout the entire experiment".

The high-pressure fixed-bed gasifier system, shown schematically in Figure 4.4, was operated in the start-up mode to bring the system to required operating conditions of temperature and pressure. The reactor was continuously purged with argon, from the start-up through the gasification step, to maintain inert condition. A long vertically mounted Lindberg Sola Basic Model 123 split-tube furnace heated the reactor. The differential char bed accommodated about 4.5 grams of char during the experimental run. Once the system was ready for gasification, steam was introduced into the reactor. Distilled water for generating steam was introduced into the system using an Eldex Laboratories, Inc. Model A-10-S metering pump. The total amount of water entering the apparatus was measured by the burette from which the water entered the inlet of the pump. The pressure in the system was regulated by a Tescom Industrial Controls Model backpressure regulator, which was placed at the reactor outlet. Pressure was monitored at both ends of the reactor using a Residuecroft pressure gauge, with a reading up to 400 psig, to ensure constant pressure condition during gasification. The water was pumped into the system once the reactor reached the desired operating condition. The argon, unreacted steam, and products from the gasifier entered the condenser after passing through the backpressure regulator. Most of the unreacted steam was condensed at this point and collected at the end of the gasification run. A drying tube packed with silica gel removed any traces of water left from the condenser outlet gas. The dry gas then entered

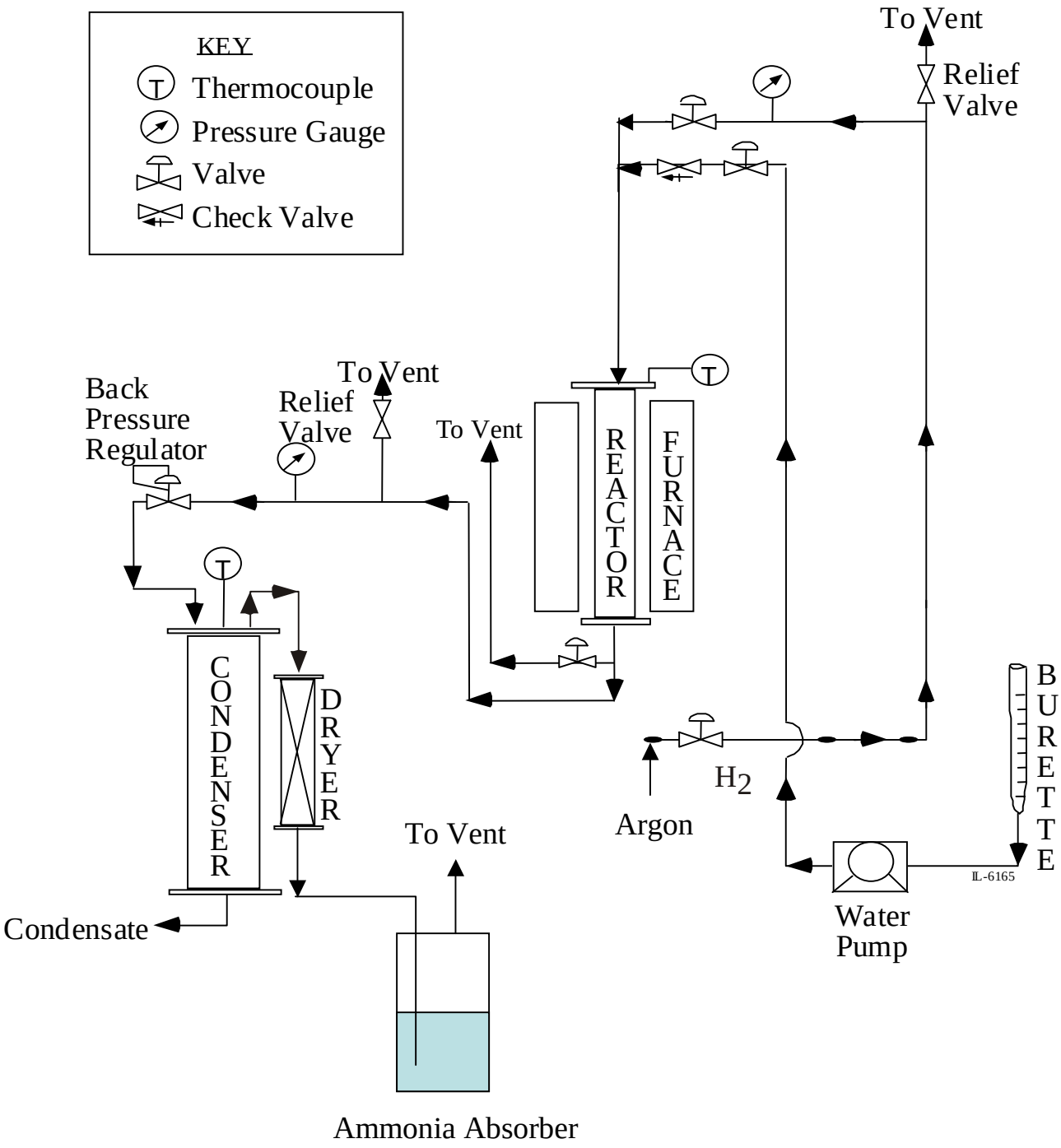

Figure 4.4: Schematic of High-Pressure High-Temperature Fixed Bed Gasifier with Ammonia Absorption System

the absorbing section of the system. The gas was rendered ammonia free in the absorbing section, where the ammonia reacted with the dilute hydrochloric acid solution.

The steam gasification step was carried out for about three hours. During the progress of the experiment, the temperature was maintained at 1300 ^{0}F. Liquid sample of the scrubbing liquor was collected every 15 minutes. These samples were titrated against caustic soda solution. The indicator used was methyl orange which turned yellow on neutralization. The quantity of hydrochloric acid consumed in the scrubbing liquor was used to calculate the quantity of ammonia liberated following the approach discussed earlier.

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Chapter V

Results and Discussion

Analysis of Broiler Litter, Residue and Absorbing Solution

Analysis of the broiler litter, residue and the absorbing solution (scrubbing liquor) was carried out by Galbraith laboratories (13). The results of the analysis by components are presented in Table 5.1. The components, which were analysed before by UTSI, are tabulated in Table 3.1 along with the analysis results of MTCI(3) and Antares group (5).

Results from Muffle Furnace Experiments

The components shown in Table 5.1 will be dealt with in the material balance worked out in Figure 5.1, where the titration of scrubbing solution result is depicted as block diagrams. The nitrogen released as ammonia is higher in most cases than the nitrogen in the litter. This is because, the nitrogen in the litter is estimated from the single analysis of the litter done by Galbraith Laboratories. It should be borne in mind that part of the nitrogen will be present as uric acid coming from the droppings of chicken, which will be non-homogenous. Hence, the nitrogen content in the litter will be non-homogenous and any single estimate of it may not be accurate.

The nine experiments of pyrolysis and gasification as described in Figure 5.1 and Table 5.2 were performed in a Barnstead Thermolyne - Model F48015 muffle furnace at atmospheric pressure. The description of the furnace and the arrangement has been described earlier in the chapter IV. The desired temperature was set and the litter was

Table 5.1 : Major Constituents of Litter, Residue and Absorbing Solution

Sample Identification	Phosphorus, wt %	Nitrogen wt %	Total Halides as chloride, wt %	Potassium wt %
Litter (as received)	1.87	2.72	0.74	2.37
Absorbing solution from Pyrolysis @1300^{0}F	<7 ppm	0.008	NM*	NM*
Residue from Pyrolysis@1300^{0}F	8.31	0.24	NM*	NM*
Absorbing Solution from Pyrolysis and gasification @1300^{0}F	< 5 ppm	0.027	1.27	NM*
Residue from Pyrolysis and gasification @1300^{0}F	8.09	0.13	2.32	NM*

