KANSAS COAL GASIFICATION

by

JERALD A. HOWELL

B.S., Kansas State University, 1977

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 1

INTRODUCTION

As the price of our petroleum and natural gas resources increase and supplies diminish, increased emphasis will be placed upon the development of alternative sources of energy. Today, these two energy resources account for 75% of the total energy consumption of the United States. Furthermore, about 50% of our petroleum is imported. It is, therefore, essential that new energy alternatives be found in order that the country's economic growth, which has been directly linked to the growth of energy consumption, can be maintained.

The conversion of the nation's vast resources of coal to liquid and gaseous fuels has been envisioned as a major contributor to the energy picture in the near future. However, for this material to play a significant role, utilization cannot be restricted to the use of only premium coal; that is, the types of coal with low sulfur, low ash, and non-caking characteristics. Research must be pursued into the utilization of our total coal reserves. A data base is needed to describe the behavior of these non-premium coals in conversion environments along with information on the quality and yield of the products which can be expected from them. This thesis will focus specifically on obtaining such information for the gasification of a high sulfur, caking coal which is native to Kansas. Further work is performed in order to determine potential benefits to be realized from the gasification of a mixture of Kansas coal and a low sulfur feedlot manure. These benefits would include the reduction of sulfur concentrations in the product gas, and the possible catalytic effect of the alkali salts found in manure. The use of feedlot manure in this manner would, in addition, allow the utilization

of a renewable energy resource which in the past has created disposal and pollution problems.

Chapter Two reviews some of the coal gasification processes which have been proposed in order to utilize "problem" coal. These processes vary in the gas-solid contacting methods employed and the process operating conditions. For processing caking coal, the common principle of the various contacting devices is to maintain a dilute coal phase to avoid agglomeration while the coal undergoes caking.

In fundamental studies of the behavior of coal during devolatilization, thermal analysis (TA) experiments have been shown to provide valuable information. These techniques continuously monitor a property of the coal (such as weight) as it is linearly heated. In this work, TA is used to study the devolatilization of a high-sulfur, high-ash, caking bituminous coal from the Rowe coal bed in Kansas. The results of this study are presented in Chapter Three. The major characteristics of the devolatilization are observed and statistically analyzed for their dependence upon experimental variables. Kinetic parameters of the devolatilization are determined and compared to those found in the literature for coal of similar ultimate and proximate analysis, but obtained using dramatically different experimental techniques.

Although many contacting devices have been proposed in coal gasification operations, fluidized beds are widely used because of their advantageous characteristics, such as good heat transfer and long residence times for the char. However, difficulties have been encountered in the operation of fluidized beds, when the material being gasified has strong caking properties and tends to agglomerate the bed. Chapter Four presents an experimental study of the steam gasification of a type of Kansas coal in a fluidized bed

reactor. The operating conditions necessary to prevent bed agglomeration are determined as well as the effect of reactor temperature on product gas yield and composition.

While the conversion of coal to gaseous fuels has received the greatest attention due to the possible affect it could have on the energy supply picture of the nation, the production of fuel gas from materials previously considered as waste is receiving increased recognition. Waste materials now under consideration as possible gasification feedstocks include municipal refuse, crop residues, feedlot manure, tires, and plastic wastes. While basic gasification studies of these materials have, in many cases, shown results which are superior to those from the gasification of coal, a major practical concern involves the reliability of supplying sufficient quantities of these substances to sustain a commercial plant operation. The utilization of these materials would not only be useful from the standpoint of providing an additional energy source, but also in the elimination of the disposal and pollution problems associated with these waste materials. Chapter Five investigates the steam gasification of a 50-50 blend of a type of high-sulfur, caking bituminous coal and feedlot manure. The potential advantages of using this type of mixture include the production of a gaseous product superior to that obtained from either component individually, and the ability to utilize these materials which now are considered undesirable for gasification feedstocks. Chapter Six summarizes the significant conclusions of this study and recommendations for future work.

CHAPTER II

REVIEW OF GASIFICATION TECHNOLOGY

COAL GASIFICATION

While the basic concept in all coal gasification processes is to decompose the coal by exposure to heat with subsequent reaction of the residual char with the gaseous environment, considerable variations in operating conditions and contacting devices exist. These variations stem primarily from the form and nature of the products desired from the gasification procedure. The literature contains scores of proposed processes which can be classified as belonging to one of three groups: Those which produce a high-heating-value gas suitable for introduction into pipelines; those which produce a low- to medium-heating-value gas which can be used locally; those in which liquids or solids are the major end product.

Coal gasification processes basically are comprised of four steps. The importance of each step will depend upon the nature of the coal feedstock, the contacting device employed, and the desired form of the end products. These four steps are:

1) Coal Pretreatment
2) Primary Gasification
3) Secondary Gasification
4) Alteration of the chemical composition of the gasification products.

Pretreatment

Pretreatment involves alteration of coal into a feedstock which is amenable to the conversion process employed. For example, certain types of bituminous coal exhibit swelling and softening tendencies when exposed to elevated temperatures (Van Krevelen, 1956). This tendency is known as caking, and is usually characterized by the coal's Free Swelling Index (FSI). Values

of the FSI range from unity for a noncaking coal to nine for a severely caking coal. As gasification proceeds, however, the softening reaches a peak and the coal subsequently resolidifies (Overturf, 1978).

Many processes using fluidized beds or moving bed reactors are unable to accommodate caking behavior without experiencing bed agglomeration problems. To destroy its caking tendency, coal is normally exposed to a mildly oxidative environment. Several techniques have been explored using static beds (Gasior et al, 1964), fluidized beds (Forney et al, 1964; Ravlick and Lee, 1967), and free-fall reactors (Gasior et al, 1965, 1967). These decaking schemes use various combinations of steam and oxygen at temperatures ranging from 400°C to 700°C. For the pretreatment to be practical, a correct combination of temperature, coal residence time and oxygen concentration must be used to accomplish decaking without an excessive loss of the coal's volatile matter. For example, Gasior et al, (1967) found that a strongly caking coal (FSI of 8.0) from the Pittsburg seam could be converted to a noncaking char (FSI of 1.0) by a two-second exposure in a free-fall reactor. A stream of 5.5 to 12.7 molar % oxygen was used at 250 to 300 psig and 560° to 680°C. The volatile matter of the coal was decreased from 35.6% to 24.9% due to this treatment.

Several processes have been able to handle various types of caking coal without pretreatment. The majority of these keep the coal concentration in the contacting device very low as the material passes through its swelling temperature range and resolidifies. In the Hydrane process, developed by the U.S. Bureau of Mines (Feldmann et al, 1972), crushed raw coal is fed to a two-zone hydrogenation reactor operated at 7 MPa and 900°C. In the first zone, the coal falls freely as a dilute cloud of particles through a hydrogen-rich gas. As the coal is heated in this zone, it loses its volatile

matter and agglomerating characteristics. The remaining char falls into a fluidized bed reactor and undergoes further gasification. The Atgas process, which can also process caking coal, injects the dried crushed coal into a molten iron bath at a temperature of 1370°C and a pressure of 5 MPa (Karnavas et al, 1972). The coal is dissolved by the molten iron where the volatile matter cracks in the presence of oxygen and steam to produce a gas composed of hydrogen and carbon monoxide. Similar to the Atgas process, the Molten Salt process (Cover, 1973) injects coal, steam and oxygen into a molten bath of sodium carbonate at 1000°C and 3 MPa. The Char Oil Energy Development (COED) process treats caking coals in a different manner from the processes mentioned previously. In this process, coal passes through a series of progressively hotter fluidized bed reactors. In each reactor, a fraction of the coal's volatile matter is released, and the temperature of each bed is chosen just below the maximum temperature to which the coal can be heated without softening sufficiently to agglomerate. The number of stages and operating temperature of each stage are determined by the caking properties of the coal used. Unlike the other gasification processes, a fuel gas is not the major product from the COED process. The product distribution from an Illinois No. 6-Seam coal was 57.1% char, 23.6% oil, 13.2% gas, and 6.1% liquid (Eddinger et al, 1965).

Another common problem associated with the use of coal in gasification processes is that many types of coal contain high sulfur concentration. During primary gasification, studies have shown that about 70% of the coal's original sulfur content is gasified at 1000°C (Suuberg, 1978) and 85% is gasified at 1800°C (Kobayashi, 1977). The majority of this sulfur appears in the form of hydrogen sulfide. In a recent survey of coal conversion technology (Howard-Smith, 1976), it is suggested that it would probably be

more efficient and, in the long run, less expensive, to desulfurize high-sulfur fuels before use rather than to resort to stack gas cleaners to reduce sulfur pollutants to acceptable levels.

A number of techniques are available for the desulfurization of coal. Removal of pyritic sulfur has been accomplished using physical processes such as magnetic separation (Howard et al, 1975) and by chemical leaching techniques, such as the Ledgemont oxygen leaching process (Agarwal et al, 1975). To effect the removal of organic sulfur often necessitates hydrogenation to produce hydrogen sulfide. However, a process, known as the Battelle Hydrothermal Coal Process (BHCP), has been reportedly able to remove 99% of the pyritic sulfur and 70% of the organic sulfur from coal using a process based on the heating of a water-coal slurry and a calcium hydroxide leaching agent at moderate temperatures and pressures (Stambaugh, 1977).

Despite the technology available for sulfur removal prior to the coal conversion process, a majority of the proposed gasification processes rely upon the removal of sulfur pollutants from the product gas stream. This is the case employed for most processes which seek to produce a pipeline-quality fuel gas. For these processes, it is necessary to remove the carbon dioxide produced during the conversion process. The acid gas removal measures needed for CO_2 also effect the removal of the principal sulfur pollutant, hydrogen sulfide.

Primary Gasification

Primary gasification is also known as devolatilization, carbonization, and pyrolysis. This phenomenon results from the exposure of coal to elevated temperatures. Under this condition, the coal liberates a hydrogen-rich volatile fraction which contains CO, CO_2, H_2O, CH_4, H_2S, other light hydrocarbons,

as well as tars, oils, phenols, and others. This decomposition is due to heat alone and will occur regardless of the gaseous environment. The solid residue has a very high carbon content and is extremely unreactive to further thermal decomposition. The volatiles formed within a coal particle include unreactive species and species which are extremely reactive (Anthony et al, 1976). The unreactive volatiles escape from the particle to the surrounding environment, but only a fraction of the reactive volatiles usually escape. The volatiles which do not escape can polymerize or crack on the hot coal surfaces to form more stable (less reactive) char and thus reduce the actual volatile yield. This view of coal devolatilization is supported by the experimental findings of increased volatile yield with decreasing particle size and reactor pressure (Anthony et al, 1974). Yields depend on the coal type and the conditions under which heating takes place. Proximate analysis, in which coal is slowly heated in an inert environment under very precisely defined conditions, has shown the volatile matter of coal to range from less than ten percent for anthracites to over 50% for lignites (Averitt, 1961). Investigations, performed using extremely rapid heating techniques under less precisely defined conditions, have shown volatile yields which are substantially greater than those found by proximate analysis (Anthony and Howard, 1976).

An important part of coal science and technology has been concerned with the yields and compositions of the products formed and the rates and mechanisms of the physical and chemical changes taking place during devolatilization. Over a wide range in rank, coal exhibits more or less definite decomposition temperatures (Burgess and Wheeler, 1926). Depending on rank, devolatilization typically begins between 350°C and 450°C (Anthony and Howard, 1976). As the temperature is increased, a rapid volatile loss is

experienced until approximately 750°C to 800°C. Prolonged heating at or above this temperature results in an increasingly slower volatile evolution. The extent of devolatilization and the factors that influence it are of primary importance to gasification processes. The char resulting from this step will determine the extent of secondary gasification needed to obtain acceptable product gas yields, and the extent of gas methanation necessary to obtain pipeline quality gas. An extensive review of investigations into the devolatilization of coal has been given by Anthony and Howard (1976).

Secondary Gasification

Secondary gasification usually concerns the gasification of the residual char resulting from the primary gasification step. Most proposed processes employ some combination of hydrogen, steam, and oxygen to accomplish this task. When a high heating value gas is the desired end product, it is desirable to produce as much methane as possible during the primary and secondary gasification steps to reduce the need for downstream water shift and methanation reactions. Studies have shown that the use of high hydrogen partial pressures during primary and secondary gasification leads to greatly increased methane production (Anthony et al, 1976). Although hydrogen reacts with char during secondary gasification, the reported rates of this reaction are relatively slow (Feldkirchner, 1963). Another effect of hydrogen is its reaction with some of the reactive volatiles formed during the primary devolatilization to produce light hydrocarbons capable of escaping from the coal particle without further reaction. The existance of this effect is supported by evidence of an increased volatile evolution in the presence of hydrogen with rates similar to that of devolatilization, and by the decrease of tars formed as the pressure of hydrogen is increased (Anthony et al, 1976).

Even though hydrogen has been shown to promote the production of methane during gasification, most of the coal gasification processes under serious consideration make use of steam and oxygen as gasification agents (Howard-Smith, 1976). Two notable exceptions are the Hydrane and Hygas processes which generate their needed hydrogen from the steam-oxygen gasification of char residual. The major differences between processes attempting to produce a high heating value gas and those producing low to medium heating value gases, are as follows: the latter processes employ air in the place of oxygen, perform no downstream methanation, and operate at lower pressures.

Product Gas Alteration

The gaseous products from the gasification steps normally contains substantial concentrations of hydrogen and carbon monoxide. Processes which produce a pipeline quality gas utilize the water shift reaction. This step reacts CO and H_2O to form CO_2 and H_2 to adjust the CO and H_2 concentrations to a 1 to 3 ratio for the subsequent methanation step. This shift reaction is a well-known process which conventionally uses an iron-chromium catalyst. However, this process has not been applied to the large scale which will be required for coal gasification processes. The shift reaction as well as the catalytic methanation reaction have not been fully studied at the pressures and feed gas compositions which will be encountered in the final cleanup step in the production of pipeline quality gas from coal (Tajbl et al, 1967). Currently, research is under way to discover the best catalysts and the mode of operation for large scale gasification operations (Wen et al, 1969; Wen, 1976).

BOVINE WASTE GASIFICATION

The use of cattle feedlot wastes as a renewable gasification feedstock has been under consideration for over the past ten years. Several advantages have been seen in the usage of this material for gasification other than just for the production of a fuel gas.

The cattle feeding industry has experienced both an increase in the number of cattle fed and marketed annually, and a growth in size of the individual feedlot operations. Feedlots with 50,000 head or more are no longer unique (Garner and Smith, 1973). Since each animal produces from 40 to 60 pounds of manure daily, the handling and disposal of this material has become a major operating problem for this industry. Due to competition from chemical fertilizers, the common disposal technique has been piling or concentrated field spreading. These techniques have created potential hazards to the environment, and have been held responsible for specific fish kills and general degradation of aqueous bodies (Garner and Smith, 1973).

Reported analysis of the elemental composition of feedlot manures (Appell et al, 1972; Martinez, 1973) have shown this material to be in many respects similar to lignite coal on a dry ash free basis. Sulfur contents were found to be normally less than one percent by weight. Depending on location, moisture and ash contents have been found to be as high as 80% and 26%, respectively. With proper pretreatment, this material could be gasified in many of the proposed processes for coal gasification.

In a conceptual economic study (Engler et al., 1975), pretreatment involved the flash drying of the material to approximately 10% moisture and size reduction to 250 μm. Pilot plant studies on the partial oxidation of manure with steam and air in a reportedly fluidized bed reactor (Beck et al, 1979), have shown product gases produced with heating values of 9.3 MJ/Nm^3

and yields, on a dry-ash free basis (daf), between 0.5 Nm^3/Kg and 1.2 Nm^3/Kg. Walawender and Fan (1978) gasified dried feedlot manure in a 23 cm fluidized bed reactor operating at atmospheric pressure between 727°C and 827°C. The bulk of the bed used in this study was composed of silica sand. The fluidization gas and heat required for the gasification were supplied by the combustion of propane. The study showed that a fuel gas with a heating value of 13.2 MJ/Nm^3 could be obtained with yields of 0.71 $Nm^3/Kg(daf)$. These results compare very favorably to those found from gasification of coal in similar environments. Reactor temperatures used in these studies were fairly low (500°C to 800°C) compared to those used in many coal gasification processes. The ability to use lower reactor temperatures is also reflected by thermogravimetric studies of the primary gasification of manure (Antal, 1979). These studies have shown devolatilization of manure to occur rapidly in the temperature range of 200°C to 400°C with a volatile yield comprising 85% of the initial sample weight.

THERMAL ANALYSIS

The term thermal analysis (TA), refers to a group of experimental techniques which all have a common operating principle: as a captive sample is heated or cooled according to a predetermined temperature-time program, a physical property of that sample is continually monitored and recorded as a function of temperature (or time). The purpose of the analysis is not merely to evaluate the physical property as a function of temperature, but also to relate the change of that property to physical or chemical alterations which occur in the sample during heating. The interpretations of thermal analysis, therefore, consists of using features of the property-temperature curve (peaks, discontinuities, slope changes, etc.) to identify thermal events, e.g., chemical reactions or physical property transitions.

Thermogravimetric Analysis

Knowledge of the rate of loss of weight of a material when heated either at a constant temperature or at a controlled rate of temperature increase is of primary importance to the understanding of the nature of the thermal decomposition process (Howard, 1963). Thermogravimetric analysis (TGA) continuously monitors sample weight in a precisely controlled temperature environment. This technique has been applied to the study of the devolatilization of coal as early as 1926 (Audibert, 1926). More recent studies have used this technique not only in the study of conversions, but also in the modeling of reaction kinetics for various complex organic substances such as coal (Gardner et al, 1974), wood (Havens, 1969; Maa and Bailey, 1978), and cellulose (Chatterjee, 1968).

LITERATURE CITED

Agarwal, J. C., R. A. Gilberti, P. F. Irminger, L. J. Petrovic, and S. S. Sareen, Mining Congress Journal, pp. 40, March, 1975.

Antal, M. J., Jr., F. E. Rogers, and H. L. Freidman, "Study of Steam Gasification of Organic Wastes," Draft Final Copy to U.S. Envir. Protect. Agency, Dept. Mechanical and Aerospace Eng., Princeton Univ., Princeton, N.J., 1979.

Anthony, D. B., J. B. Howard, H. C. Hottel, and H. P. Meissner, "Rapid Devolatilization of Pulverized Coal," Fifteenth Symposium (International) on Combustion, pp. 1303, The Combustion Institute, Pittsburg, Pa., 1974.

Anthony, D. B., J. B. Howard, H. C. Hottel, and H. P. Meissner, "Rapid Devolatilization and Hydrogasification of Bituminous Coal," Fuel, 55, 121, 1976.

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

Appell, H. R., Y. C. Fu, S. Friedman, P. M. Yavorsky, and I. Wender, "Converting Organic Wastes to Oil," Agri. Eng., 53, No. 3, 17, 1972.

Audibert, E., Rev. Ind. Minérale, pp. 115, 1926; Chem. Abs., 20, 2239, 1926.

Averitt, P., "Coal Reserves of the United States," U.S. Geological Survey Bulletin 1136, 1961.

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.

Burgess, M. J., and R. V. Wheeler, Fuel, 5, pp. 65, 1926.

Chatterjee, P. K., and C. M. Conrad, "Thermogravimetric Analysis of Cellulose," J. Poly. Sci.: Part A-1, 6, 1968.

Cover, A. E., "The Kellogg Coal Gasification Process," Synthetic Gas Production Symposium, AICHE, New York, 1973.

Eddinger, R. T., "Char Oil Energy Development," FMC Technical Report PCR-469, 1965.

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

Feldkirchner, H. L., and H. R. Linden, "Reactivity of Coals in High Pressure Gasification," Ind. Eng. Process Design Develop., 2, 153, 1963.

Feldmann, H. F., "Supplemental Pipeline Gas from Coal by the Hydrane Process," presented at 71st National Meeting of AICHE, Dallas, 1972.

Forney, A. J., R. F. Kenny, S. J. Gasior, and J. H. Field, "Fluid Bed Gasification of Pretreated Pittsburg Seam Coals," in Fuel Gasification, pp. 128, Advances in Chemistry Series, No. 69, Am. Chem. Soc., Washington, D.C., 1967.

Gardner, N., E. Samuels, and K. Wilks, "Catalyzed Hydrogasification of Coal Chars," in Coal Gasification, pp. 217, Advances in Chemistry Series, No. 131, Am. Chem. Soc., Washington, D.C., 1974.

Garner, W. and I. C. Smith, "The Disposal of Cattle Feedlot Wastes by Pyrolysis," Environmental Protection Technology Series, EPA-R2-73-096, Office of Research and Monitoring, U.S. Environmental Protection Agency, Washington, D.C., 1973.

Gasior, S. J., A. J. Forney, and J. H. Field, Ind. Eng. Chem. Prod. Res. Develop., 3, 43, 1964.

Gasior, S. J., A. J. Forney, and J. H. Field, Mining Eng., pp. 74, March, 1965.

Gasior, S. J., A. J. Forney, and J. H. Field, "Decaking of Coal in Free Fall," in Fuel Gasification, pp. 1, Advances in Chemistry Series, No. 69, Am. Chem. Soc., Washington, D.C., 1967.

Havens, J. A., "Thermal Decomposition of Wood," Ph.D. thesis, Univ. Oklahoma, Norman, 1969.

Howard, H. C., "Pyrolytic Reactions of Coal," in Chemistry of Coal Utilization, pp. 340, Supplementary Volume, H. H. Lowry, ed., Wiley, New York, 1963.

Howard, P., A. Hanchett, and R. G. Aldrich, "Chemical Cummination for Cleaning Bituminous Coal," presented at the Institute of Gas Technology Symposium, Chicago, Ill., June 26, 1975.

Howard-Smith, I., and G. J. Werner, Coal Conversion Technology, Chemical Technology Review No. 66, Noyes Data Corp., Park Ridge, N.J., 1976.

Karnavas, J. A., and others, "Atgas-Molten Iron Coal Gasification," AGA Fourth Synthetic Pipeline Gas Symposium, Chicago, 1972.

Kavlick, V. J., and B. S. Lee, "Coal Pretreatment in Fluidized Bed," in Fuel Gasification, Advances in Chemistry Series, No. 69, Am. Chem. Soc., Washington, D.C., 1967.

Kobayashi, H., J. B. Howard, and A. F. Sarofim, "Sixteenth Symposium (International) on Combustion," pp. 411, The Combustion Institute, Pittsburg, Pa., 1977.

Maa, P. S., and R. C. Bailie, "Experimental Pyrolysis of Cellulosic Material," presented at the AICHE 84th National Meeting, Atlanta, Ga., 1978.

Martinez, J., C. A., "An Experimental Study of the Production of Substitute Natural Gas by Hydrogasification of Livestock Manure," Ph.D. thesis, Dept. Chemical and Petroleum Engineering, Univ. Kansas, Lawrence, 1973.

Overturf, B. W., F. Kayihan, and G. V. Reklaitis, "Modeling and Analysis of an Integrated Coal Pyrolysis, Gasification, and Combustion Reactor System," presented at the 71st Annual Meeting of AICHE, Miami Beach, Nov. 16, 1978.

Stambaugh, E. P., and others, "Environmentally Acceptable Solid Fuels by the Battelle Hydrothermal Coal Process," Battelle Columbus Laboratories, Columbus, Ohio, June 19, 1975.

Suuberg, E. M., W. A. Peters, and J. B. Howard, "Product Composition and Kinetics of Lignite Pyrolysis," Ind. Eng. Chem. Process Des. Dev., 17, No. 1, 1978.

Tajbl, D. G., H. L. Feldkirchner, and A. L. Lee, "Cleanup Methanation for Hydrogasification Process," in Fuel Gasification, Advances in Chemistry Series, No. 69, Am. Chem. Soc., Washington, D.C., 1967.

Van Krevelen, D. W., F. J. Huntjens, and H.N.M. Dormans, "Chemical Structure and Properties of Coal XVI-Plastic Behavior on Heating," Fuel, 35, 462, 1956.

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

STUDY OF THE DEVOLATILIZATION OF A BITUMINOUS COAL USING THERMOGRAVIMETRIC ANALYSIS

INTRODUCTION

As domestic supplies of liquid and gaseous fuels diminish, increased emphasis has been placed upon the conversion of the nation's abundant coal reserves in order to reduce our dependence on imported fuels. Research has been conducted both on the development of conversion processes, and on the fundamental behavior of coal during conversion. Basic knowledge of the behavior of coal is essential for developing a coal conversion process since large variations exist between coals of different ranks, and even between coals of the same rank. These variations can necessitate changes in process operating parameters and even prohibit certain coals from being used in particular conversion processes.

In the study of various types of coal, laboratory tests can be performed to evaluate some of their characteristic properties. These tests include proximate analysis, ultimate analysis, porosity measurement, and density evaluation. Other tests yield information on the behavior of the material as it is subjected to changes in its thermal environment, such as various thermal analysis techniques, which are used to monitor the changes which occur as coal is heated.

The term Thermal Analyses (TA) refers to a group of experimental techniques which all have a common operating principle: as a captive sample is heated or cooled according to a predetermined temperature-time program, some physical property of that sample is continually monitored and recorded as a function of temperature. The purpose of the analysis is not merely to evaluate the physical property as a function of temperature, but also to relate the change of that property to physical or chemical alterations which occur in the sample during heating. The interpretations of thermal analysis data, therefore, consists of using features of the property -

temperature curve (peaks, discontinuities, slope changes, etc.) to identify thermal events, e.g., chemical reactions or physical property transitions.

Although in principle any physical property can be monitored in thermal analysis, only a small number of techniques have actually found widespread application. Table 1 summarizes the methods that have been employed. Each of these techniques yields a specific type of information about the behavior of the sample, and may be classified as belonging to one of three groups, depending on the nature of the parameter recorded:

a) methods which record the absolute value of the measured property (e.g., the sample weight, TGA).

b) methods which record the difference between some property of the sample and that of a reference material (e.g., the temperature difference, DTA).

c) methods which record the rate at which some property is changing with respect to temperature (e.g., the rate of weight change, DTG).

