STEAM GASIFICATION OF MANURE

by

S. GANESAN

B. Tech., Indian Institute of Technology, Madras, India

_____

A MASTER'S THESIS

submitted in partial fulfillment of the

requirements for the degree

MASTER OF SCIENCE

Department of Chemical Engineering

KANSAS STATE UNIVERSITY
Manhattan, Kansas

1979

Approved by:

Walter P Walawender

Major Professor

TABLE OF CONTENTS

CHAPTER I

INTRODUCTION

The recent sharp increase in the price of oil and gas caused by our dwindling reserves, increased consumption and dependence on foreign oil has caused major concern. In an effort to control the spiralling prices, cut down on our dependence on foreign oil and curb inflation, the nation has turned towards alternate sources of energy. Among these, coal, being this country's most abundant fossil fuel has been the focus of major attention. Oil shale and tar sand are two of the other main fossil fuels which have generated a lot of interest as potential sources of energy.

While these fossil fuels comprise the major portion of our energy reserves, they are not without drawbacks. The sulfur content in coal has posed a major problem as to the harmful effects it can have on the environment. The caking tendency of certain types of coals and the large ash content have created operation problems in converting the coal to a useful form of energy. With oil shale and tar sand, the prohibitive costs of processing these materials have deterred many industrial concerns from attempting to utilize these fuels to produce energy.

In the continued search for alternate energy resources many non-fossil fuels have begun to generate a lot of interest. Among these municipal solid wastes, sewage sludge, scrap rubber tires, wood, crop residues and manure are some of the materials that have been considered. Although the latter category of fuels are not as abundant as our reserves of fossil fuels, they posses one major advantage over fossil fuels in that they are replenishable. Except for rubber tires, the remaining non-fossil fuels listed above are known generally as biomass.

This study focuses on the gasification of one of these biomass fuels, namely manure, with a view to study the quality and yield of gas produced

by the said process. Apart from its abundance in the state of Kansas, its low sulfur content makes it a very attractive material for producing energy.

A review of the work done in the gasification of non-fossil fuels, particularly manure, is discussed in chapter two. The gasification processes involved vary in the nature of the contacting devices employed and operating conditions.

Chapter three presents the experimental study performed on the steam gasification of feedlot manure in a bench-scale fluidized bed reactor. The effect of temperature on the composition and yield of the produced gas is discussed. The study also focuses on the agglomeration problems encountered in the fluidized bed gasification of manure. In addition, the results from the bench-scale reactor are compared with those obtained from a pilot plant fluidized bed reactor operated under similar conditions. A discussion is presented on the similarities and differences of the results obtained in the two cases.

The importance of suitable analysis schemes to study the products of gasification processes cannot be over emphasized. Chapter four discusses the development of a gas chromatographic method of analysis employed for the qualitative and quantitative analysis of the produced gas from the gasification of coal and biomass. Chapter five summarizes the work done in this thesis with recommendations for future research in this area.

CHAPTER II

LITERATURE REVIEW ON GASIFICATION

OF MANURE

The utilization of cattle feedlot manure as a potential and renewable source of energy has received increasing attention in recent years. This attention has been caused not only by the increase in demand for alternate sources of energy but also by the mounting disposal and pollution problems created by feedlot wastes.

The development of the cattle feeding industry has resulted in the concentration of large numbers of animals in relatively small areas. It is estimated that there are almost 14 million cattle in confined feeding areas (Walawender et al., 1972). Feedlots of 50,000 or more heads are no longer uncommon (Garner and Smith, 1973). Present estimates show that the amount of wet manure produced to be about 2 billion tons/year (Walawender et al., 1972). As a result of the rapid growth of the cattle feeding industry, the accumulation of vast quantities of animal wastes has posed serious environmental hazards to air, water and land quality.

In order to overcome this problem, several alternate disposal methods have been proposed (Walawender et al., 1972, 1973). Possible conversion schemes include anaerobic digestion, gasification at ambient pressure, hydrogasification and liquefaction. Of these atmospheric gasification appears to be the most economically attractive alternative for large scale applications. (Engler, 1975; Walawender et al., 1972, 1973 a, 1973 b). The synthesis gas produced from such a process could be utilized as a low Btu gas for power generation, a starting material for ammonia synthesis or starting point for methanol production. In addition to the synthesis gas, the ash by-product from the gasification process appears to be a potential nitrogen free fertilizer (Engler et al., 1975; Davis et al., 1972).

Thus the gasification of manure serves not only to solve the disposal problem of mounting feedlot wastes but also provides a valuable contribution towards the alleviation of the energy crisis.

A survey of the literature indicated that limited information was available on the gasification of manure. Burton (1972) reported data obtained from two runs made with manure in a 38.1 cm fluidized bed reactor. The fluidizing gas was the product formed from combusting methane in air and the bed was made of silica sand. The first run was made at 1022 K and yielded 0.76 Nm^3/kg (DAF) (12.16 SCF/lb) of gas with a heating value of 10.43 MJ/Nm^3 (280 Btu/SCF). The second run, made at 1041 K yielded 0.71 Nm^3/kg (DAF) (11.30 SCF/lb) of gas with a heating value of 14.04 MJ/Nm^3 (377 Btu/SCF). Halligan et al. (1975) partially oxidized manure in a bench scale fluidized bed reactor, 3.81 cm in diameter, using a mixture of air and steam as the fluidizing gas. The temperature range investigated was (966-1069)K. and the gas yield varied from (0.604-1.232) m^3/kg (DAF), measured at (273K, 1 atm).

Smith et al (1974) partially oxidized cattle feedlot waste in a moving bed retort using a mixture of recycled product gas and air. The temperature range studied was (883-950)K and the product gas had a net heating value of 2.037 MJ/Nm^3. Mikesell et al (1978) reported limited data on the gasification of manure in a multiple hearth furnace. The feed was pyrolyzed at 1023K to yield a product gas with a heating value of 11.17 MJ/Nm^3. Martinez (1973) hydrogasified manure in a batch reactor at 839K and at pressures ranging from (1.0 - 20.4) atm. The produced gas yield was 0.54 Nm^3/kg with a heating value of 22.36 MJ/Nm^3. Garner and Smith (1973) reported data obtained from the gasification of manure in a fixed bed at 773K, the produced gas from which had a heating value of 9.1 MJ/Nm^3.

Pilot plant gasification studies on manure have been reported recently by Beck et al (1979). The process involved partial oxidation of the feedstock in a fluidized bed using a mixture of steam and air with manure being the only solid phase present. The temperature range studied was (790-909)K and the heating value of the dry produced gas varied from (8.89 – 11.96) MJ/Nm^3. Walawender and Fan (1978) reported data on the gasification of feedlot manure in a 22.9 cm fluidized bed reactor with a silica sand bed. The flue gas from the combustion of propane in air was employed as the fluidizing medium. The gasification yielded about 0.54 Nm^3 of gas per kg as received feed, with a heating value of 13.2 MJ/Nm^3 (355 Btu/SCF). The temperature range investigated varied from (1000 – 1100) K. Pattabhi Raman et al (1979) studied the effect of temperature on the gasification of manure in a fluidized bed reactor, 22.9 cm in diameter, with a bed composed primarily of silica sand. The flue gas from combusting propane in air was employed to fluidize the bed. The operating temperature varied from 900K to 994K. The higher heating value of the dry produced gas varied from 12.52 MJ/Nm^3 (336.8 Btu/SCF) to 21.58 MJ/Nm^3 (579.3 Btu/ SCF) and the gas yields reported ranged from 0.399 Nm^3/kg DAF (6.6 SCF/lb DAF) to 0.612 Nm^3/kg DAF (9.6 SCF/lb DAF).

LITERATURE CITED

Beck, S. R., W. J. Huffman, B. L. Landeene, and J. E. Halligan, "Pilot
    Plant Results for Partial Oxidation of Cattle Feedlot Manure," Ind.
    Eng. Chem. Process Des. Dev., 18, No. 2 (1979).

Burton, R. S., "Fluid Bed Gasification of Solid Waste Materials," M.S.
    Report, West Virginia University (1972).

Davis, E. G., I. L. Feld, and J. H. Brown, "Combustion Disposal of Manure
    Wastes and Utilization of the Residue," Bureau of Mines Solid Waste
    Research Program, Technical Progress Report 46, January, 1972.

Engler, C. R., W. P. Walawender, and L. T. Fan, "Synthesis Gas from Feedlot
    Manure," Enviro. Sci. Tech., 9, No. 13 (1975).

Garner, W. and I. C. Smith, "The Disposal of Cattle Feedlot Wastes by
    Pyrolysis," Environmental Protection Technology Series, EPA-R2-73-096
    (January, 1973).

Halligan, J. E., K. L. Herzog, and H. W. Parker, "Synthesis Gas from
    Bovine Wastes," Ind. Eng. Chem., Process Des. Develop., 14, No. 1
    (1975).

Martinez, J. and A. Carlos, "An Experimental Study on the Production of
    Substitute Natural Gas by Hydrogasification of Livestock Manure,"
    Ph.D. Thesis, University of Kansas (1973).

Mikesell, R. D., D. C. Hoang, and D. E. Garrett, "The Garrett Energy
    Research Biomass Gasification Process," Proc. of the 13th Inter-
    society Energy Conversion Engineering Conference, San Diego, CA,
    (1978).

Pattabhi Raman, K., W. P. Walawender, and L. T. Fan, "The Effect of Temp-
    erature on the Fluidized Bed Gasification of Feedlot Manure in a
    Pilot Plant," to be published.

Smith, G. L., C. J. Albus, Jr., and H. W. Parker, "Products and Operating
    Characteristics of the TTU Retort," presented at the 76th National
    AICHE Meeting, Tulsa, Oklahoma (1974).

Walawender, W. P., L. T. Fan, and L. E. Erickson, "Feedlot Manure and Other
    Agricultural Wastes as Future Material and Energy Resources: I. Intro-
    duction and Literature Review," Report No. 36 of the Institute for
    System Design and Optimization, Kansas State University, Manhattan,
    Kansas, April (1972).

Walawender, W. P., L. T. Fan, C. R. Engler, and L. E. Erickson, "Feedlot
    Manure and Other Agricultural Wastes as Future Material and Energy
    Resources: II. Process Descriptions," Report No. 45 of the Institute
    for Systems Design and Optimization, Kansas State University, Manhattan,
    Kansas, March 1973(a).

Walawender, W. P., L. T. Fan, C. R. Engler, and L. E. Erickson, "Feedlot Manure and Other Agricultural Wastes as Future Material and Energy Resources: III. Economic Evaluation," Report No. 46 of the Institute for Systems Design and Optimization, Kansas State University, Manhattan, Kansas, July, 1973(b).

Walawender, W. P. and L. T. Fan, "Gasification of Dried Feedlot Manure in a Fluidized Bed - Preliminary Pilot Plant Tests," presented at the 84th National Meeting of AICHE, Atlanta, GA, (1978).

CHAPTER III

STEAM GASIFICATION OF MANURE IN A
BENCH SCALE FLUIDIZED BED REACTOR

INTRODUCTION

Diminishing natural reserves, spiralling price hikes, strong dependence of foreign oil and increased demand for oil and gas have led to a continued search for alternative fuels. Coal has been by far the major focus of attention since it is the nation's most abundant fossil fuel. Oil shale and tar sand are two other main fossil fuels which have received increasing attention.

While these fossil fuels constitute the major portion of this nation's energy reserves, many non-fossil fuels have recently begun to generate much interest. Among these, scrap tires (Green, 1978), municipal solid wastes (Jones, 1977; Chiang et al., 1978), feedlot manure (Beck et al., 1979; Walawender and Fan, 1978; Pattabhi Raman et al., 1979), and agricultural crop residues (McGriff, 1973; Shafizadeh, 1975) are some of the materials that have been considered. Although the non-fossil fuels are not as abundant as our reserves of fossil fuels, they possess other advantages. Gasification studies of these materials have shown that in many cases gas yields and heating values to be superior to those from coal gasification. In addition, the low sulfur content of most of these materials coupled with the fact that unlike fossil fuels these are replenishable sources of energy, has made them very attractive as alternative fuels. This study focuses on one of these materials, namely, manure.

The rapid growth of the cattle feeding industry has resulted in the accumulation of vast quantities of animal wastes thus creating problems of environmental pollution. In an attempt to overcome this problem, several alternative disposal schemes have been proposed (Walawender et al., 1972, 1973). Some of these routes include anaerobic digestion, gasification at atmospheric pressure, hydrogasification and liquefaction. Of these

atmospheric gasification appears to be the most economically attractive alternative (Engler, et al., 1975; Walawender et al., 1972, 1973a, 1973b).