*NM – not measured

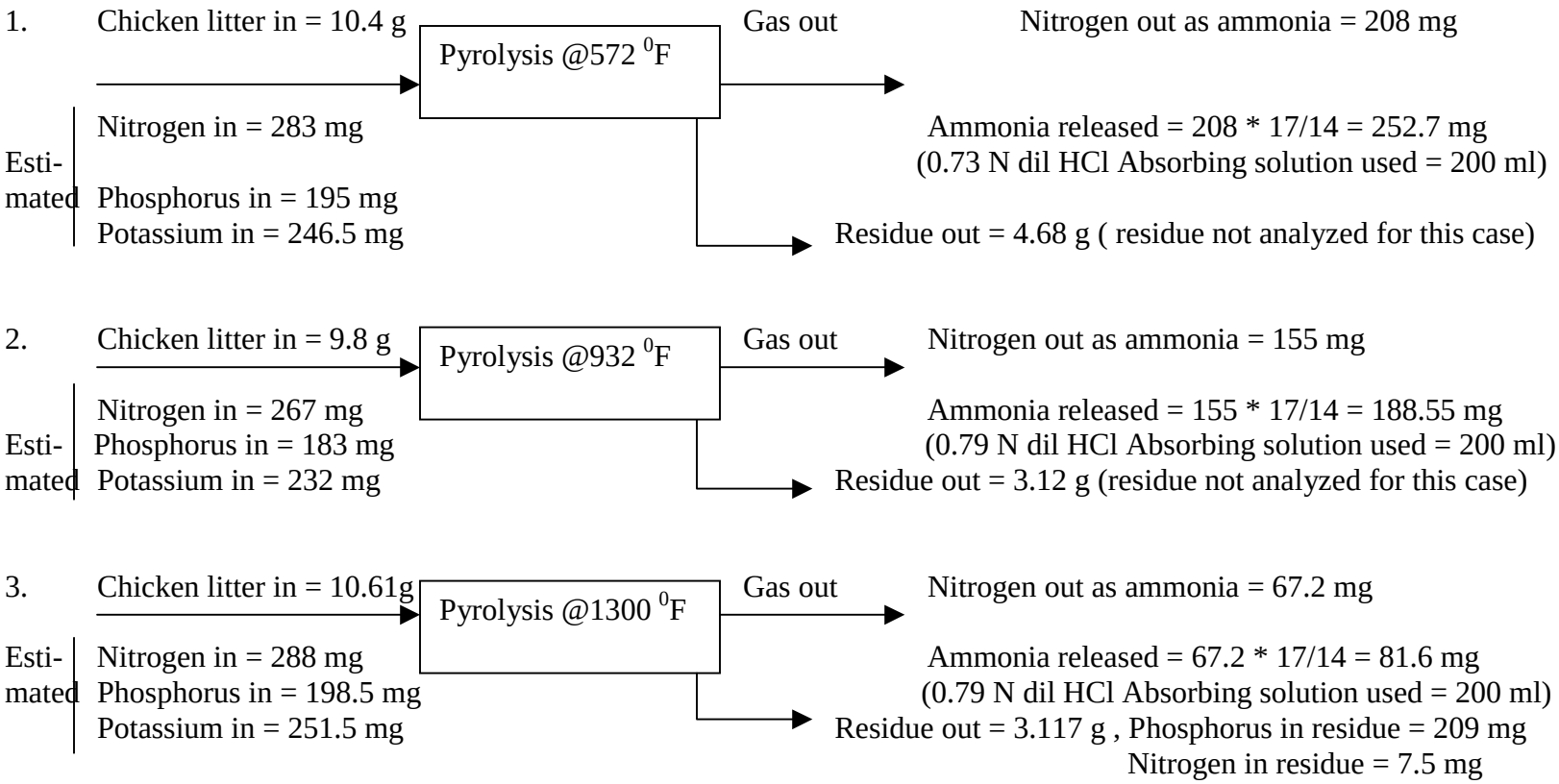


Figure 5.1: Material Balance of the Pyrolysis / Gasification Experiments Conducted in Muffle Furnace

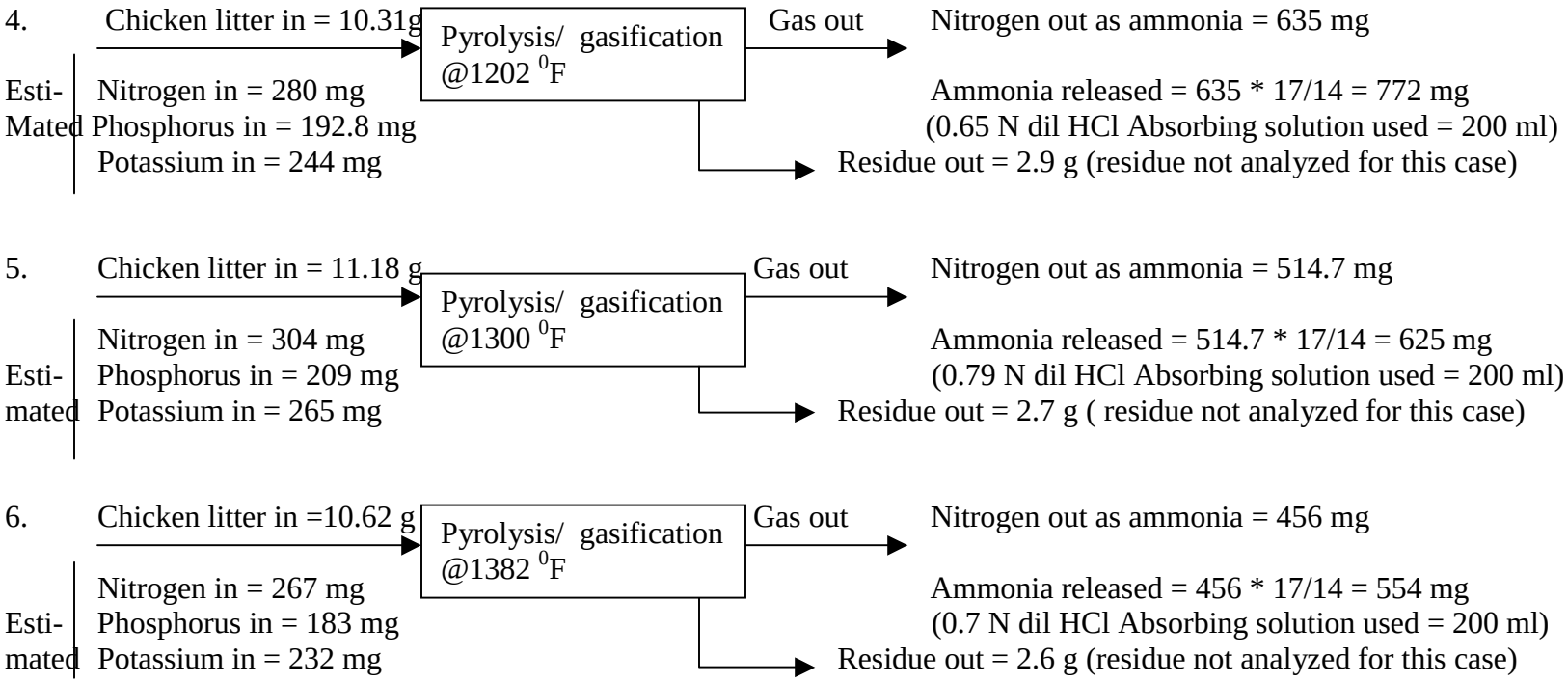


Figure 5.1: Material Balance of the Pyrolysis / Gasification Experiments Conducted in Muffle Furnace (contd.)

