Spring 1993

Rapid hydropyrolysis of coals for production of liquid hydrocarbons

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Recommended Citation

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Order Number 9400396

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Mohamed, Abdul Rahman, Ph.D.

University of New Hampshire, 1993

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RAPID HYDROPYROLYSIS OF COALS FOR PRODUCTION OF LIQUID HYDROCARBONS

BY

ABDUL RAHMAN MOHAMED

B.S., University of Southern California, 1986
M.S., University of New Hampshire, 1989

DISSERTATION

Submitted to the University of New Hampshire
in Partial Fulfillment of
the Requirement for the Degree of

Doctor of Philosophy

in

Engineering

May, 1993

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Date

Dedicated to my wife, Roslina and my daughter, Nabilah

ACKNOWLEDGEMENT

I am extremely grateful to my dissertation director, Professor V.K. Mathur for his valuable guidance and encouragement in directing the work that is presented in this dissertation. I am very fortunate to have had the benefit of his experience and confidence.

I thank my dissertation committee members, Professors Stephen S.T. Fan, Russell T. Carr, Palligarnai T. Vasudevan of the Chemical Engineering Department, Sterling A. Tomellini of the Chemistry Department and Dr. Gregory C. Glatzmaier of National Renewable Energy Laboratory, CO for examining this dissertation.

Mr. Jonathan Newell deserves a special appreciation for assisting in solving many mechanical problems I encountered from time to time.

I would also like to thank Chris McLarnon, Mohd Salahuddin, and others who have contributed to the successful completion of this study.

ABDUL RAHMAN MOHAMED

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ABSTRACT

RAPID HYDROPYROLYSIS OF COALS FOR PRODUCTION OF LIQUID HYDROCARBONS

by

ABDUL RAHMAN MOHAMED
University of New Hampshire, May, 1993

Production of fuels and chemicals from coal is becoming attractive due to potential high cost and uncertain supply of crude petroleum oil. Conventional techniques of coal liquefaction, though technically feasible, have been expensive due to hydrogen requirements, high pressure equipment, and high cost of commercial supported catalysts.

In this study, a novel technique for rapid hydropyrolysis of bituminous, subbituminous, and lignite coals has been investigated. Rapid hydropyrolysis is the process of heating at a fast rate to high temperature in a hydrogen environment. A coal sample in hydrogen atmosphere is targeted, in the absence of a catalyst, with a high intensity xenon light beam. A shuttering mechanism is incorporated to expose the coal sample only for a few seconds at a time. This technique provides the best of several processes: high heating rate of the coal sample to achieve a high carbon conversion, and control of secondary reactions via low ambient hydrogen gas temperature to potentially achieve high yields of liquid hydrocarbons. This technique also provides an effective economic alternative to the use of expensive commercial catalysts for the conventional coal liquefaction process. The operating parameters studied were exposure time, peak temperature, particle size, gaseous atmosphere, and coal rank.

The most suitable conditions for the rapid hydropyrolysis of coals were found to be 30 seconds exposure time, 900 °C peak temperature, 63 to 74 micrometer particle size, and in hydrogen atmosphere (1 atm). The total amount of coal converted to liquid

and gaseous products for bituminous coal was found to be 38.5% and decreased to 33.6% for subbituminous coal and to 32.2% for lignite. The amount of liquid hydrocarbons produced were 16.3%, 8.8%, and 3.5% for bituminous, subbituminous, and lignite coal, respectively.

In this process, a radiative heat source is used. The rapid hydropyrolysis method used in this study has several advantages over the coal liquefaction processes. It is conducted at atmospheric pressure, at a relatively shorter exposure time (less than one minute), and in the absence of a catalyst.

CHAPTER I

INTRODUCTION

The consumption of natural gas and petroleum as the source of energy in the United States has steadily increased after a brief decline resulting from measures taken after the oil crisis in the 1970s. The projected United State consumption for petroleum in 1995 is expected to be about 16.7 million barrels per day while the projected total domestic production of petroleum for 1995 is estimated to be only about 7.8 million barrels per day. This gap is expected to increase by more than ten million barrels per day by the year 2000 (Ashby, 1988). It is also likely that new energy crises would occur from time to time in the near future since most of the oil supply and its price are controlled by the country-members of OPEC. The United States will only feel safe and secure when it will be able to rely on its own energy sources.

The best way to overcome this problem is through conservation. The increase in the domestic production of petroleum will also help to reduce the dependency on foreign oil import. Another alternative is to utilize coal as a source of energy which is readily available in the United States. Coal is the most abundant source of fossil fuel energy in the United States and widely distributed. The demonstrated coal reserves in the United States are estimated to be about 490 billion tons which comprise coals in the ground considered suitable for mining with the present day technology. At the present rate of annual consumption of about 890 million tons per year, the United States has enough coal to last for several centuries (Longwell, 1990; EIA, 1991).

Currently, coal is used to generate almost half of the electric energy in the United States. However, the use of coal presents several drawbacks. Coal is difficult to mine, expensive to transport, and heavily polluting. The pollution is mainly due to the presence of mineral matter (ash), sulfur, and other impurities that limit its usefulness as a fuel. A serious drawback in the direct combustion of coal is the emissions of sulfur dioxide, nitrogen oxides, carbon dioxide, and fly ash which have serious adverse effects on both human and animal life. Therefore, combustion of coal requires the use of special equipment to reduce the emissions which increase the cost of utilizing coal as a fuel.

The solution to these problems is the conversion of coal at a reasonable cost into a clean and easily transportable form of fuel. The conversion of coal can be achieved by either the gasification or the liquefaction of coal. Coal gasification involves the conversion of coal to a mixture of carbon monoxide and hydrogen (synthesis gas) which then is passed over a catalyst to produce methane rich pipeline gas. There are a number of coal gasification processes in commercial use or in various stages of development for the production of synthesis gas in the U.S. and elsewhere in the world. These include the Lurgi, Koppers-Totzek, Winkler, and Texaco process (Hebden et al., 1981). However, there are problems with the gasification process. The reaction to produce methane from carbon monoxide and hydrogen requires nickel base catalysts which can be poisoned by various chemicals, especially sulfur. Therefore, rigorous purification is required. The catalyst can also be overheated due to the large exothermic heat release.

The ratio of hydrogen to carbon in coal is much lower compared to high heating value fuels such as gasoline. The ratio of hydrogen to carbon in coal varies from 0.3 for anthracite to about 0.9 for bituminous coal. On the other hand, the hydrogen to carbon ratio in gasoline is about 2.0 to 2.2 (Howard, 1981). Therefore, the basic concept of coal liquefaction is to add hydrogen to the coal molecule. Coal liquefaction has the potential for providing low-ash and low-sulfur products, ranging from heavy fuel to middle and light distillates. The liquefaction of coal also has several advantages over coal gasification which include: i) liquid fuel is easily storable, ii) liquid fuel is a more concentrated form of energy, iii) physical conditions for coal liquefaction are relatively milder compared to the severe operating conditions for gasification, iv) coal liquefaction requires much less chemical transformation and hydrogenation. Bituminous coal only goes from $CH_{0.9}$ to about $CH_{1.3}$ in becoming a liquid but must go all the way to CH_4 for high heating value pipeline gas. Therefore, the production of oil should be less expensive than the production of methane.

Liquid fuels and chemicals can be produced from coal by indirect coal liquefaction process. In this technique coal is first reacted with steam and gasified to produce carbon monoxide and hydrogen as in the gasification process. The carbon monoxide and hydrogen produced is then converted to liquid hydrocarbons by Fisher-Tropsch synthesis. Iron catalyst is generally used for the synthesis and the operating pressure is about 300 psig (20 atm). One of the commercial process that utilizes this technique is SASOL which is currently operating in South Africa.

There are a number of processes that have been developed for coal direct liquefaction. One of these processes is called the 'H-Coal' process. In this process hydrogen is added directly to the coal at high temperature and pressure in the presence of a catalyst to produce liquid hydrocarbons. The typical operating conditions for this process are: pressures of 20 to 24 MPa (197 to 237 atm) and temperatures of about 450 °C. Cobalt / molybdenum on alumina is normally used as a catalyst for the process (Hessley et al., 1986).

There are several problems associated with the production of liquid fuels from coal via the direct coal liquefaction process. Cobalt / molybdenum catalysts are effective for the process but expensive. The high cost of hydrogen and high pressure equipment also make the process less attractive economically compared to crude petroleum. The estimated cost for producing liquid fuels from coal is in the range of $30 to $40 per barrel (Longwell, 1990).

Possible solutions to the catalysts deactivation problems are either to develop new commercial catalysts not easily poisoned or to find low cost disposable catalysts. Mathur et al. (1982) investigated the effects of several mineral ores and ore concentrates as disposable catalyst in coal liquefaction. They reported that ores containing metals such as cobalt, molybdenum and nickel were catalytically active for the liquefaction of coal, with molybdenum oxide showing the best results.

Carbonization is another process of converting coal to valuable products. Carbonization is a process in which coal is heated in a large oven at a slow rate at a high temperature to produce metallurgical coke. The oven temperature typically ranges from

500 to as high as 1000 °C and the carbonization time can vary from several hours up to several days. Therefore, the temperature increase within the fresh coal is very slow and as a result the coal carbon matrix is not changed. The yield of liquid hydrocarbons was reported to be very little. The product distribution of liquid product collected from a carbonization process is also mostly made of high boiling point hydrocarbons.

A number of studies have been conducted to investigate rapid pyrolysis and hydropyrolysis of coal for the production of liquid hydrocarbons. Rapid hydropyrolysis is the process of heating coal at a fast rate to high temperature in a short period of time in an hydrogen environment. The heating rate is much higher as compared to the heating rate in a carbonization process. Both rapid pyrolysis and hydropyrolysis are generally operated at conditions of high temperature, high heating rate, short period of heating time, low pressure, and without the use of catalysts. Various heating techniques have been used in the rapid coal pyrolysis and hydropyrolysis studies. These include laser beam, electrical wire grid, hydrogen explosion, and electrical tube furnace. Most of the products from coal pyrolysis using a laser beam were solids and gases and no liquid hydrocarbons were produced. Other heating methods such as the heating wire grid and tube furnace gave a reasonable amount of liquid hydrocarbons from coal. However, none of these heat sources are commercially viable.

In this study, both the rapid hydropyrolysis and pyrolysis of coals, namely bituminous, subbituminous, and lignite coals using a novel concentrated light beam has been investigated. This heating method is unique in the sense that the coal particles are heated radiatively by a concentrated light beam as opposed to the conventional heating methods. The beam is targeted on a coal sample in the presence of hydrogen (hydropyrolysis) or helium (pyrolysis). The effect of this rapid heating on hydropyrolysis of coals has been investigated with particular reference to coal exposure time, peak temperature, coal particle size, and reaction atmosphere. In addition, mathematical correlations have been proposed for predicting the total coal conversion, liquid hydrocarbons and gaseous yields. A comparative analysis of this process against other liquefaction techniques has also been made.

For the purpose of this study an electrical xenon lamp with the capability of generating high heat flux is used to generate the radiative concentrated light beam. However, the use of concentrated radiation generated by either a solar beam or emitter burner is suggested for commercial scale operation. These novel heat sources will make the rapid hydropyrolysis process more commercially viable as a coal liquefaction process.

CHAPTER II

LITERATURE REVIEW

All coals contain some volatile matter as measured by a standard ASTM test. The amount of volatiles is strongly dependent upon the type and origin of the coal, with the amount of volatiles being as much as about 50% (weight) for a high volatile bituminous coal. When heated slowly (low heating rates), the volatile components of the coal are released as gases, liquids, and tars, leaving behind a carbon-ash matrix. This process has been employed in the manufacturing of metallurgical coke for many years. The carbon matrix that is left behind can also be gasified with steam and oxygen to produce hydrogen and carbonaceous gases. Gasification is an expensive process, even if the gases are purified and converted to high-value hydrocarbon liquids. However, the evolution of volatiles such as gases, liquids and tars is not limited to low heating rates only. High heating rate experiments, on the order of 50 to 10^6 °C / second have also been conducted. The volatile yields from these experiments are found to be higher than those at low heating rates.