When complex organic solids such as feedlot manure are heated to elevated temperatures, a series of chemical and physical changes occur, resulting in the evolution of gaseous products and a carbonaceous solid residue. The extent of the volatiles yield and composition will depend largely on the nature of the material, the manner of heating (Anthony and Howard, 1976), and the environment in which gasification is performed. Devolatilization studies on manure indicate volatile yields as high as 90% on a dry basis (Antal et al., 1979; Howell, 1979).

Many contacting reactors, such as fixed beds (Garner and Smith, 1973), moving beds (Smith et al., 1974), entrained beds (Mikesell et al., 1978) and fluidized beds (Burton, 1972; Beck et al., 1978; Walawender and Fan, 1978; Pattabhi Raman et al., 1979; Howell, 1979), have been employed to study the gasification characteristics of manure. Of these, fluidized beds have been widely used because of their high heat transfer characteristics, ease of operation and their capacity to maintain a uniform thermal environment.

The steam gasification of feedlot manure in a bench scale fluidized bed reactor was investigated in this study with a view to study the effect of temperature on the product gas composition and yields. The gaseous products using a bed of silica sand were compared to those from a bed made of a limestone-sand mixture. The latter was employed as a means of preventing bed agglomeration which resulted when the reactor, using a sand bed, was run for extended periods of time. In addition, the data from the bench scale reactor were compared with those obtained from a pilot plant scale fluidized bed reactor.

EXPERIMENTAL

Feedstock

The feedstock used for steam gasification was feedlot manure obtained
from the Kansas State University Beef Cattle Research Center. The original
moisture content of the manure was about 80% by weight, but the manure was
flash dried to reduce the moisture content to about 5%. It was then hammer-
milled and sieved. The size fraction used in the experiments was 14-40 mesh
(1.41 mm - 0.42 mm).

Facilities

The bench scale fluidized bed reactor is shown schematically in Figs. 1
and 2. The reactor was constructed from a 5.08 cm (2 in.) diameter schedule
40 Inconel 600 pipe, with a 10.16 cm (4 in.) diameter pipe of the same
material which served as the disengaging zone. The gas distributor con-
sisted of a packed bed containing aluminum oxide pellets 0.5 cm in diameter,
which also served as a preheating zone for the fluidizing gas. The bed was
composed of 30-50 mesh (1.42 mm - 0.95 mm) inert particles with a static
bed height of 7.62 cm (3 in). Silica sand and a limestone-silica sand
mixture were used as bed materials. The fluid bed section was separated
from the packed bed section by means of a 60 mesh (0.25mm) 316 stainless
steel screen.

Heat was supplied by means of four pairs of semi-cylindrical electrical
resistance heaters, each capable of delivering up to 2300 watts of power
with a maximum operating temperature of 1473K. Steam was generated exter-
nally in an 800 watt electrical furnace and was supplied to the reactor at
approximately 770K.

The feed was introduced into the reactor by means of a vertical feed-pipe which discharged at a height of 6.3cm above the static bed. A Vibra Screw Model SCR-20 screwfeeder with a solid core flight screw was used to supply the feedpipe at a uniform volumetric rate. A purge flow of helium was employed to aid flow through the feedpipe and to prevent backflow through the feedpipe and subsequent condensation of vapor in the feeder. To prevent the feed material from prematurely devol-atilizing before it reached the bed, the feedpipe was equipped with a water jacket which maintained the temperature below 420K.

The product gases from the reactor were sent to a cyclone where entrained fines were separated from the gas. The temperature in the cyclone was maintained at about 570K to prevent condensation of tar and steam. This was accomplished by means of a heating tape wrapped around the cyclone.

The gaseous stream leaving the cyclone was cooled to approximately 320K by means of two water-cooled heat exchangers in series. This resulted in the condensation of the fluidizing steam, which was collected in a flask. The resulting product gas carried with it a fine mist of condensable materials which were removed by passing the gas through a packing of glass wool. A column packed with Drierite ($CaSO_4$) was then used to dry the gas before it was collected in a sample bottle for analysis. A known volumetric flow of nitrogen was introduced as a tracer gas just upstream of the gas sample point. Subsequent gas analysis permitted the calculation of the produced gas flow rate from the reactor.

The temperature of the fluidized bed was monitored by means of a thermocouple placed inside the bed. The temperature was also monitored in the steam generator, cyclone, heat exchanger outlet and reactor inlet.

A pressure probe, connected to a manometer, was used to monitor the bed pressure and as a check on the quality of fluidization.

Procedure

The reactor was heated to approximately 50K above the desired operating temperature using air as the fluidizing gas for start-up. The heatup period for the reactor was about one hour. During this period, the steam generator, cyclone heater and inlet section heaters were brought to their operating temperatures of 770K, 570K and 470K, respectively. Coolant flow to the feed pipe jacket was then commenced and the air flow was replaced by steam. The volumetric flow rate of steam through the bed required to maintain the selected fluidization velocity was measured both by condensate collection downstream of the heat exchangers and by metering the water flow into the steam generator. The system reached steady state as measured by the steady collection of water condensate in about 15-20 minutes.

The pressure probe used to monitor the pressure inside the bed gave an indication of the quality of fluidization of the bed. When the bed was well fluidized, the probe fluctuated about the mean bed pressure, while a stagnant pressure reading indicated poor fluidization. The helium purge through the feed pipe was commenced just prior to the initiation of feeding. During the initial stages of feeding, the reactor temperature dropped and the power supply to the heaters had to be readjusted to maintain the set temperature.

The system required about 30 to 45 minutes after the initiation of feeding to reach steady state as determined by the reactor temperature and condensate collection. The reactor was run at steady state for about one hour during which time gas samples and condensate were collected.

The condensate was measured over four consecutive 15-minute time intervals with the gas samples being taken at the end of every 15-minute period. A known volumetric flow of nitrogen was introduced as a tracer gas just upstream of the gas sample point. Subsequent gas analysis permitted the calculation of the produced gas flow rate from the reactor.

The reactor temperature was varied between 970K and 1370K while the superficial velocity of steam was maintained at 36.6 cm/sec. The superficial velocity of the fluidizing gas corresponded to about 20 times the minimum fluidization velocity and 20% of the terminal velocity of the manure particles, while it corresponded to about 10 times the minimum fluidization velocity of the sand in the bed. The operating conditions employed are summarized in Table 1.

Chemical Analysis

The chemical analysis included proximate and ultimate analyses of the feed as well as the quantitative analysis of the product gas. The proximate analysis was performed with a Perkin-Elmer Model TGS-2 Thermogravimetric Analyzer. Ultimate analysis was performed using a Perkin-Elmer Model 240 Elemental Analyzer. Using one milligram samples, this instrument determined the weight percentages of C, H, N, O and S to within an accuracy of one half of a percent. Densities were measured using a Beckman Model 930 Air Compression Pycnometer.

Analysis of the product gas was performed using a Packard Model 417 Becker dual column gas chromatograph equipped with thermal conductivity detectors. The gas components of interest included H_2, CO, CO_2, CH_4, C_2H_4, C_2H_6, C_3H_6, C_3H_8, O_2 and N_2. A 1.83m x 0.0032m (6' x 1/8") column with No. 5A molecular sieve packing (80-100 mesh) was used for the separation and analysis of H_2, O_2, N_2, CH_4 and CO. The remaining components were

analyzed by using a 1.83m x 0.0032m (6' x 1/8") column with 80-100 mesh Porapak Q packing preceded by a 0.15m x 0.0032m (6" x 1/8") section of (80-100) mesh Porapak R packing. The Porapak R was used to shift the retention time of the H_2O peak so that it was easily separated from the other components. The gas chromatograph was operated isothermally at 350K with helium as the carrier gas. Accessories used in the analysis included a spectra-physics Autolab System-I computing integrator and a Varian Model A-25 stripchart recorder.

RESULTS AND DISCUSSION

The results of the proximate and ultimate analyses of the feed as well as the physical properties of the feed are summarized in Table 2. The results from the bench-scale reactor will be discussed in two parts.

In the first part, the effects of temperature on the steam gasification of manure are discussed and results obtained using a silica sand bed are compared with those from a bed made of 25% limestone and 75% sand. The purpose of the limestone sand mixture was to attempt to prevent agglomeration of the bed which occurred when the silica sand alone was used as bed material. It was suspected that the alkali salts present in the manure either formed a low melting solid, which at sufficiently high temperatures fused with the particles of sand or reacted with the sand to form low melting silicates, which caused the bed to agglomerate.

In the second part, the results from the bench scale reactor are compared with those from a 22.9 cm (9 inch) diameter pilot plant fluidized bed reactor run under similar conditions.

In the bench scale studies, the variation of the following parameters with temperature were noted:

(1) Concentrations of the individual components in the product gas,

(2) Higher heating value of the product gas,

(3) Gas yield per unit mass of feed,

(4) Efficiency, as measured by the fractional energy recovered in the product gas.

The results from the two types of beds used were compared. In addition, the effect of limestone on the agglomeration characteristics of the bed was examined.

Gas Composition.

The variations in the concentrations of H_2, CO_2 and CO in the product gas from the sand bed with temperature are shown in Fig. 3. Fig. 4 shows the corresponding variations of the same components using the sand-limestone bed.

Hydrogen. The composition of H_2 was not seriously affected by temperature in the sand bed. At 980K the composition was 43.5%. It decreased to 38% at 1140K before rising back to 44% at 1370K. No notable change in the concentration of H_2 was observed in the limestone bed. The composition remained essentially constant at 45% throughout the temperature range.

Carbon dioxide. Carbon dioxide from the sand bed showed a continuous decrease in concentration over the temperature range studied. At the lower temperature, 980K, it was 32.5% and with increasing temperature its value decreased to 20% at 1370K. The CO_2 concentration with the limestone bed remained approximately constant at about 28% throughout the temperature range.

Carbon monoxide. Carbon monoxide from the sand bed showed a continuous increase in concentration with temperature. It rose from 17% at 980K to 26% at 1370K, a 53% increase from its value at the lower temperature. The limestone bed showed no increase in the concentration of carbon monoxide. It remained approximately constant at 15% over the temperature range investigated.

The effect of temperature on the hydrocarbon concentrations in the sand bed are shown in Fig. 5. The concentration of methane showed a sharp increase from 4.5% at 980K to 8.5% at 1090K. There was no further increase in concentration at the higher temperatures. Ethylene concentration increased four-fold from 1.5% at 980K to 6% at 1170K before decreasing to 2% at 1370K.

Ethane and propylene showed similar trends although to a much smaller degree. Ethane varied from 0.3% at 980K to 0.7% at 1120K and back to 0.4% at 1230K. At temperatures above 1230K ethane was not detected in the produced gas. Propylene increased from 0.6% at 980K to 1.6% at 1120K and then decreased to 0.6% at 1230K. At temperatures above 1230K it was not detected in the product gas.

Fig. 6 shows the variations in the hydrocarbon concentrations from the limestone bed. The concentration of methane showed a continuous increase with temperature. Starting from a value of 5.7% at 980K, it increased to 8.3% at 1310K. This was in contrast to the sand bed where the concentration of methane remained essentially constant after an initial sharp increase. The composition of ethylene followed a trend similar to that observed on the sand bed. It increased from an initial value of 2.5% at 980K to 3.9% at 1170K before decreasing to 3% at 1310K. Ethane slowly decreased in concentration with temperature. Starting at 0.5% at 980K it decreased until it was barely detectable at about 0.1% at 1310K. The concentration of propylene remained essentially constant around 1% from 980K to 1140K beyond which it was not detected.

Heating Value of the Product Gas

The effect of temperature on the higher heating value of the product gas is shown in Fig. 7. In the sand bed, the heating value showed a small increasing trend initially before reaching a maximum at 1140K, beyond which it tapered off. At 980K it was 10.71 MJ/Nm^3 (287 Btu/SCF). The peak value at 1140K was 15.37 MJ/Nm^3 (412 Btu/SCF) and at 1370K it dropped to 13.06 MJ/Nm^3 (350 Btu/SCF).

The heating value of the product gas from the limestone bed showed no appreciable variation with temperature. It remained essentially constant

at 13.06 MJ/Nm^3 (350 Btu/SCF) throughout the temperature range. The difference in heating value between the sand and limestone beds was not very significant. The deviation of the heating value of the product gas from the sand bed was not more than 2.24 MJ/Nm^3 (60 Btu/SCF) from a line drawn at 13.06 MJ/Nm^3 (350 Btu/SCF) across the entire temperature range.