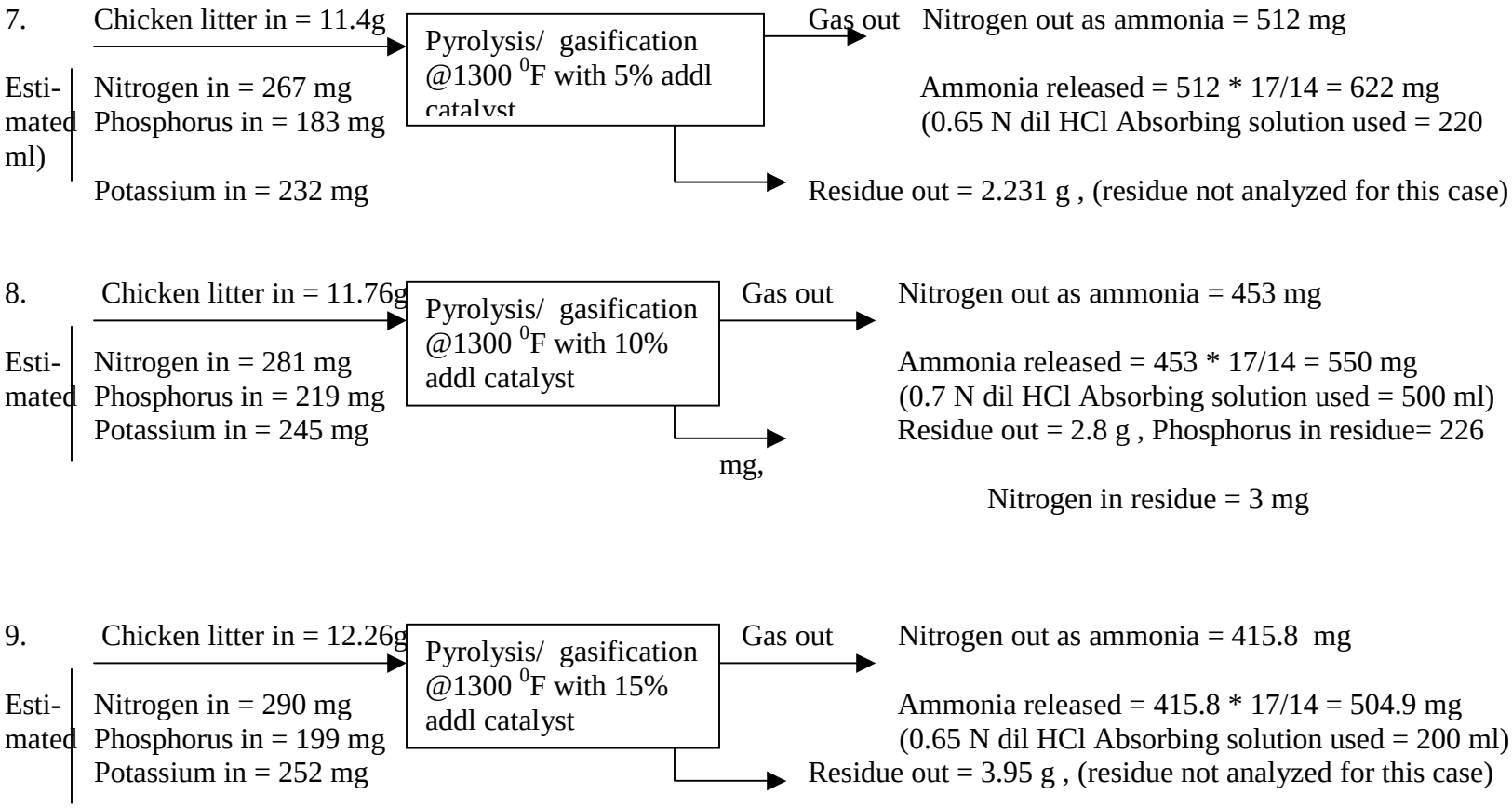


Figure 5.1: Material Balance of the Pyrolysis / Gasification Experiments Conducted in Muffle Furnace (contd.)

Table 5.2: Preliminary Tests Carried Out in Muffle Furnace at Atmospheric Pressure

Sl. No.	Description	¡mg of total NH_3 released (from titration)
1	Pyrolysis at 300^0C	253
2	Pyrolysis at 500^0C	188
3	Pyrolysis at 700^0C	82
4	Pyrolysis / gasification at 650^0C	772
5	Pyrolysis / gasification at 700^0C	625
6	Pyrolysis / gasification at 750^0C	554
7	Pyrolysis / gasification at 700^0C with 5% catalyst.	622
8	Pyrolysis / gasification at 700^0C with 10 % catalyst.	550
9	Pyrolysis / gasification at 700^0C with 15 % catalyst.	505

Note : The argon (inert gas) flow rate and steam flow rate during gasification were not measured and were not considered as a variable.

heated for 3 hours after the desired temperature was attained. During gasification experiments, water was separately boiled and vapors were fed to the furnace by the flowing argon gas. The argon gas serves two purposes here. First, it maintains an oxygen free and inert atmosphere and secondly it pressurizes and forces the steam to flow in the direction of the reactor containing chicken litter. The pyrolyzed / gasified gas was passed through a dilute solution of hydrochloric acid. The hydrochloric acid solution would absorb any ammonia and make the gas ammonia free. In the cases when only pyrolysis was carried out, the boiler would not be on line. The boiler would be on line when pyrolysis is followed by gasification in the same muffle furnace for the same sample.

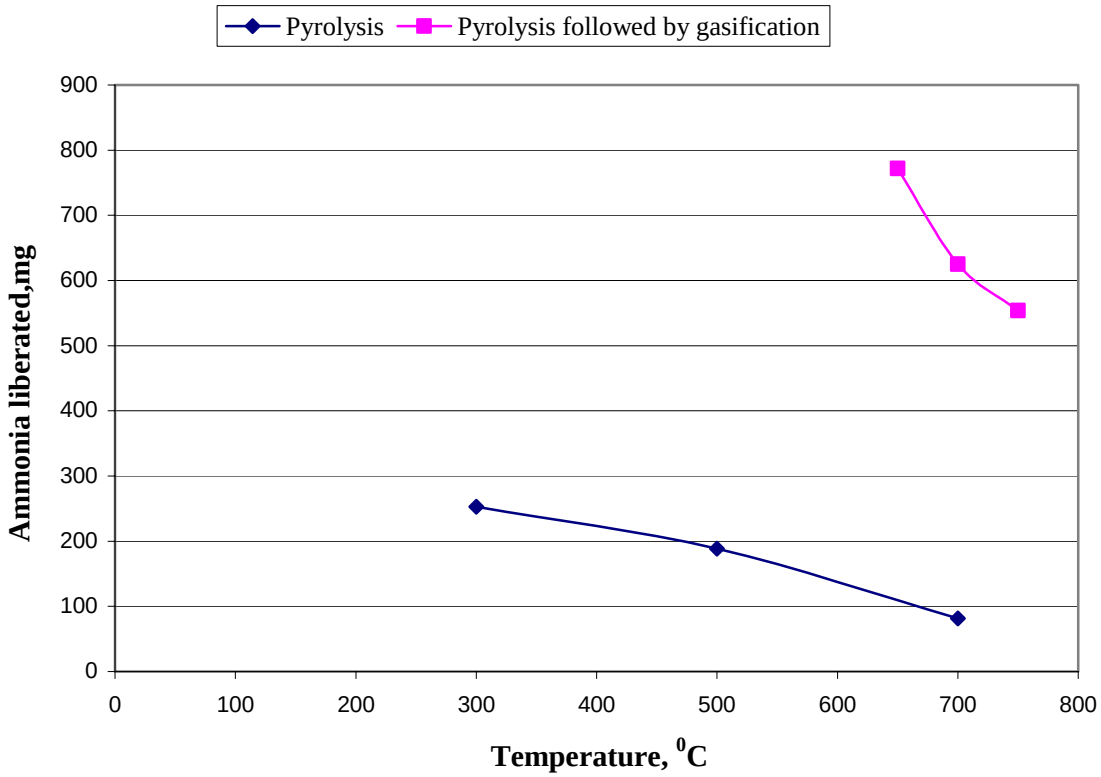
Nine cases, as described in Figure 5.1 and tabulated in Table 5.2, were studied in the muffle furnace, as preliminary experiments. The optimum conditions were then selected to perform kinetic study in the high-pressure fixed-bed system.

The ammonia that should be liberated in the case of pyrolysis/gasification was calculated from material balance on nitrogen. Nitrogen in the residue after pyrolysis, calculated, for example, from row 3 of Table 5.1, when subtracted from the nitrogen in the original litter sample will give the nitrogen liberated as ammonia, which was 341 mg of ammonia in this case. However, the results from titration of the scrubbing solution gave only 82 mg of ammonia. This difference could be due to part of the nitrogen being liberated as nitrogen gas and not having enough hydrogen to react. The titration result only gives the ammonia liberated during pyrolysis. It does not account for nitrogen released in any other form. Doing a similar balance for the case when pyrolysis is followed by gasification,

i.e., when the nitrogen in the residue after pyrolysis / gasification (calculated from row 5 of Table 5.1) is subtracted from the total nitrogen present in the original litter, the ammonia liberated theoretically was calculated as equal to 331 mg. However, the titration result gave 550 mg of ammonia. Non-homogeneity of litter could be a possible reason behind the difference in the theoretical amount of ammonia liberated and that calculated from the titration result. In both the pyrolysis and the pyrolysis followed by gasification cases, the similar material balance on the phosphorus based on the composition given in Table 5.1, showed that no phosphorus was lost in the gaseous form (refer to Figure 5.1). The phosphorus remained mostly in the residue and together with the potassium could thus provide a good component of fertilizer. Hence, in the following discussions on thermodynamics and kinetics we will limit it only to the study of nitrogen and ammonia.