Pyrolysis is the process of rapidly heating coal in an inert environment. When coal is rapidly heated in a hydrogen atmosphere the process is known as hydropyrolysis. Both the pyrolysis and hydropyrolysis processes can produce a wide range of products depending on the reaction conditions. The products can range from gases rich with methane and higher hydrocarbons, to liquids with significant amounts of benzene, toluene, and xylene (BTX), to heavy tars. Since the reaction conditions can be varied to obtain different product yields, the study of coal pyrolysis and hydropyrolysis is very important in coal conversion and utilization technologies. These processes are also considered to be inexpensive coal liquefaction processes, because they are carried out at low pressure and without catalyst consumption. Several heating methods have been utilized in conducting pyrolysis and hydropyrolysis studies. These methods include laser, electric current, entraining gas, and several other techniques.

Karn et al. (1967) have listed the advantages of lasers over other techniques for studies of high temperature coal pyrolysis and hydropyrolysis. The advantages are :

i) The energy can be focused and directed on specific areas.

ii) Heating is done by an external source without sample or product contamination.

iii) Rapid heating of the coal sample and cooling of gaseous products are possible.

Karn et al. (1967) conducted a series of rapid coal pyrolysis experiments using laser energy as the heating source. Coals of various ranks were pyrolyzed by the laser energy pulses. Samples (3/8 in. cubes) were sealed in Pyrex tubes 10 mm i.d. and 90 mm long. Five pulses of 1.5 joule of focused laser energy were irradiated on each coal sample. Gaseous products were analyzed by mass spectrometry. No liquid products were detected. A carbonaceous residue deposited on the wall of the glass tube during irradiation was examined by infrared spectroscopy. Results from experiments showed that the gaseous products were richer in hydrogen (lower carbon-to-hydrogen ratio) than their parent coals. The total gas increased as coal rank decreased, showing about a four-fold increase from anthracite to lignite. Yields of acetylene, hydrogen, carbon monoxide, and carbon dioxide generally increased between anthracite and lignite.

Shultz and Sharkey (1967) conducted a coal pyrolysis study using a ruby red laser for the laser tests. The ruby crystal had an output of 1.5 joule at 694.3 nanometer. Five pulses of energy of 1 millisecond duration were focused on 3/8 in. cubes of high volatile bituminous Pittsburgh coal. The effect of various surrounding atmospheres on the distribution of gaseous products from the laser irradiation of bituminous coal was studied. Gaseous products were analyzed by mass spectrometry. About 26 weight percent of the gas produced from coal under vacuum conditions was acetylene. The presence of argon and nitrogen were the only gases which increased the acetylene content. At pressures of 80 to 400 torr of argon and nitrogen, the acetylene content almost doubled compared with the sample irradiated under vacuum conditions. No liquid products were reported. These results indicated that the product distribution was caused by secondary reactions of the primary volatile matter in both the gas and solid phases.

Karn et al. (1969) conducted another coal pyrolysis study using laser irradiation. The effect of coal rank, coal macerals, particle size, type of laser, and temperature on product gases of coal pyrolysis were studied. Their results indicated that coal irradiated with laser light can produce gases rich in acetylene. The acetylene-to-methane ratio was shown to be related directly to the light flux at the coal surface. Temperatures were estimated from equilibrium data because they could not be measured directly due to the short duration of the laser pulse. Temperatures could be changed by varying the energy of the laser beam, the laser focus, and the type of laser (ruby, neodymium, carbon dioxide). As the light flux increased from 190 watt / cm^2 to 375 kilowatt / cm^2, the acetylene-to-methane ratio increased from zero to 3.6 for Pittsburgh seam (hvab) coal. Based on the measured gas composition and published equilibrium data, temperatures were estimated as 1160 to 1250 °K. As coal rank decreased the yield of gaseous product increased and yields of acetylene, hydrogen, and hydrogen cyanide reached a maximum for a high-volatile bituminous coal. As hydrogen and volatile matter in the maceral increased, the product gas increased and the acetylene-to-methane ratio decreased. For the smaller particles there was a decrease in methane and an increase in acetylene. No liquid was produced.

Karn et al. (1972) conducted more coal pyrolysis experiments using laser irradiation. Two lasers were used in the study: a pulsed ruby laser with a focused beam that gave an energy concentration of 55,000 watt / cm^2 and a continuous carbon dioxide laser with a focused beam giving an energy output of 140 watt / cm^2. Coal pyrolysis products using the ruby laser were 53% solid and 47% gas for a Pittsburgh seam high volatile bituminous coal. No significant amount of liquid was recovered, consistent with the results of the previous investigation. The ruby laser produced gaseous mixtures which were high in hydrogen, carbon monoxide, and acetylene. Coal pyrolysis products using the carbon dioxide laser were 29% gas and 71% solid. The only liquid observed were traces of pentane and hexane in the vapor phase. The carbon dioxide laser produced a series of hydrocarbon gases, but not acetylene, which apparently requires a higher temperature.

Beattie and Sullivan (1980) of Los Alamos Scientific Laboratory studied rapid pyrolysis of coal. A carbon dioxide laser was used to simulate concentrated sunlight. In the experiments, 2 to 5 milligram of subbituminous coal powder (0.3 to 0.15 mm diameter) were placed in a molybdenum pan which was supported by an insulator. The laser beam was passed through a KCl window to reach the sample. The composition of the evolved gases was determined by mass spectrometry. Heating rates of 1000 to 10,000 °C / second in an inert argon atmosphere resulted in rapid pyrolysis at temperatures between 400 and 800 °C.

The gases evolved were primarily carbon monoxide, hydrogen, and methane with lesser amounts of carbon dioxide and other light hydrocarbons. Yields of gaseous products increased with the time of pyrolysis. The yields of gas and tar decreased with the increased in argon pressure. The total yield of gaseous products increased with laser flux which resulted in higher equilibrium temperatures. The study also found that the total yields of gaseous products from coal samples of particle diameter between 0.074 and 0.71 mm in a flux of 89 watt / cm^2 for 12 seconds were found to be independent of particle size. The yield of methane, ethane, and propane increased with the laser flux. The yield of carbon dioxide was almost independent of flux.

Coal pyrolysis using laser heating was also studied by Pyatenko et al. (1992) in Russia. The objective of their study was to develop a method of laser heating of coal particles and to investigate the effect of particle size on the coal pyrolysis process. The results from this study showed that the total specific yield of volatile (both gaseous and tars) with regard to mass was independent of the particle size and the amount was in agreement with the amount of volatiles determined by proximate analysis.

High temperature solar pyrolysis was studied by Beattie et al. (1983) in Odeillo, France, as a way to convert subbituminous coal into light gases. The energy required for the reactions to take place was supplied by a solar furnace with a coal sample placed at the focal point of the solar beam. The solar furnace consisted of a heliostat directing light vertically upward to a 2 meter diameter, 0.85 focal length parabolic mirror. The flux falling on the sample was varied by moving the entire reactor vertically so that the sample would be positioned above and below the focal plane of the furnace. The solar flux was measured using a water-cooled calorimeter. A pyrometer was used to measure sample temperatures. Chemical analysis of the gaseous product was done using a mass spectrometer. Filters were used to study the effect of the ultraviolet and blue components of solar radiation on coal pyrolysis.

The experiments were conducted at an appropriate sample height using cut-off filters. Approximately, 50 milligram of subbituminous coal sample having particle size in the range of 0.15 to 0.30 millimeter was packed into a sample pan. The system was then evacuated and refilled with nitrogen or hydrogen gases to a pressure of approximately 630 torr. The sample was then irradiated for 12.5 seconds by manually uncovering and recovering the quartz dome with an aluminum plate. After the reaction, the system was allowed to cool down to its initial temperature. Gas yields were calculated from the pressure increase and the composition was determined using a mass spectrometer. The solid residue (char) was then weighed and the percent devolatilization was determined from the mass loss. Flux measurements were made at positions identical to the sample positions and corrected for changes in insolation with time of the day.

The devolatilization increased with increasing flux at fluxes under 200 watt / cm^2. The maximum gas yield was found to be 31 millimole / gram at a flux of 100 watt / cm^2 and decreased slightly with increasing flux. It was also found that at a radiant flux of 200 watt / cm^2 and exposure of 12.5 seconds, 51% of the coal devolatilized. The coal temperatures were measured to be in excess of 1800 °C. The gaseous product consisted of methane, carbon monoxide, carbon dioxide, ethylene, and ethane. At high flux levels (200 watt / cm^2 and greater) and experiments conducted in a nitrogen atmosphere, the combined yield of the hydrocarbons methane, ethylene, and ethane was approximately 10 mole percent. In hydrogen atmosphere this yield was approximately twice as much as it was in the inert (nitrogen) atmosphere. The yield of carbon dioxide was the same in both atmospheres with a value of 3 mole percent. The remainder of the carbon was assumed to be the carbon deposited on the reactor walls as soot-like particles. No liquid product was produced. There was also no effect of changing the wavelength distribution of sunlight on the product yields.

A coal pyrolysis study using concentrated solar thermal energy was conducted by Scholl (1992) at the National Renewable Energy Laboratory. Experiments were conducted with high-volatile bituminous coal with average particle sizes of 90, 125, and 160 micrometer. Helium was used as the reaction atmosphere and also as a carrier gas in which coal was exposed to the concentrated solar beam. Helium was chosen because it is safe and has the same thermal conductivity as hydrogen. The study was conducted in a continuous flow reactor.

Pulverized coal particles were fed into the top of a tubular, quartz reactor with dimensions of 2.5 cm outside diameter, 2.2 cm inside diameter, and 25 cm long. Gas was injected at the inlet of the reactor. The coal particles were exposed to concentrated solar flux generated by a setup called the 'High Flux Solar Furnace' as they moved down the reactor. Concentrated sunlight from the High Flux Solar Furnace's primary concentrator entered the reactor perpendicular to the coal flow. At the focal point, the concentrated solar beam had a diameter of 13 cm. A water-cooled, polished aluminum reflector was placed at the back of the reactor in an attempt to illuminate the coal particles from both sides. Concentrated solar fluxes of 100 and 200 watt / cm^2 were used in the experiments. The mass loadings of the coal were 0.06, 0.3, and 0.6 Kg / m^3.

Results from this study indicated that high quality, low viscosity liquid hydrocarbons were not produced. However, there was a trace of a very viscous tar. The composition of the tar was not determined. Gas chromatographic tests of the sample gases showed a small amount of pyrolysis gases, predominantly hydrogen. The detailed composition of the pyrolysis gases was not reported. Devolatilized coal particles recovered from the solid trap were reported to be much more porous than the parent coal. The results also indicated that the devolatilization of coal particles occurred only when the mass loading of coal particles was 0.6 Kg / m^3 regardless of the concentrated solar flux and particle average size. With lower mass loadings, there were no reactions. The amount of coal devolatilized was not reported.

Experiments by Ballantyne et al. (1984) at Avco Everett Research Laboratory, focused on using a carbon dioxide laser to heat coal particles. A laser source with power adjustable up to 15 kilowatt was used to deliver an output at a wavelength of 10.6 micrometer. Samples of powdered Pittsburgh no. 8 bituminous, Wyoming subbituminous, and Montana Rosebud subbituminous coals were transported as particulate suspensions in cold nitrogen gas (room temperature), and heated to temperatures in the range of 700 to 1700 °C by the laser beam in times ranging from 1 to 30 milliseconds. The heating rates were reported to be in the range of 10^5 °C / second. A gas chromatograph was used to analyze gas samples and Fourier Transform Infrared (FTIR) spectroscopy was used to analyze both the raw coal and solid residue samples. The experimental results showed that the carbon conversion to light volatiles for Wyoming subbituminous and Pittsburgh no. 8 bituminous coals were less than 0.2% and 0.01%, respectively. The solid product showed minimum changes in proximate and ultimate analyses relative to the raw coal.