While some thermal analysis methods have been employed for thousands of years, modern developments essentially began around the turn of this century. Since then, new methods and equipment have been developed. Recent technological development has allowed some techniques to be realized, which previously had only been concepts, and has permitted others to be extended in their applications and capabilities. During the last twenty years, an increasing number of equipment for thermal analysis have become commercially available, and there is now a wide choice of instrumentation for the more common techniques. It is no longer necessary for the individual researcher to construct his own thermal analysis equipment, unless it is required for specialized measurements.

Thermal analysis equipment has reached a stage of development where very high sensitivities and a wide range of operational conditions can be

achieved. However, great care must be employed in the interpretation of data. This is especially true when studying the devolatilization of complex substances, where the nature of devolatilization and the factors that influence it are not known. In addition, caution must be used when comparing data by investigators employing different instruments. This requires a knowledge of the instrument configuration and experimental parameters. Some of the major factors which may influence the thermogram are:

a) heating rate

b) furnace configuration

c) method of monitoring sample temperature

d) sample size and form

e) atmosphere and pressure

f) dynamic response of instrument and recording device

g) purge gas flow rates

One feature of thermal analysis equipment, which has raised doubts about its applicability in the study of some reactions, is the normally slow time-temperature program employed. Since sample properties are continually monitored with sensitive measuring devices, slow heating is necessary to maintain stability within the instrument. To the authors' knowledge, the fastest heating program commercially available today is approximately 5°C/sec (available from the Perkin-Elmer Corp.). Many investigators (e.g., Leu, 1974; Havens, 1969; Ozawa, 1965) have found that the shape and location of a thermogram is dependent upon the heating rate employed. It is for this reason that many have questioned the extrapolation of TA data to processes which realize heating rates several orders of magnitude higher than those used in TA.

In recent years, numerous techniques have been developed to monitor sample behavior under conditions more representative of those expected in actual reactor systems. These techniques have typically been applied to studies involving combustion and devolatilization of various materials, where heating rates are extremely high. In the heating of coal particles, some typical apparatus which have been used include shock tubes (Woodburn et al., 1974), plasma jets (Anderson et al., 1968), xenon flash tubes (Sharkey et al., 1964), and lasers (Joy et al., 1970). These methods have reportedly achieved heating rates as high as 400,000°C/sec (Kimber and Gray, 1967), but in many cases have also made acquisition of kinetic data virtually impossible.

In a review of proposed coal gasification processes, Hottel and Howard (1971) indicate heating rates of these processes will be as high as 10^4°C/sec. Several techniques have been devised to operate in this heating rate region, including fluidized beds (Pitt, 1962; Jones et al., 1964), electric grids (Anthony, 1974; Mentser, 1974), and entrained flow reactors (Badzioch et al., 1967, 1970; Coates et al., 1974). In contrast to the conventional thermal analysis techniques, sample changes under rapid heating are not monitored continuously; rather, only the gross change in sample characteristics can be obtained. The most common parameter studied in these experiments has been weight loss. By rapidly heating to several temperatures, a weight-loss-versus-temperature curve, similar to that obtained in thermogravimetric analysis, can be constructed. The majority of rapid heating studies done on coal have shown total conversions which have been higher that that obtained by proximate analysis, which is a slow heating technique (Anthony and Howard, 1976). However, the actual relationship between results obtained by thermal analysis and rapid heating methods remains to be determined.

In this study, the devolatilization of bituminous coal was characterized using thermogravimetric analysis. The resultant thermograms were statistically analyzed for their dependence on the instrument operating parameters (heating rate and purge gas rate) and coal particle size. Kinetic parameters of the coal were determined from the thermograms. They were analyzed and compared to the published parameters obtained by means of rapid heating techniques.

THEORETICAL

Devolatilization involves the decomposition of an organic material when exposed to elevated temperatures. The products of this decomposition are a hydrogen rich volatile fraction and a carbon rich solid residue. The complexities of the chemical reaction and transport phenomena involved in the devolatilization of complex substances, such as coal, polymers, and cellulosic wastes, make modeling efforts extremely difficult. Most researchers have resorted to empirical models to fit their data. Theoretical or mechanistic approaches to solve modeling of coal devolatilization, e.g., Cheong (1976), have predictably resulted in extremely complex expressions.

The majority of investigators who have attempted to empirically model devolatilization reactions utilize weight-loss data. The data typically has been analyzed by approaches which are analogous to those employed in the analysis of simple homogeneous reaction kinetics. In its simplest form, assuming an overall n-th order decomposition occuring uniformly throughout the particle, the rate of devolatilization may be expressed as

$$-\frac{dw}{dt} = kw^n \qquad (1)$$

where w represents the volatile matter remaining and k is the rate constant, which is typically correlated by an Arrhenius equation

$$k = k_o \exp(-\frac{E}{RT}). \qquad (2)$$

The values of n, k_o, and E are determined by fitting the model to the weight-loss-versus-temperature curve. Many methods have been proposed for the determination of these kinetic parameters. Flynn & Wall (1966) have presented a review of a number of these approaches.

Several investigators (e.g., Stone *et al.*, 1954; Shapatina *et al.*, 1960) have observed that the simple model, equation (1), is not capable of

correlating weight loss data over a wide range of temperatures, using a single set of kinetic parameters. Anthony and Howard (1976) stated that the use of a simple single-step, first order reaction model has led some investigators to incorrectly reject chemical reaction kinetics as the rate controlling step in the devolatilization of pulverized coal. This conclusion is primarily due to the low activation energies resulting from the single step parameter estimation (e.g., Berkowitz, 1960).

Cheong (1977) considered the coal molecule to made up of various types of carbon-carbon, carbon-hydrogen, and oxygen-hydrogen bonds. He classified the carbon environments into three groups:

a) aromatic carbons

b) carbons adjacent to the aromatic ring

c) all remaining carbons.

Cheong recognized that the carbon-carbon bonds involving carbons adjacent to an aromatic ring are, in general, much weaker than the other carbon-carbon bondings. He concluded that these bonds would then be the most susceptible to direct fission to release the primary reactive volatiles. Disassociation energies for some of these weak carbon-carbon bonds were shown by Benson (1968) to be in the range of 57 kcal/mole to over 100 kcal/mole.

Jünten and Van Heek (1970) theoretically demonstrated that a set of independent, parallel, first-order reactions can be approximated by a single first-order expression with an activation energy and a frequency factor lower than those of any of the parallel reactions in the set. Anthony et al. (1974) further illustrated this by fitting his weight-loss

data to both a single reaction model and a multireaction model. The single reaction model yielded an activation energy of approximately 10 kcal/mole, while the mean activation energy from the multireaction model was 50 kcal/mole. These results were obtained under experimental conditions which were assumed to virtually eliminate heat and mass transfer effects.

Attempts to develop models for larger temperature ranges have resulted in multireaction concepts. Some investigations have broken the devolatilization curve into several consecutive zones, each represented by the simple homogeneous reaction model described above (Shapatina et al., 1960; Wiser et al., 1967; Skylar, 1969). In his work on cellulose decomposition, Chatterjee (1968a, 1968b) used a model which considered a chain reaction mechanism in which the major reaction of cellulose was a two step process. In the model, the initiation step was glucosidic bond scission and the propagation step was levoglucosan formation. This treatment, included a region between the initiation and propagation zones where these two steps overlapped. Another treatment, developed by Pitt (1962) and modified by Anthony et al. (1974), envisioned a large number of independent parallel reactions for the decomposition of coal. Each of the reactions were assumed to be first order with respect to the unvolatilized material and irreversible. Therefore, for the i-th reaction,

$$\frac{dV_i}{dt} = k_i(V_i^* - V_i) \tag{3}$$

where V_i is the volatile matter resulting from the i-th reaction, V_i^* is the total potential volatile matter for the i-th reaction, and k_i is a rate constant of the Arrhenius form

$$k_i = ko_i \exp(-\frac{E_i}{RT}). \tag{4}$$

Integration of Equation 3 yields

$$\frac{V_i^* - V_i}{V_i^*} = \exp \int_0^t ko_i \exp(-\frac{E_i}{RT})dt \qquad (5)$$

where V_i^*, ko_i and E_i must be determined for each of the parallel reactions. To simplify the analysis, it was assumed that the preexponential factor, ko_i, was the same for all reactions, i.e., $ko_i = k_o$ for all i. It was also assumed that the number of reactions involved was large enough to permit the activation energy, E, to be expressed as a continuous distribution function, f(E), with f(E)dE representing the fraction of the potential total volatile loss, V*, which has an activation energy between E and E+dE. Then V_i^*, the potential volatile loss from the i-th reaction, becomes a differential part of the total V^*, or

$$V_i^* = dV^* = V^* f(E)dE \qquad (6)$$

where

$$\int_0^\infty f(E)dE = 1 . \qquad (7)$$

Integration of Equation (5) over all values of E, with the use of Equation (6), yields an expression for the total volatile material remaining

$$V^* - V = V^* \int_0^\infty \exp\{\int_0^t k_o \exp(-\frac{E}{RT})dt\} f(E)dE \qquad (8)$$

In his work, assuming isothermal conditions, Pitt (1962) constructed a f(E) curve which best fitted his data by assuming the term

$$\exp[-k_o t \exp(-E/RT)]$$

to be a step function which was zero for $E < E_t$ and unity for $E \geq E_t$, where

$$E_t = RT \ln (k_o t)$$

Anthony (1974), on the other hand, using the nonisothermal form of Eq. 8, assumed the function f(E) to be a Gaussian distribution with a mean activation

energy, E_m, and a standard deviation, σ. Thus,

$$f(E) = \frac{1}{\sigma\sqrt{2\pi}} \exp\{-\frac{(E - E_m)^2}{2\sigma^2}\} \qquad (9)$$

Using the four parameters E_m, σ, k_o and V^*, along with the time-temperature history of his experiments, Anthony was able to curve fit the devolatilization data of both Montana lignite and Pittsburg Seam bituminous coal. The parameter values found were; E_m = 48.72 kcal/mole, σ = 9.38 kcal/mole, $k_o = 1.07 \times 10^{10}$ sec^{-1} and V^* = 40.63% for the lignite and E_m = 36.89 kcal/mole, σ = 4.18 kcal/mole, $k_o = 2.91 \times 10^{9}$ sec^{-1} and V^* = 37.18% for the bituminous coal. Anthony found that by using a value of k_o equal to that of the frequency factor calculated from transition state theory (Benson, 1968) and by using the experimental value of V^*, the number of parameters needed to characterize the devolatilization curve could be reduced to two without greatly effecting the fit of the model.

The model described above has found wide acceptance, primarily because it is able to characterize the devolatilization curve over a wide temperature range using only two parameters. It accounts for, at least partially, the complex nature of coal devolatilization, but at the same time it is not excessively complex as to prohibit utilization.

EXPERIMENTAL

Materials

High Volatile C Bituminous coal from the Rowe coal bed in southeast Kansas was used in this study. Its characteristics are listed in Table 2.

Equipment

A Perkin-Elmer Model TGS-2 Thermogravimetric Analyzer was used in this study to continuously monitor weight changes in coal due to devolatilization as the sample followed a linear heating program. This instrument was chosen on the basis of its sensitivity (0.1 μg max), range of heating rates (0.3125°C/min to 320°C/min), convenience of operation, and ability to use any type of gaseous environment.

The furnace area, shown in Fig. 2, was separated from the weighing chamber in order to minimize any effect of the increasing temperature on the weighing mechanism. The weighing mechanism employed operated on the null-balance principal. Balance response time could be selected by using a low, medium, or high filter. The available response times on the TGS-2 were 0.7, 1.2, and 4 seconds, respectively. This flexibility permitted less noise at the higher sensitivities. The instrument was capable of handling samples up to 1300 mg with six full scale range settings from 0.01 mg to 1000 mg. The flow pattern of the purge gas through the system is also shown in Figure 1. Permitted purge rates through the system ranged from static to 200 cc/min. For decomposition studies in which condensible materials were formed, a positive pressure was maintained through the weighing chamber in order to protect the balance mechanism. The furnace assembly consisted of a platinum wire element wound around a cylindrical aluminum support. This element acted

alternately as a heater and temperature sensor. Heating of the sample material was accomplished by both radiative heating and convective heating by means of the purge gas entering the furnace chamber. A chromel-alumel thermocouple was positioned one to two millimeters below the platinum sample pan. The low internal mass of this furnace configuration allowed rapid temperature equilibrium and therefore permitted this instrument to attain what is probably the fastest heating rate available today for equipment of this kind.

Data collection was accomplished using a Bascom-Turner Model 8110 plotting microprocesser, which allowed permanent data storage plus data manipulation capability.

Temperature Calibration

The thermocouple mounted in the furnace was calibrated so that it monitored not just the temperature of the furnace enclosure, but of the actual location in which the sample would be placed. This calibration was performed by placing a sample of a ferromagnetic metal with a precisely known Curie point temperature in the sample pan. The weight of this metal was electrically suppressed. The furnace tube was then surrounded by a magentic field which pulled down on the metal sample. Upon heating, the point at which the sample lost its observed weight indicated the contents of the sample pan were at the Curie point temperature. The thermocouple gain potentiometer was adjusted to indicate this temperature at the point where the weight loss occurred.

Procedure

The Kansas coal used in this study was hammermilled with subsequent size classification. Samples were oven dried for 24 hours at 105°C and stored in a desicator until used. Devolatilization data were collected

over the temperature range of 130°C to 960°C. For each experiment, five hundred data points were collected. This resulted in one data point being taken for every 1.64°C of temperature rise. At the end of every experiment, oxygen was introduced into the system to burn the residual char for ash analysis. To reduce possible heat and mass transfer effects, small sample sizes (0.5 mg to 1.5 mg) of crushed coal particles were spread in a uniform monolayer in the sample pan.

The principal experimental variables, which were determined to be the most likely to affect the results, included heating rate, particle size, and flow rate of inert purge gas. Three thermograms were obtained for every combination of two heating rates, two particle size ranges, and two inert purge gas flow rates, for a total of 24 experiments. The results were statistically analyzed to determine the influence of these experimental variables.

RESULTS AND DISCUSSION

Figure 3 shows the 24 experimental thermograms taken for the devolatilization of the Kansas Bituminous coal in a nitrogen atmosphere. As this figure shows, total weight loss due to devolatilization in the temperature region of 130°C to 960°C, ranges from 32% to 41% of the initial weight of the coal on an 'as received' basis. Much of this variation can be attributed to the varying ash contents of the samples. Ash concentration ranged from 8.6% to 20% over the 24 experiments. Figure 4 shows the three experiments performed for a heating rate of 160°C/min, a particle size range of 420 μm to 840 μm, and a purge gas flow rate of 50 cc/min. The ash contents of these three runs ranged from 8.6% to 16.3%, while the final percentage of the initial weight remaining varied from 59.3% to 64.7%. The varying ash contents of the individual samples were taken into account when the affects of the experimental variables on the final weight remaining were studied.

Figure 3 shows that the region of rapid weight loss begins at approximately 450°C and essentially end around 650°C. For temperatures above 650°C, the weight loss tends to approach the final weight remaining almost asymptotically. Little could be inferred from Fig. 3 alone with regards to the affect of the various experimental conditions under which pyrolysis was carried out.

Statistical Analysis of Thermogram Characteristics

The dependence of the thermogravimetric data on the experimental variables was determined by statistically comparing the data using analysis of variance (AOV). The hypothesis to be tested was that by changing the heating rate, particle size, or purge gas flow rate, no significant effect

would be observed, with respect to characteristics of the thermograms, that could not be attributed to experimental error. The usual assumptions involved in analysis of variance are; error deviations are normally distributed, observations are random and independent, and variances from each population are equal. For the present statistical analysis, the three experimental variables were treated as fixed variables. Consequently, the data dependence was analyzed specifically with respect to the two settings used for each experimental variable. While treatment of the variables preferably would have been on the basis of random variables so that generalizations could have been drawn with respect to data dependence, this would have necessitated investigation of several more variable settings.

Any common characteristics of the thermograms which can be found to depend upon the experimental variables would be sufficient to disprove the hypothesis given above. It has been noted that other investigators (e.g. Havens, 1969; Ozawa, 1965) have noticed a lateral shift of the thermograms with respect to temperature for different heating rates, therefore, the temperature location of the maximum rate of weight loss was chosen for statistical analysis. Another common characteristic chosen for analysis was the final weight attained at 960°C. Table 4 shows the F-ratios resulting from the analysis of variance. The critical F value with a protection level of five percent was determined to be 4.75, i.e., the probability of falsely rejecting the proposed hypothesis because of a F-ratio being greater than 4.75 is only five percent. The variables determined to be significant with this level of protection are underlined in Table 4. It can be seen that in the case of the temperature at which the maximum rate of weight loss occurred, the deviations observed for the two heating rates and the two particle size ranges can not be entirely attributed to experimental

error. No dependence is seen, however, for the two purge gas flow rates. In addition, no interaction of the three experimental variables is observed. In the case of the final weight at 960°C, however, there are only two variables which do not show significance; they are gas flow rate and the particle size-flow rate interaction.

Twelve experiments were performed which involved a heating rate of 40°C/min, and similarly twelve were performed at a rate of 160°C/min. The twelve experiments were the result of three repetitions for every combination of the two particle sizes and two purge gas flow rates. The mean temperature at which the maximum rate of weight loss occurred, and the mean final weight remaining were determined for each set of the twelve experiments. These means are shown in Table 3 along with a similar averaging for the twelve experiments performed for each particle size range. The means reported for the final weight remaining are on a dry, ash-free basis. As can be seen, the location of the maximum rate of weight loss shift to higher temperatures as both heating rate and particle size are increased. The final weight remaining at 960°C increases (lower conversion) with an increase in particle size, but decreases (higher conversion) for the faster heating rate.

The observed effect of particle size on final conversion is in agreement with studies done on both coal and cellulosic materials (Anthony et al., 1974, 1976a, 1976b; Havens, 1969). Anthony et al. (1974) considered the volatile product formed during pyrolysis to be composed of both reactive nonreacted components. As particle size is increased, the residence time of the reactive volatile species in the coal particle is also increased, hence promoting secondary char forming reaction.

A great deal of uncertainty remains with regards to the role played by the heating rate in decomposition reactions. One explanation given for the observed increase in volatile yield with increasing heating rate is that a competition exists between evaporation of volatile matter and re-polymerization to form char (Chaiken, 1974). Others, however, view the heating rate as being not per se the source of the observed effects but instead parametrically related (Essenhigh, 1974). In other words, the observed effects attributed to increased heating rates may not be due to that fact alone, but rather attributable to the experimental techniques employed to attain the higher heating rates. Clarification of the effect of heating rate can only be achieved through further studies.

Kinetics of Devolatilization

Each of the 24 thermograms were fitted to the multireaction model, developed by Anthony et al (1974). The form of the model used is shown in Eq. 8 and 9 of the THEORETICAL section. Curve fits were obtained using both a three parameter and a two parameter model. For the three parameter model, the unknowns found included the mean of the normally distributed activation energies, E_m, the standard deviation from that mean, σ, and the frequency factor, k_o. For the two parameter model, the frequency factor, k_o, was assumed to have a value of 1.67×10^{13} sec^{-1} as was determined by Benson (1968). Parameter estimation was accomplished using an unconstrained, nonlinear Hooke and Jeeves optimization routine. The objective function used was the sum of the squares of the deviations between the experimental data points and those determined by the model. The numerical scheme used to determine the model parameters is included in the appendix to this manuscript.

Table 5 shows the average values of the estimated parameters from the data of the 24 experiments performed on Kansas bituminous coal. Also given

in this table are the average mean deviation and the average standard deviation between the model and experimental results. The standard deviations given for each of the five parameters in Table 5 relate the amount of spread of these terms over the 24 experiments. This table indicates that the model was capable of representing the devolatilization curve closely over the temperature range of 130°C to 960°C. Figure 5 shows an example of the model fit to a typical set of weight loss data. It can be seen from Table 5 that the two parameter model can be used without significantly affecting the fit of the model. The mean activation energies found are in the range shown in the THEORETICAL section to be expected for coal devolatilization.

Model parameters for the Kansas bituminous coal are compared in Table 5 to those found by Anthony et al. (1974) for Pittsburg Seam Bituminous coal. Table 2 indicates that this coal has essentially the same characteristics as the coal used in this study. Anthony obtained data from experiments performed in a helium atmosphere at 7MPa pressure. An electric grid was employed to obtained heating rates between 180°C/sec and 10,000°C/sec. It is not clear what effect the high pressures used in Anthony's studies had on the shape and location of his devolatilization curves. Comparison of the obtained parameters to those resulting from this study show significant similarities, even though the experimental technique employed was dramatically different. Based on this comparison, it is concluded that these two coals would fall into the same classification on the basis of their devolatilization characteristics.

Statistical Analysis of the Correlation Parameters

To determine the effect of the experimental variables on the parameter values resulting from the three parameter fitting, these parameters were

statistically analyzed in the same manner as previously used for the temperature location of the maximum rate of weight loss and final weight remaining. The results of these analysis are shown in Table 6. As before, the F-ratios which are significant (greater than the critical value of 4.75) are underlined. Model parameter means for each main experimental variable found to be significant are also shown in Table 6. These means were obtained by averaging the model parameters over the 12 experiments which involved a particular experimental variable setting. This table shows that there is no single experimental variable which has a significant effect on all three of the model parameters. The most unaffected parameter is the mean activation energy, E_m, which is seen to be influenced only by some interaction between the heating rate and particle size. Particle size, which influenced both the final weight remaining as well as the temperature position of the maximum rate of weight loss in this work, is seen in this table to affect only two terms; the standard deviation from the mean activation energy (o) and the mean deviation between the experimental and correlation results (M. Dev.). The mean values for these two terms indicate that for the larger particle size, the mean deviation between experimental and model results increases. The standard deviation from the mean activation energy (o) is seen to decrease with increasing particle size, indicating a less broad Gaussian distribution of activation energies was needed to correlate the data. Heating rate is seen to influence both the value obtained for the models' frequency factor parameter (k_o), as well as the standard deviation between the experimental thermograms and the model generated weight loss curve (Std. Dev.). The means of these two terms at the two heating rates show that the frequency factor increases with increasing heating rate, while the standard deviation is higher at

the lower heating rate. The same effect on the standard deviation between the experimental data and the fitted model (Std. Dev.), is seen for the lower purge gas flow rate. A higher purge gas rate also tends to decrease the standard deviation about the mean activation energy (σ).

CONCLUSION

The devolatilization of Kansas bituminous coal was studied using thermogravimetric analysis. Experiments were carried out in an inert environment at atmospheric pressure. Results show significant devolatilization to begin at approximately 450°C and to conclude at 650°C. Further heating to 960°C resulted in an asymptotic approach to the final weight remaining, which ranged from 59% to 68% of the initial dry, ash-free weight. Experiments were performed at two heating rates (40°C/min and 160°C/min), two particle size ranges (74μm to 149μm and 420μm to 840μm), and two inert purge gas flow rates (50 cc/min and 150 cc/min). Statistical analysis of the experimental results show that the total conversion and temperature location of the maximum rate of weight loss were influenced by both heating rate and particle size. Fitting the experimental results to the model developed by Anthony (1974) yielded parameter estimates in good agreement to those found by other investigators using dramatically different experimental techniques, for coal of the same ultimate and proximate analysis. Statistical analysis of the dependence of the model parameters on the experimental variables indicated some dependence to exist. However, no single experimental variable was found to have significant influence on all of the model parameters.

LITERATURE CITED

Anderson, L. L., G. R. Hill, E. H. McDonald, and M. J. McIntosh, "Flash Heating and Plasma Processing of Coal," Chem. Engr. Progr. Symposium Ser. No. 85, 64, 81, 1968.

Anthony, D. B., J. B. Howard, H. C. Hottel, and H. P. Meissner, "Rapid Devolatilization of Pulverized Coal," Fifteenth Symposium (International) on Combustion, p. 1303, The Combustion Institute, Pittsburg, Pa., 1974.

Anthony, D. B., J. B. Howard, H. C. Hottel, and H. P. Meissner, "Rapid Devolatilization and Hydrogasification of Bituminous Coal," Fuel, 55, 121, 1976a.

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

Badzioch, S., "Thermal Decomposition," British Coal Utilization Research Association Monthly Bulletin, 31, No. 4, 193, 1967.

Badzioch, S., and P.G.W. Hawksby, "Kinetics of Thermal Decomposition," Ind. Eng. Chem. Process Design Develop., 9, 521, 1970.

Benson, S., Thermochemical Kinetics, Wiley, New York, N.Y., 1968.

Berkowitz, N., "Mechanism of Coal Pyrolysis, I," Fuel, 39, 47, 1960.

Chaiken, R. F., U. S. Bureau of Mines, In Comments on "Rapid Devolatilization of Pulverized Coal," pg. 1316, Fifteenth Symposium (International) on Combustion, The Combustion Institute, Pittsburg, Pa., 1974.

Chatterjee, P. K., and C. M. Conrad, "Thermogravimetric Analysis of Cellulose," J. Polymer Sci., A-1, 6, 3217, 1968a.

Chatterjee, P. K. and C. M. Conrad, "Chain Reaction Mechanism of Cellulose Pyrolysis," J. Applied Polymer Sci., 12, 1859, 1968b.

Cheong, P. H., "A Modeling Study of Coal Pyrolysis," Ph.D. thesis, Calif. Instit. Technol., Pasadena, 1976.

Coates, R. L., C. L. Chen, and B. L. Pope, "Coal Devolatilization in a Low Pressure, Low Residence Time Entrained Flow Reactor," in "Coal Gasification," p. 92, Advances in Chemistry Series, No. 131, Am. Chem. Soc., Washington, D.C., 1974.

Daniels, T., Thermal Analysis, John Wiley and Sons, New York, 1973.

Essenhigh, R. H., Penn. State Univ., In Comments on, "Rapid Devolatilization of Pulverized Coal," p. 1317, Fifteenth Symposium (International) on Combustion, The Combustion Institute, Pittsburg, Pa., 1974.

Flynn, J. H. and L. A. Wall, "General Treatment of the Thermogravimetry of Polymers," J. Res. Nat. Bur. Stand.-A, 70A, No. 6, 1966.