The plot of pyrolysis and gasification temperature versus amount of ammonia liberated is shown in Figure 5.2. The ammonia liberation increases sharply while gasification is carried out after pyrolysis due to the increase of hydrogen concentration as explained earlier. The plot of percent additional catalyst in the litter versus ammonia liberated when the pyrolysis / gasification is carried out at 1300^0F is given in Figure 5.3. The catalyst added to the litter before pyrolysis and gasification was langbeinite, the chemical formula of which is $K_2Mg_2(SO_4)_3$. As shown in Figure 5.2, there is a drop in ammonia liberation with increase in pyrolysis/ gasification temperature because as explained in chapter III, ammonia forms in the presence or absence of a catalyst by a reversible reaction as shown below;

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

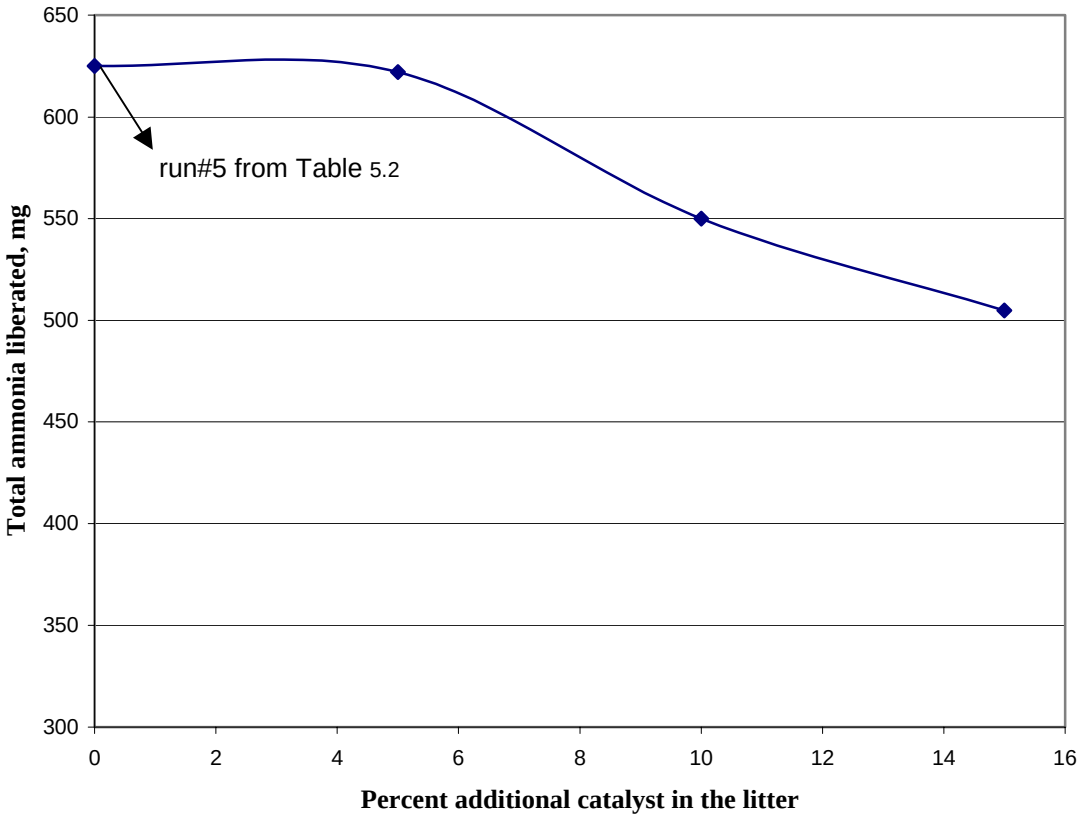


Basis: Approximately 10 gram litter

No additional catalyst

~ atmospheric pressure

Figure 5.2 : Total Ammonia Released vs Pyrolysis / Gasification Temperature



Basis: Approximately 10 gram litter

700^0C Temperature

~ Atmospheric pressure

Figure 5.3 : Total Ammonia Liberated Following Pyrolysis / Gasification vs Percent Additional Catalyst

As shown in chapter III, as the temperature increases the equilibrium constant (K_p) for the reaction decreases.

We know that,

$$K_p = \frac{P^2_{NH3}}{P_{N2} * P^3_{H2}} \quad \ldots\ldots\ldots\ldots\ldots 5.1$$

Where, P_{NH3} , P_{N2} , P_{H2} are the partial pressure of ammonia, nitrogen and hydrogen respectively.

So, as evident from equation 5.1, as K_p decreases, the partial pressure of ammonia would decrease, i.e., the amount of ammonia liberated must decrease. Hence, our observation of decrease in the quantity of ammonia liberated when the pyrolysis / gasification temperature was increased is in line with the thermodynamics.

There is a drop in the ammonia liberation with percent increase in additional catalyst in the litter. This may be because, additional catalyst may tie up with nitrogen containing species in litter and thereby reduce the availability of nitrogen for ammonia formation.

Results from Kinetic Experiment

The litter was first pyrolyzed in the muffle furnace and then gasified in the bench scale high-pressure, high-temperature fixed-bed gasifier setup. The conditions for pyrolysis were set at 700^0C, atmospheric pressure and 10% additional catalyst. During pyrolysis,

samples of the absorbing solution were collected every 15 minutes. The process was continued for 3 hours and 12 samples were collected. The titration of these samples would give the amount of hydrochloric acid reacted or in other words amount of ammonia liberated with time. The ammonia will then give the amount of nitrogen removed from litter as a function of time.

For example, if x mg of ammonia is formed at time t.

$$[N] + 3/2\ H_2 \longrightarrow NH_3$$

14 mg 17 mg

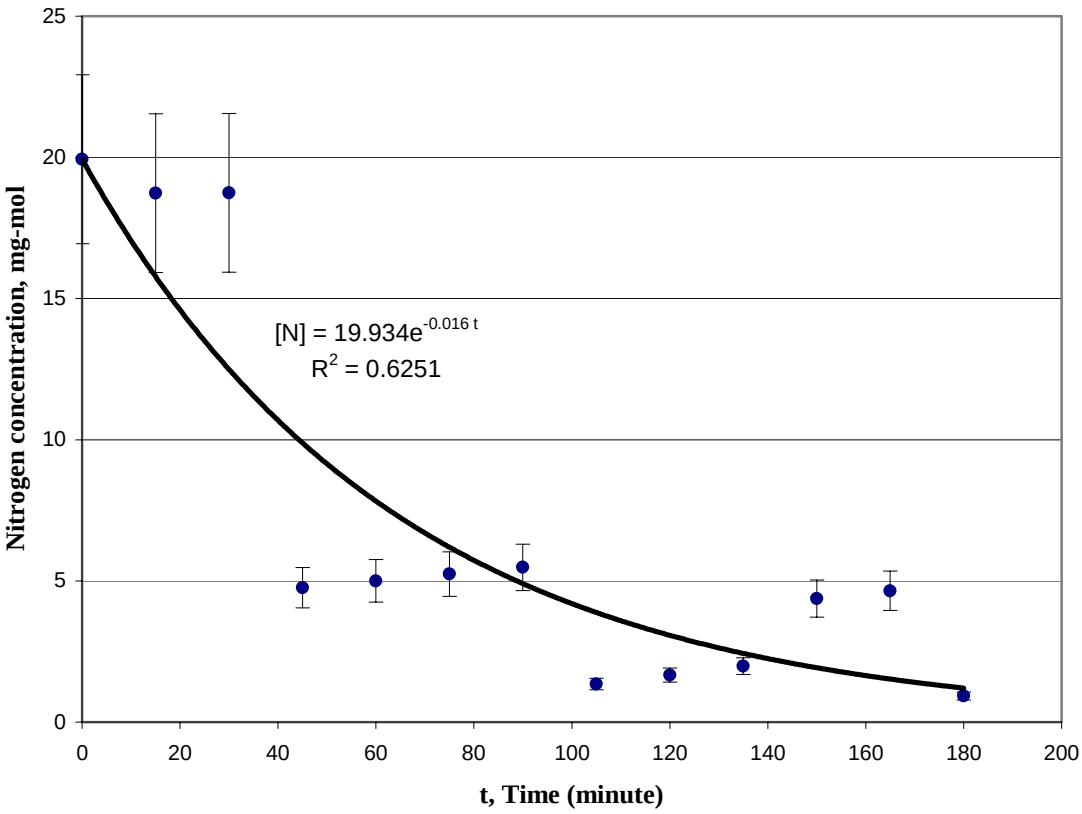
Then, x * 14/17 = x * 0.823 mg of nitrogen has been removed at time t from the chicken litter. Accordingly, the mg-moles of nitrogen in the litter versus time (minute) was plotted and shown as Figure 5.4. It was modeled as a first order process for simplicity.