Effect of Gas Composition on Heating Value

At the lower temperatures, the higher concentration of CO_2 coupled with low concentrations of CO and the hydrocarbons caused the smaller heating value of the product gas in the sand bed. The peak values of the hydrocarbons gave rise to the observed high heating value around 1170K. At still higher temperatures, the decrease in hydrocarbon concentration caused the heating value to drop down again, in spite of lower CO_2 and higher CO concentrations.

In the limestone bed, the increase in methane concentration was offset by a decrease in the concentration of the other hydrocarbons thus leading to a constant heating value over the entire temperature range.

Gas Yield

The gas yield as measured by the cubic meters of gas (at 288.6K (60°F)) per kilogram of dry ash-free feed, showed a continuous increase with temperature in both the sand and limestone beds, as shown in Fig. 8.

The sand bed showed a variation in yield which was almost linear with increasing temperature. At 980K the gas yield was 0.59 Nm^3/kg (9.5 SCF/lb). At 1370K, the yield increased to 1.3 Nm^3/kg (20 SCF/lb), more than twice the value at the lower temperature.

The gas yields from the limestone bed were significantly higher than those obtained from the sand bed. Starting at a value of 0.624 Nm^3/kg (10 SCF/lb) at 950K, the gas yield increased to about 1.436 Nm^3/kg (23 SCF/lb) at 1310K. At 1140K, the gas yield from the limestone bed was about 1.186 Nm^3/kg

(19 SCF/lb), a 35% increase over the value of 0.874 Nm^3/kg (14 SCF/lb) from the sand bed at the same temperature.

Efficiency

The efficiency, defined as the fraction of recoverable energy present in the product gas as compared to the heat of combustion of the dry ash free feed, is shown in Fig. 9. The total energy available from the product gas is its heating value multiplied by its yield. The efficiency using the sand bed showed a sharp increase from 33% at 980K to 75% at 1230K and then tapered off to a value of 85% at 1370K.

The sand-limestone bed showed a substantially higher efficiency than the silica sand bed. Starting at a value of 45% at 980K it increased more than twofold to about 84% at 1200K and then tapered off to reach a value of about 90% at 1310K.

Effect of Limestone on the Agglomerating Behavior

Agglomeration problems in the fluidized bed gasification of manure, when using sand as bed material, have been reported by a few investigators. Alpert et al., (1972) noted the formation of agglomerates of sand particles exhibiting the high temperature phases of quartz (cristobalite and tridymite). They attributed the cause of these phase transformations to the natural fluxes contained in the manure. Halligan et al., (1975) reported that the particles found in their fluidized bed consisted of agglomerates of from five to ten char-sized particles. Hercules Inc. (1975) gasified manure in a pilot plant scale fluidized bed reactor, 22.9 cm in diameter, at 1044K. They found that after approximately 7 hours of operation, the fluidized bed became semi-rigid. Some small aggregates of sand and ash were also observed.

In the present study, similar observations were noted when manure was steam gasified using a silica sand bed. The entire bed formed a semirigid mass, which prevented any further fluidization.

In an attempt to prevent this bed agglomeration, a mixture consisting of 25% limestone and 75% silica sand was employed as the bed material. It was found that this limestone-sand mixture prevented the formation of any agglomerates, thus permitting continuous operations of the fluidized bed reactor. Furthermore, as discussed above, the limestone showed no adverse effects but rather improved the gas yield significantly.

Comparison of Results of the Bench Scale and Pilot Plant Reactors

The results from the bench scale fluidized bed reactor using the limestone–sand bed were compared with those obtained in a pilot plant reactor run under similar conditions. The pilot plant reactor was a 22.9 cm fluidized bed reactor with the same bed material and was operated in the low temperature range (925K - 1025K) of the bench scale experiments. A schematic diagram of the pilot plant facility is shown in Fig. 10. A detailed description of the pilot plant reactor can be found elsewhere (Pattabhi Raman et al., 1979). Comparisons were made between the heating value, yield and efficiencies of the two systems.

Heating Values

The higher heating values of the product gases from the bench scale and pilot plant reactors are compared in Fig. 11. The heating value of the gas produced in the pilot plant reactor appeared to show a continuous decrease with increasing temperature. Starting at a value of about 19 MJ/Nm^3 (509.2 Btu/SCF) at 933K it dropped to 16.3 MJ/Nm^3 (436.8 Btu/SCF) at 1015K. The heating value of the bench scale reactor, however, was significantly lower, and stayed essentially constant at 12.5 MJ/m^3 (335.0 Btu/SCF) from 950K to 1255K.

Gas Yields

Fig. 12 shows the gas yields obtained with the bench scale and pilot plant reactors. Both reactors showed an increasing gas yield with temperature although the gas yield from the pilot plant reactor appeared to be slightly lower than the bench scale reactor. The gas yield from the pilot plant reactor showed an almost linear increase from 0.55 Nm^3/kg SCF/lb at 933K to about 0.8 Nm^3/kg SCF/lb at 1015K. The bench scale reactor also showed a linear increase in the same temperature range. The gas yield

started at 0.7 Nm^3/kg at 950K, and rose almost linearly to 1.28 Nm^3/kg at 1145K before slowly tapering to about 1.44 Nm^3/kg at 1255K. At any particular temperature, the gas yield from the bench scale reactor was about 0.1 Nm^3/kg higher than that from the pilot plant reactor.

Efficiencies

Fig. 13 shows the percentage energy recovery (or efficiency) of the two reactors. In both cases the efficiency increased sharply with increasing temperature. However, the pilot plant showed a higher efficiency than the bench scale reactor in the same temperature range. The efficiency of the pilot plant reactor increased from about 47.5% at 933K to about 63% at 1015K. In the same temperature range the efficiency of the bench scale reactor rose from about 41% to a value of about 57% at 1015K.

Comparison of the data obtained from the two reactors indicated that while the values of the gas yields from the two reactors were close to one another and followed a very similar trend with temperature, the heating values and efficiencies were markedly different. One possible explanation for the differences in heating value and efficiency while the yield remained the same, can be offered by considering the secondary reactions that can take place after devolatilization occurs (Pattabhi Raman et al., 1979; Antal et al., 1979). The extent to which these reactions take place depends on the time-temperature history of the products of devolatilization. Immediate quenching of the devolatilization products will result in a fairly high quality gas with yield on the low side. Holding these products in the high temperature environment will permit cracking reactions to take place along with reactions with steam. These result in low molecular weight compounds, especially H_2 and CO, which increase the gas yield while decreasing the heating value of the gas.

It was observed that in the pilot plant, the gases experienced a drop in temperature as they left the bed. In the bench scale reactor, the temperature of the disengaging zone was at least the same and might have been even higher than the temperature of the bed. The power supplied to the external heaters was maintained at a uniform value throughout the fluidized bed and disengaging zones, the latter being closer to the heaters than the bed itself. Furthermore, additional energy was needed to heat the fluidized bed as well as the packed bed gas distributor. These two factors could have resulted in a large temperature difference between the bed and the disengaging zone.

Since the temperature was measured by a thermocouple immersed inside the bed, the exact temperature of the disengaging zone was not known. If the temperature of the latter zone was indeed hotter than the bed, it is possible that the effect of secondary reactions in the disengaging zone caused the heating value of the product gas to remain essentially constant throughout the temperature range investigated. Hence, careful attention must be given to the temperature of the disengaging zone when obtaining data from the reactor.

It should be noted, therefore, that the bed temperature alone is not a valid point of comparison. The time-temperature history of the gas along with other factors that differ between experimental systems should be carefully considered as they can significantly affect the final gas yield and composition.

CONCLUSION

Steam gasification of manure was conducted in a bench scale fluidized reactor using a bed made of sand, and the results were compared to those using a bed made of a limestone-sand mixture. It was found that although the quality of the gas produced was not altered, [i.e., 13.06 MJ/Nm^3 (350 Btu/SCF) vs 14.28 MJ/Nm^3 (383 Btu/SCF)], the quantity of gas produced with the limestone bed was significantly higher than that of the silica sand bed [1.19 Nm^3/kg (19 SCF/lb) vs 0.874 Nm^3/kg (14 SCF/lb)]. Thus, it was concluded that the presence of limestone not only served to prevent agglomeration of the bed but also greatly improved the efficiency of the gasification process.

The data obtained with the bench scale reactor using the limestone-sand bed were also compared with those obtained from a pilot plant reactor operated under similar conditions. The results showed that while the value of the gas yields from both reactors were very close, the heating values were markedly different. It was suspected that the time-temperature history of the produced gas in the disengaging zone plays an important role in the product gas composition. Therefore, caution must be exercised in the comparison of two reactors of different sizes on the basis of temperature alone.

LITERATURE CITED

Alpert, S. B., H. Scheeline, B. Louks, F. A. Ferguson, and C. Marynowski, "Pyrolysis of Solid Waste: A Technical and Economic Assessment," Stanford Research Institute, SRI Project ECC-1886, September (1972).

Antal, M. J., Jr., F. E. Rogers, and H. L. Friedman, "A Study of the Steam Gasification of Organic Wastes," Draft Final Copy to U.S.E.P.A., Dept. of Mechanical and Aerospace Eng., Princeton Univ., Princeton, N.J. (1979).

Anthony, D. B. and J. B. Howard, "Coal Devolatilization and Hydrogasification," AICHE Journal, 22, No. 4 (1976).

Beck, S. R., W. J. Huffman, B. L. Landeen, and J. E. Halligan, "Pilot Plant Results for Partial Oxidation of Cattle Feedlot Manure," Ind. Eng. Chem. Process Des. Dev., 18, No. 2 (1979).

Burton, R. S., "Fluid Bed Gasification of Solid Waste Materials," M.S. Report, West Virginia University (1972).

Chiang, S. H., J. T. Cobb, and G. E. Klinzing, "A Critical Analysis of the Technology and Economics for the Production of Liquid and Gaseous Fuels from Waste," presented at the 84th National Meeting of AICHE, Atlanta, GA (1978).

Engler, C. R., W. P. Walawender, and L. T. Fan, "Synthesis Gas from Feedlot Manure," Enviro. Sci. Tech., 9, No. 13 (1975).

Garner, W. and I. C. Smith, "The Disposal of Cattle Feedlot Waste by Pyrolysis," Environmental Protection Technology Series, EPA-R2-73-096 (January, 1973).

Green, R., "Finding Offbeat Uses for Scrap Tires," Chemical Engineering, 85, No. 18, pp. 88, Aug. 14 (1978).

Halligan, J. E., K. L. Herzog, and H. W. Parker, "Synthesis Gas from Bovine Wastes," Ind. Eng. Chem., Process Des. Develop., 14, No. 1 (1975).

Hercules, Inc., "Pyrolysis of Dried Feedlot Manure in a Fluidhearth Reactor," Final Report to Kansas State University, No. 367-414, October (1975).

Howell, J. A., "Kansas Coal Gasification," M.S. Thesis, Kansas State University (1979).

Jones, J. L. and D. C. Bomberger, Jr., "Energy Usage and Recovery in Sludge Disposal Part 1," Water and Sewage Works, July (1977).

McGriff, E. C. and A. J. Shindala, "Agricultural Wastes," J. Water Pollut. Control Fed., 45, No. 6 (1973).

Mikesell, R. D., D. C. Hoang, and D. E. Garrett, "The Garrett Energy Research Biomass Gasification Process," Proc. of the 13th Intersociety Energy Conversion Engineering Conference, San Diego, CA (1978).

Pattabhi Raman, K., W. P. Walawender and L. T. Fan, "The Effect of Temperature on the Fluidized Bed Gasification of Feedlot Manure in a Pilot Plant," to be published, June 25 (1979).

Shafizadeh, F., "Industrial Pyrolysis of Cellulosic Materials Wood Chemistry," App. Polymer Symposium 28, pp. 153 (1975).

Smith, G. L., C. J. Albus, Jr., and H. W. Parker, "Products and Operating Characteristics of the TTU Retort," presented at the 76th National AICHE Meeting, Tulsa, Oklahoma (1974).

Walawender, W. P., L. T. Fan, and L. E. Erickson, "Feedlot Manure and Other Agricultural Wastes as Future Material and Energy Resources: I. Introduction and Literature Review," Report No. 36 of the Institute for System Design and Optimization, Kansas State University, Manhattan, Kansas, April, 1972.

Walawender, W. P., L. T. Fan, C. R. Engler, and L. E. Erickson, "Feedlot Manure and Other Agricultural Wastes as Future Material and Energy Resources: II. Process Descriptions," Report No. 45 of the Institute for System Design and Optimization, Kansas State University, Manhattan, Kansas, March, 1973(a).