Havens, J. A., "Thermal Decomposition of Wood," Ph.D. thesis, Dept. of Chemical Engineering, Univ. Okla., Norman, 1969.

Hottel, H. C. and J. B. Howard, New Energy Technology, MIT Press, Cambridge, Mass., 1971.

Jones, W. I., "The Thermal Decompositon of Coal," J. Inst. Fuel, 37, 3, 1964.

Joy, W. K., W. R. Ladner, and E. Pritchard, "Laser Heating of Pulverized Coal in the Source of a Time-of-Flight Mass Spectrometer," Fuel, 49, 26, 1970.

Jünten, H., and K. H. Van Heek, "Reaktionablaufe unter nichtisothermen Bedingungen," in Fortschritte der chemischen Forschung, Vol. 13, p. 601-699, Springer-Verlag, Berlin, 1970.

Leu, J. C., "Modeling of the Pyrolysis and Ignition of Wood," Ph.D. thesis, Dept. of Chemical Engineering, Univ. Okla., Norman, 1975.

Menster, M., H. J. O'Donnell, S. Ergun, and R. A. Friedel, "Devolatilization of Coal by Rapid Heating," in Coal Gasification, p. 1, Advances in Chemistry Series, No. 131, Am. Chem. Soc., Washington, D.C., 1974.

Ozawa, T., "A New Method of Analyzing Thermogravimetric Data," Chem. Soc. Bull. Japan, 38, 1881, 1965.

Pitt, G. J., "The Kinetics of the Evolution of Volatile Products from Coal," Fuel, 41, 267, 1962.

Rogers, R. N., "Simplified Determination of Rate Constants by Scanning Calorimetry," Anal. Chem., 44, No. 7, 1972.

Rogers, R. N., and L. C. Smith, "Application of Scanning Calorimetry to the Study of Chemical Kinetics," Thermochim Acta, 1, 1970.

Shapatina, E. A., U. A. Kalyuzhnyi, and Z. F. Chukhanov, "Technological Utilization of Fuel for Energy, 1-Thermal Treatment of Fuels," 1960. Reviewed by S. Badzoich, British Coal Utilization Research Association Monthly Bulletin, 25, 285, 1961.

Sharkey, A. G., Jr., J. L. Schultz, and R. A. Friedel, "Gases from Flash and Laser Irradiation of Coal," Nature, 202, 988, 1964.

Skylar, M. G., U. I. Shustikov, and I. V. Virozub, "Investigation of the Kinetics of Thermal Decomposition of Coals," Intern. Chem. Eng., 9, 595, 1969.

Stene, H. N., J. D. Batchelor, and H. F. Johnstone, "Low Temperature Carbonization Rates in a Fluidized Bed," Ind. Eng. Chem., 46, 274, 1954.

Van Krevelen, Properties of Polymers, Elsevier Scientific Publishing Co., New York, 1976.

Wiser, W. H., G. R. Hill, and N. J. Kertamus, "Kinetic Study of the Pyrolysis of a High-Volatile Bituminous Coal," Ind. Eng. Chem. Process Design Develop., 6, 133, 1967.

Woodburn, E. T., R. C. Everson, and A.R.M. Kirk, "Thermal Decomposition of Coal Dust in a Shock Tube," Fuel, 53, 38, 1974.

Notation

E	Activation energy, kcal/mole
f(E)	Activation energy distribution
k	Rate constant, sec^{-1}
k_o	Frequency factor, sec^{-1}
n	Reaction order
R	Gas constant, cal/mole k
t	Time, sec
T	Temperature, k
V	Volatile matter, %
V^*	Potential volatile matter, %
W	Weight remaining, %

Greek

σ	Standard deviation from mean activation energy, kcal/mole
π	Constant

Subscripts

i	i-th parallel reaction

TABLE 1. Thermal Analysis Techniques (Daniels, 1973)

Type of property	Measured physical property	Name of technique and abbreviation	
Weight	Sample weight	Thermogravimetry*	TGA
	Rate of weight-loss	Derivative Thermogravimetry*	DTG*
Thermal	Sample temperature	Heating (or Cooling) Curve*	——
	Temperature difference between sample and standard	Differential Thermal Analysis*	DTA*
	Energy difference between sample and standard	Differential Scanning Calorimetry*	DSC*
	Specific heat	Dynamic Adiabatic Calorimetry	DAC
Dimensional	Length or volume of sample	Dilatometry*	——
Mechanical	Compressibility, extensibility	Thermomechanical Analysis	TMA
	Rigidity, damping	Torsional Braid Analysis	——
Electrical	Resistance, conductance	Electrothermal Analysis	ETA
Magnetic	Magnetic susceptibility, force	Thermomagnetometry	——
Volatile Products	Total amount of volatiles	Evolved Gas Detection*	EGD*
	Nature and amount of particular volatile products	Evolved Gas Analysis*	EGA*
	Pressure of volatiles	Thermal Volatilisation Analysis	——
	Amount of condensation nuclei	Thermoparticulate Analysis	——

*ICTA recommended name or abbreviation

TABLE 2. COAL ANALYSIS

	Kansas Bituminous	Pittsburg Seam Bituminous
PROXIMATE ANALYSIS (%)		
FIXED CARBON (daf)	55.4	53.8
Volatile Matter (daf)	44.6	46.2
Moisture	2.0	1.7
Ash (dry)	16.2	12.4
Ultimate Analysis (% daf)		
C	75.0	77.0
H	5.3	5.7
N	1.4	1.2
O (by diff.)	10.9	10.2
S	7.5	5.9
ASTM Free Swelling Index	5.5	
Density (g/cc)	1.58	
Higher Heating Value ($\frac{MJ}{kg}$, As Received)	27.64	

TABLE 3. EXPERIMENTAL CONDITIONS.

Heating Rates	40°C/min and 160°C/min
Particle Size Ranges	74μm to 149μm and 420μm to 840μm
Dry Nitrogen Purge Gas Flow Rates	50 cc/min and 150 cc/min
Pressure	Atmospheric
Temperature Range	130°C to 960°C
Sample Sizes	0.5 mg to 1.5 mg

Table 4. Statistical Analysis of Devolatilization Curves

F-Ratio

$F_c = 4.75$; $\alpha = 0.05$

Variable \ Factor	Heating Rate (H)	Particle Size (P)	Purge Gas Flow Rate (G)	HXP Interaction	HXG Interaction	PXG Interaction	HXPXG Interaction
Location of Max. Rate of Weight Loss	74.39	9.97	0.13	1.61	2.34	2.54	3.44
Final Remaining Weight (daf)	10.57	6.26	1.48	7.41	10.71	0.19	7.29

Means	Heating Rate		Particle Size	
	40°C/min	160°C/min	74μm to 149μm	420μm to 840μm
Final Weight (%, daf)	48.31	43.38	43.95	47.74
Location of Max. Rate (°C)	490.17	512.25	497.17	505.25

TABLE 5. CORRELATION PARAMETERS

Correlation Parameter	3-Parameter Correlation		2-Parameter Correlation	
	Kansas Bituminous Coal	Pittsburg Seam Bituminous (7MPa) (Anthony, 1974)	Kansas Bituminous Coal	Pittsburg Seam Bituminous (7MPA) (Anthony, 1974)
Average Frequency Factor k_o, sec^{-1}	3.68×10^8	2.91×10^9	1.67×10^{13}*	1.67×10^{13}*
Standard Deviation	$\pm 2.18 \times 10^8$	——	——	——
Average Mean Activation Energy, Em, kcal/mole	36.87	36.89	54.14	50.65
Standard Deviation	$\pm$ 1.36	——	$\pm$ 1.24	——
Average Std. Dev. from Mean Activation Energy, σ, $\frac{kcal}{mole}$	4.82	4.18	7.18	7.01
Standard Deviation	$\pm$ 0.74	——	$\pm$ 1.25	——
Average Mean Deviation Data vs Model, M. Dev., (%)	$\pm$ 0.93	——	$\pm$ 0.97	——
Standard Deviation	$\pm$ 0.25		$\pm$ .21	
Average Standard Deviation, Data vs Model, Std. Dev., (%)	$\pm$ 1.55	——	$\pm$ 1.67	——
Standard Deviation	$\pm$ 0.29		$\pm$ .26	

* = Assumed Frequency Factor (Benson, 1968).

TABLE 6. STATISTICAL ANALYSIS OF CORRELATION PARAMETERS

F-RATIO

$F_c = 4.75$; $\alpha = 0.05$

Parameter \ Factor	Heating Rate (H)	Particle Size (P)	Purge Gas Flow Rate (G)	HXP Interaction	HXG Interaction	PXG Interaction	HXPXG Interaction
Frequency Factor (k_o)	<u>6.958</u>	0.105	3.531	3.794	<u>31.718</u>	0.412	0.607
Mean Activation Energy (E_m)	0.725	0.614	0.059	2.607	<u>18.708</u>	0.152	0.175
Std. Dev. from E_m (σ)	1.417	<u>10.607</u>	<u>13.959</u>	0.301	2.222	1.998	2.184
Correlation M. Dev.	4.653	<u>31.465</u>	0.181	1.054	0.906	0.023	<u>5.660</u>
Correlation Std. Dev.	<u>7.875</u>	3.556	<u>6.912</u>	1.345	2.082	0.119	0.489

Means	Heating Rate		Particle Size		Purge Rate	
	40°/min	160°/min	74μm to 149μm	420μm to 840μm	50 cc/min	150 cc/min
$k_o (sec^{-1})$	2.96×10^8	4.45×10^8				
$E_m (\frac{kcal}{mol})$			5.198	4.473		
M. Dev. (±)			0.744	1.118		
Std. Dev. (±)	1.682	1.418			1.673	1.426

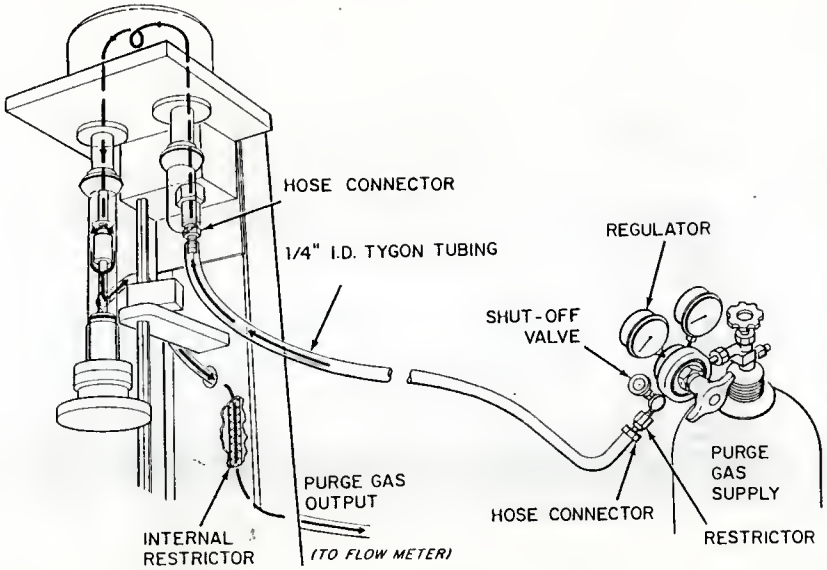

Fig. 1 Perkin-Elmer TGS-2

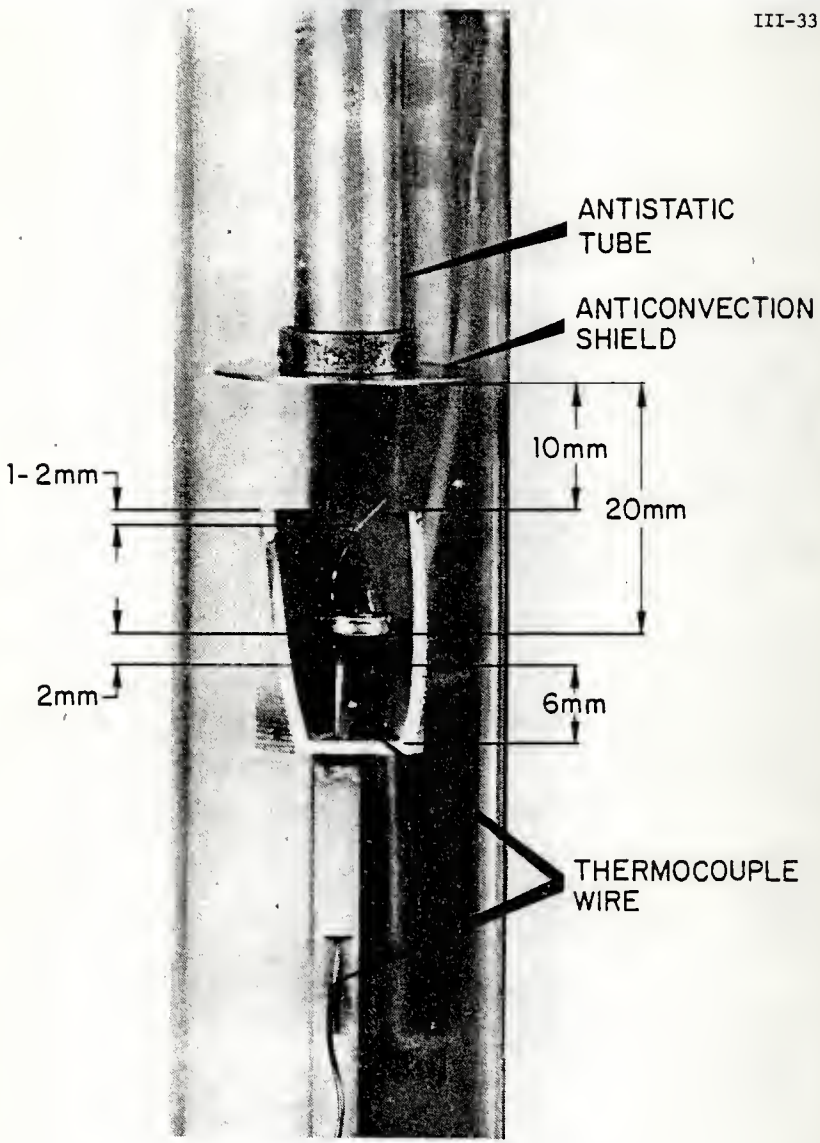

Fig. 2 TGS-2 Furnace Area

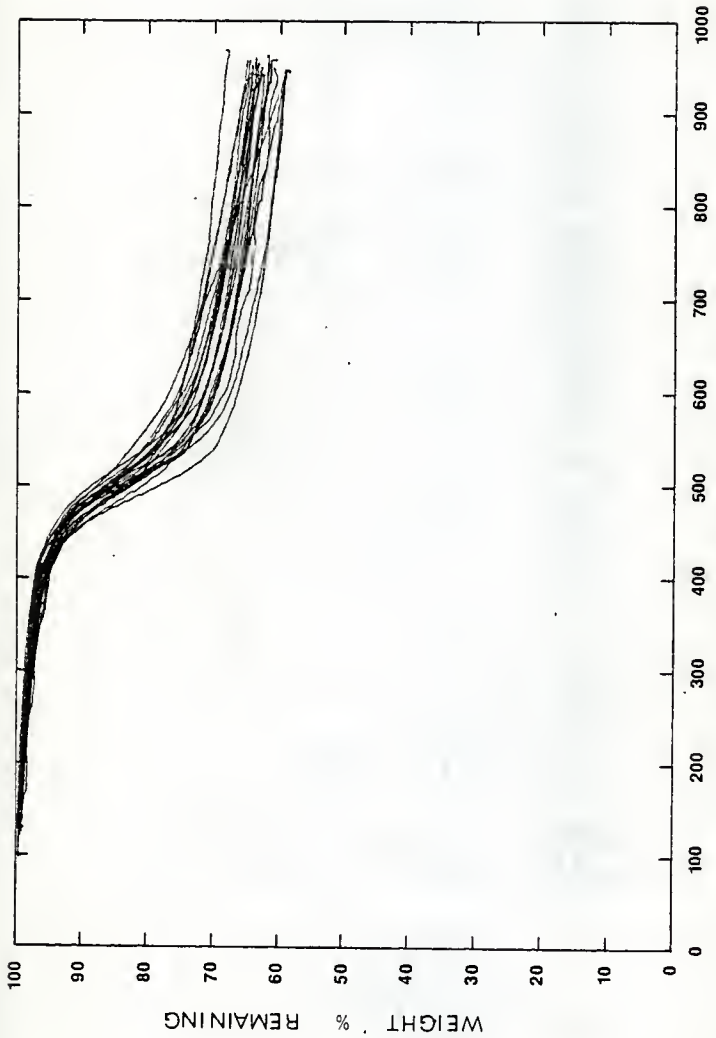

Fig. 3 Devolatilization of Kansas Coal

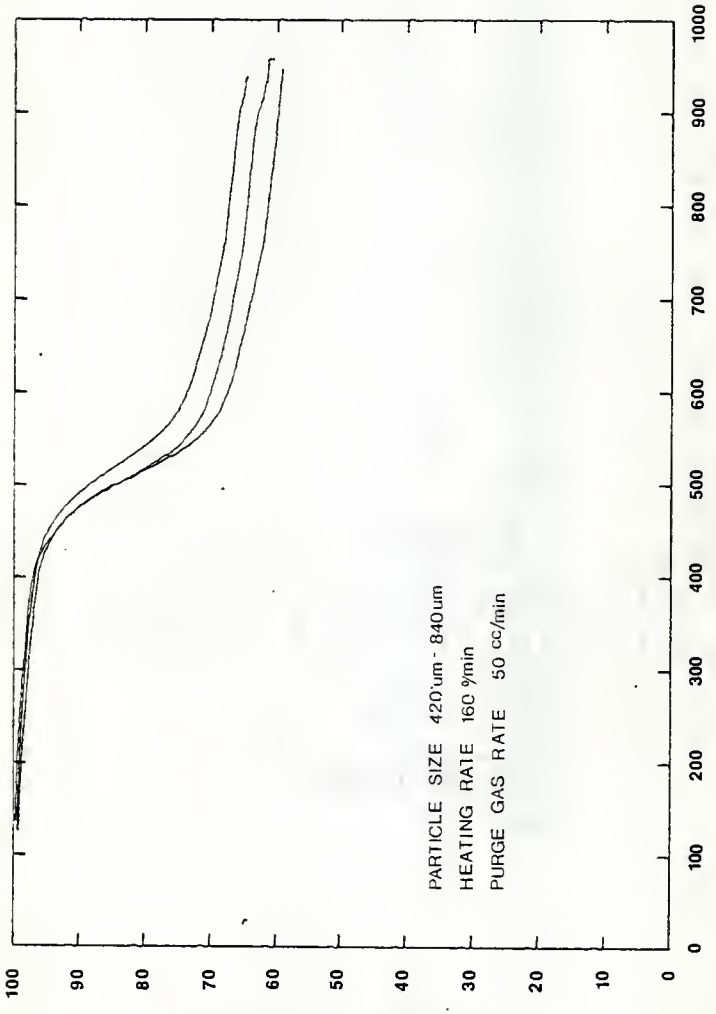

Fig. 4 Variation of Thermogram

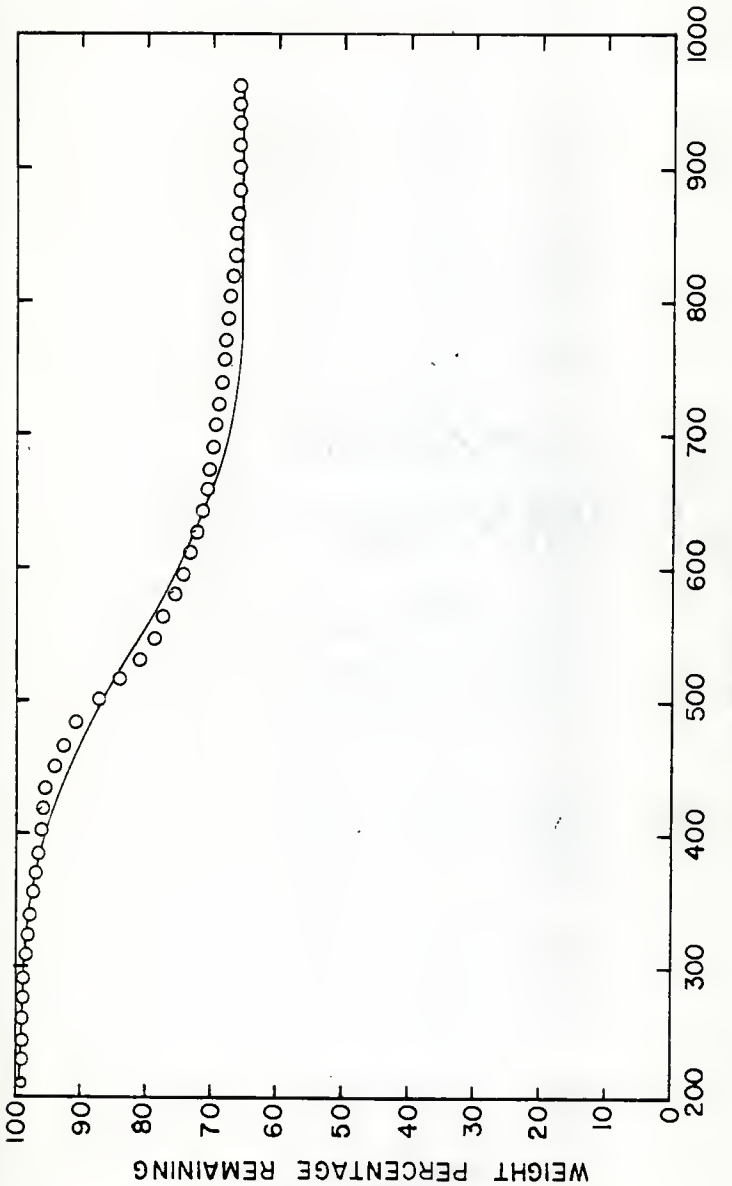

Fig. 5 Typical Model Fit

CHAPTER IV

STEAM GASIFICATION OF A CAKING BITUMINOUS COAL IN A BENCH SCALE FLUIDIZED BED

INTRODUCTION

The decline in the availability of domestic reserves of liquid and gaseous fossil fuels, coupled with the increasing unreliability of imported fuels has generated new interest in the utilization of U.S. coal reserves. The concept of decomposing coal to produce a product which is in a more useful or convenient form has been known for many years, and various processes have been conceived to accomplish this task. The majority of these processes rely upon the gasification of char with mixtures of steam, hydrogen, and oxygen. Although many contacting devices have been proposed, fluidized beds are widely used in gasification processes because of their advantageous characteristics, such as good heat transfer and long residence times for the char. However, difficulties arise in operating a fluidized bed, when the material gasified has strong caking properties and tends to agglomerate the bed.

A successful reactor design requires a thorough characterization of the feedstock. Much of this can be accomplished in the laboratory by analyzing elemental composition, porosity, density, swelling tendencies, and other properties of the feedstock. Other laboratory techniques, such as thermal analysis techniques, can provide initial estimates of the behavior of the material as it undergoes heating, such as heat effects, conversions, and temperature and pressure effects. These estimates must be verified by comparing them with experimental results obtained in an actual reactor.

Most processes for coal gasification use reactor types which have large gas to solid ratios, such as moving, entrained or fluidized beds. This not only promotes the good gas-solid contact necessary for char-gas reactions, but also tends to reduce the likelihood of agglomeration when using caking

coals. The COED process, for example, uses a series of fluidized beds of consecutively higher temperatures (Hendrickson, 1975). In each bed, a fraction of the coal's volatile matter is released, and temperature of each bed is chosen just below the maximum temperature to which the coal can be heated without agglomerating. The number of stages and operating temperatures of each stage are determined by the caking properties of the coal. Another process which can directly use a caking coal is the Hydrane process developed by the U.S. Bureau of Mines. In the first of this two-stage process, coal is reacted with hydrogen in a free fall zone where the dilute phase particle dispersion avoids agglomeration of the coal. In the second stage, the residual char is either consumed in synthesis gas production or used as a fuel for the plant power. Besides the ability to use caking coals, another advantage of this process is that only light methanation is required to remove the small amount of CO formed during hydrogasification, so that the final product meets pipeline specifications. Many processes exist which either can not use caking coals or must pretreat these coal types with mild oxidation in order to destroy their caking tendencies (Kavlick and Lee, 1967). Some of these processes include; Hygas, Lurgi, Synthane and the CO_2 Acceptor process (Howard-Smith, 1976). In this study, a bench scale fluidized bed reactor was designed and constructed for the investigation of the steam gasification of a caking bituminous coal mined in Kansas. Specifically, the effect of the reactor temperature on product gas yields and compositions was studied.

THEORETICAL

When coal is heated to elevated temperatures, a series of physical and chemical changes occur which result in the evolution of gaseous products. If heated in an inert environment, the observed gas products are the result

of coal devolatilization alone. This devolatilization begins at 350°C to 400°C and results in a hydrogen rich volatile fraction and a highly carbonaceous solid residue. The extent of volatile yield and its composition depends upon coal type and the manner of heating. Proximate analysis indicates that volatile matter ranges from less than ten percent for anthracites to over 50% for lignites (Averitt, 1961). However, captive sample techniques using rapid heating have shown that volatile yields higher than those observed by proximate analysis can be obtained (Anthony & Howard, 1976).

In the early stages of devolatilization, many types of coal undergo physical changes such as swelling and softening (Van Krevelen, 1956). As devolatilization proceeds, however, the softening process reaches a peak and subsequently the coal resolidifies (Overturf et al., 1978). This swelling tendency is normally characterized by the coal's free swelling index (FSI). Values of the FSI range from unity for a non-caking coal, to 9 for severely caking coal. A process which utilizes a caking coal must account for this property to prevent possible agglomeration within its reactor system.

Any process which involves the heating of coal in a reactive gas environment, e.g., steam, will undergo the process of devolatilization followed by a char-gas reaction. However, the yield, product distribution, and extent of problems associated with swelling phenomena are largely dependent upon the type of reactor system used and the operating conditions employed.