As per first order,

$$-\text{Ln}\ (1- X_N) = k * \text{time}$$

where, X_N , k are as described in equation 3.1 (Chapter III)

The plot of -Ln (1- X_N) versus time does not fit a straight line, as shown in Figure 5.5, with the R^2 value of 0.6251, which indicates that about 30% of the points do not agree with the equation in Figure 5.5. In future study, an online ammonia indicator/analyzer should be used to minimize errors in data collection, and also other model should be tried to represent ammonia evolution process. The pyrolyzed char was then transferred into the high-pressure, high-temperature fixed-bed gasifier system. The gasification temperature was set at 700^0C and pressure at 100 psig, which is the optimum condition suggested for gasification (4). The steam flow rate was about 0.25 ml/min, which was suggested by Turner(4) to attain optimum gasification in short time.



Fitted curve

Data point

Error Bands = + / - 15%

Basis: 10.26 gram of litter

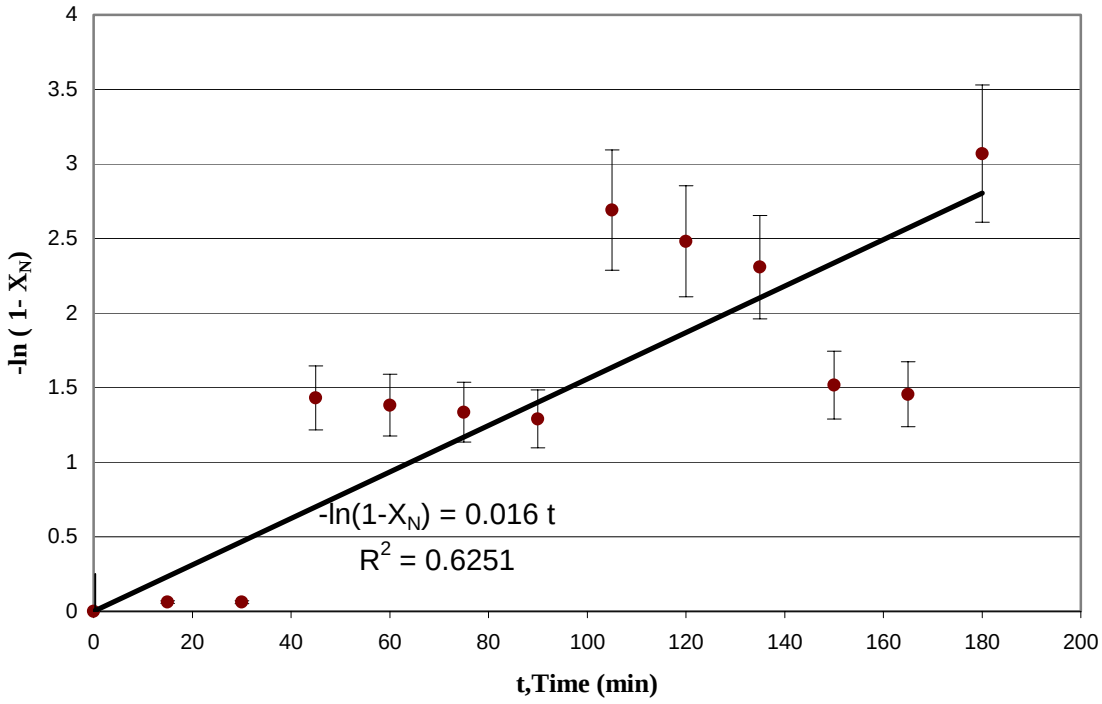
10% catalyst(langbeinite)

Temperature = 1300^0F

Pressure = atmospheric

Steam flow rate = nil

Figure 5.4 : Nitrogen Concentration in the Litter versus Time During Pyrolysis



_____ Fitted curve

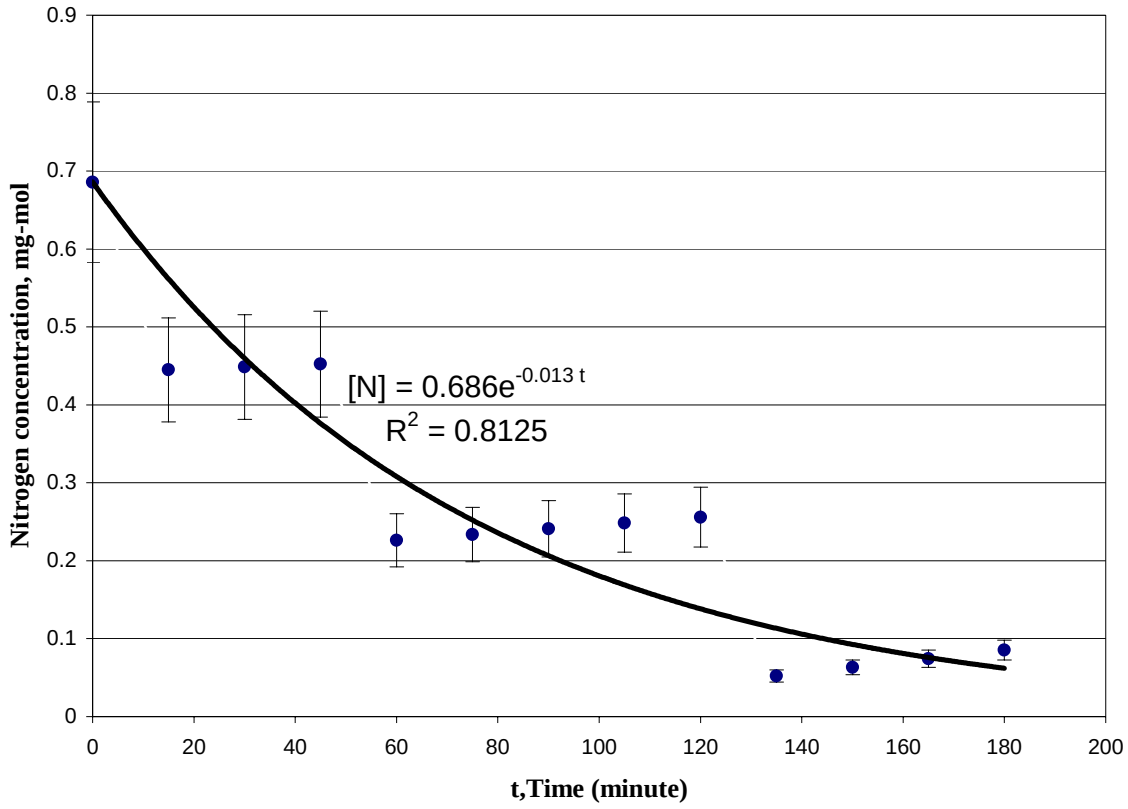
Basis: Same as in Figure 5.4

● Data point

Error Bands = +/- 15%

Figure 5.5: Testing for First Order Rate During Pyrolysis

No additional catalyst was added to the 10% langbeinite added during the pyrolysis stage. With these conditions, the gasification was carried out for 3 hours and the scrubbing liquor samples were collected every 15 minutes, just as it was done during the pyrolysis operation. The titration of these 12 samples would give the amount of hydrochloric acid reacted or in other words amount of ammonia liberated with time. As in the case of pyrolysis described above, the ammonia will then give the amount of nitrogen removed from litter with time. The mg-moles of nitrogen in litter versus time (minute) was plotted and shown as Figure 5.6. It was again modeled as a first order rate process. The plot of -Ln (1- X_N) versus time does not fit a straight line, as shown in Figure 5.7, with a R^2 value of 0.8125. which indicates that about 18% of the points do not agree with the model suggested by equation in Figure 5.7. Hence, it is suggested that better understanding of the reaction kinetics and mass transfer steps are required to incorporate in an improved kinetic equation and overall rate model. Accordingly, additional kinetic experiments with different additional catalyst loading and different temperature settings are recommended in future studies. These experiments will assist in understanding the reaction kinetics better.