Walawender, W. P., L. T. Fan, C. R. Engler, and L. E. Erickson, "Feedlot Manure and Other Agricultural Wastes as Future Material and Energy Resources: III. Economic Evaluation," Report No. 46 of the Institute for Systems Design and Optimization, Kansas State University, Manhattan, Kansas, July, 1973(b).

Walawender, W. P. and L. T. Fan, "Gasification of Dried Feedlot Manure in a Fluidized Bed - Preliminary Pilot Plant Tests," presented at the 84th National Meeting of AICHE, Atlanta, GA (1978).

Table 1. Reactor Operating Parameters

Reactor Temperature Range	970K – 1370K
Fluidizing Medium	Steam
Superficial Velocity	36.6 cm/sec
Feed Rate	1.57 gm/min
Manure Particle Size	0.42 mm – 1.41 mm

Table 2. Feedstock Analysis

PROXIMATE ANALYSIS

VOLATILE MATTER (DAF)	85.3
FIXED CARBON (DAF)	14.7
ASH (DRY)	11.5
MOISTURE	4.9

ULTIMATE ANALYSIS (DAF, Wt%)

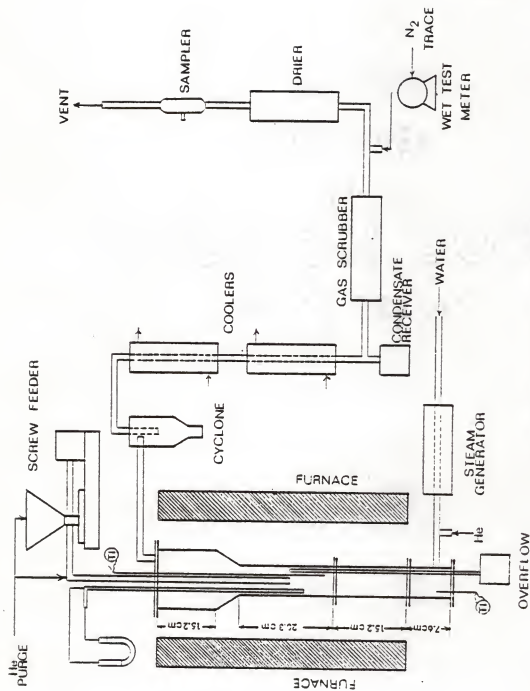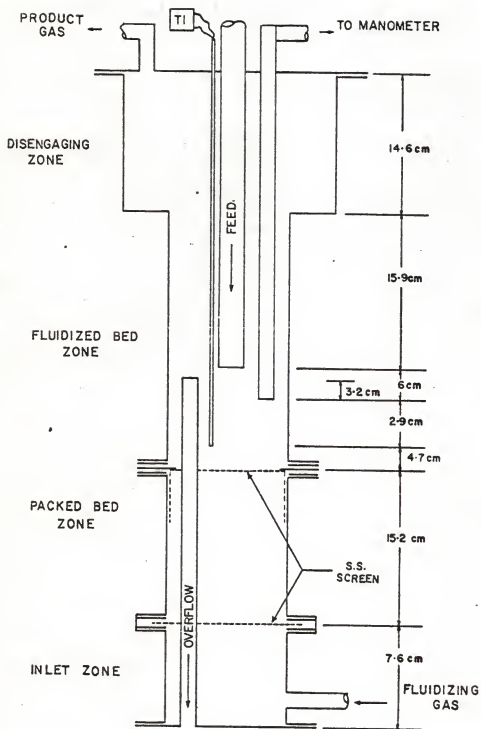|	
CARBON	50.1
HYDROGEN	6.9
NITROGEN	4.0
OXYGEN	39.0
DENSITY (g/cc)	1.37
HHV (DAF) (MJ/kg)	19.86

Figure 1. Bench Scale Reactor

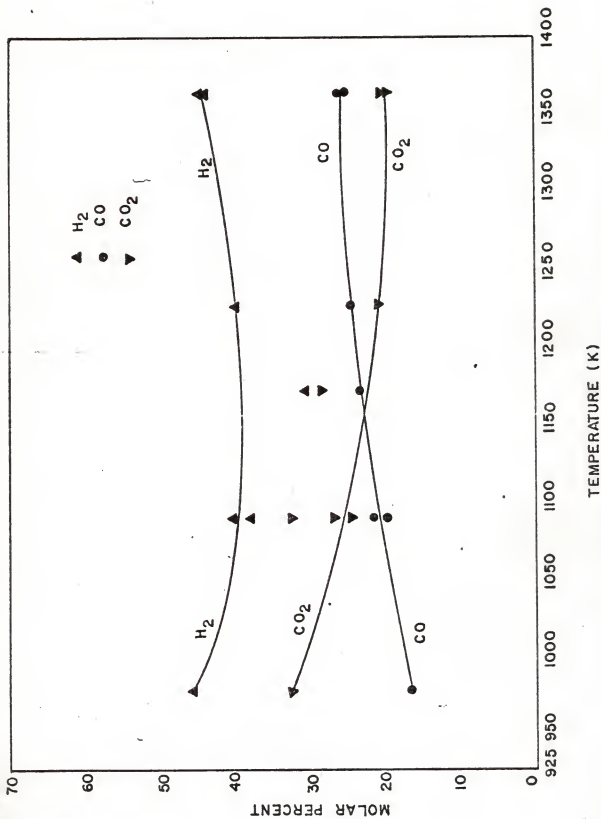Figure 2. Bench Scale Reactor Details

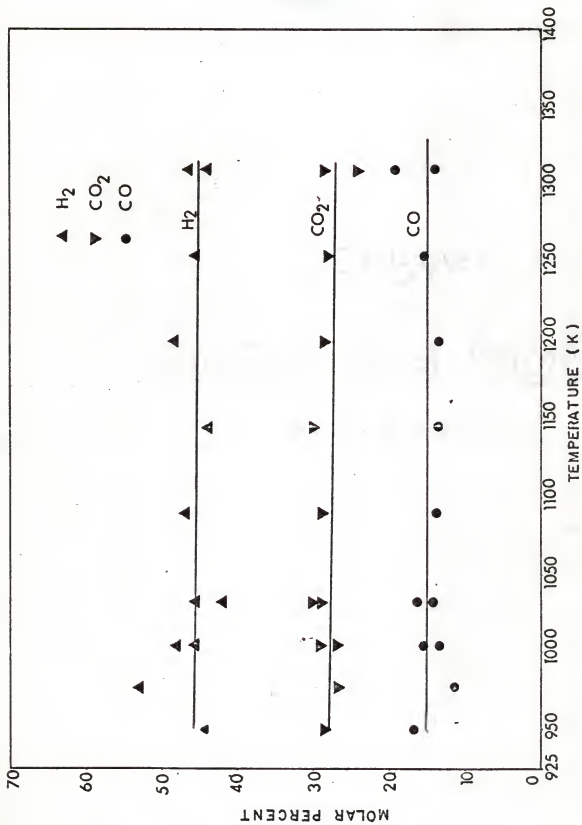Figure 3. Product Gas Composition Versus Temperature Sand Bed

Figure 4. Product Gas Composition Versus Temperature Limestone Bed
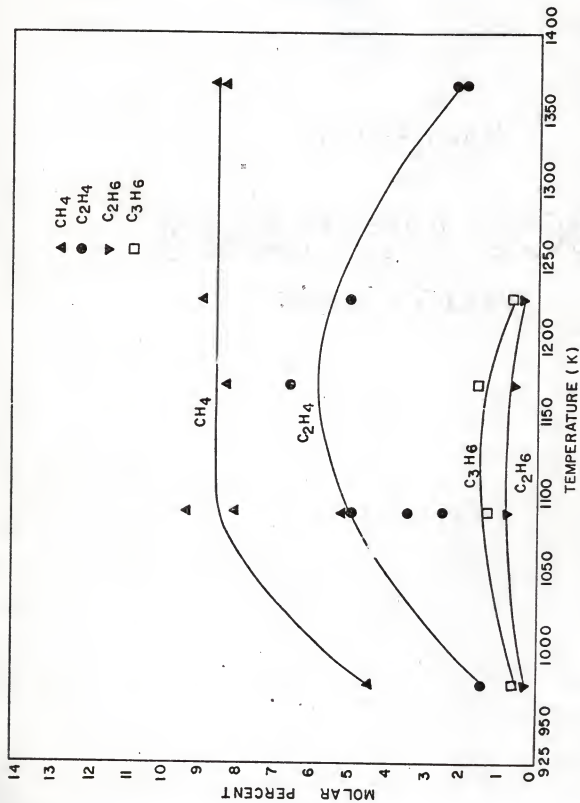
Figure 5. Product Gas Composition Versus Temperature Sand Bed
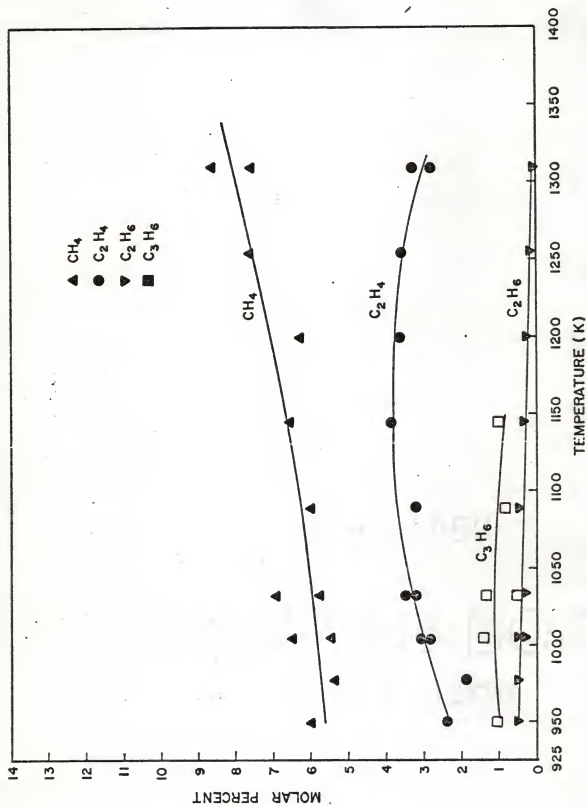
Figure 6. Product Gas Composition Versus Temperature
Limestone Bed