Gasification processes utilize combinations of hydrogen, oxygen, and steam in an attempt to increase the yield of gaseous products at the expense of the char residual. The particular gaseous environment used is dependent upon the intended use of the product gas. For example, hydrogen

has been proposed in the production of pipeline quality gas due to the high methane yields achieved (Anthony, et. al., 1974). Combinations of oxygen and steam are typically used in the production of low to medium heating value gases. Steam gasification is by far the most convenient due to the fact that steam is easily produced and readily removed from the product gas. In steam gasification, residual char is converted to carbon monoxide and hydrogen by the reaction

$$C + H_2O \rightleftharpoons CO + H_2 \qquad (1)$$

However, the introduction of steam also induces many other gas phase reactions such as

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \qquad (2)$$

$$CH_4 + H_2O \rightleftharpoons CO + 3H_2 \qquad (3)$$

While these are in no way the only possible reactions in which steam can participate, they provide a basis for studying the effects of steam on the product gas composition (von Fredersdorff, 1963).

EXPERIMENTAL

Material

A bituminous coal, from the Rowe coal bed in southeast Kansas, was steam gasified in a bench scale fluidized bed reactor under atmospheric pressure. Table 1 characterizes this material. The proximate analysis given in the table shows this coal to have a low moisture content (2%), but a large amount of ash (16.2%). The fixed carbon content and heating value place this coal in the High Volatile C Bituminous classification. Ultimate analysis indicates a high sulfur content (7.5% daf), while the free swelling index of 5.5 shows this coal to have moderate caking tendencies.

Facilities

Figure 1 shows the basic flow diagram, including the reactor, feeding

system, and gas cleanup train. Other than the disengaging zone, the reactor was constructed of 2 inch (5.08cm) schedule 40 Inconel 600 pipe, while the disengaging zone was 4 inch (10.16cm) pipe of the same material. A packed bed containing 0.5 cm aluminum oxide pellets was used as both a gas preheater and distributor. This section was separated from both the fluidized bed and inlet sections by 60 mesh 316 stainless steel screens, which were held in place by flanges and sealed with graphite gaskets. An inert fluid bed of high silica sand was maintained at an expanded height of 10 cm.

Heat was supplied by means of four pairs of semicylindrical electrical resistance heaters, each capable of delivering up to 2300 watts of power with a maximum operating temperature of 1200°C. Steam was generated externally in an 800 watt electrical furnace and was supplied to the reactor at approximately 500°C.

Coal was transported to the feed pipe by a Vibra Screw Model SCR-20 screw feeder using a solid core flight screw. Upon reaching the feed pipe, the material fell into the reactor bed aided by a helium purge flow which also prevented hot reactor gases from entering the feed pipe with subsequent condensation. Feed material was discharged from the feed pipe at the same level as the expanded bed. The feed pipe was equipped with a water jacket and vibrator to prevent the material from prematurely devolatilizing before it reached the reactor bed. Residual char overflowed to a sealed hopper beneath the reactor while product gas exited through the top plate. Entrained solids were removed from the product gas in the cyclone, which was kept at 300°C to prevent condensation of water and tar. After leaving the cyclone, the fluidizing steam was removed by cooling the gas to approximately 50°C by means of two water cooled heat exchangers in series. The resulting product gas carried with it a fine mist of condensible materials. This material

was removed by passing the gas through a glass wool packed column. Before sampling, the gas was further dried by means of a $CaSO_4$ packed column.

Procedure

The reactor temperature was varied from 700°C to 1100°C. The particle size range and superficial velocity were held constant at 210μm - 300μm and 36.7 cm/sec, respectively. Table 2 summarizes the operating conditions used in this study.

The superficial velocity of the fluidizing gas corresponds to between 20 and 30 times minimum fluidization velocity and 20% of the terminal velocity of the reactant particles (Kunii and Levenspiel, 1968). It was found that under these conditions, the voidage within the bed was high enough to avoid the agglomeration problems normally associated with the use of a caking coal. In addition, the high concentration of sand in the feed kept the carbon concentration in the fluid bed low and contributed significantly to the smooth operation of the system. However, the necessity of high inert concentrations with low feed rates severely hampered the collection of liquid and solid products needed for overall material balances.

To initiate the operation, the screw feeder was charged with the feed material and the reactor heated to approximately 50°C above the desired operating temperature while purging the system with air. Heat up to 800°C required about one hour. During this period, power was also supplied to the steam generator, cyclone heater, and inlet section heater. Before switching to steam, the inlet section and cyclone temperatures were raised to at least 200°C to prevent steam condensation. When all components of the system had reached their required temperatures, the air flow was replaced by steam, and water coolant to the feed pipe jacket was commenced. An additional 15 to 20 minutes were required for the system to reach a

steady state as observed by the steady collection of water condensate downstream of the heat exchangers. With feeding ready to begin, the feed pipe vibrator and helium purge were started. After feeding had commenced, adjustment of the power to the reactor furnaces was required to maintain the set point temperature. Normally, 30 to 45 minutes were needed after the start of feeding for the system to reach a steady state, which was determined by constant reactor temperature, solid overflow and water condensate collection. Steady state sampling was repeated for at least one hour. During this period overflow and water condensate were collected over four consecutive 15 minute time intervals. Gas samples were taken at the end of every 15 minute period.

Both inert and overall material balances were evaluated for each experimental run. Inert balances were performed by first feeding the feed material, with a known inert concentration, into a cup. This rate of inert feed was then compared to the rate of inert collected from the overflow and cyclone during the steady state period.

Product Analysis

Product gas flow rates were determined by the introduction of a known volumetric flow of nitrogen into the system just upstream of the sampling point. Subsequent gas analysis allowed calculation of the total gas flow rate. Gas analysis was accomplished using a Packard Model 417 Becker 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, H_2S, N_2 and O_2. Column packings used were a 5A molecular sieve for the separation of H_2, O_2, N_2, CO, and CH_4, while the remaining components were separated using a mixture of Porapak Q and Porapak R. The instrument was operated

isothermally at 80°C with helium as a carrier gas. Accessories used in the analysis included a Spectro-Physics Autolab System I computing integrator and a Varian Model A-25 stripchart recorder. Solid materials were analyzed with respect to both their elemental composition (C, H, N, O, S) and their proximate analysis using a Perkin-Elmer Model 240 Elemental Analyzer and a Perkin-Elmer Model TGS-2 Thermogravimetric Analyzer, respectively. Reported material balances and product gas analysis are the result of averaging the many samples taken during the steady state period.

RESULTS AND DISCUSSION

As shown in Table 3, the inert balances were between 98% and 109% of closure except for one run. The inert balance allowed calculation of the feed rate of reactable material. Inputs in the overall material balance included the total solid feed rate and fluidizing steam. Outputs included solids from the overflow and cyclone, liquid condensate, and the product gas. As shown in Table 3, the overall balances closed between 74% and 92%. The discrepancies in the overall balance closures can be attributed to condensation of tar in the cleanup train.

Effect of Reactor Temperature

Despite the problems encountered in the collection of some condensible products, analysis of the gaseous products showed consistent results with discernible trends. Figure 2 shows how the yield and heating value of the product gas are influenced by the reactor temperature. Gas yields are in terms of the dry product gas expressed in normal cubic meters (0°C, 1 atm) per kilogram of dry ash-free coal. The higher heating value is that of the unscrubbed raw product gas. It can be seen that the heating value of the product gas decreases by 30 percent between 700°C and 1100°C, while the yield increases by five folds over the same temperature range. This effect

can be more clearly seen in Fig. 3, which shows a first law efficiency of the gasification process, calculated by comparing the heating value of the product gas obtained per unit mass of coal, to the heat which could be derived from conventional coal combustion. From these figures, it is seen that while a higher heating value gas is produced at a lower reactor temperature, the total energy extracted from the coal in gaseous form increases with temperature.

Figures 4 through 7 detail the effect of reactor temperature on the product gas components. In Fig. 4 and 5, the various components are plotted versus temperature. With the exception of traces of propylene at the lower reactor temperatures, no hydrocarbons larger than ethane were present in measurable quantities. Similarly, no sulfur bearing compounds other than hydrogen sulfide were detected. Figures 4 and 5 show a general decrease in hydrocarbon concentration with increasing temperatures, and a similar decrease for hydrogen sulfide. Carbon monoxide and carbon dioxide increase over this temperature range while hydrogen remains fairly constant. In Fig. 6 and 7, the volumetric production of each gaseous species per unit mass of coal is plotted versus temperature. Since Fig. 4 shows the hydrogen concentration of the product gas remains essentially constant as yield increases by four and one half times, it would be expected that the amount of hydrogen produced would also increase by the same degree. Figure 6 shows this to be the case. This figure also indicates that after an initial increase, the amounts of carbon monoxide and carbon dioxide level off and even appear to decrease at the higher reactor temperatures. The amount of methane produced per unit mass of coal is essentially constant through this temperature range, while the production of ethane and ethylene peak between 800°C and 900°C.

Effect of Steam

To observe the effects of steam, a series of runs were performed using only nitrogen as a fluidizing agent. While the superficial velocity for these runs was low (6cm/sec) compared to the steam gasification runs, the gas compositions obtained were considered valid for general comparison. The low velocities were necessary in order that the concentration of the inert fluidizing medium did not prohibit detection and analysis of the pyrolysis gas. As it was, the nitrogen typically accounted for over 95% of the off gas collected for analysis. Product gas compositions of these runs are shown in Fig. 8 and 9.

Comparing the concentration of carbon monoxide in Fig. 8 for inert gasification to that obtained in steam gasification, it is seen that this concentration is higher when steam is present for temperatures above 800°C. This is consistent with the reaction, given by equation (1) in the THEORETICAL section, for which thermodynamics show that equilibrium is favored increasingly to the right for temperatures above 700°C. The methane concentration, which is essentially constant in inert gasification, drops off rapidly when steam is introduced. This also seems reasonable since thermodynamics indicates that the reaction given by equation (3) is also spontaneous to the right at temperatures above 700°C. The same effect is seen for both ethane and ethylene. In contrast to the increase observed in steam gasification, the concentration of carbon dioxide decreases in an inert environment. It is generally assumed that the water shift reaction, equation (2), is in equilibrium (Amundson, 1978), and thermodynamics shows that above 790°C the equilibrium for this reaction is increasingly shifted to the left. Therefore, the observed higher CO_2 concentration would be expected based

upon the three reactions under consideration. However, these reactions do not explain the observed higher concentration of hydrogen found in inert gasification. It should also be noted that while determination of the hydrogen concentration posed the most serious problem in terms of accuracy in the gas analysis due to its thermal conductivity being similar to that of the helium carrier gas, the consistency of this analysis over the large number of experiments conducted supports the data reported here.

CONCLUSIONS

It has been found that steam gasification of a caking bituminous coal in the temperature range between 700°C and 1100°C at atmospheric pressure produces a 18 $\frac{MJ}{Nm^3}$ to 11.9 $\frac{MJ}{Nm^3}$ (486 $\frac{Btu}{scf}$ to 319 $\frac{Btu}{scf}$) heating value gas. Yields range from 0.221 $\frac{Nm^3}{kg}$ (3.1 $\frac{scf}{lb}$) at 700°C to 0.99 $\frac{Nm^3}{kg}$ (15.9 $\frac{scf}{lb}$) at 1100°C. The total amount of heating value contained in the gaseous product per unit mass of coal was found to increase with reactor temperature. Comparison of product gas compositions from steam gasification to those from inert gasification indicates the concentrations of CO and CO_2 increase while those of the hydrocarbons decrease.

LITERATURE CITED

Amundson, N. R. and H. S. Caram, "Fluidized Bed Gasification Reactor Modeling. 1. Model Description and Numerical Results for a Single Bed." Ind. Eng. Chem. Process Des. Dev., 18, No. 1, 1979.

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

Anthony, D. B., J. B. Howard, H. C. Hottel, and H. P. Meissner, "Rapid Devolatilization of Pulverized Coal," Fifteenth Symposium (International) on Combustion, pp. 1303, The Combustion Institute, Pittsburg, Pa., 1974.

Averitt, P., "Coal Reserves of the United States," U. S. Geological Survey Bulletin 1136, 1961.

Hendrickson, T. A., "Synthetic Fuels Data Handbook," Cameron Engineers, Inc., Denver, Colo., 1975.

Howard-Smith, I. and G. J. Werner, "Coal Conversion Technology," Noyes Data Corp., Park Ridge, N.J., 1976.

Kavlick, V. J. and B. S. Lee, "Coal Pretreatment in Fluidized Beds," Advan. Chem. Ser. 69, 8, 1967.

Kunii, D. and O. Levenspiel, "Fluidization Engineering," John Wiley and Sons, Inc., New York, 1969.

Overturf, B. W., F. Kayihan, and G. V. Reklaitis, "Modeling and Analysis of an Integrated Coal Pyrolysis, Gasification, and Combustion Reactor System," presented at the 71st Annual Meeting of AIChE, Miami Beach, Nov. 16, 1978.

Van Krevelen, D. W., F. J. Huntjens, and H.N.M. Dormans, "Chemical Structure and Properties of Coal XVI - Plastic Behavior on Heating," Fuel, 35, pp. 462, 1956.

von Fredersdorff, C. G. and M. A. Elliott, "Coal Gasification," Chemistry of Coal Utilization, Supplementary Volume, H. H. Lowry, ed., Wiley, New York, 1963.

TABLE 1. Kansas Bituminous Coal.

Proximate Analysis (%)

Ash (dry)	Fixed C (daf)	VM (daf)	Moisture
16.2	55.4	44.6	2.0

Ultimate Analysis (% daf)

C	H	N	S	O (bydiff.)
75.0	5.3	1.4	7.5	10.9

ASTM Free Swelling Index

5.5

Density (g/cc)

1.58

High Heating Value ($\frac{MJ}{kg}$ As Received)

27.64

Table 2. Reactor Operating Parameters

Superficial Velocity	36.6 cm/sec
Temperature Range	700°C - 1100°C
Feed Rate	0.540 kg/hr
Feed Composition (coal/sand)	10% by weight
Coal Particle Size	210μm-300μm

Table 3. Results of Material Balances

Run No.	INPUTS (g/min)			OUTPUTS (g/min)				BALANCES (OUT/IN)%	
	Feed	Steam		Gas	Condensate	Solid		Inert	Overall
101289	7.602	10.0		0.101	7.875	7.017		99%	85%
201289	6.33	9.0		0.3104	7.90	5.89		100%	92%
101099	6.80	9.0		0.3777	7.65	6.32		100%	91%
101129	5.79	9.0		0.293	6.10	5.30		98%	79%
101109	16.54	0.6785		5.53	15.06	15.06		98%	83%
201129	7.89	8.0		0.695	7.25	4.07		57%	76%
201109	14.76	8.2		1.05	5.1	15.00		109%	92%
301129	8.70	7.2		0.586	3.2	8.00		99%	74%