Fitted curve

Data point

Error Bands = + / - 15%

Basis: 3.98 gram of pyrolysed char

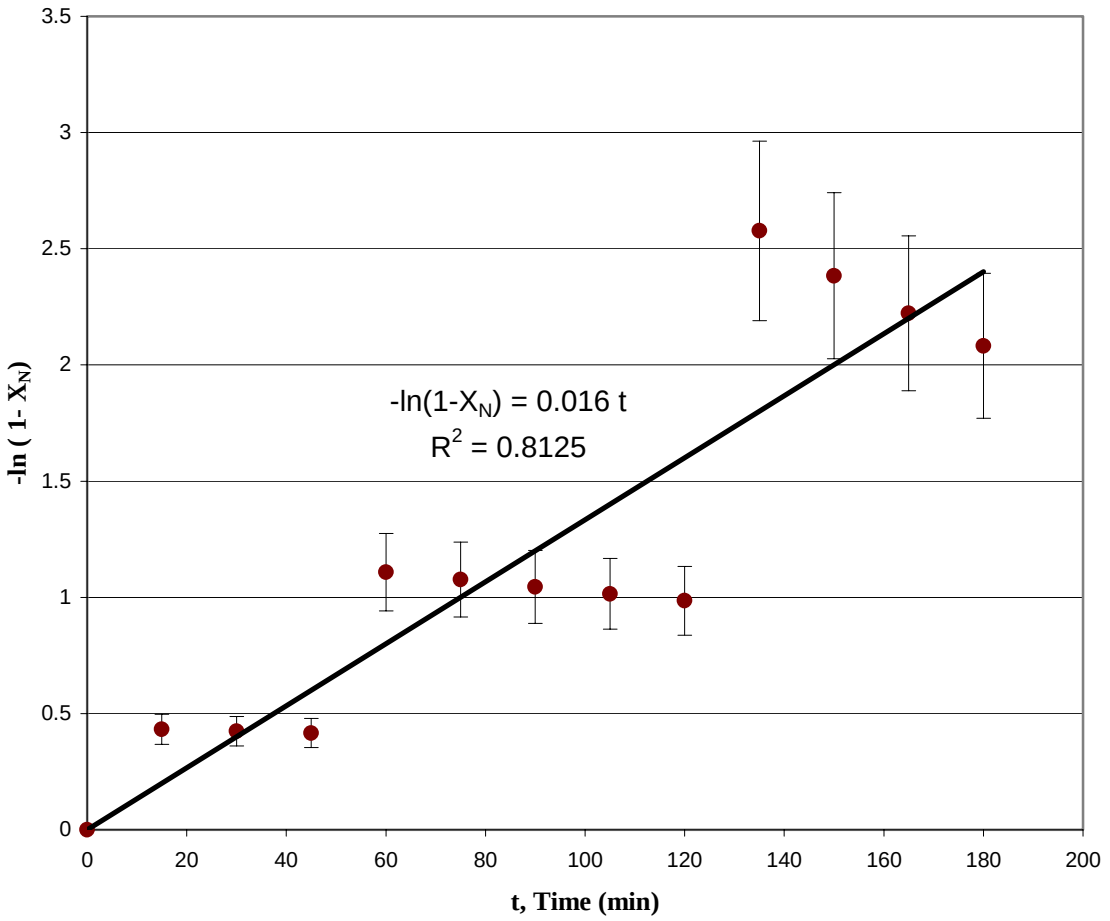
10% catalyst (langbeinite) added before pyrolysis

Temperature = 1300^0F

Pressure = 100 psig

Steam flow rate = 0.25 ml/min

Figure 5.6: Nitrogen Concentration in the Pyrolysed Char versus Time During Gasification



Fitted curve

Basis: Same as in Figure 5.6

Data point

Error Bands = + / - 15%

Figure 5.7 : Testing for First Order Rate During Gasification

Chapter VI

Economic Assessment

In the thesis "*Determining the Optimum Conditions for Catalytic Steam Gasification of Broiler Litter"* presented by *Turner(4),* he demonstrated the economic viability of a stationary poultry litter gasification plant of size ranging from 100 tons/ day to 1000 tons/ day. However, Turner did not include the fate of nitrogen and phosphorus containing species in his analysis to assess their environmental impact and the effect on economics. The previous chapters of this thesis have concentrated on all the technical aspects of this subject. In this chapter, we will concentrate on the economic impact on a 100 tons/ day litter gasification plant caused by the concerns related to phosphorus and nitrogen containing species.

As indicated in earlier chapters, and shown by MTCI (3), during gasification process the nitrogen is mostly converted into ammonia and partly liberated as gaseous nitrogen. Nitrogen release to the environment as nitrogen gas is not considered objectionable. Hence, we will not recover the nitrogen gas. A scheme is devised to recover the ammonia produced during pyrolysis and gasification as 10% (w/v) ammonium hydroxide solution, which can be sold in the market as aqua ammonia.

Turner (4) had devised a scheme for a stationary litter gasification unit. The unit was designed to operate for 330 days and process 100 tons (90.9 metric tons) of poultry litter per day. His process scheme with minor modifications is shown in Figure 6.1. The fuel

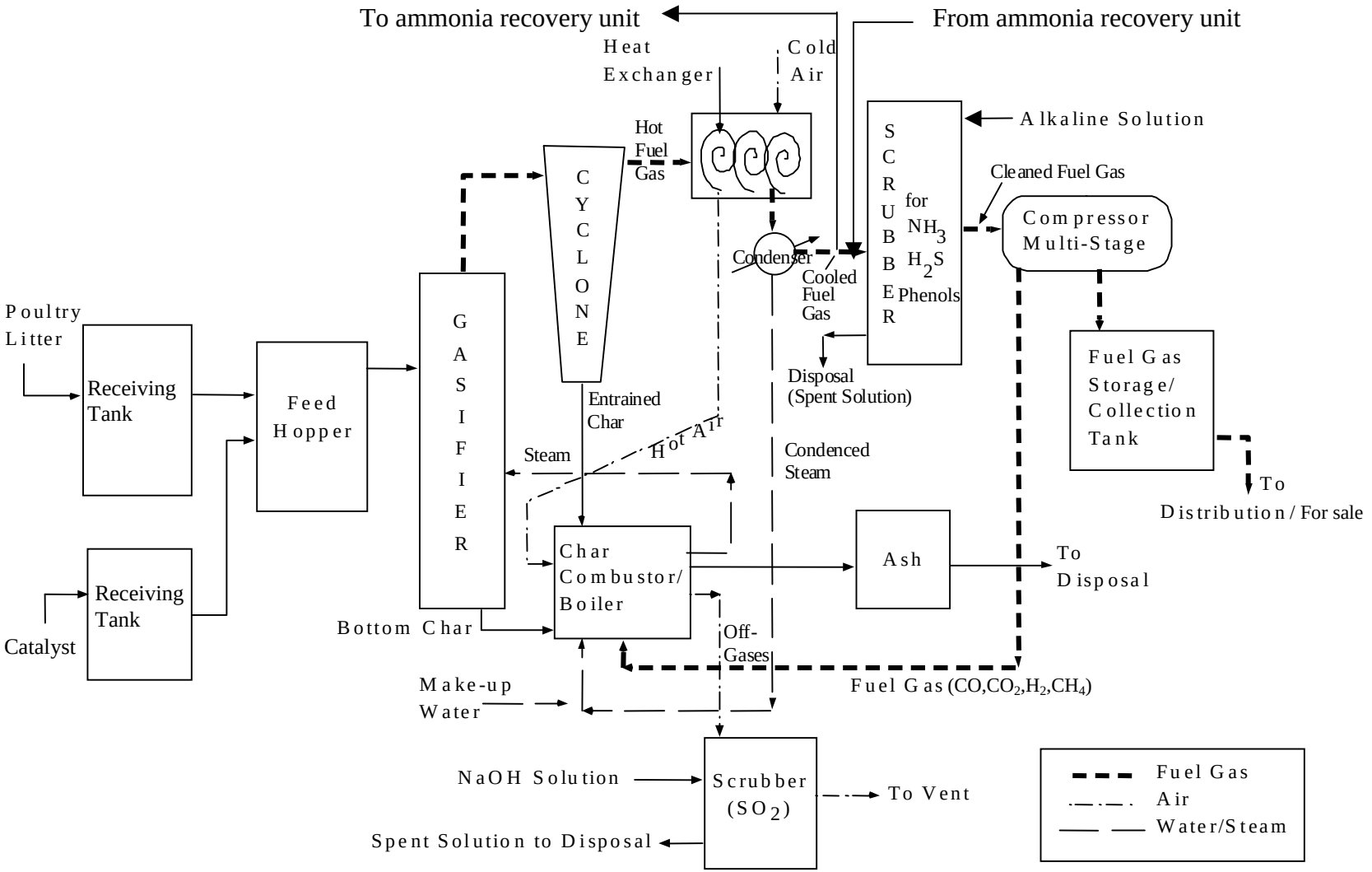
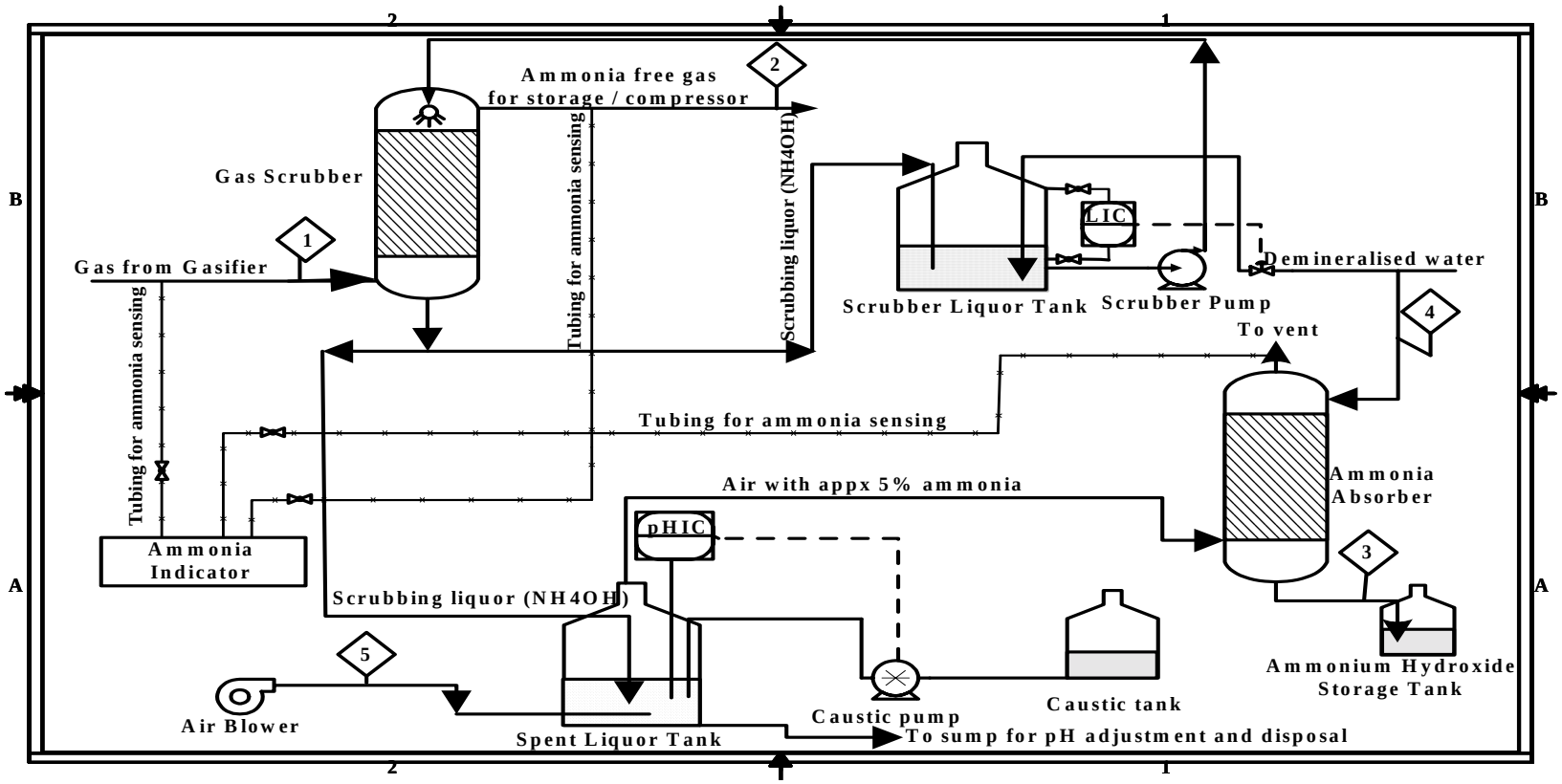