Figure 7. Product Gas Heating Value Versus Temperature

Figure 8. Product Gas Yield Versus Temperature

Figure 9. Efficiency Versus Temperature

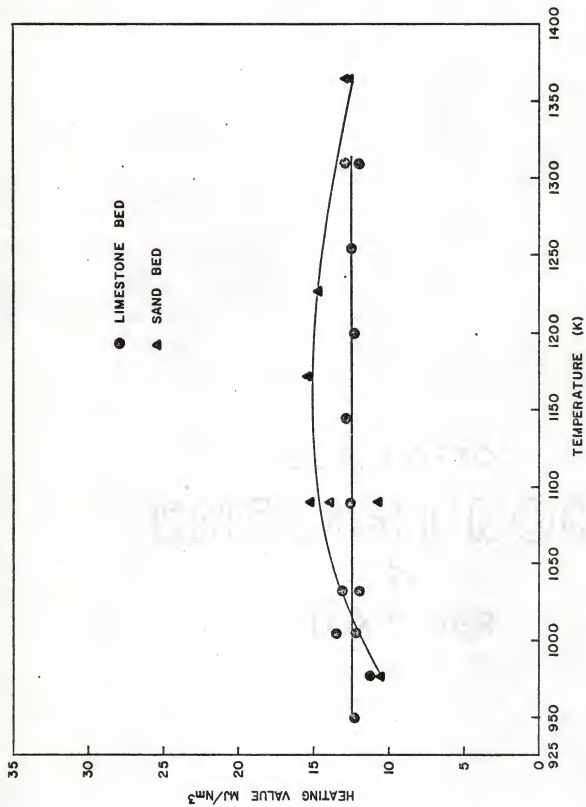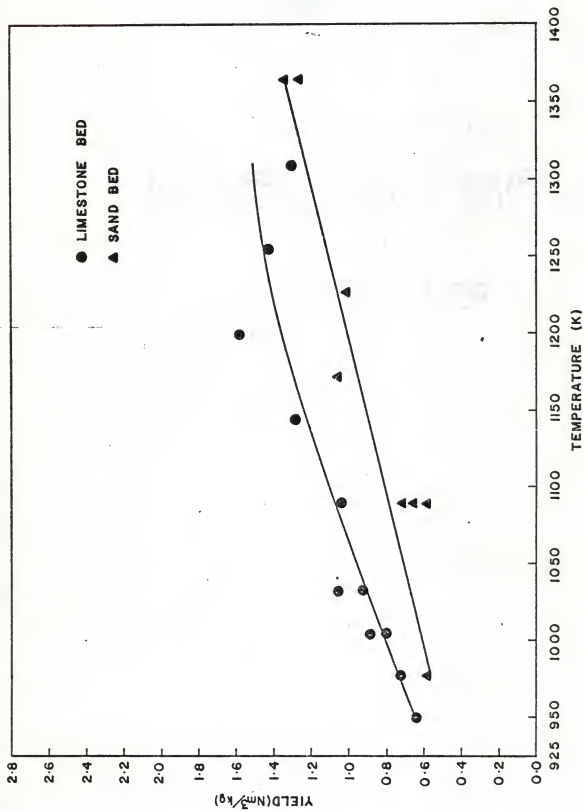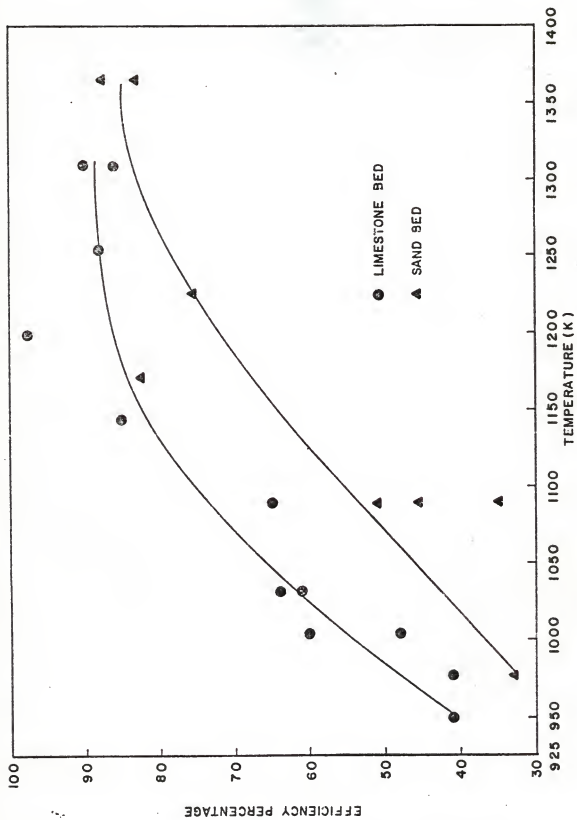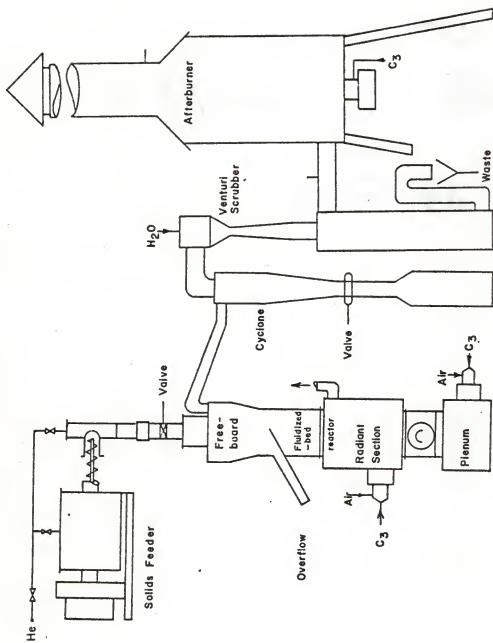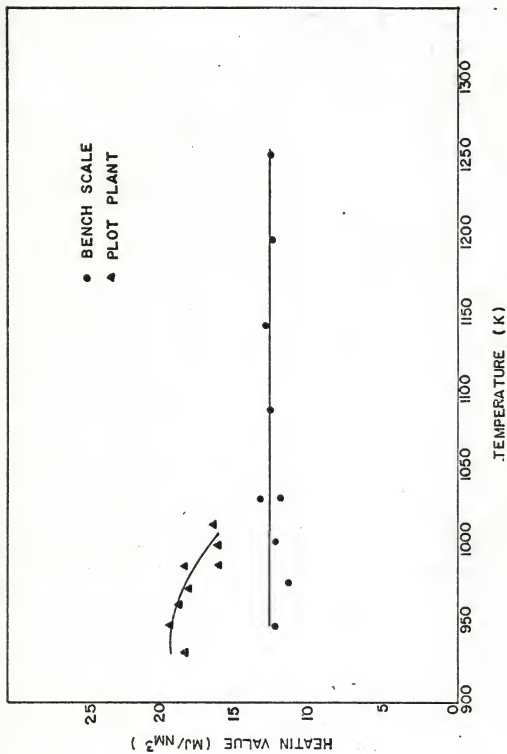Figure 10. Flow Scheme of the Pilot Plant

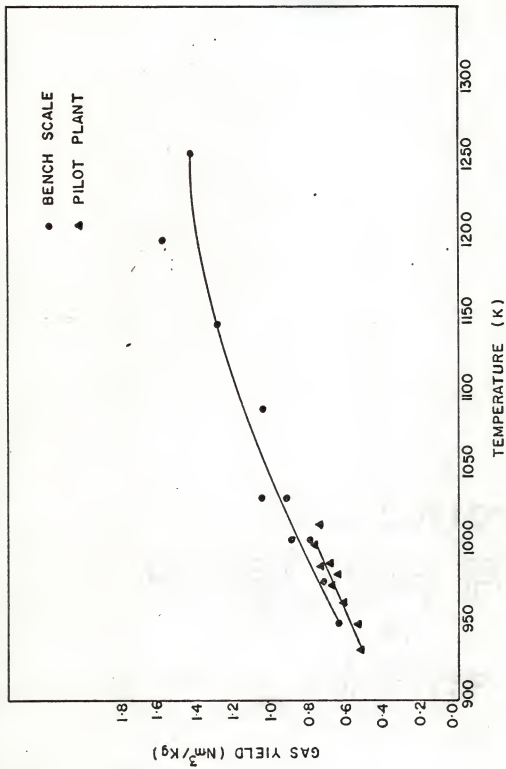Figure 11. Product Gas Heating Value Versus Temperature
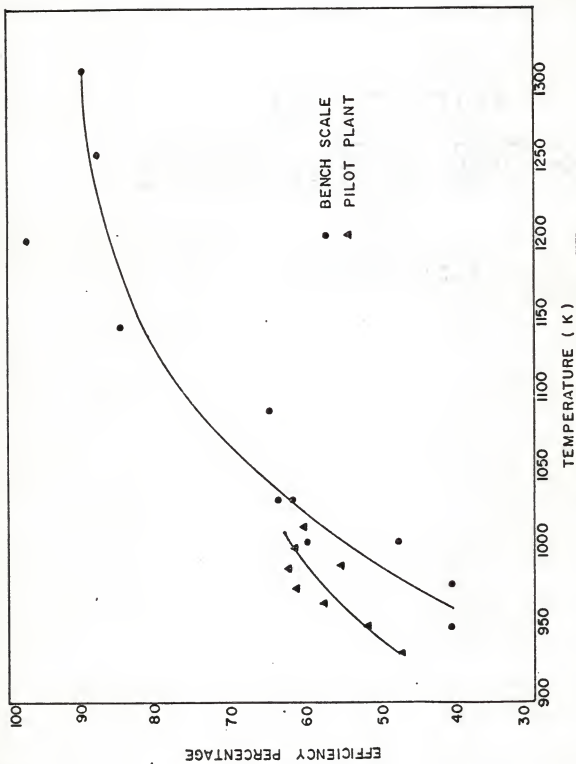
Figure 12. Product Gas Yield Versus Temperature

Figure 13. Efficiency Versus Temperature

CHAPTER IV

CHROMATOGRAPHIC ANALYSIS OF GAS MIXTURES
PRODUCED BY THE GASIFICATION OF COAL AND BIOMASS

INTRODUCTION

The decline of natural gas and petroleum reserves along with rising costs for these fossil fuels has led to a concentrated effort towards the development of alternative sources of energy. Since coal is this country's most abundant fossil fuel, it is not surprising that coal gasification has received considerable attention recently.

Although coal is the nation's most abundant source of energy for the future, it is by no means the only one. Among other fossil fuels, oil shale and tar sands are present in large amounts. Furthermore, a variety of other resources such as municipal solid waste, sewage sludge, crop residues, wood and manure are also available as potential sources of energy. The latter group of energy resources can be generally classified as biomass.

While coal and biomass in their native forms are not very desirable as fuels, they can be converted to a much more useful form of energy through the process of gasification. The gasification of these fuels results in the generation of a gas mixture containing hydrogen, the oxides of carbon, some sulfur bearing compounds, saturated and unsaturated hydrocarbons of low molecular weight, water, and depending on the method of production, appreciable amounts of nitrogen. The quality (composition) and quantity (yield) of the gas produced are highly dependent on the process conditions, including temperature, heating rate, particle size and other factors. In assessing the performance of various process options, complete material balance information is required. Therefore, a systematic procedure for the product gas analysis plays a crucial role in the development of any gasification process.

Gas chromatography has emerged as the most widespread, versatile and efficient method employed today for the qualitative and quantitative analysis of gaseous mixtures.

One of the best general definitions of chromatography has been proposed by Keulemans, (1957): "Chromatography is a physical method of separation, in which the components to be separated are distributed between two phases, one of these phases constituting a stationary bed of large surface area, the other being a fluid that percolates through the stationary bed."

In general, the stationary phase may be;

(i) A solid having adsorptive properties in which case it is called adsorption chromatography.

(ii) A liquid distributed over an inert solid support to give it a large surface area. This type has been termed "partition chromatography."

When the moving phase is a gas, there are two basic systems of chromatography (Keulmans, 1957).

    I With a Solid Staionary Phase or "Gas-Solid Chromatography"

    II With a Liquid Stationary Phase or "Gas-Liquid Chromatography"

These systems can be further classified into three groups depending on the technique employed for separation, namely,

    (a) Elution analysis

    (b) Frontal analysis

    (c) Displacement analysis

In elution analysis a small sample of the mixture is introduced into the column and is carried through the column by an unadsorbed carrier gas. The various components in the mixture travel at various speeds through the column depending on their strength of adsorption. If the differences in adsorption among them is sufficient, each component is eluted as a peak at a different time.

In frontal analysis a continuous stream of the mixture is introduced into the column. Each component, depending on its strength, is adsorbed by

the column until the latter is saturated. The component then passes through unadsorbed. This results in a series of steps on the chromatogram, each step corresponding to an additional component as it is eluted from the column.

Displacement analysis involves the use of a known concentration of a strongly adsorbed vapor, called the displacer, with the carrier gas stream. When a small sample of the mixture of interest is injected into the column, the sample components are desorbed and pushed towards the column outlet by the displacer.

Of the three techniques, elution analysis is the most widely employed method (Dal Nogare and Juvet, 1962).

The principal gases produced in the steam gasification of coal are H_2, CO, CO_2, CH_4, C_2H_4, H_2O, H_2S, C_2H_6 and C_3H_8. Some heavier hydrocarbons as well as some COS and SO_2 are produced but these are present in very small concentrations in the gaseous phase and hence can be ignored. In addition, traces of air are always present in the sample bottles used for the storage of the product gases.

The steam gasification of biomass produces most of the gases that are evolved in the gasification of coal. In addition, appreciable quantities of nitrogen may be present. Since biomass does not contain significant quantities of sulfur, the sulfur bearing gases are not present in appreciable quantities. Therefore, an analysis scheme suitable for the detection and analysis of the product gases from coal gasification can also be used for the case of biomass gasification as well.

Several gas chromatographic methods have been employed to analyze these gases qualitatively and quantitatively (Kim and Douglas, 1974). Most of these involve the use of a three column system with an analysis time of

about 15 minutes (Doran and Cross, 1966). Other methods involving temperature programming result in analysis times up to 30 minutes (Terry and Futrell, 1965).

The objective of the present work was to develop a specific procedure for the analysis of the components up to C_3 hydrocarbons in a relatively short period of time. The procedure employed gas-solid chromatography using elution analysis. Two columns with thermal conductivity detectors were employed under isothermal conditions.

THEORETICAL

When a component in a gaseous mixture is separated and eluted from the column, the difference in the thermal conductivity or some other property between the component and the carrier gas is sensed by the detector and appears as a peak on the chromatogram. The area obtained on the chromatogram is directly proportional to the amount of the component present as long as the concentration is not too large.