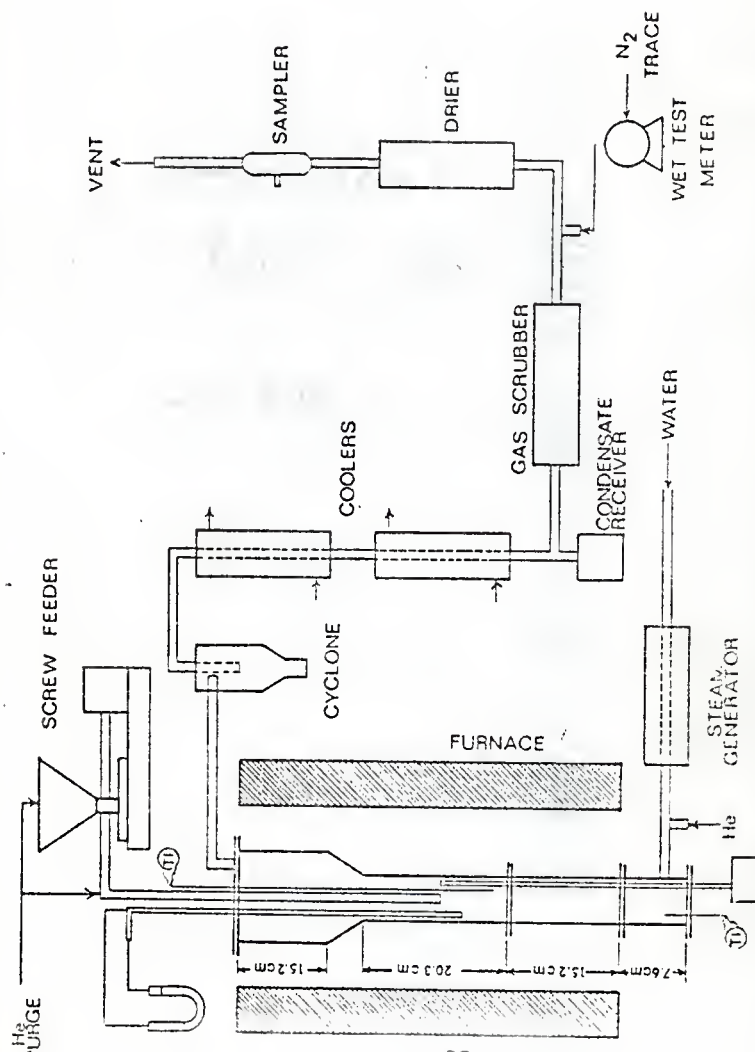

Fig. 1 Bench Scale Reactor

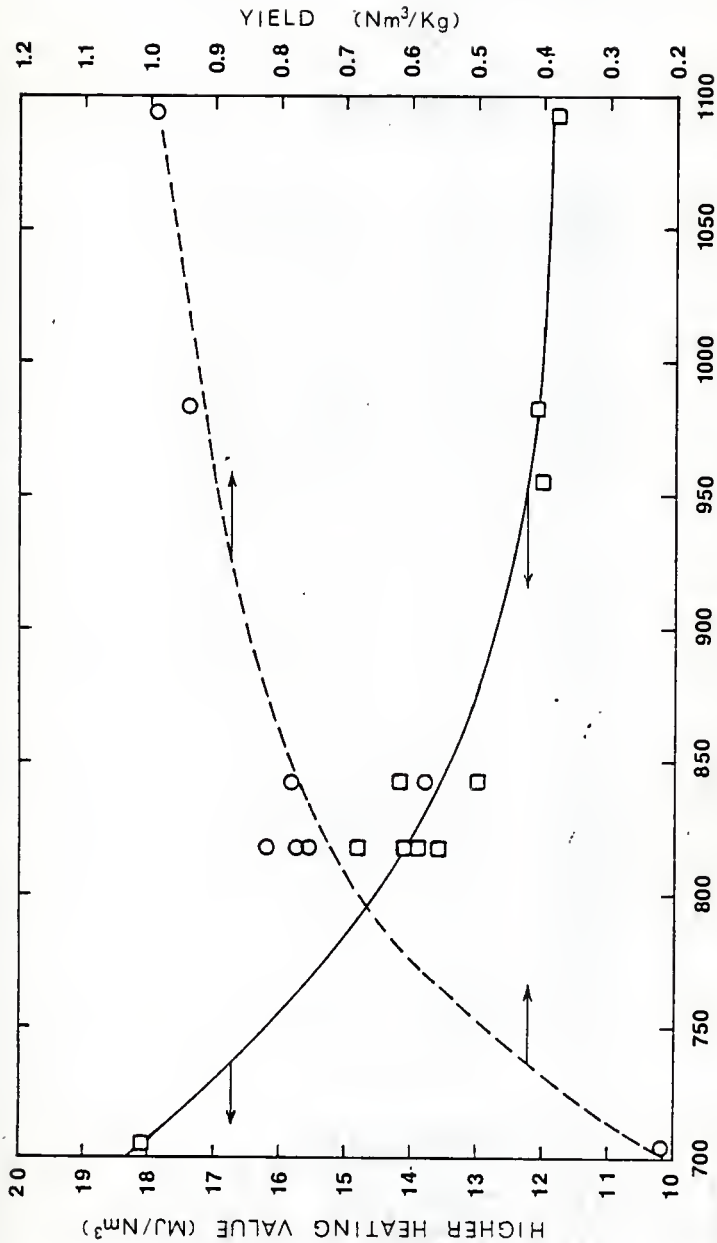

Fig. 2. Product Gas Yield and Heating Value versus Temperature

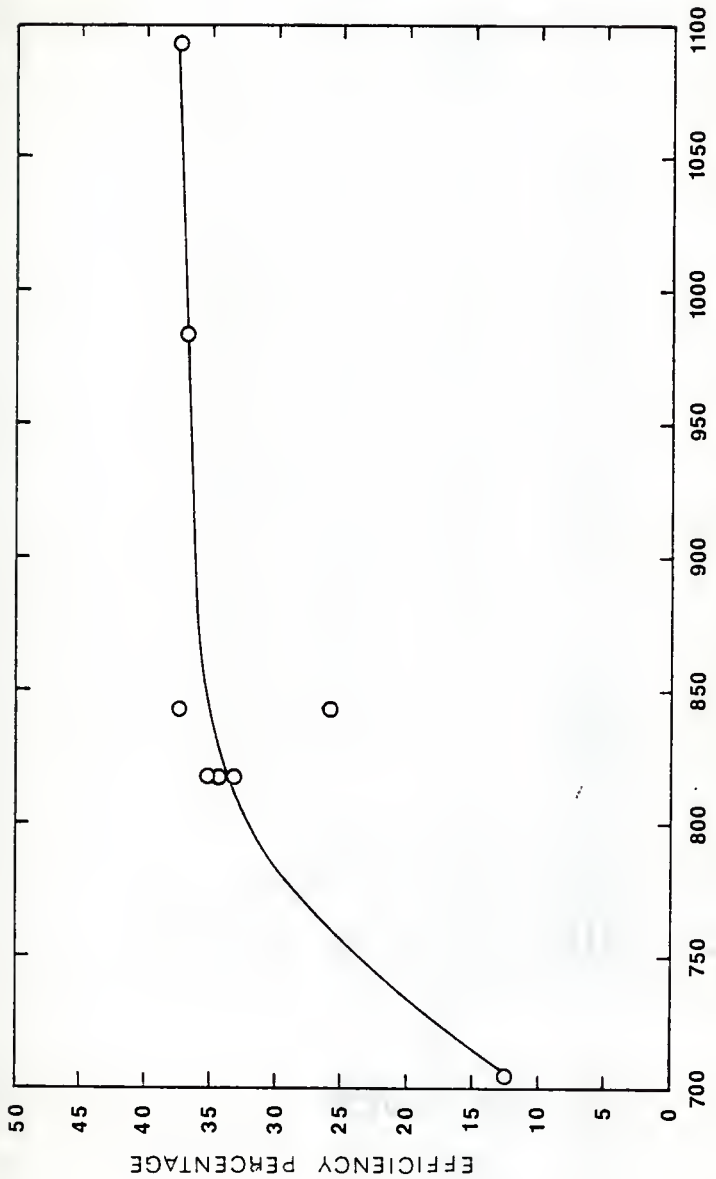

Fig. 3 Efficiency versus Temperature

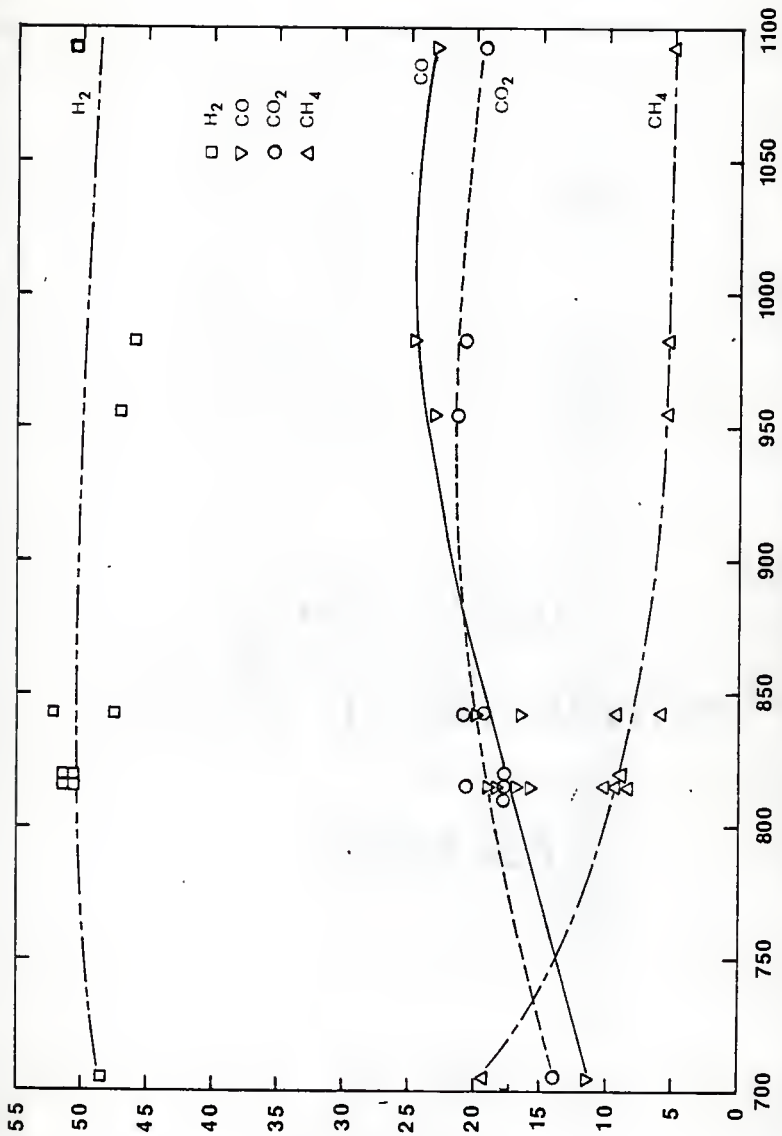

Fig. 4 Product Gas Composition versus Temperature Steam Gasification

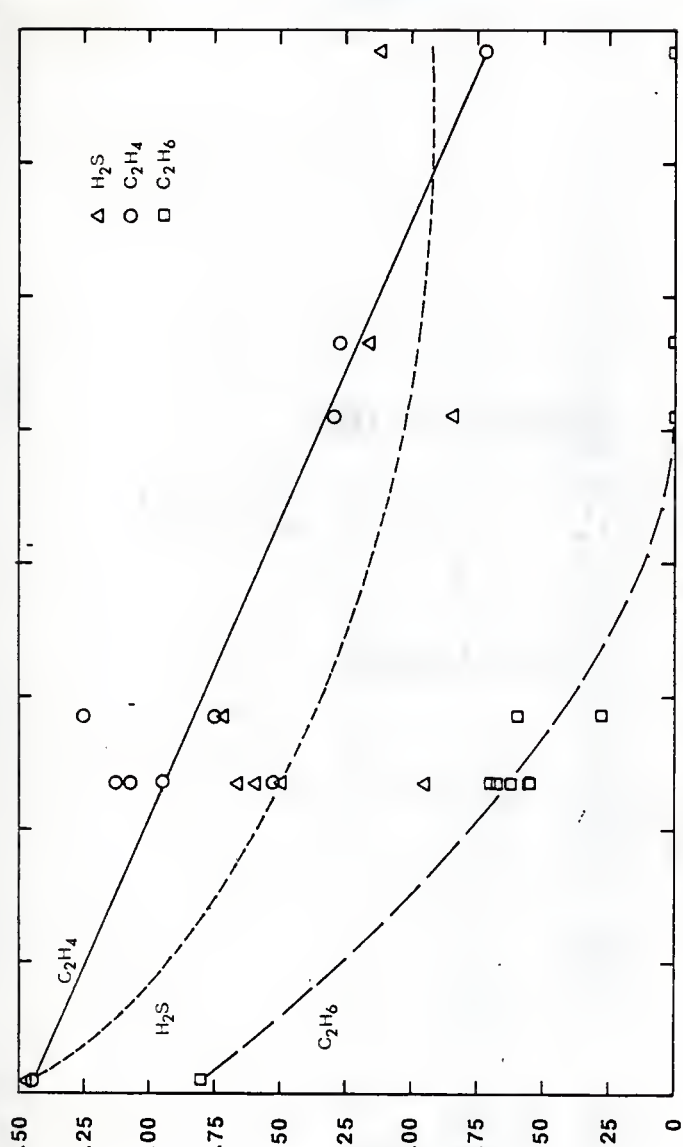

Fig. 5 Product Gas Composition versus Temperature Steam Gasification

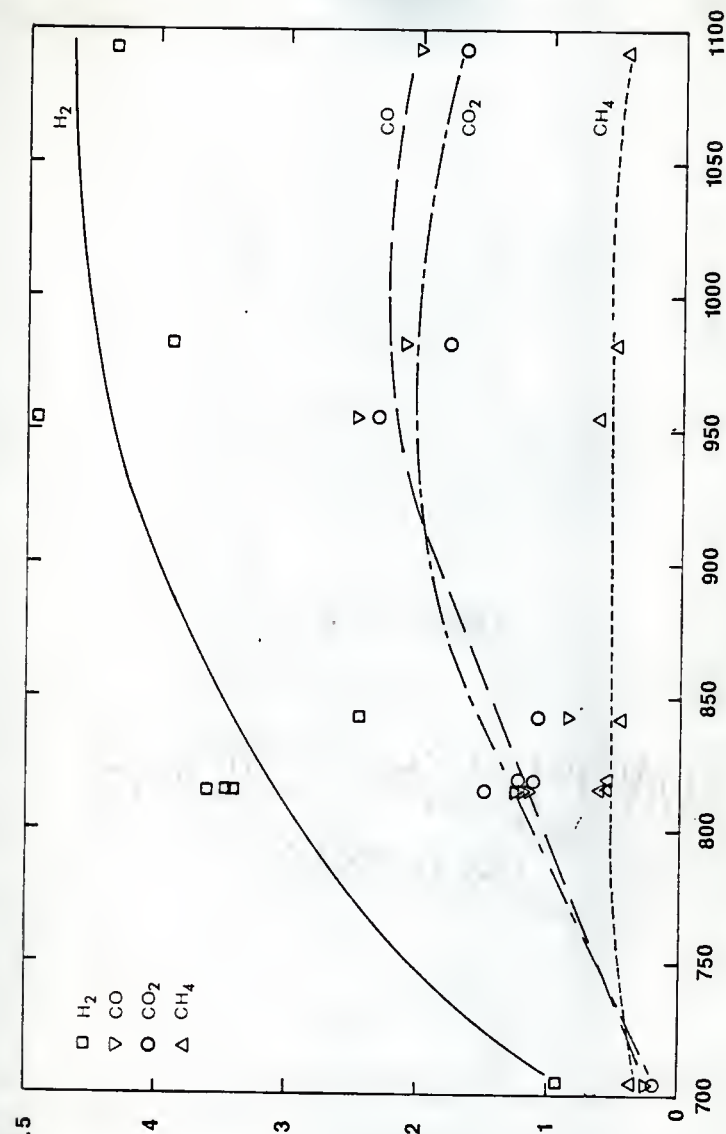

Fig. 6 Component Yield versus Temperature

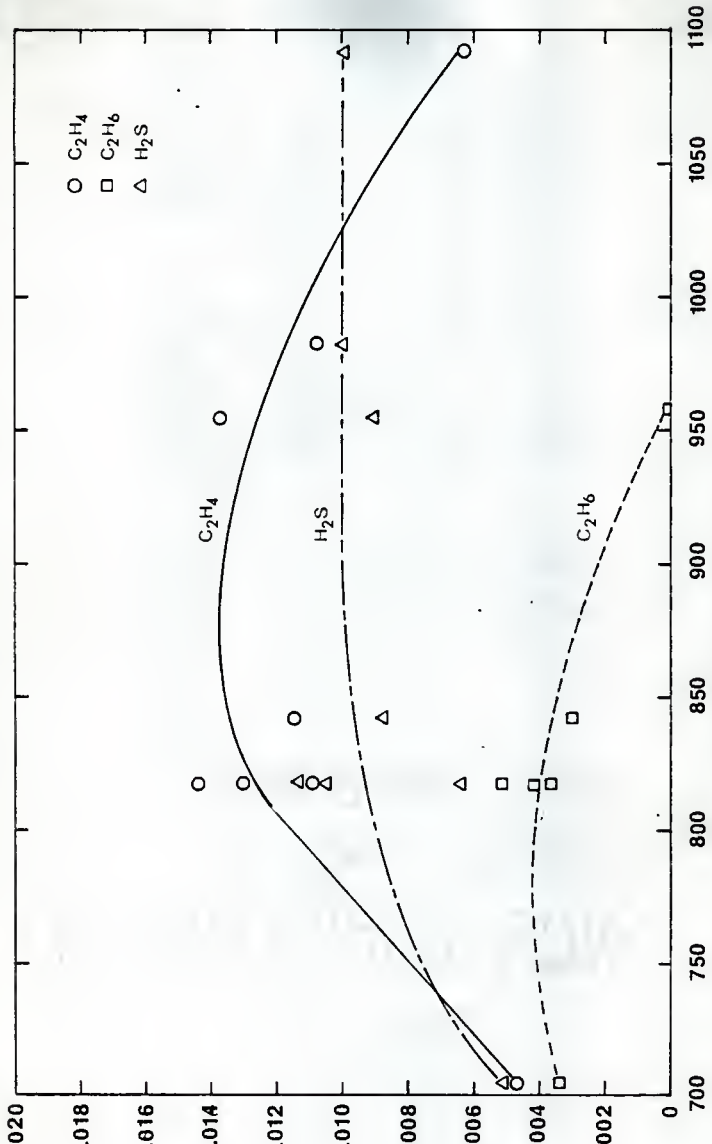

Fig. 7 Component Yield versus Temperature

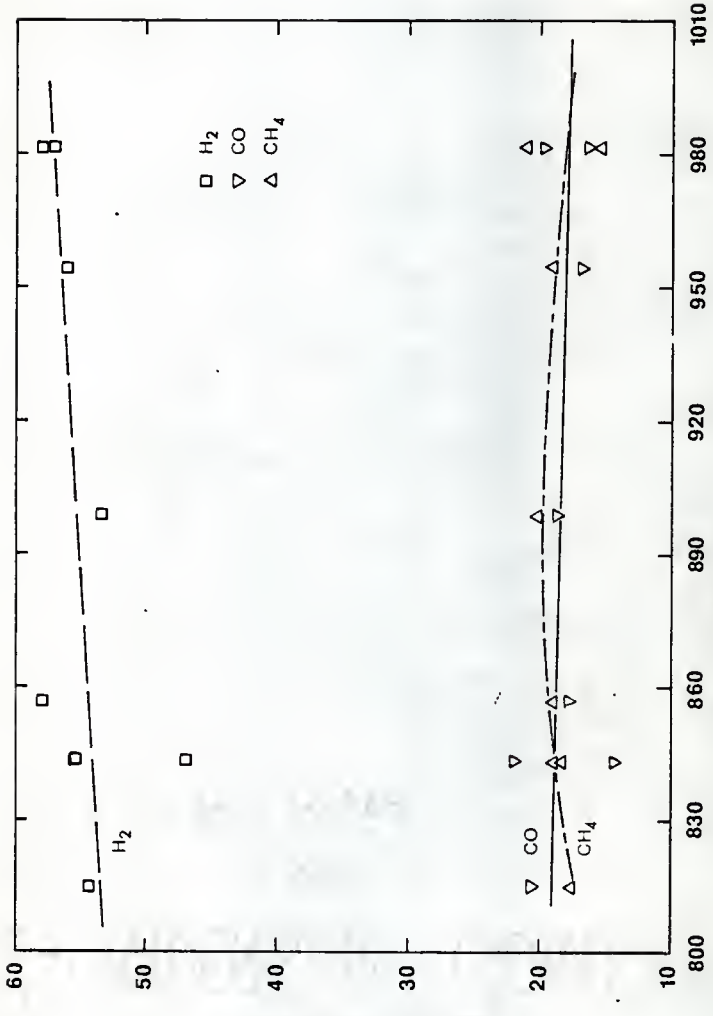

Fig. 8 Product Gas Composition vs Temperature Inert Gasification

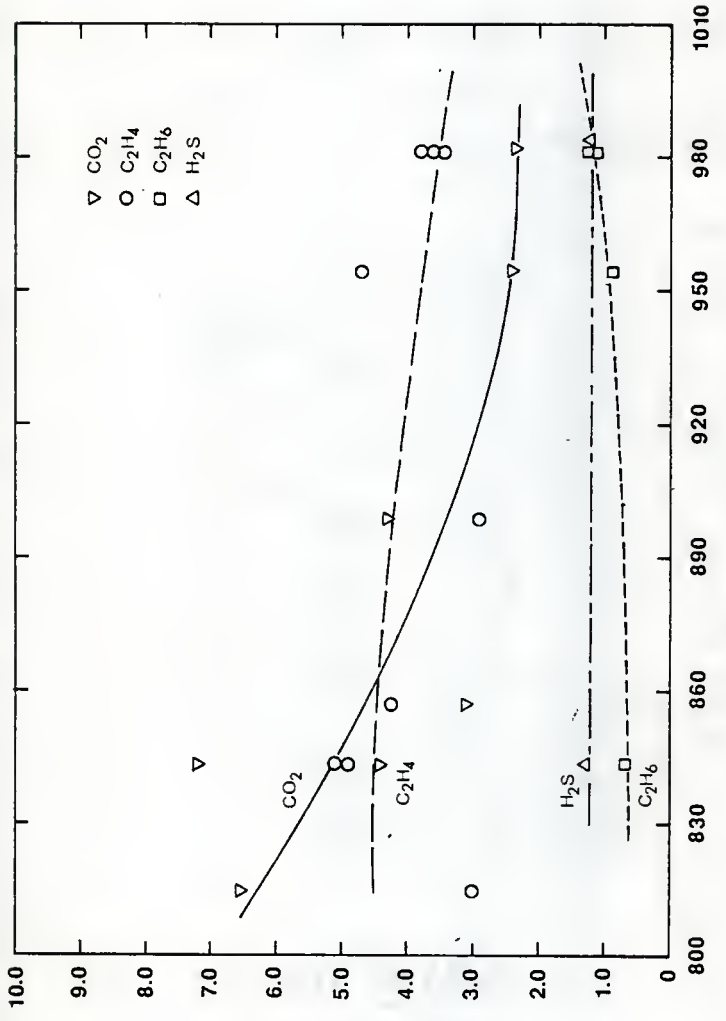

Fig. 9 Product Gas Composition vs Temperature Inert Gasification

CHAPTER V

STEAM GASIFICATION OF A MIXTURE OF FEEDLOT WASTE AND A CAKING BITUMINOUS COAL IN A BENCH SCALE FLUIDIZED BED REACTOR

INTRODUCTION

High prices and pending shortages of conventional liquid and gaseous fossil fuels have accelerated the search for new energy alternatives to alleviate the current energy problems which face the United States. A major effort is now being made for the conversion of coal into liquid and gaseous energy forms as substitutes for petroleum and natural gas.

Coal is by far the most abundant fossil fuel in the United States today. Many processes are in various stages of development to utilize this vast resource to its fullest extent. However, the usage of this material is not without its drawbacks. For example, many types of mid-western bituminous coal have high sulfur contents, high ash contents, and severe caking tendencies. For this reason, many coal gasification processes have mainly employed low sulfur, low ash, non-caking bituminous, subbituminous, and lignite coal. This is not to imply that these types of problem coals cannot be used for gasification. Several processes have been conceived specifically to handle these types of coal, such as the COED and Hydrane processes (Hendrickson, 1975). In other processes, caking tendencies can be eliminated by appropriate coal pretreatment. This normally involves a mild oxidation step, which has been found to destroy the coal's caking properties (Kavlick, 1967). In addition, many techniques have been developed to satisfy environmental concerns when gasifying high sulfur coal. These include physical separation of sulfur from the coal prior to gasification, and removal of sulfur bearing compounds from the gasification product.

In order for alternate energy processes to have a significant impact on the solution of the nation's energy shortages, the processes

cannot rely on the use of only the premium coal. Work has begun not only on the conversion of 'problem' coal, but also on the conversion of materials which have previously been considered worthless, or at least economically unattractive with respect to their potential as possible energy resources. Examples of materials which are now receiving serious consideration include tires (Green, 1978), municipal wastes (Jones, 1977; Pober & Brown, 1977; Chiang et al, 1978), livestock manure (Huffman et al, 1978, 1979; Walawender and Fan, 1978), and agricultural crop residues (McGriff, 1973; Shafizadeh, 1975). Gasification studies of these materials have shown gas yields and product heating values to be, in many cases, superior to those found for coal gasification. In addition, in contrast to the high sulfur caking bituminous coal, municipal waste, livestock manure, and agricultural crop residues have low sulfur contents and no caking tendencies. However, the steady collection of sufficient quantities of these materials to sustain a commerical plant operation has been a major concern. For example, large scale gasification of cattle manure would necessitate location of the facility in close proximity to a large feedlot operation (Walawender and Fan, 1978). Similarly, most programs which convert organic waste to energy treat each type of residue as an independent entity. As a result, many concentrations are deemed too small to support waste-to-energy systems (Tillman, 1976). Consideration is now being given to the possible combination of different gasification feedstocks in order to capitalize on their individual advantages and minimize their individual drawbacks.

The major objective of mixing two dissimilar materials is to obtain a feedstock which is superior to either one of the components alone. This concept has been recognized for both its economic as well as its technical

advantages. Tillman (1976), considered the mixture of wood and urban wastes as a gasification feedstock. The resulting blend was drier than the wood alone and contained fewer inorganics than the municipal waste. Similarly, an economic study by Abdallah (1979) found that corn stover would be an attractive supplement to coal in steam-electric power plants in the north central United States. To the author's knowledge, however, there have been no comparable studies of the potential advantages which could be realized from the gasification of a blend of coal and a non-fossilized material.

Numerous reasons can be cited in favor of blending coal with non-fossilized materials. Probably the most significant of these is the utilization of these renewable fuels, which in the past have led to disposal and pollution problems. In comparison with bituminous coal, these materials typically have higher volatile contents and very little sulfur. In a gasification operation, this would hopefully lead to a higher quantity product gas with greater yields and lower sulfur compound concentrations. Feedlot manure not only has these advantages, but it is also found to contain significant quantities of the alkali metals (Davis et al, 1972). A recent study has shown that addition of weak acid salts of potassium to an Illinois caking bituminous coal not only prevented swelling and agglomeration, but also increased the rate of gasification and allowed gasification to be accomplished at a relatively low fluid bed reactor temperature of 700°C (Gallagher and Marshall, 1978).

This study investigates the potential advantages associated with the gasification of a mixture of a high sulfur, caking bituminous coal and a low sulfur, non-caking feedlot manure. Comparisons were made between the

use of the coal-manure blend and the use of the individual components as possible gasification feedstocks. These comparisons were accomplished on three experimental levels. The first level entailed the characterization of the three feed-stocks with respect to their ultimate analysis, proximate analysis, density, and heating value. In the second level of experimentation, thermogravimetric analysis was used to monitor the devolatilization of each material and the mixture. The final level of experimentation involved the steam gasification of a mixture of coal and manure in a bench scale fluidized bed reactor. Product gas yields and compositions were studied as a function of reactor temperature and compared to those obtained from the gasification of coal and manure individually.

THEORETICAL

When complex organic solids, such as coal and manure, are heated to elevated temperatures, a series of physical and chemical changes occur which result in the evolution of gaseous products. If heated in an inert environment, the organic solids produce as a result of devolatilization, a hydrogen rich volatile fraction and a highly carbonous solid residue. The extent of volatile yield and its composition will depend upon the material gasified and the manner of heating (Anthony and Howard, 1976). Proximate analysis for different types of coal indicates that volatile matter ranges from less than ten percent for anthracites of over 50% for lignites (Averitt, 1961). Studies on dairy cattle manure show volatile yields as high as 90% on a dry basis (Antal et al, 1979).

In the early stages of devolatilization, many types of coal undergo physical changes such as swelling and softening (Van Krevelen, 1956). As devolatilization proceeds, however, the softening process reaches a peak and subsequently the coal resolidifies (Overturf et al., 1978). The swelling tendency is characterized by the coal's free swelling index (FSI). Values of the FSI range from unity for non-caking coal, to 9 for severely caking coal. A process which utilizes a caking coal must account for this property in order to prevent possible agglomeration within its reactor system.

Any process which involves the heating of coal or manure in a reactive gas environment, e.g., steam, will undergo the process of devolatilization followed by a char-gas reaction. However, the yield, product distribution, and extent of problems associated with swelling phenomena are largely dependent upon the type of reactor system used and the operating conditions employed.

Gasification processes utilize combinations of hydrogen, oxygen, and steam in an attempt to increase the yield of gaseous products as the expense of the char residual. The particular gaseous environment used is dependent upon the intended use of the product gas. For example, hydrogen has been proposed in the production of pipeline quality gas due to the high methane yields achieved (Anthony, et. al., 1974). Combinations of oxygen and steam are typically used in the production of low to medium heating value gases. Steam gasification is by far the most convenient due to the fact that steam is easily produced and readily removed from the product gas.

In steam gasification, residual char is converted to carbon monoxide and hydrogen by the reaction

$$C + H_2O \rightleftharpoons CO + H_2 \qquad (1)$$

However, the introduction of steam also induces many other gas phase reactions, such as,

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \qquad (2)$$

$$CH_4 + H_2O \rightleftharpoons CO + 3H_2 \qquad (3)$$

While these are not the only possible reactions in which steam can participate, they provide a basis for studying the effects of steam on the product gas composition (von Fredersdorff, 1963).

EXPERIMENTAL

Materials

The materials used included a bituminous coal from the Rowe coal bed in southeast Kansas and feedlot manure obtained from the Kansas State University Beef Cattle Research Center. Characteristics of these two materials are listed in Table 1. Pretreatment of the coal included hammermilling and size classification. The manure was collected from a concrete surfaced feedlot; the concrete surface kept the inert content to the reasonable level of about 15%. Collection was followed by flash drying, hammermilling, and size classification.

Facilities

The flow diagram of the bench scale fluidized bed reactor employed is sketched in Figure 1. Other than the disengaging zone, the reactor was constructed of a 2-inch (5.08 cm) schedule 40 Inconel 600 pipe, while the disengaging zone was a 4-inch (10.16cm) pipe of the same material. A packed bed containing 0.5 cm aluminum oxide pellets was used as both a gas preheater and distributor. This section was separated from both the fluidized bed and inlet sections by 60 mesh 316 stainless steel screens, which were held in place by flanges and sealed with graphite gaskets. An inert fluid bed of high silica sand was maintained at an expanded height of 10 cm.

Heat was supplied by means of four pairs of semicylindrical electrical resistance heaters, each capable of delivering up to 2300 watts of power with a maximum operating temperature of 1200°C. Steam was generated externally in an 800 watt electrical furnace and was supplied to the reactor at approximately 500°C.

Feed was transported to the feed pipe by a Vibra Screw Model SCR-20 screw feeder using a solid core flight screw. Upon reaching the feed pipe,

the material fell into the reactor bed aided by a helium purge flow which also prevented hot reactor gases from entering the feed pipe and subsequent condensation. Feed material was discharged from the feed pipe at the same level as the expanded bed. The feed pipe was equipped with a water jacket and vibrator to prevent the material from prematurely devolatilizing before it reached the reactor bed. Residual char overflowed to a sealed hopper beneath the reactor while product gases exited through the top plate. Entrained solids were removed from the product gas in the cyclone, which was kept at 300°C to prevent condensation of water and tar. After leaving the cyclone, the fluidizing steam was removed by cooling the gas to approximately 50°C by means of two water cooled heat exchangers in series. The resulting product gas carried with it a fine mist of condensible materials. This material was removed by passing the gas through a glass wool packed column. Before sampling, the gas was further dried by means of a $CaSO_4$ packed column.

Procedure

The reactor temperature was varied from 700°C to 1100°C. The particle size ranges were held constant at 210um - 300um for coal and 420um - 840um for manure. Superficial velocity was maintained at 36.7 cm/sec. Table 2 summarized the operating conditions used in this study.

The superficial velocity of the fluidizing gas corresponds to between 20 and 30 times minimum fluidization velocity and 20% of the terminal velocity of the reactant particles (Kunii and Levenspiel, 1968). It was found that under these conditions, the voidage within the bed was high enough to avoid the agglomeration problems normally associated with the use of a caking coal. In addition, the high concentration of sand in the feed kept the carbon concentration in the fluid bed low and contributed

significantly to the smooth operation of the system. However, the necessity of high inert concentrations with low feed rates severely hampered the collection of liquid and solid products needed for overall material balances.

To initiate the operation, the screw feeder was charged with the feed material and the reactor heated to approximately 50°C above the desired operating temperature while purging the system with air. Heating up to 800°C required about one hour. During this period, power was also supplied to the steam generator, cyclone heater, and inlet section heater. Before switching to steam, the inlet section and cyclone temperatures were raised to at least 200°C to prevent steam condensation. When all components of the system had reached their required temperatures, the air flow was replaced by steam, and water coolant to the feed pipe jacket was commenced. Additional 15 to 20 minutes were required for the system to reach a steady state as observed by the steady collection of water condensate downstream of the heat exchangers. With feeding ready to begin, the feed pipe vibrator and helium purge were started. After feeding had commenced, adjustment of the power to the reactor furnaces was required to maintain the set point temperature. Normally, 30 to 45 minutes were needed after the onset of feeding for the system to reach a steady state, which was determined by the reactor temperature, solid overflow and water condensate collection. Steady state sampling was repeated for at least one hour. During this period overflow and water condensate were collected over four consecutive 15 minute time intervals. Gas samples were taken at the end of every 15 minute period.

Chemical Analysis

Rates of product gas flows were determined by the introduction of a known volumetric flow of nitrogen into the system just upstream of the sampling point. Subsequent gas analysis allowed calculation of the total gas flow rate. Gas analysis was accomplished using a Packard Model 417

Becker 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, H_2S, N_2 and O_2. Column packings used were a 5A molecular sieve for the separation of H_2, O_2, N_2, CO, and CH_4, while the remaining components were separated using a mixture of Porapak Q and Porapak R, which are polymers of different cross linkages. The instrument was operated isothermally at 80°C with helium as a carrier gas. Accessories used in the analysis included a Spectro-Physics Autolab System I computing integrator and a Varian Model A-25 stripchart recorder. Reported material balances and product gas analysis are the result of averaging the many samples taken during the steady state period.

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 determined using a Beckman Model 930 Air Compression Pycnometer. A Perkin-Elmer Model TGS-2 Thermogravimetric Analyzer was used to obtain proximate analysis information, as well as to study the course of devolatilization for each material. The TGS-2 is capable of continuously monitoring sample weight as the material undergoes a linear heating program. Heating rates from 0.3125° C/min to 320°C/min are available with an upper temperature limit of 1000°C. Samples of sizes up to one gram may be used in any gaseous environment. Thermogravimetric data were recorded on a Bascom-Turner Model 8110 plotting microprocessor. This device allowed data points to be collected as fast as one point every 50 microseconds and also permitted permanent data storage and data manipulation.

RESULTS AND DISCUSSION

To aid interpretation of the experimental results, ultimate, proximate and thermogravimetric analyses of the three types of feedstock employed were carried out. The results from these analyses are presented first. They are followed by the presentation and analysis of the results from the bench - scale fluidized bed.

Proximate Analysis

The proximate analysis given in Table 1 illustrates some of the potential benefits to be expected from blending manure and bituminous coal. Comparing these two materials it is seen that manure has almost twice the volatile content of coal, but substantially more moisture. Analysis of the mixture shows that a 50-50 blend has a volatile content which is the average of the two individual components. This results in the mixture having a volatile content which is 46% greater than that of the coal alone. As would be expected, the moisture and ash content of the mixture is the average of the two components. In general, however, the moisture content of the mixture can vary significantly depending upon initial moisture content of the manure. In its raw form, manure can contain as much as 80% moisture by weight.

Ultimate Analysis

While the ultimate analysis shows only slightly more hydrogen in manure, coal has substantially more carbon and sulfur and substantially less nitrogen and oxygen. Analysis of the resulting blend in relation to that of coal shows a feedstock with 17% less carbon, twice as much nitrogen, two and one half times as much oxygen, and one half as much sulfur. As a

result of this, the heat of combustion of the mixture is approximately 23% lower than that of coal.