Figure 6.1: Schematic of Stationary Gasification System (4)

gas from the heat exchanger outlet will be fed to an ammonia recovery unit (being suggested in this study) and the outlet from the ammonia recovery unit will be fed to the scrubber inlet (in Turner's (4) scheme). The scrubber will scrub the H_2S, phenol and any trace of tar. The ammonia will not be absorbed in the scrubber because it will use an alkaline scrubbing solution. Ammonia is sparsely soluble in an alkaline solution. However, some H_2S, phenol and other organics may be in ammonia solution. So, in the future if dissolution of H_2S and phenol poses a major problem to the ammonia recovery unit, we may put the ammonia recovery unit after the scrubber envisaged by Turner to take care of the H_2S and phenol. The ammonia recovery unit is shown in Figure 6.2.

As shown in the scheme in Figure 6.2, the ammonia will be absorbed from the gasified fuel gas in the absorber by means of water at room temperature. As we have found before, the ammonia liberation kept on changing because of the non-homogeneity of the litter. Hence, we have envisaged an online ammonia indicator for continuous monitoring. The equipment sizing is based on 100 tons/day litter gasification and 3 tons/day of ammonia liberation. The ammonia liberation of 3 tons/day is a conservative value and is estimated based on the fact that about 300 mg of ammonia was liberated when we pyrolyzed/ gasified 10 g of litter which is 3%, although the ammonia liberation was as high as 772 mg in a particular case (refer Table 5.2). These higher amounts can also be taken care with the over design of equipments suggested. The exact amount of release of ammonia is very difficult to predict and hence the conservative estimate of 3 tons/day is used. The equipments will be designed for a higher load of 7-8 tons/day of ammonia



Stream Description

Stream no.	Flow rate	Ammonia	Temperature
1	62, 000 scf / hr	5 % by volume (approximately)	ambient
2	56, 000 scf / hr	1 ppm	ambient
3	150 gallons / hr	10 % by weight of the solution	ambient
4	150 gallons / hr	nil	ambient
5	20000 ft^3 /hr	nil	ambient

Figure 6.2 : Schematic for Ammonia Recovery Unit

liberation, so that the unit can take care of the higher load. A continuous stream of aqua ammonia will be taken and collected in a spent liquor tank. The pH of the solution in the tank will be maintained at 10.5 by means of pH control. At that pH all the ammonia will be released when the air blower operates. The ammonia will then be absorbed in the ammonia absorber, which will be pure 10% by weight of aqua ammonia. The aqua ammonia will be collected in ammonium hydroxide storage tank. The spent liquor from the spent liquor tank will contain permissible amount of chloride, which will be sent to a sump. The pH will be adjusted to a neutral value (pH = 7) in the sump before disposal.

From the ammonium hydroxide storage tank ammonium hydroxide will be taken out and marketed. The incoming gas to the absorber and the outgoing gas will be continuously monitored by an on-line ammonia analyzer for ammonia. The outgoing gas will have traces of ammonia (below 1 ppm). The material balance for the unit is shown in Figure 6.2. The entire operation is carried out at room temperature.

The cost estimate is based on 330 days of operation of the plant.

In the present economic assessment, we will first assess the cost of the ammonia recovery unit and then incorporate it with the total cost of the 100 tons / day gasification plant worked out by Turner (4). The operating expenses worked out by Turner are shown in Table 6.1. Since, the requirement of demineralized water is small (approximately 250 gallons / hr), we assume that we can use the steam condensate or prepare it locally. The requirement of caustic soda and hydrochloric acid will be very small (few liters per hour). Hence we are assuming that

Table 6.1 : Operating Costs (4)

Sl. No.	Item	Price ($/year)
1	Labor	$600,000.00
2	Materials	$122,000.00
3	Transportation	$118,800.00
4	Utilities	$98,000.00
	Total	**$938,800.00**

there would be no additional operating expense due to the ammonia recovery unit. The operating expenses already considered by Turner (4), will take care of the operating expenses arising due to these additional items.