The simplest method of calculating the concentration of a component based on the area obtained on the chromatogram is by the Raw Area Normalization (RAN) method (Young, 1975a). The assumptions made in this method are:

    (1) The peak area is directly proportional to the amount of the component, for all components.

    (2) The detector sensitivity is the same for all the components.

    (3) All compenents appear as peaks on the chromatogram.

Thus for any component i, by the first assumption,

$$(\text{Amount of } i) \propto (\text{Area})_i$$

or

$$(\text{Amount of } i) = k_i (\text{Area})_i \qquad \text{1(a)}$$

where k_i is a proportionality factor. The second assumption makes the proportionality factor, k_i, the same for all the components. Hence,

$$(\text{Amount of } i) = k (\text{Area})_i, \text{ for all } i \qquad \text{1(b)}$$

By using the third assumption,

$$\%(i) = \frac{(\text{Amount of } i) \times 100}{\sum_{J=1}^{N} (\text{Amount of } j)} \qquad \text{1(c)}$$

where N is the total number of components eluted from the column.

It follows therefore from equations 1(a) and 1(b) that

$$\%(i) = \frac{(Area)_i \times 100}{\displaystyle\sum_{j=1}^{N} (Area)_j} \qquad\qquad 1(d)$$

Although the Raw Area Normalization method is suitable for many components whose thermal conductivities are close to each other, the steam gasification of coal and biomass produces hydrogen which has a very high thermal conductivity ($0.209 \frac{W}{(m)\,(K)}$) whereas all the other components have relatively low thermal conductivities (($4.18 - 33.47$) x $10^{-3} \frac{W}{(m)\,(K)}$). Therefore this method introduces very large errors.

To account for the differences in thermal conductivities between the various components, the "raw" area obtained on the chromatogram for each component is corrected by using an area correction factor. This is also known as relative response factor or calibration factor (Young, 1975b).

Calibration factors for a large number of components are tabulated and are available in the literature (Rosie et al., 1957, Messner et al. 1959). The calibration factors are based on a reference component, benzene, which is usually assigned a calibration factor of 100. Although these tabulated values may be used as a guide or rough approximation, they tend to vary with the particular conditions and instrument employed when a high degree of accuracy in the analysis is required.

In this work, the determination of the calibration factors and the calculation of the concentrations of the mixture components were accomplished by the use of a Spectra-Physics Autolab System I integrator, used in conjunction with the gas chromatograph. A suitable reference component present in the mixture was chosen and assigned a calibration factor of 1000. Although the reference component is usually assigned a calibration factor

of 1.0 (Young, 1975c), the System I integrator permitted only a value of 1000. The calibration factor for any other component was then calculated from the relation:

$$\frac{(Area)_i \times (CF)_i}{(Area)_{Ref} \times 1000} = \frac{(Concentration)_i}{(Concentration)_{Ref}} \tag{2}$$

which is modified to reflect that all components do not bear the same relation between concentration and area. Rearrangement of equation (2) defines the calibration factor as

$$(CF)_i = \frac{(Concentration)_i}{(Concentration)_{Ref}} \times \frac{(Area)_{Ref}}{(Area)_i} \times 1000 \tag{3}$$

where $(CF)_i$ refers to the calibration factor of the i-th component (Young, 1975c).

Normally, when two or more columns are needed to separate a gas mixture, the procedure adopted is to choose a component that appears as a distinct peak in all the columns so that its concentration can be used to tie the areas of the various componets that are eluted from the different columns. However, in the present analysis, it was not possible to adjust the column conditions so that a common component was present as a distinct peak in both columns. Hence the following method specific to the analysis at hand, was developed.

Calibration

A calibration gas mixture, containing 62.94% N_2, 4.07% CH_4, 7.99% CO, 18.02% CO_2, 2.99% C_2H_4, 1.99% C_2H_6, 1.00% C_3H_6 and 1.00 C_3H_8 was run through the molecular sieve column and the calibration factors of the components CH_4 and CO were evaluated by using equation (3) with N_2 as a reference component (CF = 1000). This was possible since the other

components in the mixture were adsorbed by the molecular sieve column. As noted in the sample calcuation, the compositions of these components were adjusted prior to applying equation (3). The calibration factor for oxygen was determined by injecting a sample of air into the molecular sieve column. Equation (3) was used to calculate this value.

In the Porapak column, N_2, CO and CH_4 appear as one peak and hence N_2 cannot be used as a reference in that column to calculate the calibration factors of the other components. Therefore, an overall calibration factor was calculated for the peak containing these three components. (Actually there were four components present since a small amount of air was always present, thus giving rise to an oxygen peak in the molecular sieve column. In the Porapak column, O_2 was eluted along with N_2 CO and CH_4 as a single peak).

Due to limitations of the Spectra-Physics Autolab System I integrator, the reference component was always assigned a calibration factor of 1000 when operated in the calibration mode. However, as will be seen in the sample calculation, the overall calibration factor calculated for the mixture of N_2, O_2, CH_4 and CO was very close to 1000 and hence no significant error was introduced. In the analysis mode however, no such limitation was present, thus permitting the overall calibration factor to be assigned to the peak of mixtures in the Porapak column.

The overall calibration factor is defined by the equation

$$\text{Overall Calibration Factor(OCF)} = \frac{\sum\limits_{i=1}^{M} (CF)_i \, (\text{Area})_i^{MS}}{\sum\limits_{i=1}^{M} (\text{Area})_i^{MS}} \qquad (4)$$

where M is the number of peaks that appear in the molecular sieve column, namely four in the case of calibration (O_2, N_2, CH_4, and CO). The superscript MS refers to the molecular sieve column.

In the following it will be shown that the use of an overall calibration factor is equivalent to the use of a reference component that appears as a distinct peak in both columns. Consider the case where N_2 appears as a distinct peak in the molecular sieve and Porapak columns and is used as a reference component. Then from equation (3) the calibration factor of any component i can be expressed as

$$(CF)_i = \frac{(CF)_{N_2} (Area)^P_{N_2}}{(Concentration)_{N_2}} \times \frac{(Concentration)_i}{(Area)^P_i} \tag{5}$$

where the superscript P refers to the Porapak column. Now, rearranging equation (5) leads to

$$\frac{(CF)_{N_2} (Area)^P_{N_2}}{(Concentration)_{N_2}} = \frac{(CF)_i (Area)^P_i}{(Concentration)_i} \tag{6}$$

Application of this equation to N_2, H_2, O_2, CH_4 and CO yields the expression

$$\frac{(CF)_{N_2} A^P_{N_2}}{[N_2]} = \frac{(CF)_{H_2} A^P_{H_2}}{[H_2]} = \frac{(CF)_{O_2} A^P_{O_2}}{[O_2]} = \frac{(CF)_{CH_4} A^P_{CH_4}}{[CH_4]} = \frac{(CF)_{CO} A^P_{CO}}{[CO]} \tag{7}$$

where A^P_i and [i] denote the area and concentration of component i on the Porapak column respectively.

Now, if

$$\frac{a}{b} = \frac{c}{d} = \frac{e}{f} = \cdots$$

by using the componendo et dividendo rule of algebra we can obtain the expression

$$\frac{a}{b} = \frac{c}{d} = \frac{e}{f} = \ldots = \frac{a + c + e + \ldots}{b + d + f + \ldots} \tag{8}$$

Employing this expression, equation (7) becomes

$$\frac{(CF)_{N_2} A^P_{N_2}}{[N_2]} = \frac{\sum\limits_{j=1}^{M} (CF)_j A^P_j}{\sum\limits_{j=1}^{M} [j]} \tag{9}$$

where M is the number of components which appear as a single peak on the Porapak column. We have defined the overall calibration factor by equation (4). Since the same gas mixture was used for both the molecular sieve and Porapak columns,

$$(OCF) = \frac{\sum\limits_{i=1}^{M} (CF)_j A^{MS}_j}{\sum\limits_{j=1}^{M} A^{MS}_j} = \frac{\sum\limits_{i=1}^{M} (CF)_j A^P_j}{\sum\limits_{j=1}^{M} A^P_j} \tag{10}$$

which can be expressed as

$$(OCF) \sum\limits_{j=1}^{M} A^P_j = \sum\limits_{j=1}^{M} (CF)_j A^P_j \tag{11}$$

Substituting this expression on the right hand side of equation (9) we obtain

$$\frac{(CF)_{N_2} A^P_{N_2}}{[N_2]} = \frac{(OCF) \sum\limits_{j=1}^{M} A^P_j}{\sum\limits_{j=1}^{M} [j]} \tag{12}$$

Substitution of this expression back into equation (5) yields

$$(CF) = \frac{(OCF) \sum\limits_{j=1}^{M} A^P_j}{\sum\limits_{j=1}^{M} [j]} \times \frac{[i]}{A^P_i} \tag{13}$$

Equation 13 is used to evaluate the calibration factors of the various components that appear as peaks in the Porapak column.

The calibration factors for hydrogen were evaluated by using a calibration mixture containing 5.95% H_2, 1.07% H_2S and 92.98% N_2. This mixture was run through the molecular sieve column. The column adsorbed the H_2S so that only H_2 and N_2 appeared as peaks on the chromatogram. Nitrogen was then used as a reference to evaluate the calibration factor for hydrogen with the aid of equation (3).

Analysis

In the analysis mode a similar procedure was followed. After several calibration runs were made to ensure that the calibration factors calculated were consistent, these values were then used to evaluate the concentration of the components of the product gas mixture.

The unknown gas mixture was run through the molecular sieve column to determine the concentrations of H_2, O_2, N_2, CH_4 and CO.

Applying equation (7) to the molecular sieve column, for any two components i and j,

$$\frac{(CF)_i A_i^{MS}}{[i]} = \frac{(CF)_j A_j^{MS}}{[j]} = \frac{\sum\limits_{j=1}^{M} (CF)_j A_j^{MS}}{\sum\limits_{j=1}^{M} [j]} \tag{14}$$

where M is the number of columns eluted from the molecular sieve column. Now if the concentrations are adjusted to sum up to 100 percent on the molecular sieve column, then

$$\sum\limits_{j=1}^{M} [j] = 100 \tag{15}$$

Hence,

$$\frac{(CF)_i A_i^{MS}}{[i]} = \frac{\sum\limits_{j=1}^{M} (CF)_j A_j^{MS}}{100}$$

or

$$[i] = \frac{(CF)_i A_i^{MS}}{\displaystyle\sum_{j=1}^{M} (CF)_j A_j^{MS}} \times 100 \qquad (16)$$

Equation (16) was used to calculate the concentrations of the components eluted through molecular sieve column. The overall calibration factor was then calculated using equation (4) and this value was introduced as the calibration factor for the peak of mixtures in the Porapak column. The overall calibration factor was calculated for every run since it depends on the concentrations of the components in the gas mixture which appear on the molecular sieve column.

A sample of the unknown gas was then run through the Porapak column to determine the concentrations of CO_2, C_2H_4, C_2H_6, C_3H_6, C_3H_8 and H_2S.

For this column, equation (16) can be applied with the peak of mixtures considered as a single component with the overall calibration factor as its calibration factor. This yields the expression

$$[i] = \frac{A_i^P (CF)_i \times 100}{[A_{mix}^P (OCF) + \displaystyle\sum_{j=1}^{N} A_j^P (CF)_j]} \qquad (17)$$

where the second term in the denominator refers to the components which are eluted as distinct peaks on the Porapak column. N is the number of such components eluted.

EXPERIMENTAL

Facilities

A Packard Model 417 dual column gas chromatograph equipped with thermal conductivity detectors and helium as carrier gas was used for the analysis of the product gases. The injection port, detectors and column oven were equipped with independent temperature controllers. The column oven was also equipped with a linear temperature programmer. An independent power supply was used to supply the current to the detectors. A schematic diagram of the gas chromatograph is shown in Figure 1.

Gas samples usually about 0.3 ml, were injected through the injection ports into the column, using a 0.1 ml - 1.0 ml capacity syringe. The sample mixture was swept through the column by the carrier gas.

The carrier gas was continuously supplied at a constant flow-rate, which was regulated by a two-stage regulator at the gas cylinder and the pressure regulators and valves in the flow controller unit of the gas chromato graph. The column oven temperature was controlled automatically at 80°C within close limits, ($\pm$ 0.05°C) to provide maximum retention time reproducibility.