Thermogravimetric Analysis

To assess possible interactions between the individual components of the coal-manure mixture, the process of devolatilization was followed using thermogravimetric analysis (TGA). Figure 2 shows representative thermograms for coal, manure, and the coal-manure mixtures. The operating conditions for this figure included a heating rate of 40°C/min and a purge gas rate of 50 cc/min. Particle sizes used were 37um to 44um for manure and 74um to 149um for coal. Illustrated in Figure 2 are three families of curves, representing the devolatilization of coal, manure, and the coal-manure mixture. While the experimental conditions were the same, much variation is observed within each family of curves. This is attributed to the variation of ash content for the individual samples used. For both coal and manure, ash content ranged from ten percent to twenty percent of the initial dry weight. In this figure, coal is the uppermost group of devolatilization curves, and is seen to lose between 32% and 42% of its initial weight when heated to 960°C. The lowermost group of curves represents the devolatilization of manure. Here, the total weight loss ranges from 71% to 77%. The coal-manure mixture thermograms are seen to lie between those of coal and manure. The total weight loss of the mixture varies from 52% to 57% of the initial sample weight.

Comparing the devolatilization curve for coal to that of manure, it is seen that significant devolatilization of coal begins essentially where manure devolatilization ends. The range of rapid weight loss for

manure is 150°C to 400°C while that for coal is 400°C to 600°C. These two devolatilization steps are clearly identifiable in the thermogram of the mixture. In addition, the mixture curve is seen to be essentially the average of the thermograms of the individual components.

Heating Values of Product Gases

Steam gasification of the bituminous coal in the temperature range of 700°C to 1100°C, resulted in product gases with heating values between 11.87 MJ/Nm^3 and 18.09MJ/Nm^3. Heating values for the product gas obtained from manure gasification in the same temperature range were between 11.27 MJ/Nm^3 and 16.21 MJ/Nm^3. The coal-manure mixture produced a 12.86 MJ/Nm^2 to 16.08 MJ/Nm^3 heating value gas. These heating values may be compared to that of natural gas which has a value of approximately 37MJ/Nm^3.

Sulfur Contents of the Product Gases

Hydrogen sulfide was the only sulfur bearing compound detected in the product gas from the gasification of the bituminous coal. At 700°C, the concentration of this compound was analyzed to be 2.5% of the product gas. No sulfur compounds were detected for the gasification of manure. The effect of mixing coal and manure was to reduce the concentration of H_2S in the product gas by 50% compared to that obtained from coal alone.

Effect of Reactor Temperature

Steam gasification basically seeks to react the residual char resulting from devolatilization with steam in order to produce hydrogen and carbon monoxide. For manure, proximate analysis and thermogravimetric analysis showed the amount of residual char to be relatively

small in comparison to that for coal. In addition, the devolatilization of manure occurred at lower temperatures than did the devolatilization of coal. Therefore, the reactor temperature used for the gasification of the coal-manure blend had to depend upon that needed to devolatilize the coal and promote the carbon-steam reaction of the coal char residual. Equilibrium considerations show that the carbon-steam reaction is increasingly promoted for temperatures above 700°C (von Fredersdorff, 1963). Thus the bench scale reactor was operated between this temperature and the upper limit of the reactor, which was 1100°C.

Due to the low reactant feed rate and holdup in the cooling train, meaningful collection of condensible materials was prohibited. Table 3 indicates that although inert balances closed in the range between 97% and 100%, total overall material balances were found to close in the range between 52% and 91%. The low overall balances for the manure runs stem from the fact that these runs were made without inert sand in the feed material. The char product was totally retained in the fluid sand bed, with no observed collection in the overflow or cyclone hoppers.

Table 4 shows the yields, heating values, and product gas compositions for the experiments performed. From this table comparisons of the product gas of the coal-manure mixture are made to the product gases of coal and of manure at three different temperatures.

Comparing the gas produced from manure to that from coal, it is seen that the compositions of the two product gases are substantially different at the lower reactor temperatures. At 700°C, the product gas from manure contains a much larger quantity of carbon oxides than that from coal.

This can be attributed to the significantly higher oxygen content of the manure feedstock. As temperature increases and the carbon-steam reaction becomes more important, the difference in carbon oxide concentrations of the two materials decreases, until at 1100°C they are essentially the same. It is also seen that while the combined concentration of carbon oxides produced from manure remains essentially constant between 700°C and 1100°C, the concentration increases from 25% to over 42%,in the case of coal. This can be attributed to the substantial difference between the amount of residual char available for the carbon-steam reaction for manure and coal. The low carbon oxide production from coal at the lower reactor temperature, and the increase in this concentration with increasing temperature indicate the carbon-steam reaction plays a major role in the final gas composition. For manure, however, the essentially constant high carbon oxide concentration between 700°C and 1100°C, suggests that the majority of the carbon oxide concentration results from reaction of carbon with the oxygen inherent to the manure, and not from the carbon-steam reaction. The result of using the available carbon in this manner is reflected in the hydrocarbon concentrations. At 700°C, the total hydrocarbon concentrations of the product gases are 23.5% and 7.0% for coal and manure, respectively. At 1100°C, these percentages have changed to 7.0% and 10.6%, respectively.

Product gases from the blend of coal and manure show lower carbon oxide concentrations than those experienced for manure and lower hydrogen sulfide condentrations than those for coal. For most components, the concentrations in this gas are close to the average of those found for manure and coal.

Table 4 shows, for all three of the gasification feedstocks, that the concentration of carbon dioxide is higher than that of carbon monoxide at the lower reactor temperatures. As temperature increases however, this fact is reversed, with CO becoming the dominate carbon oxide component. There have been several reactions proposed in gasification processes which involved CO and CO_2 (von Fredersdorff, 1963). These include the three reactions given in the THEORETICAL section, which also involve steam, and in addition the reaction of carbon dioxide with the fixed carbon in the char to produce carbon monoxide. The only one of these reactions which has normally been assumed to be in equilibrium at the reactor exit conditions is the water shift reaction, equation (2) of the THEORETICAL section (Amundson, 1979). Being an exothermic reaction, the equilibrium concentrations would be shifted in favor of the reactants, CO and H_2O, as reactor temperature is increased. The other three reactions mentioned, are endothermic and result in the production of carbon monoxide. Therefore, the observation that carbon monoxide becomes the dominate form of carbon oxide compounds, would be expected with respect to the proposed reactions.

For temperatures above 700°C the heating values of the product gases from both the blend and manure are higher than that of coal. The high heating value for the coal gas at 700°C is due to the low concentration of carbon oxides and high methane content. As temperature increases, however, the concentration of methane decreases dramatically, which is attributed to the reaction of methane and steam as shown by equation (3) of the THEORETICAL section. This is in contrast to that observed in the gasification of manure, which shows an increase in methane concentration between 700°C and 1100°C. With respect to equation (3) of the THEORETICAL section, this indicates that the production of methane increases at a

faster rate than does the rate of reaction of methane and steam. The opposite is indicated in the case of coal.

Gasification of an equal weight ratio of coal and manure at reactor temperatures greater than 700°C has the effect of increasing the heating value of the product gas by 8% over that produced from coal alone. Product gas yields shown in Table 4 indicate that the results are compatible with the results of TGA, in that gas yield of the blend is roughly the average of that from coal and manure on a dry ash free basis. However, it is interesting to note that the effect of reactor temperature on the yields of coal and manure is different. Yields from coal are seen to increase by over 250% between 700°C and 815°C, with only a 26% increase between 815°C and 1100°C. Manure, on the other hand, experiences only a 12% increase between 700°C and 815°C. Between 815°C and 1100°C, the yield from manure increases by over 120%.

The combined effect of heating value and yield for each material is expressed in Table 4 as the total energy recovered in gaseous form per unit mass of feed. This shows that the gas from the blend is always higher than that from coal. The efficiencies shown in this table are defined as the total heating value of the product gas yielded per unit mass of feed divided by the heat of combustion of the feed material. It can be seen that the addition of manure to a coal feedstock increases this efficiency parameter. At 1100°C, the efficiency of the blend is over 51% compared to 35% for coal alone. The percentage of the carbon in the feed which is converted to product gas is also seen to be higher for the blended feed than for coal.

CONCLUSION

A mixture of 50% feedlot manure and 50% bituminous coal was gasified with steam in the temperature range of 700°C to 1100°C. Results indicate that with respect to the total energy recovered in gaseous form per unit mass of reactable solid, the gasification of the blend yields a higher value than if coal was used alone. In this temperature range, gasification of the blend results in higher efficiencies and better conversion of carbon to the final product gas than gasification of coal alone. In addition, the blend yields higher concentrations of light hydrocarbons and 50% less hydrogen sulfide than in the gasification of coal alone. The data indicate that for an equal weight ratio of coal and manure, the resulting gasification product is essentially the average of the product gases which would be obtained from gasification of the two components individually.

Literature Cited

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

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.

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.

Gallagher, J. E., Jr., and H. A. Marshall, "Production of SNG from Illinois Coal via Catalytic Gasification," presented at the AICHE Symposium on Reaction Engineering in Processing Solid Fossil Fuels," Miami Beach, Fla., Nov., 1978.

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

Hendrickson, T. A., Synthetic Fuels Data Handbook, Cameron Engineers, Inc., Denver, Colo. 1975.

Huffman, W. J., W. W. Liberick, Jr., "EPA's R&D Program in Pyrolytic Conversion of Wastes to Fuel Products," presented at the ACS Symposium on Advances Thermal Processes for Conversion of Solid Wastes and Residues, Anaheim, Ca., March 16, 1978.

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

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

Kavlick, V. J., and B. S. Lee, "Coal Pretreatment in Fluidized Bed," in Fuel Gasification, Advances in Chemistry Series, No. 69, Am. Chem. Soc., Washington, D.C., 1967.

Kunii, D. and O. Levenspiel, Fluidization Engineering, John Wiley & Sons, Inc., New York, 1969.

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

Overturf, B. W., F. Kayihan, and G. V. Reklaitis, "Modeling and Analysis of an Integrated Coal Pyrolysis, Gasification, and Combustion Reactor System," presented at the 71st Annual Meeting of AICHE, Miami Beach, Nov. 16, 1978.

Pober, K. and H. Bauer, "From Garbage-Oil," Chemtech, pp. 164, March, 1977.

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

Tillman, D. A., "Mixing Urban Waste and Wood for Gasification in a Purox Reactor," in Thermal Uses and Properties of Carbohydrates and Lignins, pp. 141, F. Shafizadeh, K. V. Sarkanen, and D. A. Tillman, ed., Academic Press, New York, 1976.

Van Krevelen, D. W., F. J. Hantjens, and H.N.M. Dormans, "Chemical Structure and Properties of Coal XVI - Plastic Behavior on Heating," Fuel, 35, 462, 1956.

von Fredersdorff, C. G. and M. A. Elliott, "Coal Gasification," in Chemistry of Coal Utilization, Supplementary Volume, H. H. Lowry, ed., Wiley, New York, 1963.

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. Feedstock Analysis

	KANSAS BITUMINOUS COAL	FEED LOT MANURE	MIXTURE 50-50 wt.%
PROXIMATE ANALYSIS			
FREE SWELLING INDEX	5.5	——	——
VOLATILE MATTER (daf)	44.6	85.3	65.1
FIXED CARBON (daf)	55.4	14.7	34.9
ASH (dry)	16.2	12.8	14.5
MOISTURE	2.0	9.4	5.7
ULTIMATE ANALYSIS (daf, wt.%)			
CARBON	75.0	50.1	62.6
HYDROGEN	5.3	6.9	6.1
NITROGEN	1.4	4.0	2.7
OXYGEN	10.9	39.0	25.0
SULFUR	7.5	0	3.8
DENSITY (g/cc)	1.58	1.37	1.48
HHV (as received) $(\frac{MJ}{kg})$	27.64	15.00	21.32
HHV (dry, ash free) $(\frac{MJ}{kg})$	31.74	19.86	25.80

TABLE 2

Bench Scale Experimental Parameter

Reactor Temperature:	700°C - 1100°C
Fluidizing Medium:	Steam
Superficial Velocity:	36.7 cm/sec
Feed Rate:	9.0 gm/min
Feed Compositions:	
Coal and Coal-Manure Mix Experiments:	90% Sand/ 10% Reactant
Manure Experiments:	100% Reactant
Particle Sizes:	coal - 210μm to 300μm
	manure - 420μm to 1000μm
	sand - 420μm to 595μm

TABLE 3

MATERIAL BALANCE RESULTS

RUN NUMBER	Temp.	INPUTS (g/min)		Feedstock	OUTPUTS (g/min)			BALANCES (OUT/IN)	
		Feed	Steam		Gas	Condensate	Solids	INERT	OVERALL
101289	700	7.602	10.0	coal	0.101	7.875	7.017	99%	85%
101099	815	6.80	9.0	coal	0.3777	7.650	6.32	100%	91%
301129	1100	8.70	7.2	coal	0.582	3.20	8.00	99%	74%
204169	700	1.70	9.6	manure	0.619	5.30	—	—	52%
101049	815	2.40	9.0	manure	1.002	9.10	—	—	89%
104169	1100	1.7	7.0	manure	1.31	3.80	—	—	59%
102019	700	9.26	10.0	coal-manure	0.175	4.413	8.475	97%	68%
101309	815	8.75	9.0	coal-manure	0.422	5.067	8.248	99%	77%
102189	1100	9.60	8.0	coal-manure	0.591	1.447	8.89	100%	62%

TABLE 4

Experimental Results

TEMPERATURE	700°C			815°C			1100°C		
Molar %	coal	manure	50-50 Blend	coal	manure	50-50 Blend	coal	manure	50-50 Blend
H_2	48.6	43.5	39.7	51.0	33.3	41.4	50.3	44.4	47.8
CH_4	19.3	4.5	13.1	8.7	9.3	9.1	5.2	8.6	7.4
CO	11.4	17.1	16.5	16.9	25.6	21.7	23.2	25.7	21.6
CO_2	14.0	32.4	24.5	19.4	24.5	22.2	19.4	19.3	21.1
C_2H_4	2.4	1.5	2.45	1.9	5.2	3.1	0.7	2.0	1.8
C_2H_6	1.8	0.3	1.4	0.6	0.76	0.5	ND	ND	ND
H_2S	2.5	ND	1.1	1.4	ND	0.8	1.1	ND	0.4
C_3H_6	ND	0.7	1.3	ND	1.32	1.1	ND	ND	ND
HHV ($\frac{MJ}{Nm^3}$)	18.09	11.27	16.08	13.87	16.21	15.00	11.87	13.59	12.86
Yield (Nm^3/kg)	0.192	0.374	0.236	0.684	0.418	0.593	0.864	0.931	0.835
Yield(Nm^3/kg,daf)	0.221	0.481	0.290	0.779	0.554	0.730	0.992	1.196	1.027
Energy Recovered (MJ/kg, daf)	4.00	5.42	4.66	10.80	8.98	10.95	11.78	16.25	13.21
Efficiency	12.6	27.3	18.1	34.0	45.2	42.4	37.1	81.9	51.2
Carbon Conversion	8.4	30.7	16.3	27.8	44.6	39.7	34.9	73.7	47.2

ND = Not Detected

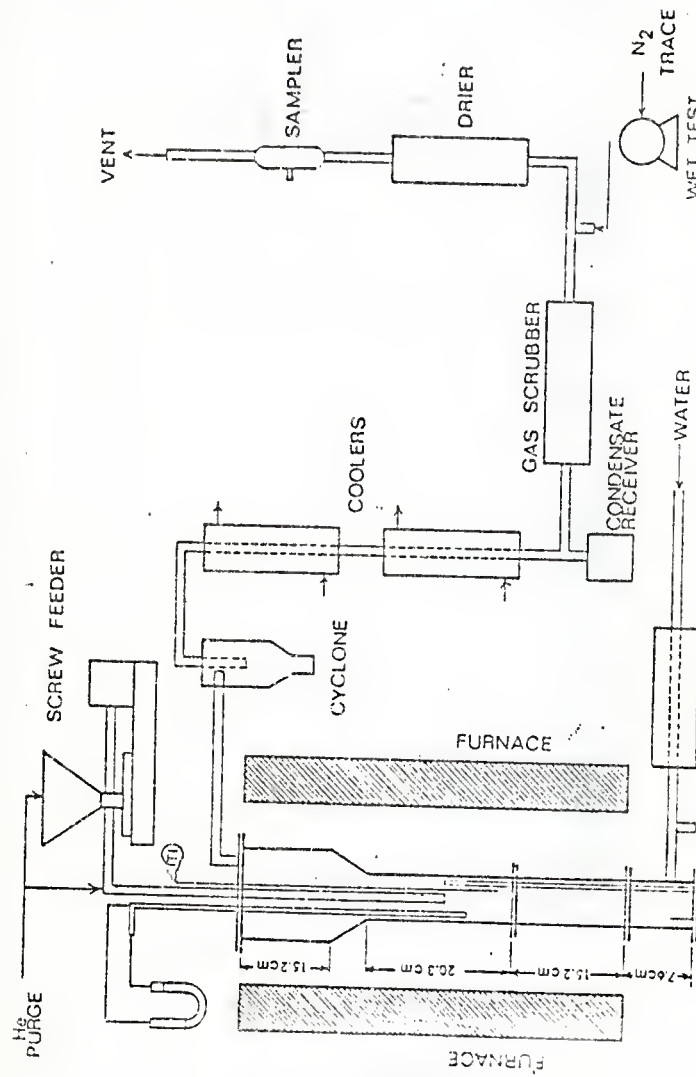

Fig. 1 Bench Scale Reactor

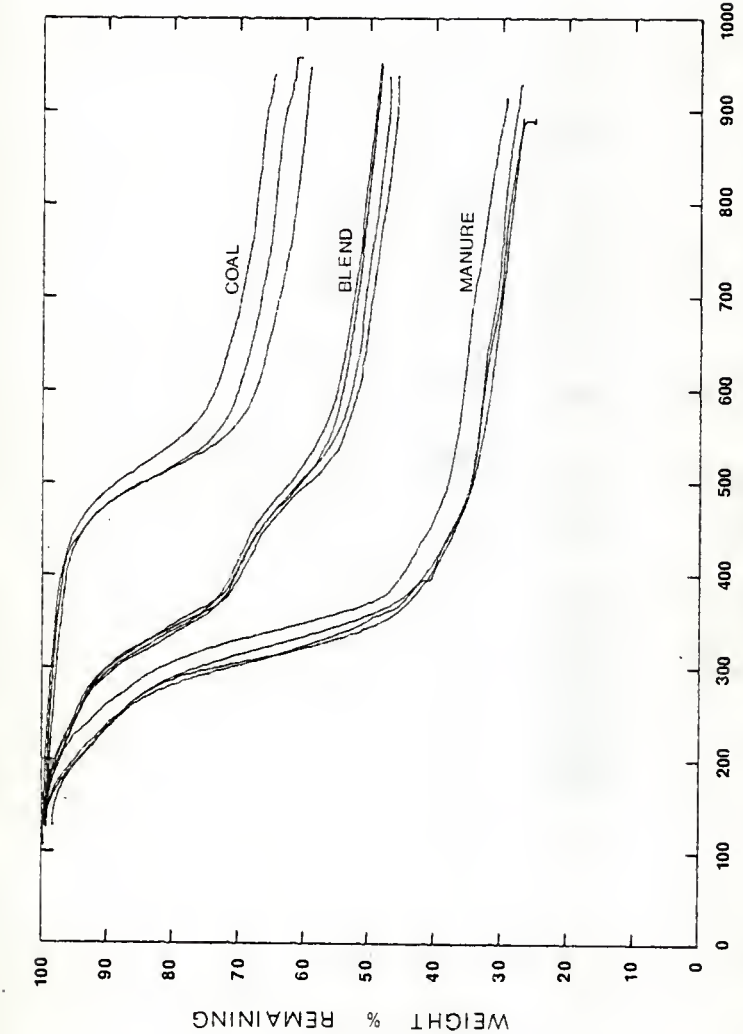

Fig. 2 Thermograms of Coal, Manure, and Coal-Manure Blend.

CHAPTER VI

CONCLUDING REMARKS

This chapter summarizes the conclusions presented in Chapters III, IV, and V. Recommendations for future work are also presented.

Thermogravimetric Analysis

The devolatilization of a Kansas bituminous coal was studied using thermogravimetric analysis. Experiments were carried out in an inert environment at atmospheric pressure. Results showed significant devolatilization to occur in the temperature range between 450°C and 650°C. Further heating to 960°C resulted in an asymptotic approach to the final weight remaining, which ranged from 59% to 68% of the initial dry, ash free weight. Statistical analysis showed that the final weight remaining was influenced by the two heating rates (40°C/min and 160°C/min) and two particle size ranges (74 μm to 149 μm and 420 μm to 840 μm) used in this study.

Fitting of the thermograms to a multireaction model using a normally distributed activation energy, yielded mean activation energies in the range expected for coal devolatilization. These parameters were compared to those determined by other investigators employing extremely rapid heating techniques. The comparison showed excellent agreement with coal of similar ultimate and proximate analysis. Statistical analysis showed that the model parameters were influenced by the experimental variables. However, no single experimental variable was found to have influence on all of the model parameters. The parameter found to be the least sensitive to experimental conditions, was the mean activation energy.

Bench Scale Reactor

A high sulfur, high ash, caking bituminous Kansas coal was steam gasified in a bench scale fluidized bed reactor at atmospheric pressure in the

temperature range of 700°C to 1100°C. Agglomeration problems, normally associated with the gasification of caking coal in fluid bed reactors, were successfully countered by feeding into a fluid bed consisting primarily of inert sand and by using a superficial fluidization velocity of 36.6 cm/sec.

The product gas consisted primarily of hydrogen, methane, and carbon oxides. Heating values ranged from 18 MJ/Nm^3 at 700°C to 11.9 MJ/Nm^3 at 1100°C. Yields obtained ranged from 0.221 Nm^3/Kg at 700°C to 0.99 Nm^3/Kg at 1100°C on a dry, ash free basis. Hydrogen sulfide concentrations ranged from 2.5% at 700°C to approximately 1.0% at 1100°C. This gas could be used on a local basis as either a medium heating value fuel gas or as an industrial feedstock.

Steam gasification of an equal weight ratio of Kansas bituminous coal and feedlot manure was performed. Results indicate that with respect to the total energy recovered in gaseous form per unit mass of reactable solid, the gasification of the blend yields a higher heating value than if coal was used alone. Gasification in the temperature range of 700°C to 1100°C resulted in better carbon conversion to the final product gas than in the case of coal. Compared to coal alone, the blend yielded higher concentrations of light hydrocarbons and 50% less hydrogen sulfide. The data indicated that for an equal weight ratio, the gasification product is essentially the average of the product gases which would be obtained from the gasification of the two components individually.

Recommendations

Further work needs to be done on the dependence of the nature of devolatilization with respect to heating rates and particle sizes. The thermogravimetric work accomplished in this study can easily be extended to investigations

employing different pressures and gaseous environments. This information would be of primary importance to the understanding of the gasification process. Addition of an evolved gas analysis system to the thermogravimetric analyzer would provide needed data on the process of evolution of the various components during the course of gasification.

The bench scale work accomplished in this study concentrated on the dependence of the characteristics of the gaseous product on the reactor temperature. Further work should investigate other operational parameters such as pressure, particle size, and superficial velocity. In addition, modifications should be performed to allow for the collection and analysis of the condensible products resulting from the gasification process.

APPENDIX A

PARAMETER ESTIMATION OF KINETIC MODEL

Presented in this appendix is the method used to determine the parameters of the multireaction kinetic model developed by Anthony et al. (1974) for the devolatilization of coal.

The form of the mathematical model to be fitted is

$$\frac{V^* - V}{V^*} = \frac{1}{\sigma\sqrt{2\pi}} \int_{E_m - 2\sigma}^{E_m + 2\sigma} \exp[-k_o \int_0^t \exp(-\frac{E}{RT})dt - \frac{(E - E_m)^2}{2\sigma^2}]dE. \quad (1)$$

The unknown parameters of this model which were used to correlate the thermogravimetric data of a Kansas bituminous coal were E_m, σ, and k_o. The devolatilization data was obtained experimentally over the temperature range of 130°C to 960°C. The total potential volatile yield, V^*, was approximated by the total weight loss at 960°C.