Ubhayakar et. al (1976), Stickler et al. (1974), and Ubhayakar et al.(1977) at Avco-Everett also performed comparable experiments where cold coal particles were injected into very hot combustion gases to achieve rates of heating comparable to the laser experiments. Pittsburgh seam bituminous coal particles were rapidly devolatilized in combustion gases that were produced in an oil burner. The burner used no. 2 fuel oil which was burned in oxygen enriched air.

The effect of several experimental parameters on the weight loss of the pyrolyzed coal was studied. These parameters were: mass fraction of coal fed into the combustion gas (0 to 0.12), the input gas temperature (1500 to 2000 °C), coal particle size, and the residence time (7 to 70 milliseconds). The reactions were conducted at atmospheric pressure with heating rates of up to 10^5 °C / second. Gas samples were analyzed using gas chromatograph and infrared spectrometer. The results indicated that thermal devolatilization of up to 68% of the dry, ash-free coal could be obtained within residence times of 70 milliseconds.

Antal et al. (1980) studied the use of concentrated solar radiation to achieve pyrolysis of solid biomass materials. Light emitted from a 5 kilowatt tungsten halogen lamp simulating concentrated solar radiation was focused on kraft lignin samples. The flux levels within the reactor were estimated to be greater than 150 watt / cm^2. Gas was introduced at the bottom of the reactor and flowed in the opposite direction to the falling particles which were introduced into the reactor by a gravity feeder. The particles completely pyrolyzed as they were exposed to the radiant heat area. The distribution of products formed from the pyrolysis was not reported. The results of the study suggested that the pyrolysis technique using concentrated sunlight can be commercialized.

Granger et al. (1970) conducted coal pyrolysis experiments using a pulse of light generated from a xenon flash tube as a source of heat. The flash heating technique enabled rapid heating of coal particles and rapid quenching of evolved volatile products in the relatively cool surrounding. A thin layer of coal particles with sizes less than 10 micrometer was heated in argon and argon / 23% oxygen atmospheres for about 1 millisecond by a pulse of light. Incident energy on the coal was varied from 8 to 60 kilojoule / m^2. Tar yields as high as 30% of the coal weight were reported when experiments were conducted in an argon atmosphere with an incident energy of about 45 kilojoule / m^2. However, after the tar yield reached this maximum it began to decrease with increasing incident energy indicating secondary reactions. Gaseous product was mainly made up of hydrogen, carbon monoxide, methane, ethylene, and acetylene and other light hydrocarbons. The yields of carbon monoxide, hydrogen, and acetylene increased with increasing incident energy. The production of tar in the oxygen / argon environment was about 24% with an increase in carbon dioxide and carbon monoxide yields and a decrease in hydrocarbons compared to experiments conducted in argon. This indicated that ignition took place in the presence of oxygen.

Rapid devolatilization and hydrogasification of bituminous coal was studied by Anthony et al. (1976). In this study, a monolayer of coal particle samples (5 to 10 milligram) were supported on wire mesh heating elements and electrically heated in an atmosphere of hydrogen, helium, and mixtures of the two gases. This technique allowed rapid heating of the coal powders and rapid cooling of the products formed since the reactor and the surrounding gas were at room temperature during the reaction. Pittsburgh seam high-volatile bituminous coal with an average particle size of 70 micrometer was used in most experimental runs, but larger coal particles were used to study the effect of particle size. Sample weight loss (volatiles yield) was determined by weighing the wire mesh and coal before and after heating. The effect of several experimental variables on the measured coal weight loss (volatiles yield) was investigated. The experimental variables were: residence time (0 to 20 seconds), heating rate (65 to 10^4 °C / second), final temperature (400 to 1100 °C), total pressure (0.001 to 70 atmospheres), hydrogen partial pressure (0 to 70 atmospheres), and particle size (70 to 1000 micrometer).

The results of the study indicated that the yields of volatiles under these conditions increased significantly with decreasing total pressure, decreasing particle size, increasing hydrogen partial pressure and increasing final temperature, but only slightly with increasing heating rates. Most of the weight loss occurred during the heat up period. After a short time (2 to 3 seconds), the increase in weight loss was negligible. The composition of the gaseous products formed and the analysis of tar were not reported.

Rapid pyrolysis of lignite and bituminous coals was also investigated by Suuberg et al. (1979). The experiments were similar to those conducted by Anthony et al. (1976). Montana Lignite and Pittsburgh no. 8 Bituminous coal samples were used in this study. About 10 milligram of pulverized coal samples were placed on a stainless steel screen. The screen acted both as a sample holder and as an electrical heating element. The samples were heated at heating rates of 100 to 10^4 °C / second to a temperature as high as 1100 °C. The holding times at the final temperature varied from 0 to 30 seconds. Other experimental parameters studied included the pressure (10^{-4} to 100 atmosphere) and the coal particle size in the range of 74 to about 1000 micrometer. The sample weight loss (volatile yields) of the original coal and product compositions were studied as the function of these experimental variables. Since only the screen and coal samples were heated, the volatiles were rapidly quenched upon escaping from the coal particles. All the experiments were conducted in a helium atmosphere.

Coal samples were heated at a rate of 1000 °C / second to the final temperature and immediately allowed to cool. The result from these experiments showed that as volatile yields from both lignite and bituminous coals increased with increasing final temperatures. The tar yield from the bituminous coal pyrolysis at temperatures in the range 850 to 1000 °C was about 23 weight percent of the original coal which was four to five times more than the tar yield produced from the lignite coal pyrolysis (about 5 percent). The study also found that the heating rate had a negligible effect on the total yields or product distributions from both the lignite and bituminous coals over the range studied (100 to 10^4 °C/ second). This result is in agreement with the findings by Anthony et al. (1976) for bituminous coal.

Graff et al. (1976) conducted hydropyrolysis experiments of Illinois no. 6 coal at a pressure of 100 atmospheres. The reactor was made of a 316 stainless steel tube 6.35 millimeter outside diameter, 5.1 millimeter inside diameter, and 300 millimeter long. The reactor was capable of withstanding pressures up to 100 atmosphere and a temperature of 1000 °C. About 10 milligram of coal powders were deposited as a thin ring at a selected position in the reactor.The reactor tube was then heated resistively by electrical current. The effect of heating rate, vapor residence time, and solid contact time on the product distribution (weight percent of carbon in the coal that was converted to various products) was studied.

The study found that the yield of the pyrolysis reaction (in nitrogen atmosphere) was substantially lower than the yield of the hydropyrolysis reaction (in hydrogen atmosphere). The aromatics (benzene, toluene, and xylene) yields in the pyrolysis reaction was about one-fifth of that in hydropyrolysis. The heating rate of the coal sample was varied from 20 to 1400 °C / second. Increasing the heating rate from 20 to 640 °C / second increased the yields of BTX and light saturated hydrocarbons by about

3 and 1.5 times, respectively. This result indicated that rapid heating of coal resulted in extensive fragmentation of the coal structure while a low heating rate (20 °C / second) resulted in extensive repolymerization of the primary volatiles. However, increasing the heating rate from 640 to 1400 °C / second did not increase the product yield substantially. This result indicated that the heating rate of 640 °C / second was high enough for rapid hydropyrolysis of coal.

Additional experiments were conducted by Dobner et al. (1976) using the same experimental setup to study the effect of reaction temperature on the product yields. In all the tests, Illinois No. 6 coal was heated at 650 °C / second in 100 atmospheres hydrogen pressure with a solid contact time of 10 seconds and vapor residence time of 0.6 second. The reaction temperature was varied from 620 to 980 °C. The carbon conversion to methane increased from 5% at 620 °C to 38% at 980 °C. The carbon conversion of BTX increased steadily from less than 1% at 620 °C to a peak at 800 °C with a yield of about 11.6%. However, the yield of BTX decreased as the temperature was further increased to 980 °C. The BTX yield was about 3.5% at reaction temperature of 980 °C. This result suggested that above 800 °C, the BTX liquids that were produced from the coal hydropyrolysis reaction were then cracked into lighter hydrocarbons such as methane and ethane.

Fallon et al. (1980) at Brookhaven National Laboratory conducted a series of experiments on flash hydropyrolysis of lignite and subbituminous coals. Flash hydropyrolysis is a short residence time (1 to 10 seconds) non-catalytic coal hydrogenation process in which coal is converted directly to liquid and gaseous hydrocarbon products. In this study, North Dakota lignite and New Mexico subbituminous coals, ground to less than 150 micrometer particle size, were hydrogenated with preheated hydrogen in a 1 inch diameter by 8 foot long entrained down flow tubular reactor. Experimental variables included the reactor pressure (500 to 2500 psi), reactor temperature (700 to 900 °C) and residence time (2.4 to 9.6 seconds). The heat up rate of coal particles was calculated to be in the order of 30,000 to 50,000 °C / second. Gas chromatography was used to determine gaseous products which included carbon monoxide, carbon dioxide, methane, ethane, benzene, toluene, and xylene (BTX). The results from the study showed that flash hydrogenation of lignite and subbituminous coals operating at 2000 to 2500 psi reactor pressure and 750 to 775 °C temperature produced about 10% and 13% of BTX, respectively. Other products that were formed from the process included higher boiling point liquid hydrocarbons, methane and ethane gases.

Duncan et al. (1979) at the Institute of Gas Technology (IGT) investigated the hydropyrolysis of lignite coal from North Dakota. The study was conducted in a bench scale entrained flow reactor in which hydrogen and coal were heated concurrently to temperatures between 760 to 816 °C with residence times of 2 to 4 seconds. The hydrogen-to-coal ratio was varied from 10 to 95.5 weight percent of coal and the reactor was operated in the pressure range of 1500 to 2000 psig. The reactor in a helical coil shape of 1/8 inch diameter and 80 foot long was heated externally. Coal particles heat up rates on the order of 50,000 °C / second have been reported. Results from the investigation showed that as high as 49% of the feed carbon was converted to gases and liquids. The principal gases were reported to be methane, ethane, propane, carbon monoxide, and carbon dioxide. The liquids contained high concentrations of benzene, toluene, and xylene (BTX) and other hydrocarbons.

A short residence time hydropyrolysis technique for coal gasification of Montana Rosebud subbituminous was studied by Hamshar and Bivacca (1979) of Cities Service. The experiments were conducted in a straight or helical entrained flow dilute phase externally heated reactor. The preheated hydrogen and coal were mixed rapidly at the injector located at the top of the reactor. The products were then quenched immediately by a stream of cryogenically-cooled hydrogen, terminating any further reactions. Quenched reaction products were then separated and collected in a char receiver and two condensers.

The operating conditions were varied in the ranges of 790 to 955 °C reactor temperature, 34 to 109 atmosphere total pressure and 0.3 to 3.5 seconds vapor residence time. Results from the study showed that carbon conversion at levels of 50% could be achieved in 3 seconds vapor residence time at a temperature of 855 °C, and hydrogen pressure of 100 atmosphere. However, about 30% of the carbon was converted to methane. The yield of light oils reached a maximum of about 5% and was independent of the reactor temperature within the range studied. Maximum yield of benzene, toluene, and xylene (BTX) was reported to be about 10%, at vapor residence times of 1 to 3 seconds, 100 atmosphere pressure, and 855 °C reactor temperature.

Researchers at Rockwell International (Oberg et al., 1982) performed a series of experiments where they used rocket engine technology to rapidly heat coal particles by contact with hot hydrogen. The rapid heating promotes the formation of primary volatile compounds. These experiments appear to partially control secondary reactions of primary volatile by virtue of free radical quench with hydrogen, but still with a hot environment. Typical carbon yields were 60 - 70%, with upwards of 30 - 40% of the volatile converted to BTX type liquids. Because of the rocket engine mixing, the total pressure was very high, 500 - 1500 psig.

Mohamed and Mathur (1993) conducted rapid hydropyrolysis of bituminous coal. A bituminous coal sample in hydrogen atmosphere was targeted, in the absence of a catalyst, with a high intensity xenon light beam, simulating concentrated sunlight. A shuttering mechanism was incorporated to expose the coal sample only for a few seconds at a time. Experiments have been conducted at a heat flux of 96 watt/cm^2 and coal surface temperature of 900°C in hydrogen atmosphere (1 atm). Under these conditions, about 16 percent by weight of the moisture ash free bituminous coal was converted to liquid product. A G.C. simulated distillation technique shows that about 25% of the liquid produced has a boiling point below 200°C (gasoline range).