Components of the sample mixture travelled through the column at different rates due to differences in their strength of adsorption and emerged as separate components. Each component that emerged from the column was carried into the detector by the carrier gas. The detector oven was heated by independent heaters and its temperature controlled within close limits ($\pm$ 2°C) to prevent sample condensation and maintain detector stability. An electrical signal was generated by the detector proportional to the concentration of compound sensed by it. The column elutant, after passing through

the detector was vented. The two columns employed for the analysis con-
sisted of the following:

(i) A 1.83m x 0.0032m (6' x 1/8") column packed with 80-100 mesh molecular
     sieve No. 5A packing for the analysis of H_2, O_2, N_2, CH_4 and CO.

(ii) A 1.83m x 0.0032m (6' x 1/8") column packed with 80-100 mesh Porapak
     Q preceeded with a 0.1524m x 0.0032m (6" x 1/8") section of 80-100
     mesh Porapak R, for the analysis of CO_2, H_2O, H_2S, C_2H_4, C_2H_6, C_3H_6
     and C_3H_8. The Porapak R section was used to shift the retention time
     of water so that it did not interfere with the peaks from any of the
     other components.

     The detector response was fed to a Spectra-Physics Autolab System I
integrator. The integrator was employed for the calculation of the peak
areas as well as for calibration and analysis of the gas mixture. A Varian
Model A-25 Strip-chart recorder connected to the integrator was used to
record the peaks as an indicator that they were separated from one another.

Procedure

     The column oven of the gas-chromatograph was heated and maintained at
80°C. The injection ports and the thermal conductivity detectors were
maintained at a temperature of 150°C. The carrier gas flow rate was 30 ml/
min through both columns. Other control settings on the gas chromatograph
and its accessories were:

Gas chromatograph attenuation = 1

Detector Bridge Current = 100 milliamperes

Integrator peak width = 5

Slope sensitivity = 15

Plateau test = 5

Integrator attenuation to the recorder = 1

Recorder chart speed = 25 inch/hour

Recorder attenuation = 5 milliamps (full scale)

The sample (0.3 ml) was injected into the molecular sieve column to analyze for H_2, O_2, N_2, CH_4 and CO. The C_2 and C_3 hydrocarbons as well as CO_2, H_2O and H_2S were adsorbed by this column. The gases that were resolved and analyzed in the molecular sieve appeared as one peak in the Porapak column. The results of these two columns were then combined to yield the overall concentration of the various species present in the product gas mixture.

It was found that after about 100 hours of operation the activity of the two columns gradually decreased. This decrease in activity was observed when the peaks on the chromatogram were no longer sharp and the separation of the various peaks became progressively worse, thus necessitating in the reactivation of the columns.

The columns were reconditioned by heating them to 240°C for about 8-10 hours with a small flow of helium through them. If the gas mixture analyzed contained sulfur bearing compounds, the latter were adsorbed by the molecular sieve column. In this case it was necessary to heat the molecular sieve to 300°C to drive away those components. Since the highest temperature at which the Porapak column could be operated was 250°C, above which temperature the porous polymer beads which constitute the packing begin to degenerate, it was necessary to remove the Porapak column from the gas chromatograph for this regeneration. Reconditioning the columns was not very effective after about 500 hours of operation and hence the columns were replaced with fresh packing after that period of time.

It was also necessary to change the septa in the injection ports of the gas chromatograph after about 30 samples were injected, in order to prevent gas leaks through them.

The gas samples collected from the experiments were stored in 250 ml. gas sample bottles fitted with stopcocks and a sideport with a septum. Samples of 0.3 ml were withdrawn through the latter with a gastight syringe to be injected into the gas chromatograph. The syringe was flushed at least twice with the gas sample to eliminate any possible contamination before injection into the column. The samples could be stored in the gas sample bottles for at least two days before any change in the concentrations of the components due to leaks was observed.

In spite of all precautions taken to eliminate leaks, a small amount of air (about one percent) was always present as observed by a small oxygen peak in the molecular sieve column. However, the amount present was consistent with all the samples that were run, and the analysis was corrected to an airfree basis to eliminate this problem.

Calibration Standards

Two calibration standard gas mixtures were employed to determine the calibration factors of the various gases produced in the gasification of coal and biomass. The first gas mixture consisted of 62.94% N_2, 4.07% CH_4, 7.99% CO, 18.02% CO_2, 2.99% C_2H_4, 1.99% C_2H_6, 1.00% C_3H_6 and 1.00% C_3H_8. The second gas mixture consisted of 92.98% N_2, 1.07% H_2S and 5.98% H_2. The second mixture was necessary since it was not possible to store a mixture of H_2, C_2H_4 and C_3H_6 at high pressures which would have resulted in the hydrogenation of the unsaturated hydrocarbons.

SAMPLE CALCULATION

A sample calculation of the gas analysis procedure is given below

Calibration Mode

The standard gas mixture containing 62.94% N_2, 4.07% CH_4, 7.99% CO, 18.02% CO_2, 2.99% C_2H_4, 1.99% C_2H_6, 1.00% C_3H_6 and 1.00% C_3H_8 was run through the molecular sieve column and the areas obtained on the integrator were as follows: (The oxygne peak was too small and hence was ignored.)

component	Area
N_2	130,538
CH_4	6,783
CO	16,010

Using N_2 as the reference component with an assigned calibration factor of 1000, the calibration factor for CH_4 was calculated according to equation (3) as

$$(CF)_{CH_4} = \frac{[CH_4]}{[N_2]} \frac{A_{N_2}}{A_{CH_4}} \times CF_{N_2}$$

$$= \frac{(5.43)}{(83.92)} \frac{(130538)}{6783} \times 1000 = 1245$$

Similarly for CO

$$(CF)_{CO} = \frac{[CO]}{[N_2]} \frac{A_{N_2}}{A_{CO}} \times CF_{N_2}$$

$$= \frac{(10.65)}{(83.92)} \frac{(130538)}{(16010)} \times 1000 = 1035$$

Here the concentrations of N_2, CO and CH_4 were adjusted to make their sum 100 percent.

The same standard gas mixture was then run through the Porapak column and gave rise to the following areas on the integrator. In this column N_2, CH_4 and CO appeared as one peak. (Traces of air are also included

in that peak but the area, being too small, was ignored).

Component	Area
N_2, CH_4 and CO	55822
CO_2	15472
C_2H_4	2637
C_2H_6	1830
C_3H_6	930
C_3H_8	1034

The mixture of N_2, CH_4 and CO was taken as the reference and assigned a calibration factor of 1000. As explained in the THEORETICAL section, in the calibration mode the integrator permitted only a value of 1000 for the reference component. However, the overall calibration factor for the standard mixture was calculated by using equation (4) and was found to be 1014, thus introducing no significant error in the calculations of the calculations of the calibration factors of the other components. Since the individual calibration factors of CH_4 and CO are close to 1000, the overall calibration factor, calculated by using CH_4, CO and the reference component N_2, was close to 1000.

The calibration factors of the remaining components were calculated as follows using equation (13).

$$(CF)_{CO_2} = \frac{[CO_2]}{[\text{mixture}]} \quad \frac{A \text{ mixture}}{A_{CO_2}} \times CF \text{ mixture}$$

$$= \frac{(18.02)}{(75.00)} \cdot \frac{55822}{15472} \times 1000$$

$$= 867$$

similarly

$$(CF)_{C_2H_4} = 844$$

$$(CF)_{C_2H_6} = 809$$

$$(CF)_{C_3H_6} = 800$$

$$(CF)_{C_3H_8} = 720$$

Calibration for H_2 was done in a similar manner with a standard gas mixture containing 92.98% N_2, 1.07% H_2S and 5.98% H_2. The molecular sieve column adsorbed the H_2S and hence only the H_2 and N_2 peaks were seen on the chromatogram. The areas obtained on the integration were as follows: (The oxygen peak was too small and hence was ignored).

Component	Area
H_2	200
N_2	153,923

The calibration factor of H_2 was calculated by

$$(CF)_{H_2} = \frac{[H_2]}{[N_2]} \frac{(A_{N_2})\ (CF)_{N_2}}{(A_{H_2})}$$

$$= \frac{(6.01)}{93.99} \times \frac{15,393 \times 1000}{200}$$

$$= 49,211$$

Since H_2S did not appear as a peak, the concentrations of H_2 and N_2 were adjusted to make their sum 100 percent.

The calibration factor for H_2S was not calculated since the gas mixture did not contain any detectable amounts of H_2S. In the case where the latter gas is present, it can be calibrated using the standard mixture containing 92.98% N_2, 1.07% H_2S and 5.98% H_2 employing the Porapak column, where H_2S appears as a distinct peak on the chromatogram.

Analysis mode

A sample of the gas produced by the steam gasification of manure was run through the molecular sieve and gave rise to the following areas on the integrator.

Component	Area
H_2	336
O_2	1,403
N_2	82,040
CH_4	5,689
CO	14,612

The concentrations of the components on the molecular sieve were calculated as follows:

Let

$$A_{EQ} = (CF)_{H_2} A_{H_2} + (CF)_{N_2} A_{N_2} + (CF)_{O_2} A_{O_2} + (CF)_{CH_4} A_{CH_4} + (CF)_{CO} A_{CO}$$

$$= (49,211)\ 336 + (1,000)\ 82,090 + (1,000)\ 1,403 + (1,245)\ 5,689$$
$$+ (1,035)\ 14,612$$
$$= 1.22 \times 10^8$$

Then, by using equation (16),

$$[H_2] = \frac{(CF)_{H_2} A_{H_2} \times 100}{A_{EQ}}$$

$$= \frac{(49,211)\ 336}{1.2218 \times 10^8} \times 100$$

$$= 13.5\%$$

similarly

$$[O_2] = 1.15\%$$
$$[N_2] = 67.14\%$$
$$[CH_4] = 5.80\%$$
$$[CO] = 12.38\%$$

The overall calibration factor was calculated using equation (4) as

$$OCF = \frac{A_{EQ}}{A_{H_2} + A_{O_2} + A_{N_2} + A_{CH_4} + A_{CO}}$$

$$= 1174$$

Another sample of the same gas mixture was run through the Porapak column. The overall calibration factor calculated from the run made on the molecular sieve column was introduced as the calibration factor for the mixture of peaks. The areas obtained on the integrator were as follows. The peak obtained for H_2O was ignored as the analysis was performed on a water free basis.

Component	Area
H_2, O_2, N_2, CH_4 and CO	57731
CO_2	14205
C_2H_4	1745
C_2H_6	575
C_3H_6	859
C_3H_8	0

The concentration of the components on the Porapak column were calculated as follows:

$$\text{Let } A_{EQT} = (CF)_{mix}A_{mix} + (CF)_{CO_2}A_{CO_2} + (CF)_{C_2H_4}A_{C_2H_4}$$

$$+ (CF)_{C_2H_6}A_{C_2H_6} + (CF)_{C_3H_6}A_{C_3H_6} + (CF)_{C_3H_8}A_{C_3H_8}$$

$$= (1,174)57.731 + (867)14,205 + (844)1,745 + (809)575 + (800)859$$

$$= 82,717,084$$

Then

$$[CO_2] = \frac{(CF)_{CO_2}A_{CO_2}}{A_{EQT}} \times 100 = \frac{(867)14,205}{82,717,084} \times 100$$

$$= 14.89\%$$

similarly,

$$[C_2H_4] = 1.78\%$$
$$[C_2H_6] = 0.56\%$$
$$[C_3H_6] = 0.83\%$$
$$[mix] = 81.94\%$$

Since [mix] = 81.94% the concentrations calculated on the molecular sieve were modified as follows

$$[H_2] = (13.53)\ (0.189)$$
$$= 11.08\%$$
$$[O_2] = (1.15)\ (0.819)$$
$$= 0.94\%$$
$$[N_2] = (67.14)\ (0.819)$$
$$= 4.75\%$$
$$[CO] = (12.38)\ (0.819)$$
$$= 10.14\%$$

The composition of the product gas is summarized below.

Component	Concentration
H_2	11.08
O_2	0.94
N_2	54.99
CH_4	4.75
CO	10.14
CO_2	14.89
C_2H_4	1.78
C_2H_6	0.56
C_3H_6	0.83
C_3H_8	0.00

The oxygen present in the analysis was due to contamination of the gas sample bottles and syringe and therefore the gas composition was adjusted to exclude oxygen. The final gas composition was given as follows:

Component	Concentration
H_2	11.60
O_2	0.00
N_2	53.86
CH_4	4.97
CO	10.62
CO_2	15.59
C_2H_4	1.86
C_2H_6	0.59
C_3H_6	0.87
C_3H_8	0.00

ERROR ANALYSIS

An error analysis was made to determine the relative standard error for each component present in a standard gas mixture.