The experimental weight loss data was obtained as the sample was linearly heated. A typical time-temperature history for a run made with a heating rate of 160°C/min is shown in Fig. 1. Since the time-temperature data was recorded using the Bascom-Turner Model 8110 microprocessor in digital form, it was possible to use this information for the time integral of equation (1). However, it was found that the recorded temperature increase was normally within 10°C of that which would have been predicted using the nominal linear heating rate selected (eg. 40°C/min or 160°C/min). It was found that the parameter estimations obtained from the model were insensitive to whether the nominal linear heating rate or the actual time-temperature history was used. Therefore, the time integral in equation (1) was changed to an integral over temperature using the linear heating rate

$$\beta = \frac{dT}{dt} \quad (2)$$

with the boundary conditions

$$T = T \text{ at } t = t$$

$$T = T_o \text{ at } t = 0.$$

Using these in equation (1) yields

$$\frac{V^* - V}{V^*} = \frac{1}{\sigma\sqrt{2\pi}} \int_{E_m - 2\sigma}^{E_m + 2\sigma} \exp\left[-\frac{k_o}{\beta} \int_{T_o}^{T} \exp\left(-\frac{E}{RT}\right) dT - \frac{(E - E_m)^2}{2\sigma^2}\right] dE \qquad (3)$$

The lower limit of the temperature integral of equation (3) can be set to zero without affecting the correlation results. Letting $x = (-E/RT)$, the temperature integral becomes

$$\int_0^T \exp\left(-\frac{E}{RT}\right) dT = \frac{E}{R} \int_{-\infty}^{x} \frac{e^x}{x^2} dx. \qquad (4)$$

Integration by parts results in

$$\frac{E}{R} \int_{-\infty}^{x} \frac{e^x}{x^2} dx = \frac{E}{R} \left[-\frac{e^x}{x} + \int_{-\infty}^{x} \frac{e^x}{x} dx\right] \qquad (5)$$

Integration of the right hand side of equation (5) can be accomplished using the approximation (Jahnke, 1960),

$$E_i(-y) = \int_{-\infty}^{-y} \frac{e^t}{t} dt = \frac{e^{-y}}{-y} \left\{A - \frac{B}{y} + \frac{C}{y^2} - \frac{D}{y^3} + \frac{E}{y^4} - \frac{F}{y^5} + \frac{G}{y^6} - \frac{H}{y^7} \pm 3.5 \times 10^{-4}\right\} \qquad (6)$$

where

$A = 0.9999965$

$B = 0.9989710$

$C = 1.9487646$

$D = 4.9482092$

$E = 11.7850792$

$F = 20.4523840$

G = 21.1491469

H = 9.5240410

and y is a real, positive number. This approximation is valid for y > 2. Letting x = -y = t, and substituting into equation (5) yields

$$\frac{E}{R}\int_{-\infty}^{x}\frac{e^x}{x^2}\,dx = \frac{E}{R}\left\{\frac{e^x}{x}\left[A' + \frac{B}{x} + \frac{C}{x^2} + \frac{D}{x^3} + \frac{E}{x^4} + \frac{E}{x^5} + \frac{G}{x^6} + \frac{H}{x^7}\right]\right\} \qquad (7)$$

or

$$\frac{E}{R}\int_{-\infty}^{x}\frac{e^x}{x^2}\,dx = \frac{E}{R}\,P(x). \qquad (8)$$

The coefficients B through H, of the polynomial in equation (7) are the same as those of equation (6). The value of A' is -0.0000035. Replacement of the temperature integral in equation (3) by the approximation in equation (8) results in the final form of the correlation

$$V^* - V = \frac{V^*}{\sigma\sqrt{2\pi}}\int_{E_m-2\sigma}^{E_m+2\sigma}\exp\left\{-\frac{k_o E}{\beta R}\,P(x) - \frac{(E-E_m)^2}{2\sigma^2}\right\}dE. \qquad (9)$$

A Hooke and Jeeves pattern search technique (Hwang, et al., 1969) was used to estimate the parameters E_m, σ, and k_o. The objective function to be minimized was the sum of the squares of the differences between the experimental weights remaining and those predicted from equation (9). While 500 data points were available for this curve fit, it was found that by using only 50 (every tenth data point), the estimated parameters were not significantly affected.

Notation

E	Activation energy, kcal/mole
E_m	Mean activation energy, kcal/mole
k_o	Frequency factor, sec^{-1}
R	Gas constant, cal/mole k
T	Temperature, k
T_o	Initial Temperature, k
t	Time, sec
t'	Exponential term, -E/RT
V	Volatile matter
V^*	Potential volatile matter
x	Exponential term, -E/RT
y	Exponential term, E/RT

Greek

β	Linear heating rate, k/sec
π	Constant
σ	Standard deviation, kcal/mole

LITERATURE CITED

Anthony, D. B., J. B. Howard, H. C. Hottel, and H. P. Meisner, "Rapid Devolatilization of Pulverized Coal," Fifteenth Symposium (International) on Combustion, pp. 1303, The Combustion Institute, Pittsburg, Pa, 1974.

Hwang, C. L., L. T. Fan, and S. Kumar, "Hooke and Jeeves Pattern Search Solution to Optimal Production Planning Problems," Institute for Systems Design and Optimization, No. 18, Kansas State Univ., 1969.

Jahnke, E., Emde, and F. Lösch, Tables of Higher Functions, sixth ed., McGraw-Hill Book Co., Inc., New York, 1960.

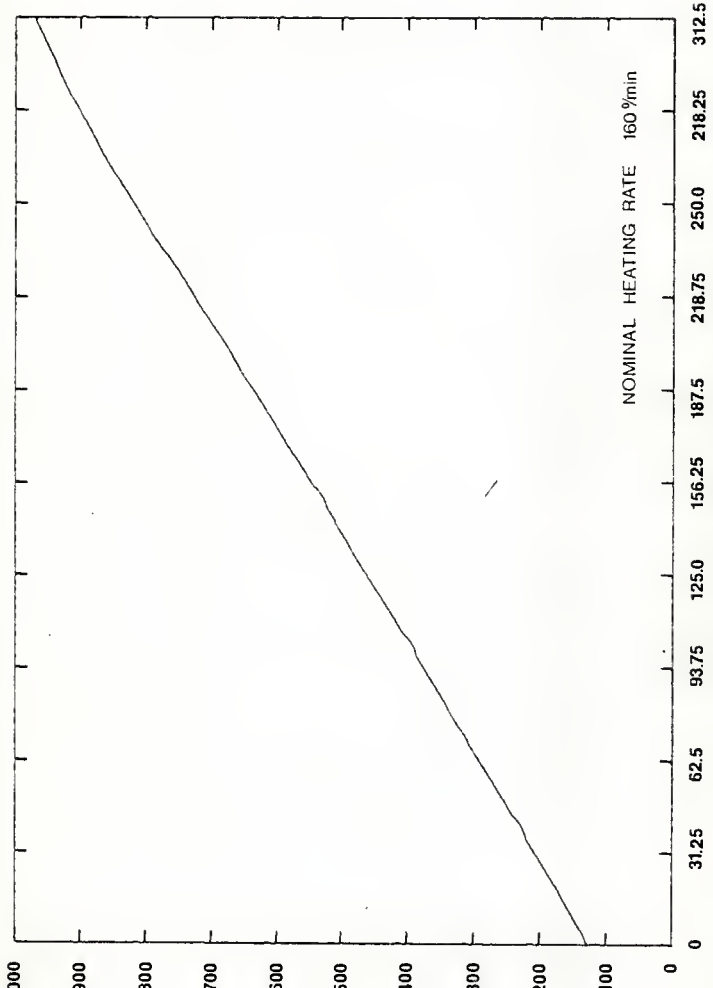

Fig. 1 Time-Temperature History

```
FORTRAN IV G LEVEL 21          MAIN          DATE = 79125          10/26
C
C
C     THIS PROGRAM IS MENT TO DETERMINE THE OPTIMIZED PARAMETERS TO
C     THE KINETIC MODEL DEVELOPED BY ANTHONY BY USING A HOOKE AND
C     JEEVES PATTERN SEARCH SCHEME.  AT MOST FOUR PARAMETERS CAN BE
C     DETERMINED;  FINAL CONVERSION, MEAN ACTIVATION ENERGY, FREQUENCY
C     FACTOR, AND STANDARD DEVIATION FROM THE MEAN ACTIVATION ENERGY.
C     IT IS ASSUMED THAT THE MEAN ACTIVATION ENERGY  AND IT'S STANDARD
C     DEVIATION ARE ALWAYS TO BE DETERMINED.  HOWEVER THE FREQUENCY
C     FACTOR AND/ OR THE FINAL CONVERSION MAY BE SPECIFIED AS CON-
C     STRAINTS.  IF ALL FOUR PARAMETERS ARE TO BE DETERMINED, THE
C     NUMBER OF STAGES AND THE NUMBER OF DIMENSIONS TO BE SPECIFIED
C     ARE BOTH FOUR.  ALSO THE VALUE OF 'NCONST' IS SET TO ZERO.  IF
C     THE FINAL CONVERSION IS KNOWN, THIS VALUE IS ENTERED AS 'WF',
C     THE VALUE OF 'NCONST' IS 1, AND THE  NUMBER OF STAGES (NS) AND
C     THE NUMBER OF DIMENSIONS (ND), MUST BOTH BE 3.  IF THE FRE-
C     QUENCY FACTOR IS KNOWN, NCONST=2, ND=NS=3, AND THE VALUE OF THIS
C     FACTOR IS ENTERED AS KO.  IF WF AND KO ARE BOTH KNOWN, THEN
C     NCONST=3,NS=ND=2.
C
C     THE PROGRAM IS SET TO HANDLE THERMOGRAVIMETRIC DATA FURNISHED BY
C     MAGNETIC TAPE.  IT IS ASSUMED THAT THE TAPE DATA IS THAT FROM
C     TRANSFERRED FROM A BASCOM-TURNER MODEL 8110 RECORDING MICRO-
C     PROCESSOR.
C
C
C
C     IF NCONST = 0;  WF=PHI(1),EM=PHI(2),KO=PHI(3),SIGMA=PHI(4); ND=4
C
C     IF NCONST = 1;  EM=PHI(1),KO=PHI(2),SIGMA=PHI(3); ND=NS=3.
C
C     IF NCONST = 2;  WF=PHI(1),EM=PHI(2),SIGMA=(3);  ND=NS= 3.
C
C     IF NCONST = 3;  EM=PHI(1),SIGMA=(2);  ND=NS= 2.
C
C
C     INPUT SEQUENCE:
C     1.)  NAME ; TITLE
C     2.)  INITIAL TEMPERATURE (TC,DEG C);  FINAL TEMPERATURE (TF,DEG
C     C);  NUMBER OF TGA DATA POINTS TO BE READ FROM TAPE (NM);  ASH
C     CONTENT OF SAMPLE (ASH, %);  HEATING RATE (HR,DEG/MIN);  NCONST;
C     TIME INTERVAL BETWEEN DATA POINTS (TI,SEC).
C     3).  NUMBER OF TGA POINTS FOR EVALUATION (EG., EVERY 5TH POINT,
C     NSKIP).
C     4.)  VALUE OF KO, IF IT IS TO BE SPECIFIED.  IF NO
C     CONSTRAINTS ARE USED (I.E. FOUR PARAMETERS ARE TO BE OPTIMIZED,
C     NCONST=0,WITH ND=NS=0),LEAVE THIS CARD OUT.
C     5.)  PRINTING FLAG
C     6.)  # OF STAGES, # OF DIMENSIONS
C      7.)  INITIAL VALUES ; STEP SIZES ; FINAL STEP SIZES.
C
C
C
0001          DIMENSION X(50), BASE0(50),BASEN(50),DEL(50),TITLE(60)
0002          DIMENSION TGR(550),TGC(550)
0003          COMMON NS,ND,DELTA(50),N,IPRINT,NE,NO,    NM,    T,BB,TGA(550)
0004          COMMON                          ASH,TI,HR,TC,TF
```

```
FORTRAN IV G LEVEL  21                  MAIN                    DATE = 79125          13/4

0005              COMMON NSKIP,NCONST,WF,AKC,MZ,SIG,EM
0006             106 FORMAT (16,60A1)
0007             110 FORMAT (1I0I5)
0008            1000 FORMAT ('-BEFORE EXPLORATORY MOVES   ',9X,I3,1X5E18.5/(40X5E18.
                    /))
0009            1001 FORMAT ('-NO. OF STAGES  ',I3,'   NO. OF DIMENSIONS   ',I3)
0010            1002 FORMAT ('1     PROBLEM NO. ',I6,10X,60A1)
0011            1010 FORMAT (' AFTER EXPLORATORY  MOVES   ',9X,I3,1X5E18.5/(40X5E18.
                   /))
0012            1011 FORMAT (' BASE POINT NUMBER  ',I5)
0013            1019 FORMAT(2F10.1,I5,2F10.4,I5,F10.4)
0014            1020 FORMAT ('-AFTER PATTERN MOVE         ',9X,I3,1X5E18.5/(40X5E18.
                    /))
0015            1021 FORMAT(10F4.1)
0016            1022 FORMAT(5E16.4)
0017            1050 FORMAT (' TOTAL EVALUATIONS OF THE FUNCTION  =',I4)
0018            1120 FORMAT ('-STEP SIZE     ', 5E15.4 /(16X,5E15.4))
0019            1121 FORMAT (' STARTING POINT', 5E15.4 /(16X,5E15.4))
0020            1130 FORMAT ('-OBJECTIVE FUNCTION  ',E16.6/' OPTIMAL POINT ',5E18.5
                   1/(15X,5E18.5))
0021            1200 FORMAT ('- FAILED PATTERN MOVE , RETURN TO LAST BASE POINT')
0022            1201 FORMAT (' FAILED EXPLORATORY MOVES ,CHECK THE STEP SIZE')
0023            1220 FORMAT ('- STEP SIZE REDUCED TO '  ,5E14.4/(23X,5E14.4))
0024            1221 FORMAT ('-  FINAL STEP SIZES     ',5E14.4/(23X,5E14.4))
0025            1300 FORMAT(8E15.4)
0026            1301 FORMAT(2E15.4)
0027            1302 FORMAT(///' TEMPERATURE INTERVAL IS',F6.1,' TO',F6.1,
                    ////' NUMBER OF TGA DATA POINTS IS',I3,//' TGA ASH CONTENT IS',
                    /F8.4,//' HEATING RATE IS',F10.4,//' EVERY  ',I2,' TH TGA DATA P
                    /INT IS USED FOR OPTIMIZATION',//' CONSTRAINT FLAG IS',I3,
                    ///' FINAL CONVERSION IS',F6.1,//' FREQUENCY FACTOR IS',E15.4)
0028            1303 FORMAT(///' TEMPERATURE INTERVAL IS',F6.1,' TO',F6.1,
                    ////' NUMBER OF TGA DATA POINTS IS',I3,//' TGA ASH CONTENT IS',
                    /F8.4,//' HEATING RATE IS',F10.4,//' EVERY  ',I2,' TH TGA DATA P
                    /INT IS USED FOR OPTIMIZATION',//' CONSTRAINT FLAG IS',I3,
                    ///' FREQUENCY FACTOR IS',E15.4)
0029            1304 FORMAT(///' TEMPERATURE INTERVAL IS',F6.1,' TO',F6.1,
                    ////' NUMBER OF TGA DATA POINTS IS',I3,//' TGA ASH CONTENT IS',
                    /F8.4,//' HEATING RATE IS',F10.4,//' EVERY  ',I2,' TH TGA DATA P
                    /INT IS USED FOR OPTIMIZATION',//' CONSTRAINT FLAG IS',I3)
0030            1305 FORMAT(//' TEMPERATURE INTERVAL IS',F6.1,' TO',F6.1,
                    ////' NUMBER OF TGA DATA POINTS IS',I3,//' TGA ASH CONTENT IS',
                    /F8.4,//' HEATING RATE IS',F10.4,//' EVERY  ',I2,' TH TGA DATA P
                    /INT IS USED FOR OPTIMIZATION',//' CONSTRAINT FLAG IS',I3,
                    ///' FINAL CONVERSION IS',F6.1)
0031            6608 FORMAT(I2)
0032            6609 FORMAT(A4)
0033            6611 FORMAT(10F10.1)
0034            6615 FORMAT(///10X,' TAPE FILE CONTENTS')
0035            6616 FORMAT(///10X,' CORRECTED DATA')
0036            6619 FORMAT(/10X,' CORRECTED FINAL CONVERSION =',F5.1)
0037            6790 FORMAT(//5X,' OBJECTIVE FUNCTION=',E15.5)
0038            8000 FORMAT(//' MODEL RESULT USING OPTIMIZED PARAMETERS',////T2,' T'
                    /T15,' TGA:W',T25,' CORR:W',T35,' TGA-CORR')
0039            8003 FORMAT(/T2,F7.2,T15,F5.1,T25,F5.1,T35,E11.4)
0040            1250 N=0
0041                 MZ=0
                C        SET EVALUATION COUNTER TO ZERO
```

```
FORTRAN IV G LEVEL  21                  MAIN              DATE = 75125        10/28

                /F6.4,///' HEATING RATE IS',F10.4,///' EVERY  ',I2,' TH TGA DATA PO
                /INT IS USED FOR OPTIMIZATION',///' CONSTRAINT FLAG IS',I3,
                ///' FINAL CONVERSION IS',F6.1)
0035          6608 FORMAT(I2)
0036          6609 FORMAT(A4)
0037          6611 FORMAT(10F10.1)
0038          6615 FORMAT(///10X,' TAPE FILE CONTENTS')
0039          6616 FORMAT(///10X,' CORRECTED DATA')
0040          6619 FORMAT(/10X,' CORRECTED FINAL CONVERSION =',F5.1)
0041          6790 FORMAT(//5X,' OBJECTIVE FUNCTION=',E15.5)
0042          6800 FORMAT(//' MODEL RESULT USING OPTIMIZED PARAMETERS',////T2,' T',
                /T15,' TGA:W',T25,' CORR:W',T35,' TGA-CORR'I
0043          8003 FORMAT(/T2,F7.2,T15,F5.1,T25,F5.1,T35,E11.4)
0044          1250 N=0
0045               MZ=0
              C       SET EVALUATION COUNTER TO ZERO
0046               NN=1
0047               NE=0
0048               NOASE=0
              C       READ PROBLEM NUMBER,IF IT IS ZERO PROGRAM GOES TO STOP
0049               READ(5,108,END=101) NAME,TITLE
0050               IF(NAME.EQ.0)  GO TO  101
0051               PRINT 1002,NAME,TITLE
0052               READ(5,1019)TO,TF,NM,ASH,HR,       NCONST,TI
0053               READ(5,6608)NSKIP
0054               READ(9,6609)HEADER
0055               READ(9,6609)DEADER
0056               READ(9,1021)(TGA(K),K=1,NM)
0057               IF(NCONST.EQ.0)WRITE(6,1304)TO,TF,NM,ASH,HR,NSKIP,NCONST
0058               IF(NCONST.EC.0)GO TO 9000
0059               IF(NCONST.EQ.2.OR.NCONST.EQ.3)GO TO 9001
0060               WF=TGA(NM)
0061               IF(NCONST.EQ.1)WRITE(6,1305)TO,TF,NM,ASH,HR,NSKIP,NCONST,
                  /WF
                   GO TO 9000
0062          9001 IF(NCONST.EQ.3)GO TO 9002
0064               READ(5,1300)AKO
0065               IF(NCONST.EQ.2)WRITE(6,1303)TO,TF,NM,ASH,HR,NSKIP,NCONST,
                  /AKO
                   GO TO 9000
0067          9002 READ(5,1300)AKO
0068               WF=TGA(NM)
0069               IF(NCONST.EQ.3)WRITE(6,1302)TO,TF,NM,ASH,HR,NSKIP,NCONST,
                  /WF,AKO
0070          9000 CORREC=0.0
0071               IF(TGA(1).EQ.100.)GO TO 6613
0072               CORREC=100.-TGA(1)
0073          6613 DO 7000 I=1,NM
0074               TGC(I)=TGA(I)
0075               TGC(I)=TGA(I)+CORREC
0076               IF(TGC(I).GT.100.)TGC(I)=100.
0077          7000 CONTINUE
0078               IF(NCONST.EQ.1.OR.NCONST.EQ.3)WF=TGC(NM)
0079               IF(NCONST.EQ.1.OR.NCONST.EQ.3)PRINT 6619,WF
0080               DO 6614 II=1,NM
0081               TGA(II)=TGC(II)-TGC(NM)
0082          6614 CONTINUE
0083               OB=1.
```

```
FORTRAN IV G LEVEL  21                  MAIN                    DATE = 75125          10/22

0064                HR=HR/60.0
0065                TF=TF+273.
0066                READ 110,IPRINT
                C      NS = NUMBER OF STAGES
                C      ND = NUMBER OF DIMENSIONS
0067                READ 110,NS ,ND
                C      READ THE STARTING POINT,INITIAL STEP SIZE AND TERMINATING
                C      STEP SIZE
0068                READ (5,1022)(BASEN(I),I=1,ND),(DELTA(I),I=1,ND),(DEL(I),I=1,ND)
0069                PRINT 1001,NS,ND
0070                PRINT 1120,(DELTA(I),I=1,ND)
0071                PRINT 1121,                    (BASEN(I),I=1,ND)
                C      X = CURRENT VARIABLE VECTOR
                C      BASEN = CURRENT BASE POINT
                C      BASEO = LAST BASE POINT IN THE SEARCH
                C      FX = FUNCTION VALUE AT X
                C      FXBN = FUNCTIONAL VALUE AT CURRENT BASE POINT
                C      FXBO = FUNCTIONAL VALUE AT OLD BASE POINT
0072                PRINT 6615
0073                PRINT 6611,(TGR(I),I=1,NM)
0074                PRINT 6616
0075                PRINT 6611,(TGC(I),I=1,NM)
0076                FXBN = OBJECT(BASEN)
0077              1 DO 10 I=1,ND
0078             10 X(I) = BASEN(I)
0079                FX = FXBN
0100                IF(IPRINT.GE.1)    PRINT 1000,NN,(X  (I),I=1,NC),FX
                C      EXPLORATORY MOVES
0101                NBASE=NBASE+1
0102                CALL EXPLAV(FX,X)
0103                IF(IPRINT.GE.1)   PRINT 1010,NE, (X(I),I=1,ND),FX
0104                IF(IPRINT.EQ.2)                PRINT 1011,NBASE
0105                IF(FX.GE.FXBN)   GO TO 3
                C      SET NEW BASE POINT
0106              2 DO 20 I=1,ND
0107                BASEO(I) = BASEN(I)
0108                BASEN(I) = X(I)
0109             20 CONTINUE
0110                FXBN = FX
0111                NNB=NE
                C      PATTERN MOVE
0112                DO 21 I=1,ND
0113                X(I) = BASEN(I)*2.  -  BASEO(I)
0114             21 CONTINUE
0115                FX = OBJECT(X)
0116                IF(IPRINT.GE.1)   PRINT 1020,N,(X  (I),I=1,ND),FX
0117                IF(IPRINT.GE.1)   PRINT 1000,N,(X  (I),I=1,ND),FX
                C      EXPLORATORY MOVES
0118                NBASE=NBASE+1
0119                CALL EXPLAV(FX,X)
0120                IF(IPRINT.GE.1)      PRINT 1010,NE, (X(I),I=1,NC) ,FX
0121                IF(IPRINT.EQ.2)                PRINT 1011,NBASE
0122                IF(FX.LT.FXBN)  GO TO 2
0123                IF(IPRINT.GE.1)        PRINT 1200
                C      PATTERN MOVE HAS FAILED
0124                NN=NNB
0125                NBASE=NBASE-1
0126                GO TO 1
```

```
FORTRAN IV G LEVEL  21                  MAIN              DATE = 75125          10/28

0127            3 CONTINUE
0128              IF(IPRINT.GE.1)         PRINT 1201
                C        CHECKING OF THE CURRENT STEP SIZE
                C        IF IT IS SMALL ENOUGH  STOP
                C        IF IT IS LARGE REDUCE IT TO HALF AND GO BACK
0129              DO 30 I=1,ND
0130              IF(DELTA(I).GE.DEL(I))  GO TO 31
0131             30 CONTINUE
0132              GO TO 100
0133             31 DO 35 I=1,ND
0134              DELTA(I) = DELTA(I)*0.5
0135             35 CONTINUE
0136              IF(IPRINT.GE.1)         PRINT 1220,(DELTA(IS),IS=1,ND)
0137              GO TO 1
0138            100 PRINT 1130,FXBN,(BASEN(I),I=1,ND)
0139              PRINT 1221,(DELTA(IS),IS=1,ND)
0140              PRINT 1030,N
0141              PRINT 8000
0142              MZ=1
0143              AAA=OBJECT(BASEN)
0144              WRITE(6,6790)AAA
0145              GO TO 1250
0146            101 STOP
0147              END
```

```
FORTRAN IV G LEVEL  21                  EXPLMV          DATE = 79125          10/28

0001              SUBROUTINE EXPLMV (FX,X)
0002              COMMON NS,NO,DELTA(50),N,IPRINT,NE,NB,    NM,    T,BB,TGA(5501
0003              COMMON                              ASH,TI,HR,TC,TF
0004              COMMON NSKIP,NCONST,AF,AKC,MZ,SIG,EM
0005              DIMENSION X(50)
0006           100 FORMAT(' EXPLORATORY MOVE IN X(',I3,') DIRECTION',I3,5E18.4/
                 1(40X,5E18.4))
0007           101 FORMAT(1H )
0008              IF(IPRINT.EQ.2)     PRINT 101
0009              DO 201 I=1,NO
0010              X(I) = X(I) + DELTA(I)
0011              FXI = OBJECT(X)
0012              NE = N
0013              IF(IPRINT.EQ.2)     PRINT 100,I,N,(X(J),J=1,NO),FXI
0014              IF(FXI-FX)  200,180,180
0015           180 X(I) = X(I) - 2.*DELTA(I)
0016              FXI = OBJECT(X)
0017              NE = N
0018              IF(IPRINT.EQ.2)     PRINT 100,I,N,(X(J),J=1,NO),FXI
0019              IF(FXI-FX) 200,181,181
0020           181 X(I) = X(I) + DELTA(I)
0021              NE=N-2
0022              IF(IPRINT.EQ.2)     PRINT 100,I,NE,(X(J),J=1,NO),FX
0023              GO TO 202
0024           200 FX = FXI
0025           202 CONTINUE
0026           201 CONTINUE
0027              RETURN
0028              END
```

```
FORTRAN IV G LEVEL  21                  OBJECT              DATE = 79125          10/28

0001                FUNCTION OBJECT (PHI)
0002                DIMENSION  PHI(50)
0003                COMMON NS,ND,DELTA(50),N,IPRINT,NE,NB,    AM,    T,BB,TGA(550)
0004                COMMON                                ASM,TI,HR,TU,TF
0005                COMMON NSKIP,NCONST,WF,AKC,MZ,SIG,EM
0006          9005  FORMAT(/T2,F7.2,T15,F5.1,T25,F5.1,T35,E11.4)
0007                AC=(-1)**.0000035
0008                BC=.998971
0009                CC=1.9487646
0010                DC=4.9482092
0011                EC=11.7850792
0012                FC=20.4523840
0013                GC=21.1491469
0014                HC=9.5240410
0015                R=1.987
0016                N=N+1
0017                OBJECT=0
0018                IF(NCONST.EQ.1)GO TO 9005
0019                IF(NCONST.EQ.2)GO TO 9006
0020                IF(NCONST.EQ.3)GO TO 9007
0021                WF=PHI(1)
0022                EM=PHI(2)
0023                AKC=PHI(3)
0024                SIG=PHI(4)
0025                GO TO 9008
0026          9005  EM=PHI(1)
0027                AKC=PHI(2)
0028                SIG=PHI(3)
0029                GO TO 9008
0030          9006  WF=PHI(1)
0031                EM=PHI(2)
0032                SIG=PHI(3)
0033                GO TO 9008
0034          9007  EM=PHI(1)
0035                SIG=PHI(2)
0036          9008  CONTINUE
0037                NI=NM+1
0038                DO 1000 JNI=1,NI
0039                IF(JNI.EQ.1)BB=1.0
0040                T=TG+(JNI-1)*HR*TI*NSKIP+273.
0041                IF (T.GT.TF) GOTO 9012
0042                IF (BB.EQ.0.0) W=0
0043                IF (BB.EQ.0.0) GOTO 7777
0044                A=EM
0045                B=4*SIG
0046                C=.4840801*B
0047                W=.040637I9*(FUNC(A+C)+FUNC(A-C))
0048                C=.9180156*B
0049                W=W+.0903240B*(FUNC(A+C)+FUNC(A-C))
0050                C=.1300857*B
0051                W=W+.1303053*(FUNC(A+C)+FUNC(A-C))
0052                C=.1621267*B
0053                W=W+.1561735*(FUNC(A+C)+FUNC(A-C))
0054                W=B*(W+.1651197*FUNC(A))
0055                IF(W.LE..01)BB=0
0056          7777  JNO=(JNI-1)*NSKIP+1
0057                IF(MZ.EQ.0)GO TO 7779
0058                BBJECT=TGA(JNO)-W
```

```
FORTRAN IV G LEVEL  21                  OBJECT          DATE = 79125        10/28

0059                WRITE(6,8003)T,TGA(JNC),W,OBJECT
0060          7779  ABJECT=(TGA(JNO)-W )**2
0061                OBJECT=OBJECT+ABJECT
0062          1000  CONTINUE
0063          9012  RETURN
0064                END
```

```
FORTRAN IV G LEVEL  21                  FUNC                    DATE = 75125          10/28

0001                FUNCTION FUNC(E)
0002                COMMON NS,NO,DELTA(50),N,IPRINT,NE,NB,    AM,    T,BB,TGA(550)
0003                COMMON                          ASH,TI,HR,TO,TF
0004                COMMON NSKIP,NCONST,WF,AKC,MZ,SIG,EM
0005                AC=(-1)*.0000035
0006                BC=.956971
0007                CC=1.94R7646
0008                DC=4.9482092
0009                EC=-11.785C792
0010                FC=20.4523840
0011                GC=21.1491409
0012                HC=9.5240410
0013                R=1.987
0014                RHO=(100-WF)/SIG/(2*3.14159)**.5
0015                X=(-1)*E/R/T
0016                P=EXP(X)/X*(AC+BC/X+CC/X**2+DC/X**3+EC/X**4+FC/X**5+GC/X**6+HC/
                   /X**7)
0017                V=AKC*E/HR/R*P+(1-EM)**2/2./SIG**2
0018                IF(V.GE.100.)GO TO 7000
0019                FUNC=RHO*EXP((-1)*AKC*E/HR/R*P-(E-EM)**2/2./SIG**2)
0020                GO TO 7001
0021           7000 FUNC=0.
0022           7001 RETURN
0023                END
```

APPENDIX B

BENCH SCALE FLUID BED REACTOR

The fluidized bed reactor used in this work was designed to study endothermic reactions at atmospheric pressure and in a temperature range from ambient to 1200°C. Due to the size of the fluidized bed, the effect of the internals (feedpipe, overflow pipe, pressure probe, and thermocouple) was to break the bubbles which were formed at the distributor plate. Since the internals occupied less than 12% of the cross sectional area of the bed, they did not overly affect solid movement within the bed.