Rapid hydropyrolysis of resid oil study was also conducted by Mohamed, Salahuddin, and Mathur (1993). Samples of atmospheric and vacuum resid oil were targeted, in the absence of a catalyst, with a high intensity xenon light beam. Experiments using atmospheric and vacuum resid oils have been conducted at a heat flux of 96 watt/cm^2, heating rate of 60 to 70 °C/sec, temperatures in the range of 700 - 940°C, and exposure times in the range of one to six minutes in a hydrogen atmosphere (1 atm). Under these conditions, about 56% by weight of atmospheric resid oil and 48%

by weight of the vacuum resid oil were converted to liquid products (acetone soluble). A G.C. simulated distillation technique shows that about 17% and 13% of the liquid produced (acetone soluble) has a boiling point below 300°C (gasoline and kerosine range) for atmospheric and vacuum resid oil, respectively. The details of the study are presented in Appendix B.

Kinetic models and correlations have been developed to determine the rate of pyrolysis and hydropyrolysis of coal and also to predict the product yields. Mechanisms of coal pyrolysis and hydropyrolysis reactions have also been postulated to describe the reactions. Model compounds which are usually pure chemicals have been used to study coal thermal reactions. The use of these model compounds is developed from observations of coal structures. Coal structure constitutes several type of functional groups which are attached to one another. These functional groups include aromatic nuclei (naphthalene, anthracene, etc.), hydroaromatic structures (hydrogenated aromatic nuclei), alkyl chains (ethyl, methyl, etc.), alkyl bridges (methylene, ethylene, etc.), and oxygen groups (carboxylic acid groups, etc.).

Several studies have been conducted to investigate the thermal reactions of these model compounds and to correlate the results to those of actual coal reactions. Short residence time pyrolysis of pulverized coals and coal model compounds were conducted by Lester et al. (1982). Three bituminous coals: Pittsburgh seam, Illinois no. 6, and Mo-Kan and two coal model compounds: L-cystine and thianthrene were used in the study. Pyrolysis experiments were conducted in a shock tube with heating rates of approximately 3 x 10^6 °K / second, at temperatures in the range 1000 to 2000 °K and a nitrogen atmosphere. L-cystine is an aliphatic disulfide and thianthrene is a sulfur heterocyclic compound both of which have been suggested to be present in coal. The rate of coals and model compounds pyrolysis was modelled using an assumed first order rate equation. The kinetic parameters for pyrolysis of several coals and model compounds were reported.

Bruinsma et al. (1988, 1 and 2) conducted a series of experiments on gas phase pyrolysis of coal related aromatic model compounds in a coiled tube flow reactor. Several heterocyclic and related compounds were pyrolyzed in an argon atmosphere. These included monocyclic compounds, dibenzo derivatives, benzo derivatives, and other comparative compounds. The kinetics parameters for pyrolysis reaction of selected coal model compounds were reported.

A number of mathematical models and correlations have been developed to predict the product yield and distribution based on results from coal pyrolysis and hydropyrolysis studies. Mathematical models developed on weight loss data have been used extensively to describe coal pyrolysis reactions.

Peters and Bertling (1965) proposed an empirical correlation for rapid coal pyrolysis. The study suggested that rapid pyrolysis or degasification of coal represents a process which was empirically similar to the evaporation of water in the drying of coke. A zero order kinetics was proposed for the rapid degasification of coal reaction. The reaction rate was reported to be dependent on the degasification temperature, coal particle size, and the duration of reaction.

A detailed reaction mechanism and a mathematical model for coal pyrolysis have been proposed by Chermin and Van Krevelen (1957) to interpret the reaction quantitatively. The model which was based on the consecutive reaction theory, gave a satisfactory explanation of coal gasification or pyrolysis process.

The reaction mechanism for coking coal was suggested to be:

$$\mathbf{P} \xrightarrow{k_1} \mathbf{M} \qquad \text{(A)}$$

$$\mathbf{M} \xrightarrow{k_2} \mathbf{R} + \mathbf{G}_1 \qquad \text{(B)}$$

$$\mathbf{R} \xrightarrow{k_3} \mathbf{S} + \mathbf{G}_2 \qquad \text{(C)}$$

where,

k_1, k_2, k_3 = reaction rate constants

P = original coal

M = metastable intermediate

R = semi coke

S = coke

G_1 = primary gas

G_2 = secondary gas

Reaction [A] could be considered as the depolymerization stage of coal to form an intermediate also known as metastable products. In the second stage, the intermediate products are cracked to form primary gas and resolidified to form semi coke as shown in equation [B] (recondensation process). Finally, semi coke further degasified to form coke and gas as shown in equation [C] (secondary degasification). All these equations were assumed to be first order reactions. Based on this reaction mechanism, a mathematical model was proposed for coal pyrolysis.

Che et al. (1979) developed a coal pyrolysis kinetic model to predict the yields of tar and gas in an entrained flow reactor. The model covered the range of experimental data and conditions for the Flash Pyrolysis Process developed by Occidental Research Corporation, CA. The pyrolysis reactions were considered to be first order with respect to the amount of material remaining.

Oko et al. (1979) studied the mechanism of short residence time hydropyrolysis reaction for Montana Rosebud subbituminous coal in an entrained flow reactor. The range of operating conditions for hydrogasification of the coal were : 825 to 1000 °C temperature, 34 to 160 atm of pressure, 0.4 to 14.0 seconds particle residence time, and hydrogen to coal weight ratio of 0.1 to 1.2. Factors affecting the formation of products were studied. These factors included temperature, pressure, vapor residence time, coal to hydrogen ratio, solid residence time, and particle diameter. The following equations and correlations were reported:

Total fraction of carbon converted:

$$X = \exp\left[-\frac{3276}{T} + 0.1282\, ln\, t + 1.761\right] \qquad r = 0.91 \qquad (2.1)$$

Fraction of carbon conversion into methane plus ethane:

$$y_g = \exp\left[-\frac{9428}{T} + 0.4457\ ln\ P_{H_2} + ln\ t + 4.63\right] \qquad r = 0.93 \qquad (2.2)$$

Fraction of conversion into liquid hydrocarbons:

$$y_e = \exp\left[0.273\ ln\ P_{H_2} + 0.96\ ln\ t - 4.373\right] \qquad r = 0.67 \qquad (2.3)$$

Fraction of carbon conversion to benzene, toluene, and xylene:

$$y_b = \exp\left[-\frac{6814}{T} + 0.265\ ln\ t + 2.899\right] \qquad r = 0.87 \qquad (2.4)$$

where,

T = temperature in °K

P_{H2} = hydrogen partial pressure in atm.

t = residence time of solids in the reactor in seconds

The results showed that gas residence time, hydrogen-to-carbon ratio, and particle size did not have any significant effect on the conversions. The Arrhenius activation energy for Montana Rosebud subbituminous coal was found to be 27 kcal / mol. This indicated that the reaction was chemically controlled.

Reaction modelling and correlation for flash hydropyrolysis of coal in an entrained flow reactor was proposed by Bhatt et al. (1980) and Fallon et al. (1981). The data used to determine the kinetic rate parameters were collected from experiments conducted in a 2 lb / hour, 1 inch i.d. x 8 foot long entrained tubular reactor operated in the range of 500 to 900 °C reactor temperature, 500 to 3000 psi hydrogen pressure, and 1 to 10 seconds coal residence time. The reaction model based on a single coal particle surrounded by hydrogen gas was developed to describe the reaction.

Kobayashi et al. (1976) proposed an empirical model for early stages of coal pyrolysis in a flow furnace. The heating rates were calculated to be about 10^4 to 2×10^5 °K / second for an oven operated in the range of 1000 to 2100 °K.

The model consisted of two competing overall reactions:

$$\begin{array}{lcccc} \text{Coal} & \xrightarrow{k_1} & \text{Volatile 1} & + & \text{Residue 1} \\ (C) & & (V_1) & & (R_1) \\ & & (\alpha_1) & & (1 - \alpha_1) \end{array}$$

and

$$\begin{array}{lcccc} \text{Coal} & \xrightarrow{k_2} & \text{Volatile 2} & + & \text{Residue 2} \\ (C) & & (V_2) & & (R_2) \\ & & (\alpha_2) & & (1 - \alpha_2) \end{array}$$

where α_1 and α_2 were mass coefficients. The first reaction was assumed to be dominant at a relatively low temperature leading to the asymptotic volatile yield α_1. At high temperatures the second reaction was assumed to become faster than the first one, resulting in larger volatile yields. The data collected from rapid pyrolysis of lignite gave an activation energy of 25 kcal / mol and 40 kcal / mol for the two reactions.

Pitt (1962) studied the kinetics of the evolution of volatile products from high volatile coal in a fluidized carbonizer. The reactions were conducted at constant temperatures in the range of 300 to 650 °C for times ranging from 10 seconds to 100 minutes. It was assumed that coal was made of different components of equal molecular weight, and that on decomposition, each component lost the same proportion of volatile products over the temperature range studied. The study suggested that coal is made up of many components which decomposed independently, and the decomposition reactions have a wide range of activation energies.

Wiser et al. (1967) conducted a kinetic study for the pyrolysis of a high volatile bituminous coal. Experiments were conducted at constant temperatures ranging from 409 to 497 °C for a given long period of time. A mathematical model in the form of:

$$\frac{dV}{dt} = k\left(V^{*} - V\right)^{n} \tag{2.5}$$

was used to fit the data where V^{*} is the ultimate yield of the coal and V is the cumulative amount of volatiles produced up to time t. The value of n (order of the reaction) changed during the coal pyrolysis. The reactions were approximately second order for the first 60 minutes of coal pyrolysis, with an activation energy of 36.6 kcal / mol. The next 100 minutes of pyrolysis was reported to be a first order reaction, with an activation energy of 5.36 kcal / mol. A zero order reaction was observed at times above approximately 300 minutes until the end of the reaction.

Anthony et al. (1975) conducted coal pyrolysis experiments using electrically heated wire mesh screen. Montana Lignite and Pittsburgh seam no. 8 coals were pyrolyzed at various heating rates to 1000 °C. The first order kinetic model ($n=1$) was used to fit the data and determine the rate parameters. The kinetic parameters were reported.

Kobayashi et al. (1976) utilized the first order Arrhenius type rate equation to model coal pyrolysis reactions. The study reported that the activation energies for both lignite and bituminous coals were about 25 kcal / mol. Lester et al. (1982) studied pyrolysis reactions of three bituminous coals: Pittsburgh seam, Illinois no. 6, and Mo-Kan. The study reported the activation energies and frequency factors for the three bituminous coals to be 103.8 kilojoule / mol and 4.9×10^6 second^{-1}, respectively.

Sugawara et al. (1990) studied hydropyrolysis of five non-caking and two caking coals using a free fall pyrolyzer in a hydrogen stream at atmospheric pressure and at temperatures up to 960 °C, with a heating rate of about 6000 °K / second. The first order Arrhenius rate equation was used to determine the rate parameters for various coals although the experiments were conducted in a hydrogen atmosphere. Since the effect of hydrogen pressure on the total coal conversion is negligible, the Arrhenius rate equation can be used for both pyrolysis and hydropyrolysis reactions conducted at atmospheric pressure. The rate parameters for seven type of coals were reported.

Juntgen and Van Heek (1968, and 1979) and Juntgen (1984) studied the effect of heating rate on coal pyrolysis and hydropyrolysis. The heating rates studied ranged from 10^{-2} to 10^5 °C / minute (1.67×10^{-4} to 1.67×10^3 °C / second). The theory of non-isothermal reaction kinetics was used to study the effect of temperature and heating rate on the coal devolatilization. A mathematical model was developed to determine rate parameters which included activation energy and frequency factor for coal pyrolysis reaction. Results from coal (19.1% volatile matter) pyrolysis at different heating rates (10^{-2} to 10^{5} °C / minute) gave a mean activation energy of 42.1 kcal / mol and a mean frequency factor of 10^{-11} minute^{-1}. The experimental results agreed with the theory.