Several calibration runs were made with the standard gas mixture containing the carbon oxides and hydrocarbons to determine the average calibration factor for each component. A similar series of runs were made with the standard mixture containing hydrogen. Using the average calibration factors, 20 analysis runs were performed to obtain the mean concentration, standard deviation, relative standard error and the confidence limits at 95% confidence level. The results are shown in Table 1.

VERIFICATION OF METHOD OF ANALYSIS

The method adopted for the calibration and analysis of the gases as well as the calibration factors evaluated were verified as follows. An overall mass balance was done around a burner operating under starving air conditions. A mixture of propane and air were partially combusted to produce a gas mixture containing H_2, N_2, CH_4, CO, CO_2 and H_2O. Water was also injected into the burner to control the temperature of the same. The gas mixture produced was analyzed using the gas chromatograph. A good closure verified that the gas analysis technique was substantially correct. A block diagram of the inlet and outlet streams of the burner is shown in Figure 2.

The input streams were as follows:

Component	Flowrate
Propane	0.4305 SCFM = (2.9931 lb/hr) = (1.3576 kg/hr)
Air	7.313 SCFM = (33.326 lb/hr) = (15.1163 kg/hr)
Water	4.229 lb/hr = (1.918 kg/hr)

The output streams were as follows:

Component	Flowrate
Steam	5.0891 lb/hr (2.3084 kg/hr)

The composition of the product gas was as follows:

Component	Concentration (%)
H_2	4.25
N_2	78.89
CH_4	0.20
CO	5.10
CO_2	11.57

Dry gas flow was 439.77 SCF/hr (12.45 Nm^3/hr)

The average gas molecular weight is

$$= [(4.25 \times 2) + (78.89 \times 28) + (0.2 \times 16) + (5.10 \times 28)$$
$$+ (11.57 \times 44)]/100$$
$$= 28.72$$

Total weight of dry gas produced was evaluated by

$$PV = nRT$$
$$PV = W/M \ RT$$
$$1 \times 439.77 = \frac{W}{28.72} \times 0.73023 \times 520$$
$$W = 33.2617 \ \text{lb/hr} \ (15.0872 \ \text{kg/hr})$$

Net output $= (33.2617 + 5.0891) \ \text{lb/hr}$

$$= 38.351 \ \text{lb/hr} = (17.3956 \ \text{kg/hr})$$

Net input $= (2.9931 + 33.326 + 4.229) \ \text{lb/hr}$

$$= 40.5481 \ \text{lb/hr} = (18.3922 \ \text{kg/hr})$$

closure $= 94.58\%$

A good closure thus indicated that the analysis method employed was substantially correct.

CONCLUSION

A gas chromatographic scheme, using a dual column gas chromatograph equipped with thermal conductivity detectors was developed for the detection and analysis of the gas produced from the gasification of coal and biomass. The gases analyzed included H_2, O_2, N_2, CH_4, CO, CO_2, H_2S, C_2H_4, C_2H_6, C_3H_6 and C_3H_8. The method of analysis and the calibration factors calculated were verified by making an overall mass balance around a burner operating under starving air conditons, the products of which were analyzed by the gas chromatograph. An error analysis was also performed to determine the accuracy of the procedure.

LITERATURE CITED

Dal Nogare, S., and R. S. Juvet, Gas-Liquid Chromatography, John Wiley & Sons, 1962.

Doran, T., and J. P. Cross, "Single Sample Analysis of the Mixture of O_2, N_2, CH_4, CO, CO_2, C_2H_6, C_3H_8 and n-C_4H_{10}," J. Gas Chromatog., July 1966, pp. 260-262.

Keulmans, A.I.M., Gas Chromatography, Reinhold Publishing Corp., New York, 1957.

Kim, A. G., and L. J. Douglas, "Gas Chromatographic Method for Analyzing Gases Associated with Coal," [Washington] U.S. Bureau of Mines, 1974.

Messner, A. E., D. M. Rosie, and P. A. Argabright, "Correlation of Thermal Conductivity Cell Response with Molecular Weight and Structure: Quantitative Gas Chromatographic Analysis," Anal. Chem. 31, 230-233 (1959).

Rosie, D. M., and R. L. Grob, "Thermal Conductivity Behavior: Importance in Quantitative Gas Chromatography," Anal. Chem., 29, 1263-1264 (1957).

Terry, J. O., and J. H. Futrell, "A Three-Column, Two-Detector Gas Chromatographic Method for the Simultaneous Analysis of a Mixture of Fixed Gases and Hydrocarbons," Anal. Chem., 37, 1165-1167 (1965).

Young, I. G., "A Review of Post-Run Calculation Techniques in Gas Chromatography: Part I," American Laboratory, pp. 27-36, February, 1975(a).

Young, I. G., "A Review of Post-Run Calculation Techniques in Gas Chromatography: Part II," American Laboratory, pp. 37-44, June 1975(b).

Young, I. G., "A Review of Post-Run Calculation Techniques in Gas Chromatography: Part III," American Laboratory, pp. 11-21, August, 1975(c).

Notations Used

$(Area)_i$, A_i	Area of the ith component
$(Area)_i^{MS}$, A_i^{MS}	Area of the ith component on the molecular sieve column
$(Area)_i^P$, A_i^P	Area of the ith component on the Porapak column
$(Area)_{Ref}$	Area of the reference component
$(CF)_i$	Calibration factor of the ith component
%(i)	Percentage composition of the ith component
[i]	Molar concentration of the ith component
[mix]	Concentration of mixture
MS	Molecular sieve column
(OCF)	Overall calibration factor
P	Porapak column
Ref	Reference component

Table 1

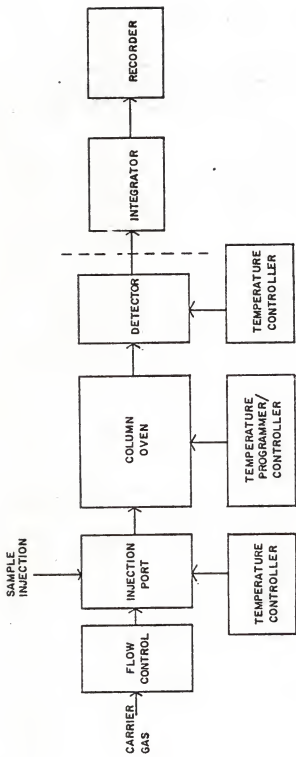|	Mean	Std. deviation	Relative Std. Error	95% Confidence Limit
H_2	6.05	0.186	3.07	$\pm$ 0.133
N_2	83.58	0.758	0.907	$\pm$ 0.354
CH_4	5.47	0.333	6.089	$\pm$ 0.156
CO	10.76	0.438	4.071	$\pm$ 0.205
CO_2	18.35	0.605	3.296	$\pm$ 0.322
C_2H_4	3.051	0.187	6.129	$\pm$ 0.099
C_2H_6	2.023	0.165	8.156	$\pm$ 0.088

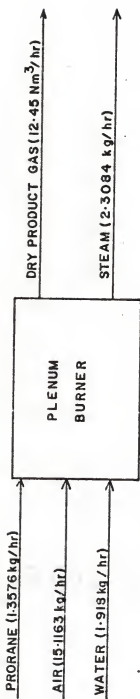Figure 1. Schematic Diagram of the Gas Chromatograph.

Figure 2. Block Diagram of the Inlet and Outlet Streams of the Plenum Burner

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

A summary of the conclusions drawn in chapters III and IV are presented in this chapter. In addition, recommendations for future work in this area are discussed.

Bench Scale Reactor

Feedlot manure was steam gasified in a bench scale fluidized bed reactor, using a silica sand bed, at atmospheric pressure. The temperature range investigated was from 950K to 1370K, with the superficial velocity of steam maintained at 36.6 cm/sec.

The produced gas consisted primarily of hydrogen, methane and carbon oxides, with smaller concentrations of the heavier hydrocarbons. Heating values ranged from 10.71 MJ/Nm^3 at 980K to 13.06 MJ/Nm^3 at 1370K. Gas yields varied from 0.59 Nm^3/kg (DAF) at 980K to 1.3 Nm^3/kg (DAF) at 1370K.

In an attempt to prevent bed agglomeration, which resulted when using a silica sand bed, a bed composed of 25% limestone and 75% silica sand was employed. It was found that this bed successfully prevented any agglomeration. Heating values of the produced gas from this bed remained essentially constant at 13.06 MJ/Nm^3 throughout the temperature range studied. Gas yields varied from 0.624 Nm^3/kg (DAF) at 950K to 1.436 Nm^3/kg (DAF) at 1310K.

Thus it was found that the limestone-sand bed not only prevented bed agglomeration, but also increased the gas yields significantly, thereby improving the efficiency of the gasification process.

The data obtained from the bench scale reactor were also compared to those from a pilot plant reactor operated under similar conditions. The results showed that while the gas yields from both reactors were very close, the heating values were markedly different. It was suspected that the time-temperature history of the produced gas and the temperature of the disengaging zone can affect the gas composition significantly.

Gas Chromatographic Analysis

A gas chromatographic scheme was developed for the detection and analysis of the gas produced from the gasification of coal and biomass. The gases analyzed included H_2, O_2, N_2, CH_4, CO, CO_2, H_2S, C_2H_4, C_2H_6, C_3H_6 and C_3H_8. The method of analysis and the calibration factors calculated were verified by making an overall mass balance around a burner operating under starving air conditions, the products of which were analyzed by the gas chromatograph. An error analysis was also performed to determine the accuracy of the procedure.

Recommendations

This study focussed on the effect of temperature on the gas composition and yields when manure was gasified with steam. Further work need be done on the effects of other variables such as superficial velocity, particle size of feed and pressure. In addition, the effects of other fluidizing gases such as H_2 and combinations of steam, air and H_2 need to be investigated. Recycle of product gas is another process variable which can be studied further.

With regard to bed agglomeration, the effects of varying concentrations of the limestone-sand mixture need to be studied with a view to improve gas yields. The cause and prevention of bed agglomeration has to be investigated more thoroughly to understand this phenomenon better. The effectiveness of various salts in preventing bed agglomeration and improving the efficiency of the gasification process is yet another area that needs further investigation.

Collection and analysis of condensible products resulting from the gasification process can provide valuable information and hence the reactor

should be suitably modified for such a task. In addition, modifications to allow for the continuous removal of char and ash from the bed would greatly help in the prolonged operation of the reactor.

ACKNOWLEDGMENT

STEAM GASIFICATION OF MANURE

by

S. GANESAN

B. Tech., Indian Institute of Technology, Madras, India

─────────────────────

AN ABSTRACT OF A MASTER'S THESIS

submitted in partial fulfillment of the

requirements for the degree

MASTER OF SCIENCE

Department of Chemical Engineering

KANSAS STATE UNIVERSITY
Manhattan, Kansas

1979

Feedlot manure, from the Kansas State University Beef Cattle Research Center, was steam gasified at atmospheric pressure, in a bench scale fluidized bed reactor composed primarily of silica sand. The temperature range investigated was from 980K to 1370K, with the superficial velocity maintained at 36.6 cm/sec. Heating values of the gaseous product ranged from 10.71 MJ/Nm^3 at 980K to 13.06 MJ/Nm^3 at 1370K. Gas yields varied from 0.59 Nm^3/kg (DAF) at 980K to 1.3 Nm^3/kg (DAF) at 1370K.

In an attempt to prevent bed agglomeration, which was observed with runs made with the silica bed, a mixture composed of 25% limestone and 75% sand was employed. The results obtained with the latter bed, in the temperature range 950K – 1310K, showed that the heating value of the produced gas remained essentially constant at 13.06 MJ/Nm^3, while the gas yield varied from 0.624 Nm^3/kg (DAF) at 950K to 1.436 Nm^3/kg (DAF) at 1310K. Thus it was found that the limestone-sand bed not only prevented bed agglomeration but also served to increase the gas yields significantly.

The data obtained from the bench scale reactor were also compared with those from a pilot plant reactor operated under similar conditions. The results showed large differences in heating values of the produced gas from the two reactors. It was suspected that the time-temperature history of the produced gas in the disengaging zone plays an important role in the product gas composition.

A gas chromatographic scheme was also developed to analyze the gaseous products formed from the gasification of coal and biomass. The gases analyzed included H_2, O_2, N_2, CH_4, CO, CO_2, H_2S, C_2H_4, C_2H_6, C_3H_6 and C_3H_8. The method of analysis was verified by making a mass balance around a burner operating under starving air conditions, the products from which were analyzed by the gas chromatograph. An error analysis was also performed to determine the accuracy of the procedure.