The reactor system consists of three primary sections; the reactor section, the gas clean up system, and the gas sampling and analysis section (Fig. 1).

Figure 2 shows the fluidized bed reactor section. This section consists of four zones; the disengaging zone, fluidized bed, packed bed, and gas inlet zone. The reactor was constructed of Inconel 600 alloy due to its temperature resistance and capability to withstand rapid heating and cooling. Flanges, flange bolts, nuts and washers were also made of Inconel 600. Graphite gaskets were used at the flange connections. Except for the disengaging zone, the reactor was constructed of two inch (5.08 cm) schedule 40 pipe. The disengaging zone was a four inch (10.16 cm) schedule 40 pipe whose wall thickness had been reduced to be the same as that of the two inch section. The flaired connection between the fluid bed zone and the disengaging zone was 18-gage Inconel sheet metal. Top and bottom plates were made of 1/8 inch (0.32 cm) Inconel plate metal.

The inlet section was 7.62 cm in height and allowed the fluidization gas to uniformly enter the packed bed zone. This section contained a

thermocouple and pressure tap so that the entering gas conditions could be monitored. A 60 mesh screen made of 316 stainless steel separated the inlet section from the packed bed zone. The packed bed zone was packed with five millimeter aluminum oxide balls, was 15.24 cm in height, and served as both a gas distributor and gas preheater. The packed bed was separated from the fluidized bed by another 60 mesh stainless steel screen, which both contained the packed bed and prohibited the filtering of the fluid bed into the packing. The fluidized bed zone was 20.32 cm in height, which together with the 15.24 cm disengaging zone brought the overall height of the reactor to 58.42 cm. The reactor was externally heated by four pairs of semi-cylindrical electrical resistance heaters. Each pair delivered up to 2300 watts of power with a maximum sustained operating temperature of 1200°C.

All reactor internals entered the bed through either the top or bottom plates. The overflow pipe extended from the fluidized bed, through the packed bed and inlet section, and exited through the reactor bottom plate.

Reactant was introduced to the reactor via gravity feeding. The reactant was transported to the feed pipe using a Vibra Screw Model SCR-20 screw feeder. The feeder was equipped with a one cubic foot (0.028317 m^3) conical hopper, a 3/8 inch (1 cm) solid core flight screw, and a variable speed screw drive capable of volumetric flows up to 0.1 cubic feet (0.0028317 m^3) per hour. The screw drive was designed with a closed loop feedback system, which immediately compensated for any variations between actual speed and the set point. A helium purge was introduced at the top of the feed pipe to prevent hot reactor gases from traveling up the feed pipe and prematurely decomposing the feed. The reactor was equipped with a

dual pressure probe, which allowed both bed pressure and pressure drop across the bed to be monitored. The fluid bed temperature indicator used was a chromel-alumel thermocouple with a 1/8 inch (0.32 cm) Inconel sheath.

Gas exiting from the reactor passed through a ½ inch (1.27 cm) stainless steel tube to the cyclone. Using tangential entry, this device removed fine solid particles from the gas stream. The cyclone was maintained at approximately 500°C to prevent condensation of tar and water vapor. After leaving the cyclone, the gas was cooled to 50°C by two counter current, water cooled, shell and tube heat exchangers. A flask at the end of these exchangers collected water condensate and water soluble materials. Further cleaning was done by means of a dry scrubber packed with glass wool. This device proved to be extremely effective in removing the fine condensible mist traveling with the gas, with very little pressure drop. Before sampling, moisture was removed by passing the gas through a $CaSO_4$ packed tube. Gas samples were then collected in 250 ml sampling bottles, and the remainder of the gas was vented.

Auxiliary equipment included a steam generator for experiments involving steam gasification, and facilities needed for introduction of a tracer gas for the determination of product gas flow rates. For steam gasification, the trace gas used was nitrogen, which was added to the flow stream just before the sampling point. Using a wet test meter, the volumetric flow rate of nitrogen was known precisely. From gas analysis, the concentration of nitrogen in the product gas allowed computation of the rate of product gas generation.

The reactor system described above was the result of many modifications to the original design. As experience was obtained in construction and operation, originally conceived materials and configurations often gave

way to alternatives. For example, the packing material used in the packed bed zone had to be totally inert in a steam atmosphere and temperatures up to 1200°C. It also needed to have a high heat capacity, high physical strength, and good gas distribution capabilities, without having an excessive heatup time or a large pressure drop. The three materials considered included the aluminum oxide pellets, quartz wool, and Inconel metal shavings. Inconel was not used due to its poor gas distribution capabilities. Quartz wool tended to layer and slump, promoting gas channeling and hence uneven fluidization. Aluminum oxide pellets were used since this material was compatible with all of the operational requirements.

A stainless steel screen was used to separate the packed bed from the fluidized bed. It was found that anchoring the screen in the flange located at this position caused the screen to tear and breakup due to its expansion during heating. In addition, it was almost impossible to prevent gas leakage through the flange regardless of the gasket material employed. To avoid these, the screen was designed in the form of an inverted cup. This allowed free expansion of the screen during heating and eliminated the observed leakage through the flange. The cup was prevented from vertical movement by the packed bed below and from above by a stainless steel disk held by the reactor flanges. This stainless steel disk had an inside diameter which was slightly less than that of the reactor (Fig. 2).

In order to maintain proper fluidization, it was found to be critical that there be no gas leakage through the flange at the position of the distributor screen. It was observed that these leaks created dead zones in the fluid bed and increased the chance for agglomeration. During normal steady state operation, the temperature in the space between the reactor and the surrounding furnaces was typically 50°C to 100°C above that inside the

reactor. While the reactor operated in a reducing atmosphere, the exterior of the reactor, as well as, the flange gaskets were exposed to air. Under these conditions, it was found that most common gasket materials could not survive. The gasket material used was essentially pure graphite, which was rated to withstand temperatures up to 1650°C in a non-oxidative environment. To protect the graphite from oxidation, a high temperature coating, specifically designed for this type of application, was used.

Using a fluidization velccity which was 20 to 30 times the minimum needed to achieve fluidization, and feeding a mixture of silica sand and coal, agglomeration of the fluid bed was rarely experienced. More commonly, agglomeration would occur either in the feed pipe or in the reactor section above the fluid bed. Feed pipe clogs were attributed to the caking nature of the feed material, and it was therefore necessary to keep this material cool as it passed through the feed pipe. This was accomplished by jacketing the feed pipe and pumping water to the base of the jacket, where the water would become steam and pass back up the jacket, carrying with it the latent heat of water vaporization. Experiments showed that this technique, using a cooling water flow rate of 150 cc/min, was able to keep the hottest poiut in the feed pipe below 300°C with the fluid bed operating at 1000°C. Two other factors were found to influence the tendency to form feed pipe clogs; feed pipe position in the fluid bed, and vibration of the feed pipe. Once a clog had developed in the feed pipe, it was found that by taping the pipe, the clog could be dislodged without disruption of the experimental run. By mounting a low amplitude, high frequency vibrator directly on the feed pipe, the frequency at which clogs developed dramatically decreased. Even though a fluidized bed of this size is normally assumed to be essentially

a completely stirred tank reactor, the solid-gas ratio is still higher at the distributor plate that at the bed surface. This explains the observation that uninterrupted feeding was easier to obtain when feeding was attempted at greater distances from the distributor plate. However, when feeding took place over the expanded fluid bed, the tendency was for the reactant to cake on the sides of the reactor above the bed. The optimum feeding point in order to prevent both feed pipe and reactor clogs was determined to be slightly below the level of the expanded fluid bed, as was determined by the height of the overflow pipe.

Use of the methods described above, which were necessary in order to permit continuous operation using a caking coal, created difficulties in the collection and analysis of the gasification products. Most of these problems resulted from the necessity of having low feed rates of reactable material, and high fluidization velocities. Typically, total feed rates ranged from six to ten grams per minute. However, as much as 90% of the feed material was inert sand and only the remaining 10% was reactant. Reactor overflow was normally over 95% inert, which made the elemental analysis for C, H, N, O, and S extremely difficult. In attempts to pyrolyze coal in an inert gaseous environment, the gas samples usually contained over 95% inert gas. In steam gasification, however, it was possible to completely remove the fluidizing steam before samples were drawn for analysis.

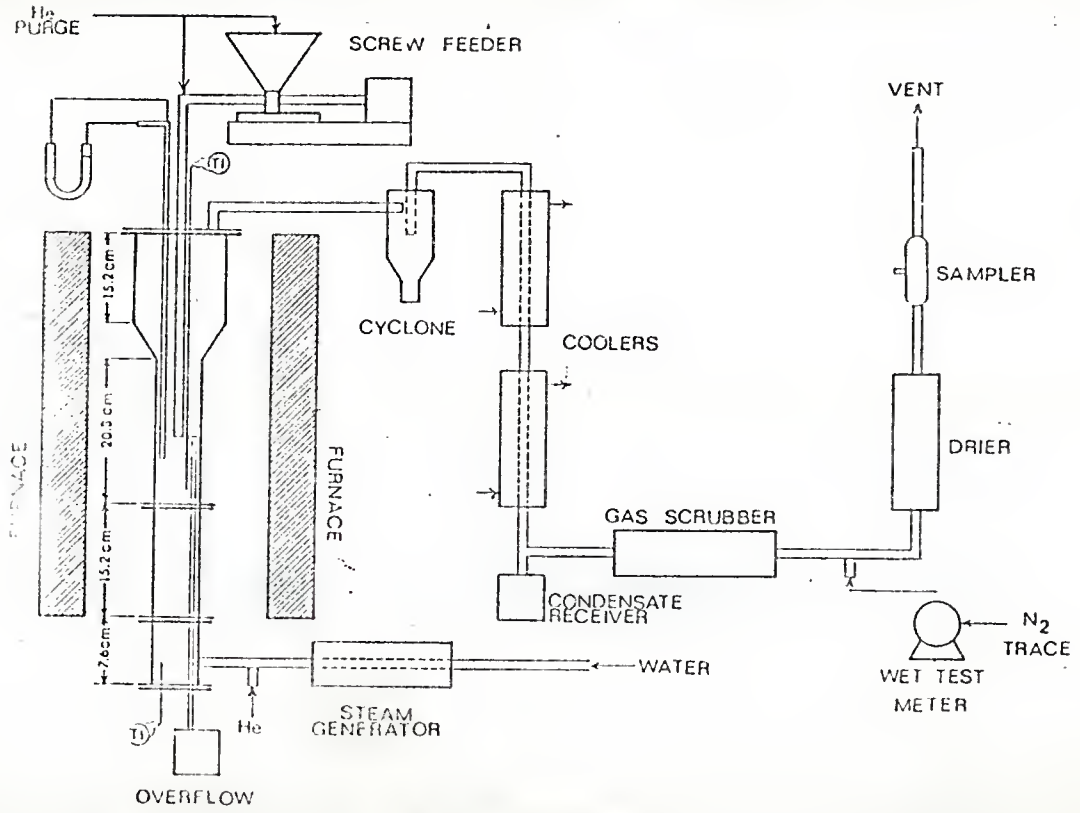

Fig. 1 Bench Scale Reactor

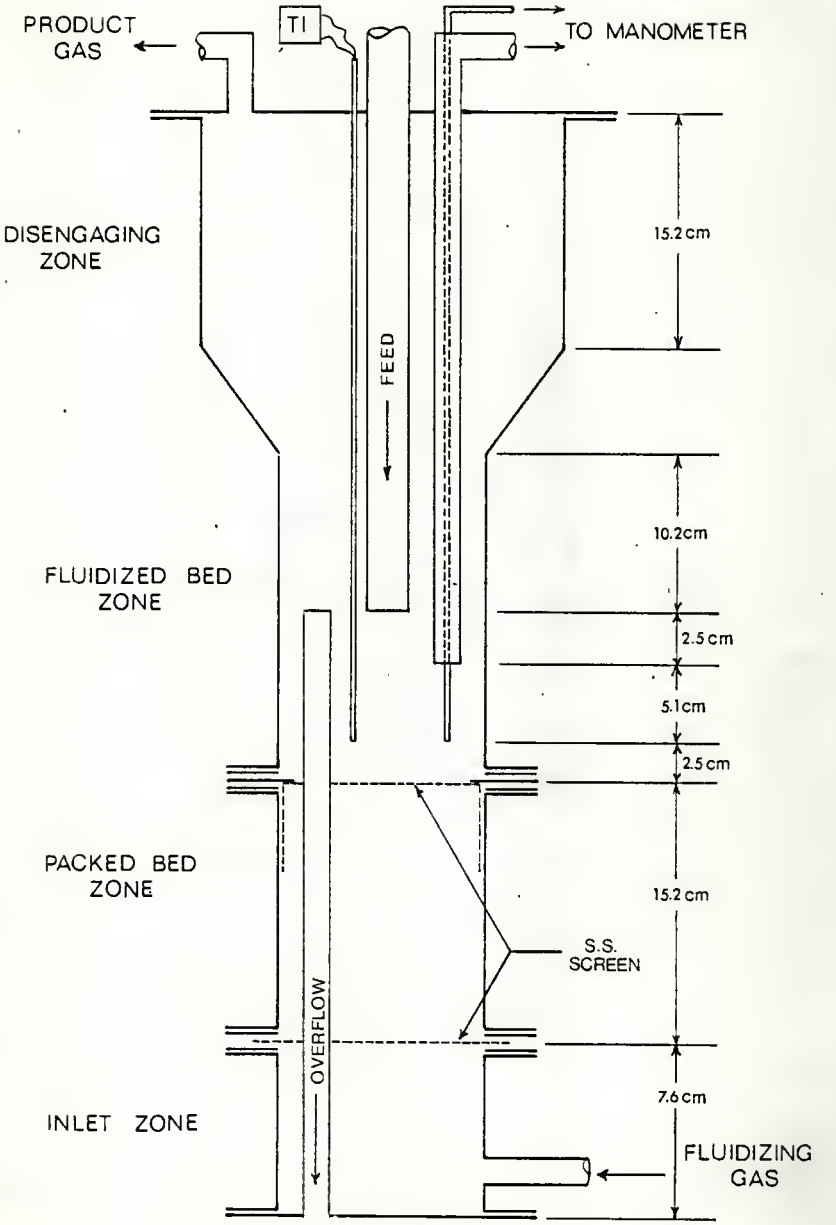

Fig. 2 Fluid Bed Reactor Section

APPENDIX C

CHEMICAL ANALYSIS

Gas analysis was accomplished using an off line, dual column, Packard Model 417 Becker Gas Chromatograph with thermoconductivity 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, H_2S, and N_2. To perform this analysis, the column packings used were a 5A molecular sieve for the separation of H_2, N_2, CO, and CH_4, and a mixture of Porapak Q and Porapak R for the separation of CO_2, C_2H_4, C_2H_6, C_3H_6, C_3H_8, and H_2S. The instrument was operated isothermally at 80°C with helium as a carrier gas. Accessories used in the gas analysis included a Spectra-Physics Autolab System I computing integrator, and a Varian Model A-25 strip chart recorder.

Calibration was accomplished using a standard gas mixture of the above components with a certified composition. Mixture No. 1 contained 1% C_3H_8, 1% C_3H_6, 1.99% C_2H_6, 2.99% C_2H_4, 4.07% CH_4, 7.99% CO, 18.02% CO_2, and the balance N_2. The second calibration mixture contained 5.95% H_2, 1.07% H_2S, and the balance was N_2. Calibration factors (K_f) relating peak areas to concentrations for each of the above mentioned components were determined by first injecting the No. 1 mixture into the molecular sieve column. Nitrogen was chosen as the reference gas and given an arbitrary calibration factor, $(K_f)_{ref}$, of 1000. Based on this, the K_f values of CO and CH_4 were calculated by the equation

$$(K_f)_i = (K_f)_{ref} \times \frac{(conc)_i}{(conc)_{ref}} \times \frac{(Area)_{ref}}{(Area)_i} \qquad i = 1, \ldots, 4 \qquad (1)$$

The No. 2 calibration mixture was then injected into the molecular sieve column to determine the calibration factor for H_2. The four components which were separated by the molecular sieve, appeared as a single broad peak when

the calibration mixtures were injected into the Porapak column. As in the case of nitrogen in the molecular sieve column, this broad peak was assigned a calibration factor, $(K_f)_{mix}$, of 1000 in the Porapak column. The K_f values for the components separated by the Porapak column were then calculated by the equation

$$(K_f)_i = (K_f)_{mix} \times \frac{(conc)_i}{(conc)_{mix}} \times \frac{(Area)_{mix}}{(Area)_i} \quad i = 1, \ldots, 6 \qquad (2)$$

In the analysis mode, the concentrations of the four components separated by the molecular sieve were calculated by the equation

$$(conc)_i = [(K_f)_i \times (Area)_i] \; / \; [\sum_{i=1}^{4} (K_f)_i \times (Area)_i] \times 100$$

$$i = 1, \ldots, 4 \qquad (3)$$

The same equation was used for the six components separated by the Porapak column. However in this case the summation in the denominator of eq. (3) was over seven components. The seventh peak being that of the four components determined by the molecular sieve. The calibration factor for this peak was no longer taken to be 1000, but rather was calculated by the equation

$$(K_f)_{mix} = [\sum_{i=1}^{4} (K_f)_i \times (Area)_i] \; / \; [\sum_{i=1}^{4} (Area)_i] \qquad (4)$$

Solid materials were analyzed with respect to both their elemental composition and their proximate analysis using a Perkin-Elmer Model 240 Elemental Analyzer and a Perkin-Elmer Model TGS-2 Thermogravimetric Analyzer, respectively.

The Perkin-Elmer Model 240 Elemental Analyzer is an extremely accurate instrument for determining the C, H, N, O, and S concentrations in a solid or liquid sample. The instrument can operate in three modes depending on

the elements to be analyzed. In the first mode, for C, H, and N analysis, the sample is completely combusted at 1000°C to CO_2, H_2O, and N_2 in an excess of O_2, with He as a carrier gas. After removing excess oxides, the gas is analyzed for the above compounds by thermoconductivity detectors. First, the conductivity of the mixture is measured before and after passing through a column of magnesium perchlorate, which removes any water present. The change in conductivity is proportional to the H_2O removed. Similarly, the remaining gas is monitored before and after passing through a column of Ascarite (a sodium hydrate-asbestos absorbent) which removes any CO_2 present. The change in conductivity after this treatment is proportional to the amount of CO_2 which was removed. The conductivity of the remaining gas is compared to the thermoconductivity of a stream of pure helium. The difference observed is proportional to the amount of nitrogen in the mixture.

For sulfur analysis, the sample is again combusted at 1000°C over tungstic oxide which acts as an oxygen donor. Sulfur dioxide and other gases are passed through calcium chloride, 8-hydroxyquinoline, and free copper to remove water, halogens, and oxygen. The thermal conductivity of the gas is then measured before and after the SO_2 is selectively absorbed by silver oxide at 250°C.

The third mode of operation is the determination of oxygen content. Here, the sample is pyrolyzed (in the absence of oxygen) at 1000°C, over platinized carbon, where oxygen is converted to carbon monoxide. The carbon monoxide and other gases pass through free carbon at 900°C and through a column of Ascarite where any acid gases are removed. The gases then move through copper oxide at 670°C where the carbon monoxide is further oxidized to carbon dioxide. After any basic gases are removed in the water trap (magnesium perhlorate), the carbon dioxide is determined in the same manner as in the CHN analysis mode.

The Model 240 Elemental Analyzer uses sample sizes between one and three milligrams. To obtain reproducible results, a weighing device capable of measuring to the nearest microgram was recommended. For this purpose a Perkin-Elmer Model AD-2Z microbalance was used. Accuracies obtainable using the elemental analyzer and microbalance combination should be within 0.5%. However, due to the heterogeneous nature of coal and feedlot manure, it was difficult to draw a one milligram sample which was representative of the entire bulk. Therefore at least three samples were analyzed and the results averaged.

NOTATION

Area = Area of chromatograph peak

conc = Concentration of gas component, molar %

K_f = Calibration factor

Subscripts

i = i-th gas component

ref = Reference component

mix = Mixture of H_2, CO, CH_4, N_2

ACKNOWLEDGMENT

I would like to thank my advisors Prof. W. P. Walawender and Prof. L. T. Fan for their support and guidance in this work. I would also like to thank Mr. S. Ganesan, Mr. K. P. Raman, and Ms. T. L. Howell for their help in the experimentation. Appreciation is expressed to the Engineering Experimental Station, Kansas State University, for their financial support under Grant No. 52460-0607 (Energy Study Project).

KANSAS COAL GASIFICATION

by

JERALD A. HOWELL

B.S., Kansas State University, 1977

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

A study was undertaken to investigate the generation of fuel gas by the gasification of high sulfur, caking coal and feedlot manure native to the state of Kansas. A High Volatile C Bituminous coal from the Rowe coal bed in southeast Kansas was used along with a feedlot manure obtained from the Kansas State University Beef Cattle Research Center.

A fundamental study of the devolatilization of coal was performed using thermogravimetric analysis. Results showed devolatilization, in an inert environment, at atmospheric pressure, to occur in the temperature region between 450°C and 650°C. Kinetic modeling of the devolatilization, using a multireaction model, resulted in a mean activation energy of 36.87 kcal/mole. This value is in the region expected for coal devolatilization, and compared well with values obtained by other investigators using rapid heating techniques. The model parameters were statistically examined and found to be influenced by the experimental conditions employed. However, no single experimental variable was found to affect all of the model parameters.

Kansas coal was steam gasified at atmospheric pressure in the temperature range between 700°C and 1100°C in a bench scale fluid bed reactor composed primarily of sand. Using a feedstock which consisted of 90% sand and 10% coal, and using a superficial velocity of 36.7 cm/sec, it was found that the caking tendency of this coal could be eliminated. Heating values of the gaseous product ranged from 18 MJ/Nm^3 (486 Btu/scf) at 700°C to 11.9 MJ/Nm^3 (319 Btu/scf) at 1100°C. Yields were 0.221 Nm^3/kg (3.1 scf/lb) at 700°C and 0.99 Nm^3/kg (15.9 scf/lb) at 1100°C. Hydrogen sulfide content in the product gas ranged from 2.5% at 700°C to 1.0% at 1100°C.

To reduce sulfur content and obtain increased gas yield per unit mass of feed, an equal weight ratio of coal and feedlot manure was gasified in

a bench scale fluidized bed reactor composed primarily of sand. Results showed the H_2S concentration in the product gas to be reduced by 50%. Heating values of the product gas were 16.1 MJ/Nm^3 (431.5 Btu/scf) at 700°C and 12.86 MJ/Nm^3 (345.2 Btu/scf) at 1100°C. Yields ranged from 0.29 Nm^3/kg (4.66 scf/lb) at 700°C to 1.03 Nm^3/kg (16.47 scf/lb) at 1100°C. Results indicated the product from the gasification of the coal-manure blend was essentially the average of the products resulting from the individual components.