Niksa et al. (1984) also studied the effect of heating rates on coal pyrolysis. A time-resolved weight loss from bituminous coal was measured during the heat-up period. The heating rates were varied from 10^{2} to 10^{4} °K / second independent of reaction temperatures (up to 1300 °K). A model developed by Juntgen and Van Heek for non-isothermal coal pyrolysis was used in the study. The activation energy and frequency factor for Pittsburgh seam no. 9 high volatile bituminous coal were reported to be 17.2 kcal / mol and 7050 second^{-1}, respectively.

The study also correlated the amount of volatile matter left and heating rates. The amount of volatile matter left at particular temperatures for different heating rates can be expressed as:

$$X(m_2) = X(m_1)^{\frac{m_1}{m_2}} \tag{2.6}$$

and

$$X = \left(\frac{V^* - V}{V^*} \right) \quad (2.7)$$

where,

V = volatile yield (weight loss) at temperature T in weight percent

V^* = ultimate yield in weight percent

m_1, m_2 = constant heating rates in °K / second

X = fraction of volatile left

Tsai (1982) suggested that coal particle size was important in determining whether the coal devolatilization rate was chemically or heat transfer controlled. The critical particle size above which devolatilization rate shifts from chemically controlled to heat transfer controlled varies with heating rates. The critical particle size for a heating rate of less than 100 °C / second was reported to be 2000 micrometer.

CHAPTER III

MATERIALS, EXPERIMENTAL EQUIPMENT, AND EXPERIMENTAL PROCEDURE

Coal rapid hydropyrolysis experiments are conducted in a batch system. Details of the materials used, experimental equipment, and the experimental procedure are discussed in this section.

Materials

The major materials used in this study consist of bituminous, subbituminous, and lignite coals, hydrogen and helium gases, acetone, and tetrahydrofuran. The coals used were bituminous (Kentucky no. 9), subbituminous (Montana Rosebud), and lignite (North Dakota Beulah) obtained from the Pennsylvania State University, Coal Research Section. The proximate and ultimate analyses of each coal sample are presented in Table 3.1 - 3.3.

Hydrogen and helium gases of 99.99 % purity supplied by Northeast Airgas Inc. were used for coal hydropyrolysis, and analytical grade acetone is used as a solvent to collect liquid hydrocarbon product. Analytical grade tetrahydrofuran was used to wash the equipment.

Table 3.1

Proximate and Ultimate Analyses of Coal Sample

Coal sample : Kentucky no. 9 bituminous coal

Proximate Analysis

	As Recd. (%)	Moist. Free (%)	Moist., Ash Free (%)
Moisture	6.81		
Ash	11.42	12.25	
Volatile	38.38	41.18	46.93
Fixed Carbon	43.40	46.57	53.07

Ultimate Analysis

	As Recd. (%)	Moist. Free (%)	Moist., Ash Free (%)
Ash	11.42	12.25	
Carbon	64.66	69.39	79.08
Hydrogen	4.74	5.09	5.80
Nitrogen	1.17	1.26	1.44
Total sulfur	3.92	4.21	4.80
Oxygen	7.27	7.80	8.89
Calorific value (Gross, Btu/lb)	11823	12687	

Source: Pennsylvania State University, Coal Research Section.

Table 3.2

Proximate and Ultimate Analyses of Coal Sample

Coal sample : Montana Rosebud subbituminous coal

Proximate Analysis

	As Recd. (%)	Moist. Free (%)	Moist., Ash Free (%)
Moisture	21.58		
Ash	9.85	12.56	
Volatile	32.68	41.67	47.66
Fixed Carbon	35.89	45.77	52.34

Ultimate Analysis

	As Recd. (%)	Moist. Free (%)	Moist., Ash Free (%)
Ash	9.85	12.56	
Carbon	53.62	68.37	78.19
Hydrogen	2.89	3.69	4.22
Nitrogen	0.72	0.92	1.05
Total sulfur	0.91	1.16	1.33
Oxygen	10.43	13.30	15.21
Calorific value (Gross, Btu/lb)	9047	11536	

Source: Pennsylvania State University, Coal Research Section.

Table 3.3

Proximate and Ultimate Analyses of Coal Sample

Coal sample : North Dakota Beulah Lignite coal

Proximate Analysis

	As Recd. (%)	Moist. Free (%)	Moist., Ash Free (%)
Moisture	33.38		
Ash	6.37	9.56	
Volatile	37.36	56.08	62.01
Fixed Carbon	22.89	34.36	37.99

Ultimate Analysis

	As Recd. (%)	Moist. Free (%)	Moist., Ash Free (%)
Ash	6.37	9.56	
Carbon	44.07	66.15	73.14
Hydrogen	2.68	4.03	4.46
Nitrogen	0.60	0.90	1.00
Total sulfur	0.49	0.74	0.82
Oxygen	12.40	18.62	20.59
Calorific value (Gross, Btu/lb)	7370	11062	

Source: Pennsylvania State University, Coal Research Section.

Experimental Equipment

A pyrex reactor with a quartz cover plate, high intensity light equipment (power supply, lamp housing and 1000 watt lamp), gas chromatograph, asymptotic calorimeter, three axis manipulator, type K thermocouple with digital thermometer, gas pump, safety bag, pressure gauge, and analytical balance capable of weighing to the nearest 0.0001 gram are the major equipment used during the course of this study.

Experimental Setup. The coal rapid hydropyrolysis experiments are carried out in an experimental set-up as shown in Figure 3.1. The experimental setup consists of a pyrex reactor, gas supply equipment, and a high intensity light assembly with a shuttering arrangement.

Hydrogen and helium gases are supplied from high pressure cylinders. Hydrogen gas is passed through several safety devices before entering the reactor as a precaution : (i) a flame arrestor (model 6103) supplied by Matheson is used to stop the gas supply if flashback occurs and to extinguish the flame before it reaches the gas supply and (ii) a check valve (Nupro, 1/3 psi) supplied by Maine Valve and Fitting Co. to prevent any back-mixing.

A pressure gauge is used to check for any leak in the system before each experiment is conducted for safety consideration. A teflon safety bag is used to prevent any pressure buildup during the experiment. Finally, a gas pump is used to purge the system with helium and the hydrogen before each experiment.

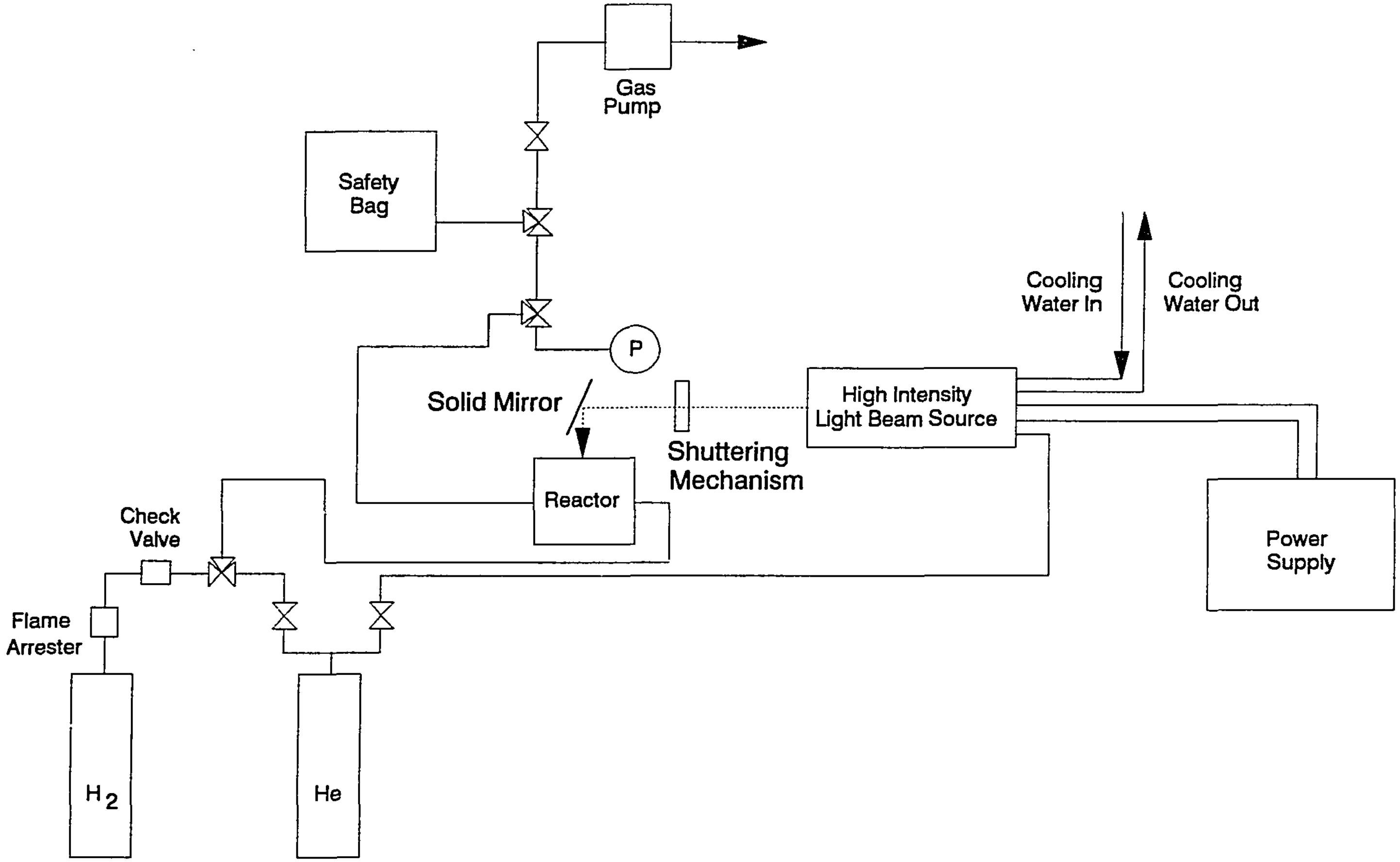

Figure 3.1: Schematic Diagram of the Experimental Set-up

The details of the high intensity light assembly with shuttering arrangement and reactor design are discussed in the next two sections.

High intensity Light Assembly With Shuttering Arrangement. The high intensity light beam is produced by xenon light equipment supplied by Photon Technology International Inc., NJ. The light source equipment consists of two units: a power supply and the lamp housing. The power supply (LPS 1000) is designed to operate with high pressure xenon, mercury, or xenon-mercury arc lamps in the range of 100 to 1000 watts and is capable of delivering 100 watt/cm^2 flux. The appropriate voltage for the lamp is automatically selected and the power of the lamp is adjusted by varying the current. The instrument is also equipped with a low operating circuit, in which case the lamp current can be reduced to as low as 20 % of the normal value. Voltage and current are displayed during each operation. The power supply is air cooled.

The arc lamp housing (02-A-5001) is designed to accommodate selected xenon, mercury, or mercury-xenon arc lamp with a power rating up to 1000 watts. The housing uses an f/4 elliptical reflector, which gives a high reflection efficiency. With the f/4 reflector, a horizontal beam of light is focused at a distance 407.1 mm from the front window. The front window is made of quartz so that wavelengths of light greater than 250 nanometers (nm) can pass through. The lamp housing is water cooled and sealed, so that a venting system is not required. Also, it is designed for nitrogen or helium purging to prevent the production of ozone.

The light source, a 1000 watt xenon arc lamp (02-1000X) with a spectral emission in the range of 250 nm to 2500 nm, is assembled in the lamp housing. The spectral emission curve for the xenon lamp is shown in Figure 3.2 (Photon Technology International Inc.). A xenon lamp is used in this study because its spectral emission curve is similar to those of sunlight. The lamp can be operated at various power levels and is capable of delivering up to a 100 watt/cm^2 flux beam at 1000 watts power level.

A shuttering mechanism is designed and incorporated between the window and the reflective solid mirror to expose the coal sample for a few seconds at a time. A 45 degree reflective solid mirror is used to change the orientation of the high intensity light beam from horizontal to vertical. The reflective solid mirror is coated with magnesium fluoride to achieve maximum reflectance. The solid mirror is cooled by forced air to avoid the loss of the magnesium fluoride coating.