The total capital investment estimated by Turner (4) is shown in Table 6.2. Capital costs include purchase prices for equipment, instrumentation and piping. These costs for the additional ammonia recovery unit are presented in Table 6.3. The capital costs were estimated using the charts and correlation from Peters and Timmerhaus (8), and were adjusted for inflation using the Marshall and Swift index for industries. The cost of the ammonia analyzer was obtained from Southeastern Automation group (15). Table 6.4 gives the additional costs for installing plant equipment. These additional costs are assumed as a percentage of the total purchase cost of the equipments considered for costing in Table 6.3. The equipment costs and the additional costs given in Table 6.3 and 6.4 represent the direct costs associated with the

Table 6.2: Total Capital Investment Excluding Ammonia Recovery Unit (4)

Sl. No.	Item	Purchase Cost ($)
1	Delivered Equipment	989,000
2	Equipment Installation	514,280
3	Instrumentation & Controls	118,680
4	Piping	178,020
5	Electrical	128,570
6	Building, land, yard improvements	34,000
7	Engineering and supervision	356,000
8	Construction cost	360,000
9	Contractor's fee	63,500
10	Process/Project Contingency	324,500
	TOTAL	3,066,550

Table 6.3 : Capital Costs for the Ammonia Absorption System

Sl No.	Item	Purchase Cost
1	Ammonia Absorber of carbon steel (2 nos.)	$ 120,000
2	Tanks (2 nos.) of carbon steel	$ 15,000
3	Tanks (2 nos.) of stainless steel	$ 22,500
4	Ammonia Analyser (1 no.)	$ 35,000
5	Scrubber pump (1 no.) of carbon steel trim	$ 2000
6	Caustic pump (1 no.)	$ 2000
7	Air blower (1 no.)	$ 12,000
	Total	$208,500

capital investment. These costs when combined with the direct cost of the whole gasification plant (after taking care of the inflation) estimated by Turner (4), is equal to;

$ 208,500 (Total as in Table 6.3) + $ 170,970 (Total as in Table 6.4) +

$ 1,962,550 (Turner's estimate, sum of first six components of Table 6.2) * 1.025 (cost index from Marshall & Swift) = $ 2,392,000. The Indirect cost, Process Contingency and Contractor's Fee considered by Turner will just be inflated for the present value. These components will not increase because of the additional equipment. The total revised capital cost for the 100 tons / day broiler plant is tabulated in Table 6.5.

Table 6.4 : Additional Costs for Installing Plant Equipment

Sl. No.	Item (% Purchase Price)	Purchase Cost
1	Purchased Equipment Installation (52%)	$ 108,420
2	Instrumentation and Controls (12%)	$ 25,020
3	Piping (18%)	$ 37,530
	Total	$ 170,970

To figure annual cost, factor 25% for depreciation, tax, etc, of the capital costs. That total equals $889,600 (= 0.25 * **$ 3,558,350**). The operating costs estimated by Turner (4) are quite conservative and presented in Table 6.1. Assuming no inflation on this cost, the annual cost is $ 1,828,400 (= 938,800 , from Table 6.1 + 889,600, depreciation etc, mentioned above).

To determine the payback period, the gross revenue must be determined. The net profit is then determined by subtracting the annual cost from the gross revenue. The original capital investment is then divided by this net profit to find the payback period.

For the gross revenues, 100 tons of litter will be processed per day, with the fuel gas being sold at $14.52 per million Btu (4). Also, the residue recovered from the litter has a fertilizer value. By the method used by Antares group (5) to calculate the fertilizer value of the residue, our residue will have a value of $35.6 per ton of residue. The method of calculating the fertilizer value is as shown below in Table 6.6. We will be generating approximately 10

Table 6.5: Total Capital Cost for Broiler Litter Plant Including Ammonia Recovery Unit

Sl. No	Item	Cost
1	Total Direct cost [sl. No. 1 to 6 from Table 6.2 * 1.025 (cost index) + Total of Table 6.3 + Total of Table 6.4]	$ 2,392,000
2	Indirect cost	$ 768,750
3	Process / Project Contingency	$ 332,600
4	Contractor's Fee	$ 65,000
	Total	**$ 3,558,350**

tons/day of the residue, which gives revenue of $356 per day (= $ 117,480 per year).

The 3600 gallons / day of 10% ammonium hydroxide solution will be relatively pure with no major impurities. So, according to the quote from Ideal Chemicals & Supply Co. of Memphis, Tennessee, the ammonium hydroxide solution can be sold at $ 0.26 / lb of ammonia delivered to Tullahoma. We will not be delivering anywhere. So, we will consider $ 0.20 / lb of ammonia. This gives a revenue of $ 290 per day (= $ 95700 per year). This and the revenue generated by selling fuel gas and residue amounts to $ 2,578,380 ($ 2,365,200, for fuel gas @$14.52/ MMBtu taken from Turner's thesis + $ 117,480, for residue + $ 95,700, for aqua ammonia). So, the annual net profit will be approximately $ 749,980 ($ 2,578,380 – $ 1,828,400,the annual cost). The payback with this net revenue will be 4.75 years. This case is representative of high price of gas.

Table 6.6: Approximation of the Fertilizer Value of the Residue

Item	Total , %	Available, %	$/lb of nutrient	$/ton of ash
P_2O_5	8	4	0.22	17.6
K_2O	15	7.5	0.12	18
			Total	**35.6**

Under a low energy value scenario the fuel gas would be sold at $9.85 per million Btu (as considered by Turner). The total gross revenue in that case will be $ 1,817,780 ($1,604,600, for fuel gas @ $9.85/ MMBtu + $ 117,480, for residue + $ 95,700, for aqua ammonia), and so the annual net profit would be negative (-$10,620). There is no chance of payback at these particular conditions. So, under the low energy value case, a 100 tons / day plant will not be profitable. It needs to be scaled up to 500 or 1000 tons /day plant as suggested by Turner (4) to make it profitable.

The cost of disposing the scrubbing liquor by giving it to a third party for disposal will be very high because the pH of the solution would be high and it needs additional treatment prior to disposal of the solution. According to a preliminary estimate about $0.70 per gallon would be required to be paid to a third party for disposal of the aqua ammonia liquor. This will amount to about $ 4,200 per day, or $1,386,000 per year. The above estimate is from Safety-Kleen (14). They were considering deep well injection in Plaquemine, Louisiana. The above disposal option is not recommended for its uneconomical nature.

According to Agency for Toxic Substances and Disease Registry (ATSDR) (12), the Permissible Exposure Limit (PEL) for ammonia set by Occupational Safety and Health Administration (OSHA) is 50 ppm. However, according to ATSDR, ammonia is considered to be toxic only at very high concentration. Usually it is present everywhere in the environment as a part of the nitrogen cycle. Hence no ongoing studies on adverse impact of ammonia on the environment were identified. According to Environmental Protection Agency, ammonia is not listed as a pollutant because it is an accidental release pollutant. So, the particular state environmental agency will have to be consulted while implementing a project related to ammonia release. Accordingly, the ammonium hydroxide liquor formed after absorbing ammonia from the fuel gas may be fed to an air stripper after pH adjustment, where the ammonium hydroxide liquor will be stripped of ammonia. We can then release the air containing ammonia, in case that is the only alternative available for ammonia disposal. After air stripping the ammonia concentration will be much below the threshold limit of 50 ppm.

Chapter VII

Conclusions and Recommendations

Conclusions

Based on the results from this preliminary study, we can make the following conclusions;

- Gasification of poultry litter poses a serious threat to environment if the nitrogen and phosphorus containing species in the litter are not taken care in an environmentally acceptable manner.
- The nitrogen is released as ammonia during pyrolysis / gasification of the litter. The ammonia can be scrubbed off from the fuel gas using demineralized water, before the fuel gas is supplied to other customers as a source of energy.
- About 300 mg of ammonia is released when 10 g of litter is gasified. So, for the litter gasification plant of 100 tons/day, the estimated amount of ammonia released would be about 3 tons/day. However, as per Table 5.2, we got a greater amount of ammonia released in certain cases due to non-homogeneity of the chicken litter.
- The percentage of phosphorus remaining in the residue after gasification is complete will be about 8 wt % and potassium will be about 15 wt%.
- As suggested by Turner(4), a higher capacity of 500 to 1000 tons/day is required for the scale of the gasification plant to make it profitable.
- Bench scale data does not support a first order overall rate expression for ammonia evolution from the chicken litter.

- The amount of ammonia released during pyrolysis/ gasification of litter reduces with temperature in accordance with equilibrium shift suggested by equation 5.1.
- The amount of ammonia released during gasification of litter also reduces with increase in catalyst loading.

Recommendations

Based on the above conclusions, following are the recommendations;

- An online ammonia analyzer needs to be installed on the fuel gas line, to monitor the rate of ammonia liberation continuously and easily. This would avoid the error involved in the wet chemistry method (titration method) used in this study.
- An ammonia scrubbing system needs to be installed in the litter gasification plant so that the fuel gas will be ammonia-free. It will be economically feasible to recover this captured ammonia and sell it as ammonium hydroxide solution.
- Additional kinetics experiments with different additional catalyst loading and different gasification temperature needs to be carried out to better model the overall process for ammonia liberation.
- There is a need to evaluate more litters, some doped with additional nitrogen containing species such as urea to evaluate effect of chemically bound nitrogen in litter.

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