Reactor Design. The coal hydropyrolysis reactor is designed and constructed to have several characteristics that make this investigation unique from other rapid coal hydropyrolysis studies. With this reactor, rapid heating rates of coal and quenching of the coal volatiles and products in the relatively cool surrounding gases and on the reactor wall are possible. The rapid coal hydropyrolysis is conducted in a batch system rather than a continuous one due to the equipment limitations. However, this system is found to be excellent to study the effects of the process variables on the product characteristics.

The coal hydropyrolysis reactions are conducted in a cylindrical pyrex reactor. The details of the hydropyrolysis reactor are shown in Figure 3.3. The reactor is 74

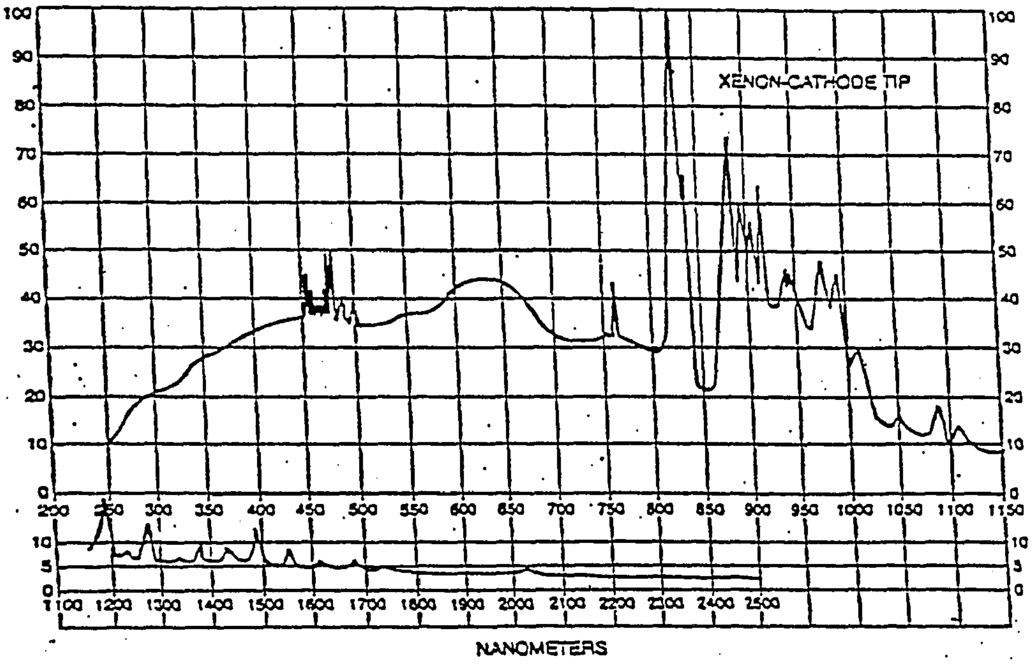

Figure 3.2: Spectral Emission for Xenon Compact Arc Lamps

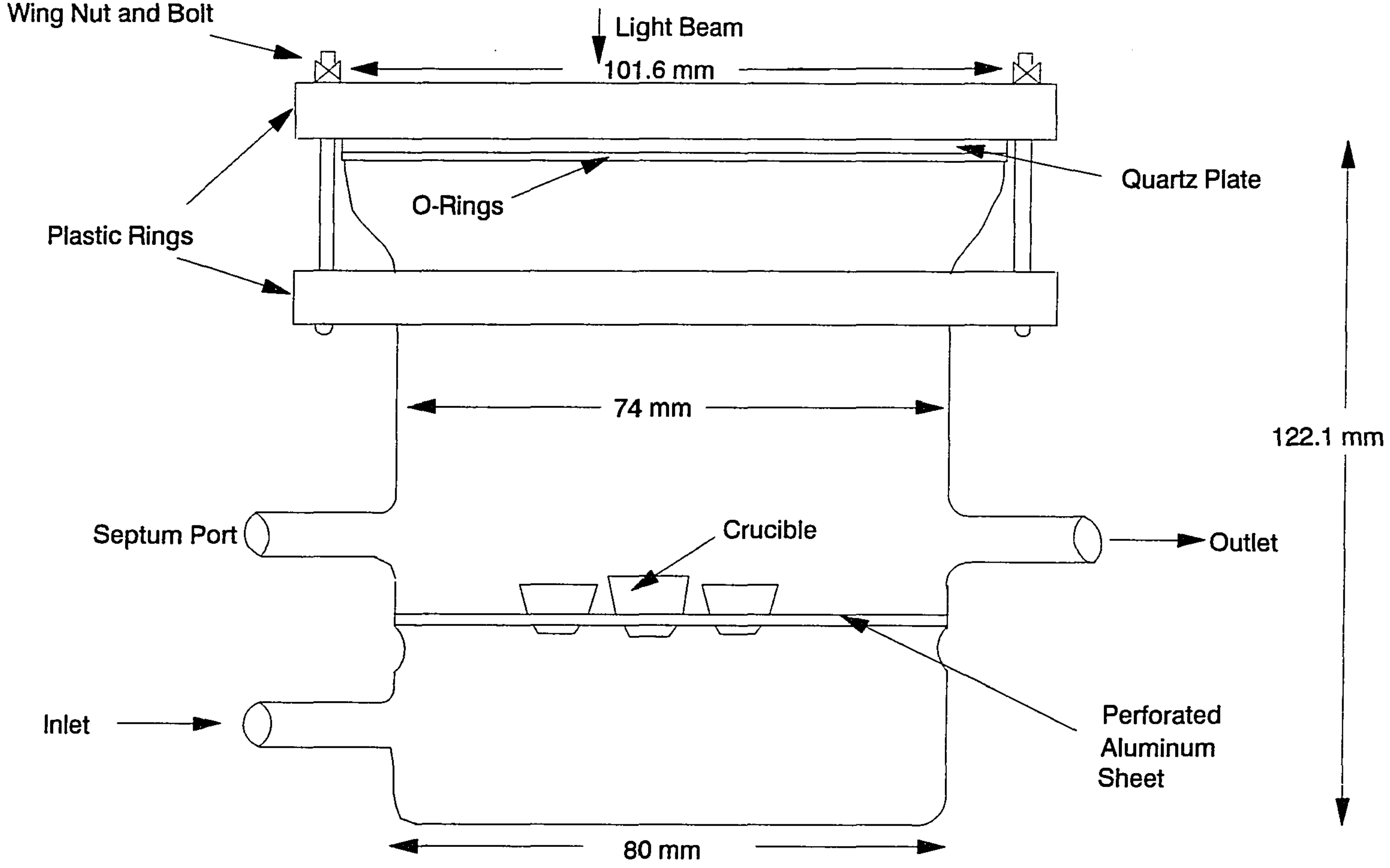

Figure 3.3: Structural Details of Hydropyrolysis Reactor

millimeters (mm) i.d., 80 mm o.d., and 122.1 mm high with a thicker wall at the top of the reactor to accommodate a 75 mm o-ring to provide a gas seal. A quartz cover plate and 75 mm o-ring are placed at top of the reactor opening to allow the high intensity light to pass through. The dimension of the quartz plate is 101.6 mm diameter and 3.2 mm thick. The inlet and outlet tubing to the reactor are located at the bottom and top of the reactor respectively. A gas sampling port is also located at the top of the reactor on the opposite side of the reactor outlet.

The light beam from the high intensity light equipment moves horizontally. A 45 degree reflective solid mirror is used to change the orientation of the high intensity light beam from horizontal to vertical. The beam now enters the reactor from the top through the quartz plate which serves as a lid as well as a window for the entering beam. The arrow shown in Figure 3.3 represents the image of the light beam.

The top view of the reactor configuration is shown in Figure 3.4. Coal particles are placed in four low wide-form crucibles. The dimensions of a crucible are 18 mm diameter at the top and 12 mm high. About 0.003 gram of the dry coal is placed in each crucible. These crucibles are placed about 22 mm apart from one another on a perforated aluminum sheet of about 1 mm thick, which acts as a support. Only one sample of coal is exposed to the light beam at a time since the diameter of the light beam at the focal point is about 8 mm. Each coal sample is exposed to the radiant heat by positioning the sample at the focal point of the beam. Up to four coal samples can be placed in the reactor for the rapid hydropyrolysis reaction. By this arrangement, a significant amount of products can be collected for each experimental run. The gaseous product is analyzed

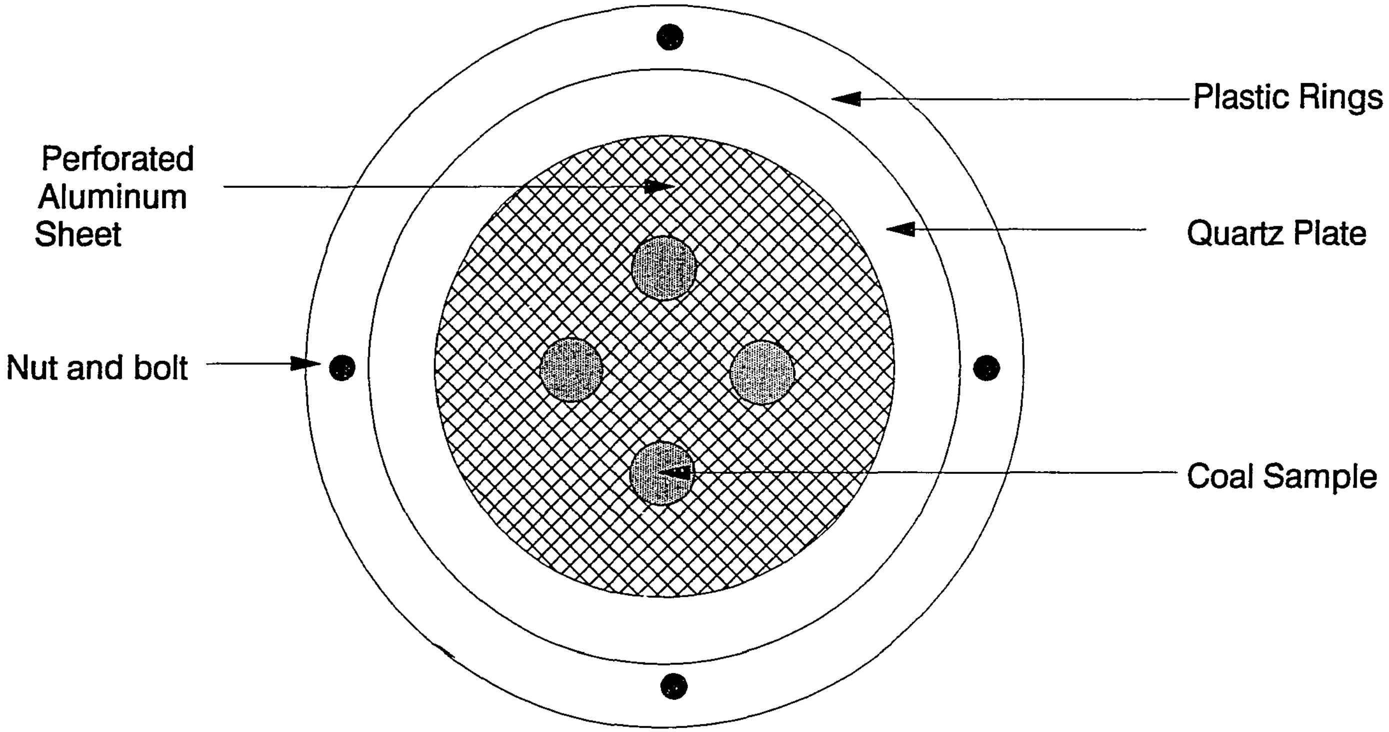

Figure 3.4: Top View of Hydropyrolysis Reactor

after each run. The results show that the gas sample is rich in hydrogen indicating that the amount of hydrogen is adequate for the rapid hydropyrolysis of each coal sample.

Both hydrogen and helium atmospheres are used for the rapid coal pyrolysis work. Helium is used for this study for several reasons. First, the thermal conductivity of helium matches with that of hydrogen in the temperature range of interest. Secondly, it is inert and is used for conducting pyrolysis experiments as a comparison to those in hydrogen atmosphere. Finally, it is used to purge the reactor several times to remove all of the air before hydrogen is passed through. This is to avoid the mixing of air and hydrogen which can lead to an explosion.

Heat Flux and Temperature Measurements

An asymptotic water cooled calorimeter (C-1300-A-300-72) with a calibrated curve supplied by Hy-Cal Engineering, CA is used to measure the heat flux of the high intensity beam at the focal point where the sample is to be located. The asymptotic calorimeter is made of solid copper with the front surface coated with carbon black. The diameter of the calorimeter is about 25 mm. The calorimeter is mounted on a three axis manipulator and positioned to intercept the focused high intensity light beam at its focal point. The output from the calorimeter is sent to a volt meter. A calibrated curve is used to determine the amount of heat flux absorbed by the calorimeter from the millivolt output reading of the volt meter.

A digital thermocouple thermometer (model DP41-TC) is used with type K (Chromel - Alumel) thermocouple to determine the temperature of the high intensity light beam. The thermocouple is placed on a coal surface in helium at the beam focal point. The voltage output from the digital thermometer is sent to a personal computer using a data acquisition program called LABTECH NOTEBOOK supplied by Laboratories Technologies Corp. and hardware supplied by Metrabyte Corp., MA. The output is continuously recorded by the computer.

Throughout this study, the gaseous and liquid samples are analyzed for their characteristics. A gas chromatograph (HP 5890 Series II) with an integrator (HP 3396 Series II) supplied by Hewlett Packard, CA is used for these analyses. Details of the analytical procedures are provided later.

Experimental Procedure

The detailed procedures for conducting coal rapid hydropyrolysis and analysis of products are as follows:

Hydropyrolysis of Coal. Coal as received is sampled for various sizes (63 to 74, 354 to 420, and 707 to 841 micrometer), dried overnight at 110 °C, and is stored in a desiccator. Coal samples of a preselected particle size weighing about 0.003 gram each are placed in four porcelain crucibles (in a thin layer) with a total coal sample of 0.012 gram. These coal samples in crucibles are then placed on a perforated aluminum sheet which acts as a support in the reactor as discussed earlier. A 75 mm o-ring is placed on the top of the reactor. The quartz plate lid is then clamped to the reactor. This assembly is then connected to the rest of the system.

The system is then purged with helium three or four times to drive out any air and keep the contents of the reactor in a total helium atmosphere. The system is then purged with hydrogen to keep the reactor contents in hydrogen when necessary. This is conducted to prevent any mixing of air with hydrogen which can lead to an explosion hazard. The inlet and outlet to and from the reactor are then closed so that the rapid coal hydropyrolysis reaction can be carried out in a batch system. A pressure gauge is used to check for any leaks in the system.

The light beam equipment is then turned on while the shutter is closed. The power is adjusted to a low level (less than 100 watts). At this power level no reaction is observed. The shutter is then opened to allow the beam to pass enabling the coal sample to be positioned at the beam focal point. The shutter is closed and the power is adjusted to a desired level. The shutter is then opened to expose the sample to rapid heating for only a given short period of time. The duration of the light beam exposure is controlled by the shutter. After the reaction, the reactor is then allowed to cool down for a few minutes to room temperature before another coal sample is exposed. The same procedure is then repeated with the other coal samples.

After all the four samples have been exposed and the reactor and its contents have been allowed to cool down, a gas sample is taken through the septum port (before the quartz plate is removed). The gas sample is analyzed using the gas chromatograph as is discussed later. The quartz plate is then removed. Both the reactor and the quartz lid are washed with analytical grade acetone. The acetone soluble product oil is then transferred into a sample bottle and is subjected to gas chromatographic simulated distillation later.

The reactor and the quartz lid are then washed with analytical grade tetrahydrofuran for cleaning purposes before another run is to be conducted. The tetrahydrofuran wash is analyzed by the gas chromatograph. No liquid hydrocarbons were detected.

After the acetone soluble product is subjected to the simulated distillation technique by gas chromatograph, acetone is evaporated from the sample using helium. The product oil is then weighed, labeled, and stored. Crucibles with carbon residue and ash are also weighed. The carbon residue and ash are then labeled, and stored.

Product Analysis. Gas chromatography is widely used since it is one of the most reliable instruments to determine the composition of liquid and gaseous mixtures. Considerable time and effort have been spent in this study to develop a gas chromatographic procedure that is capable of separating liquid products by boiling point cuts. Gaseous products are also analyzed using gas chromatography.

Carbon-hydrogen-nitrogen analysis is carried out to determine the amount of carbon in the coal sample and hydropyrolysis products.

Liquid Product Analysis. The liquid product sample (acetone soluble) is subjected to ASTM D2887-89 standard test method for boiling point range distribution of various hydrocarbon fractions by gas chromatography. This procedure is also known as a gas chromatographic simulated distillation technique for boiling point measurements. In this test, a sample is introduced into a gas chromatographic column that separates hydrocarbons in the order of increasing boiling point. The column temperature is raised at a constant rate and the areas under the chromatogram peaks are recorded throughout the analysis. Boiling points are assigned to the axis from a calibration curve, obtained under the same conditions by running a known mixture of hydrocarbons covering the boiling range expected for the sample. From these data, the boiling range distribution for the liquid sample is obtained. The significance of this procedure is that a gas chromatographic technique for the determination of the boiling range of hydrocarbons can be used inspite of the fact that the quantity of the liquid sample is very small and conventional ASTM distillation method cannot be used. This method is also widely used in other research laboratories such as Pittsburgh Energy Technology Center and is known to give reasonably good results.

A 6'x 1/8" o.d. stainless steel column packed with 5 % OV-1 phase loading on a 100/120 mesh Chromosorb WHP solid support supplied by Hewlett Packard, CA is used for the above analysis. The following operating conditions are found to be suitable for the separation : injection port temperature of 350 °C, detector temperature of 350 °C, initial column temperature of 35 °C, initial time of 0 minute, program rate of 8.0 °C / minute, final column temperature of 320 °C, final time of 15 minutes, and carrier gas (helium) flow rate of 30 ml / minute. A flame ionization detector is employed due to its inherent sensitivity for hydrocarbons. Any compound which burns in a hydrogen / oxygen flame will be detected by the flame ionization detector. A sample size of 0.8 microliter is used for this analysis.

Column Preparation. The gas chromatographic column must be conditioned at a temperature above the maximum experimental operating temperature to achieve a satisfactory gas chromatographic analysis. Conditioning of the column is done according to the following steps :

1) System is checked for leaks.

2) The column is connected to the injection port only (not to the detector).

3) Carrier gas (helium) flow rate is set at 20 ml / minute.

4) Initial oven temperature is set at 35 °C for 30 minutes.

5) Rate of temperature increase is 2 °C / minute.

6) Final temperature is 340 °C for about 16 hours.

Calibration. After the column has been conditioned, the gas chromatography conditions are set to meet the desired conditions. For calibration, a known mixture of hydrocarbons (normal paraffins) in acetone is injected into the chromatograph. This mixture of hydrocarbons of known boiling points covers the boiling range of the product sample with at least one compound in the mixture having a boiling point lower than the initial boiling point of the sample. The areas under the chromatographic peaks for the calibration are also compared to the known composition of a standard mixture. The standard mixture consists of a solution of 0.033% by weight n-tetradecane, n-pentadecane, and n-hexadecane, respectively in hexane. The standard mixture is supplied by Hewlett Packard, PA. The relative areas agree well with the composition of the standard mixture.

Data on retention times of peak maxima for each component are obtained. A calibration table based upon the results of the analysis the calibration mixture by recording the retention time of the peak maxima and the boiling point for each component in the mixture is prepared. The retention time of each peak versus the corresponding normal boiling point of that component in degrees Celsius is then plotted. This calibration plot is used to obtain boiling point data for the liquid product sample (acetone soluble) from rapid hydropyrolysis experiments.

Gaseous Product Analysis. The gaseous product is analyzed using the gas chromatograph with a different column and operating conditions than the one used for determining boiling point temperature for the liquid product. A 15'x 1/8" stainless steel column packed with 60/80 mesh Carboxen-1000 is used to analyze the gaseous sample. This column is effective in analyzing permanent gases (hydrogen, oxygen, nitrogen, carbon monoxide, and carbon dioxide), C_1-C_2 hydrocarbons (methane, ethane, acetylene, and ethylene), and sulfur containing gases. The column is supplied by Supelco, Inc., PA.

The following operating conditions are found to be suitable for analyzing a gaseous product : injection port temperature of 225 °C, detector temperature of 225 °C, initial column temperature of 35 °C, initial time of 5 minutes, program rate of 20 °C / minute., final column temperature of 220°C, final time of 15 minutes, and carrier gas (helium) flow rate of 30 ml / minute. A thermal conductivity detector is used to detect the permanent gases and hydrocarbons in the sample. A sample size of 50 microliter is used for this procedure.

The same technique used for conditioning the previous column is applied to the Carboxen-1000 column except the final temperature is maintained at 225 °C for about 16 hours.

Calibration. After the column has been conditioned, the gas chromatograph operating conditions are set at the values mentioned earlier. A sample of a standard gas mixture of permanent gases and C_1-C_2 hydrocarbons with a known composition is used to determine both the qualitative and the quantitative aspects of the gas chromatographic analysis of the gaseous product mixture. The standard gas mixture (Scotty II) is supplied by Supelco, PA. The results agree with the known retention time and composition of the standard mixture. Each retention time is identified with an individual compound in the gas. The composition of gaseous product from coal hydropyrolysis reaction is then estimated based on the retention time of individual component in the gas.

Percent Coal Conversion (Liquid Hydrocarbons + Gas)

The percent conversion of coal is calculated on moisture and ash free (maf) basis. It is assumed that the ash present in the coal remained chemically the same at the end of the experiment.

The percent coal conversion (total yield) is calculated as :

$$\%\ \text{conversion} = \frac{\text{initial weight of coal (maf) - residue (maf)}}{\text{Initial weight of coal (maf)}} \times 100$$

The percent coal converted to liquid product (acetone soluble, b.p. < 425 °C) is calculated as:

$$\% \text{ of liquid} = \frac{\text{weight of liquid produced}}{\text{initial weight of coal (maf)}} \times 100$$

The percent of coal converted to gaseous product is calculated as :

$$\% \text{ of gases} = \% \text{ conversion} - \% \text{ liquid}$$

CHAPTER IV

RESULTS AND DISCUSSION

The objectives of this investigation was to study the rapid hydropyrolysis and pyrolysis of lignite, subbituminous, and bituminous coals for the production of light distillates (gasoline and kerosine boiling ranges) using a high intensity light beam as a heating source. The experiments were first conducted using Kentucky no. 9 high volatile bituminous coal in both hydrogen and helium atmospheres. Similar experiments were then conducted using Montana Rosebud subbituminous and North Dakota Beulah lignite coals. The experimental studies were conducted as follows:

i) Heat flux and temperature measurements,

ii) Rapid hydropyrolysis of coal for various exposure times to obtain the most suitable time for maximum coal conversion and production of liquid hydrocarbons,

iii) Using the most suitable exposure time obtained in (ii) to rapidly hydropyrolize coal at various peak temperatures,

iv) Using the most suitable exposure time and peak temperature obtained in (ii) and (iii) to rapidly hydropyrolize coal of various particle size,

v) Using the most suitable exposure time, peak temperature, and coal particle size obtained in (ii), (iii), and (iv) to conduct rapid heating of coals in helium atmosphere (pyrolysis) and compare the results against those obtained from experiments conducted in hydrogen atmosphere (hydropyrolysis),

vi) Conduct a gas chromatography simulated distillation of the liquid produced by the coal rapid hydropyrolysis at the most suitable conditions of exposure time, peak temperature, particle size and reaction atmosphere,

vii) Conduct a gas chromatographic analysis of the gaseous product produced by the coal rapid hydropyrolysis reaction obtained at the most suitable conditions of exposure time, peak temperature, particle size and reaction atmosphere,

viii) Calculate the carbon conversions of the bituminous coal to various products,

ix) Using the same experimental procedure discussed above to study rapid hydropyrolysis of other ranks of coal,

x) Investigate the mechanism of coal rapid hydropyrolysis reaction and do a statistical correlation of the effect of experimental variables on the product yields,

xi) Compare results from this study with other coal conversion processes.

The experimental variables held constant during the study were the amount of coal used for each experimental run and the reactor pressure. Preliminary test runs were conducted to ensure that the equipment was functioning satisfactorily. The amount of coal char, ash, and liquid hydrocarbons (acetone soluble) formed were weighed. The amount of coal used minus char and ash residue was the measure of the amount of the total weight loss of the coal sample (total coal conversion). The amount of liquid hydrocarbons (acetone soluble) collected was the measure of the degree of coal hydropyrolysis to distillate products (less than 425 °C). The difference between these values was the amount of coal converted to gases. All the percent conversions are calculated on moisture and ash free (maf) basis. It is assumed that the ash present in the coal remained chemically the same at the end of the experiment.

The discussion of results of this study has been divided into five sections A, B, C, D, and E. In Section A, measurements of heat flux and temperature at the focal point of the high intensity light beam for various power levels of the beam generating equipment have been discussed. The results of the effect of exposure time, peak temperature, coal particle size, and atmosphere on rapid hydropyrolysis of Kentucky no. 9 high volatile bituminous coal have been discussed in Section B. A discussion of the results from the gas chromatographic simulated distillation of the liquid product (acetone soluble) and the gaseous composition obtained at the most suitable conditions of exposure time, peak temperature, particle size, and reaction atmosphere has also been presented in this section. In Section C, discussion of results of rapid hydropyrolysis for various ranks of coal (bituminous, subbituminous, and lignite) has been presented. In Section D, the mechanism of the coal rapid hydropyrolysis is investigated and statistical correlations to determine the effect of each experimental variable on the product yields have also been presented. Finally, the results from this study are then compared to other coal conversion processes in Section E.

Section A. Heat Flux and Temperature Measurements

An asymptotic water cooled calorimeter was used to measure the heat flux at the focal point of the high intensity beam. A calibration curve was provided for the instrument by the manufacturer. Heat flux at various power levels were measured. The details of heat flux measurements at the high intensity beam focal point have been discussed in the experimental procedure section. Results from the heat flux measurement are presented in Table 4.1. The results are also plotted and shown in Figure 4.1. The heat flux increased almost linearly with power level within the range measured. At a power level of about 549 watts the heat flux measured was 69.6 watt / cm^2 and increased to 96.8 watt / cm^2 at power level of about 1084 watts.

A type K (Chromel - Alumel) thermocouple with a digital thermocouple thermometer was used to measure the surface temperature of the coal particles located at the focal point of the high intensity light at various power levels. The thermocouple is placed on the coal surface in helium atmosphere. Results of these measurements are presented in Table 4.2. The temperature measurement was also plotted as a function of power levels and is shown in Figure 4.2. The peak temperature increased linearly with power level within the range measured. The peak temperature increased from 654 °C at about 393 watts to 940 °C at about 1079 watts.

The temperature profile as a function of time was also measured and the voltage output from the digital thermocouple thermometer was transmitted to a personal computer for recording purposes. The temperature profile is shown in Figure 4.3. The temperature increased from room temperature to around 900 °C in about 14 seconds with the power level operating at 1000 watt.

Table 4.1

Heat Flux Measurements at Focal Point of High Intensity Light Beam

Power Level (watt)	Heat Flux (watt / cm^2)
549.1	69.6
594.4	70.7
655.2	72.7
661.9	73.5
688.0	74.2
697.0	74.9
746.2	77.2
838.4	82.5
854.8	83.2
913.0	87.1
919.1	87.1
961.4	89.4
980.7	90.8
1075.7	96.5
1083.6	96.8

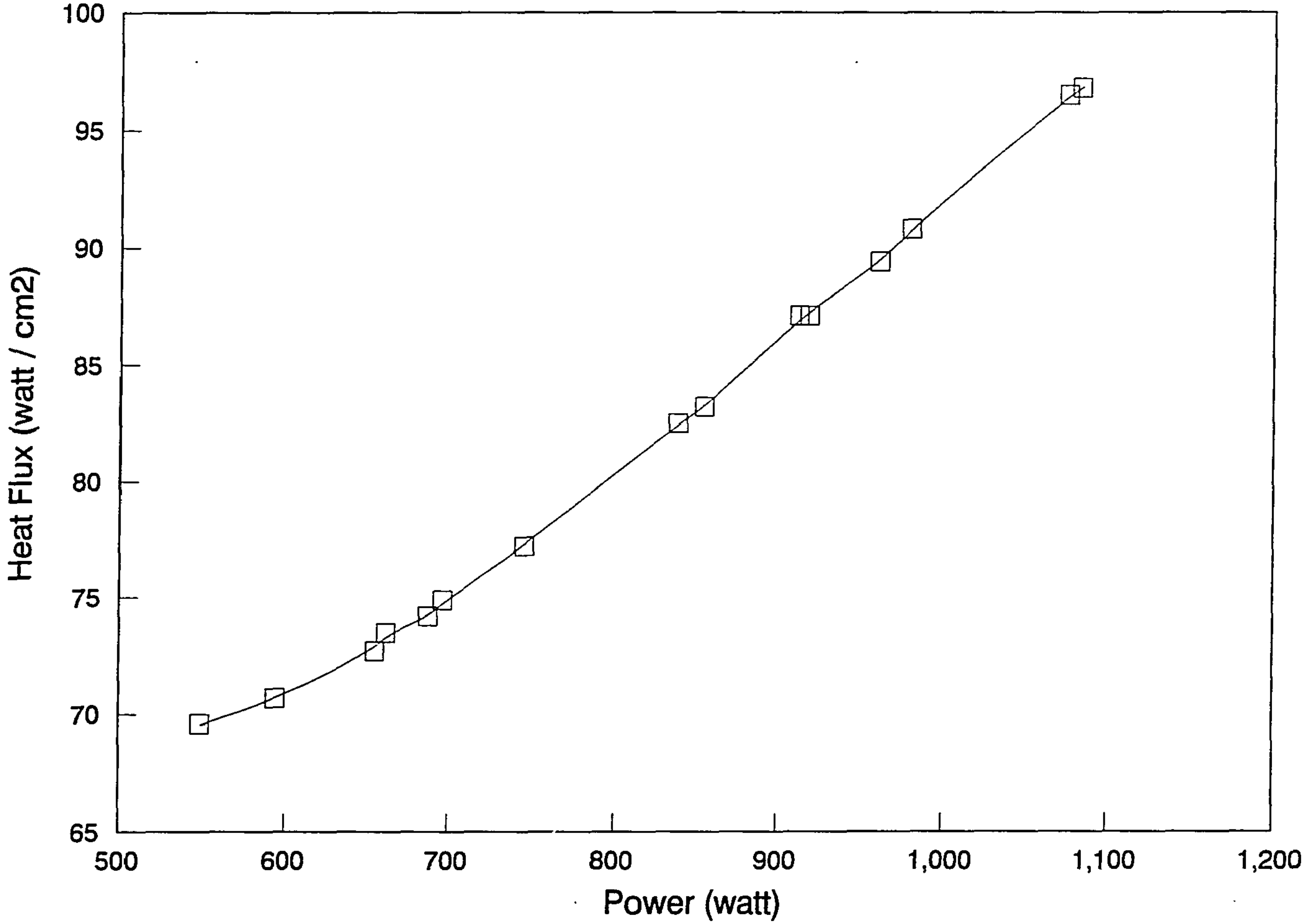

Figure 4.1: Heat Flux of Light Beam Versus Required Power

Table 4.2

Temperature Measurements at Focal Point of High Intensity Light Beam

Power Level (watt)	Temperature (°C)
392.8	654
426.0	690
471.8	698
498.6	700
526.4	720
569.6	735
577.2	736
597.8	766
643.2	767
663.1	770
735.0	809
800.0	834
811.8	828
886.8	859
900.0	872
962.6	897
999.6	907
1073.5	933
1078.6	940

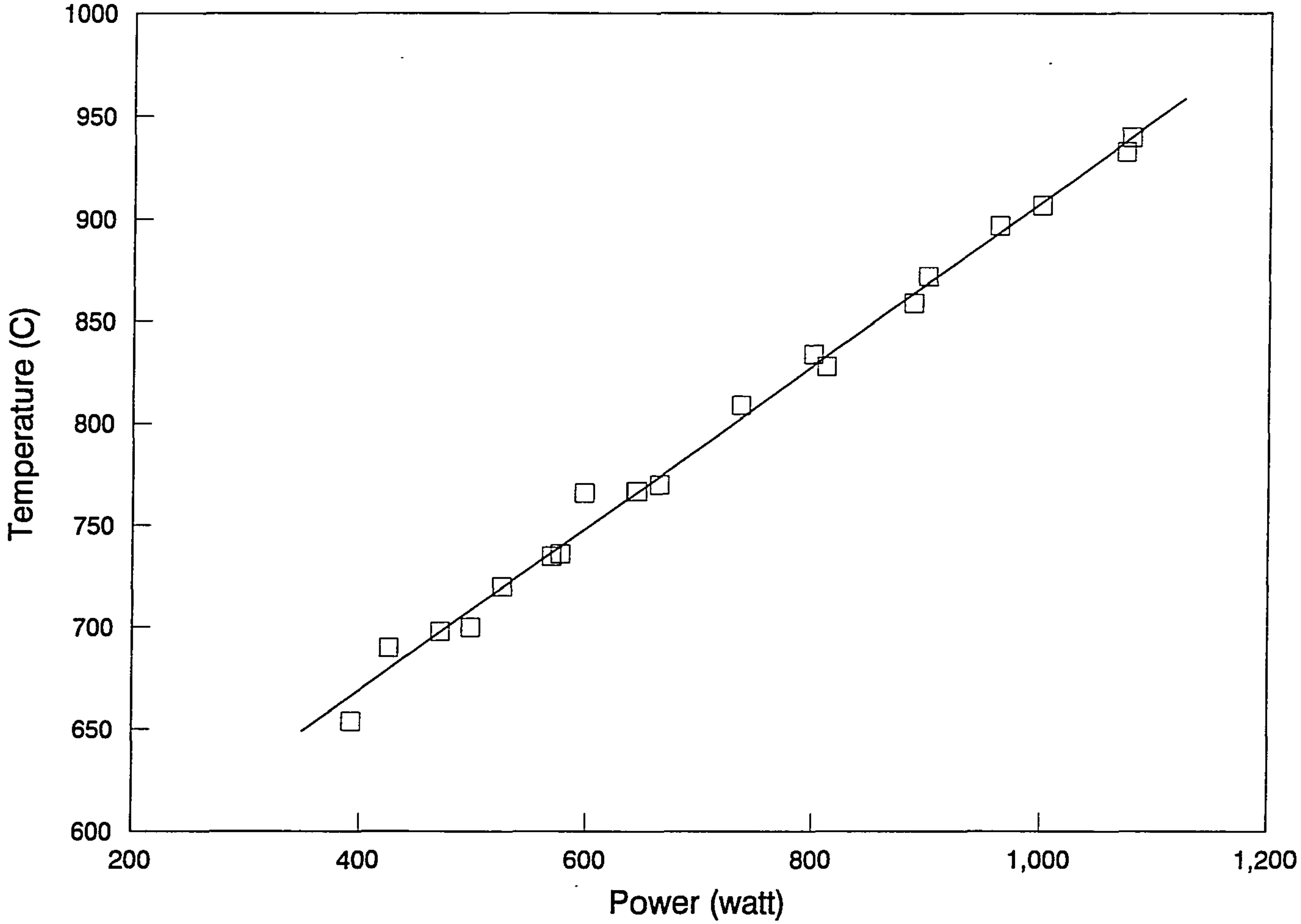

Figure 4.2: Temperature at the Focal Point Versus Required Power

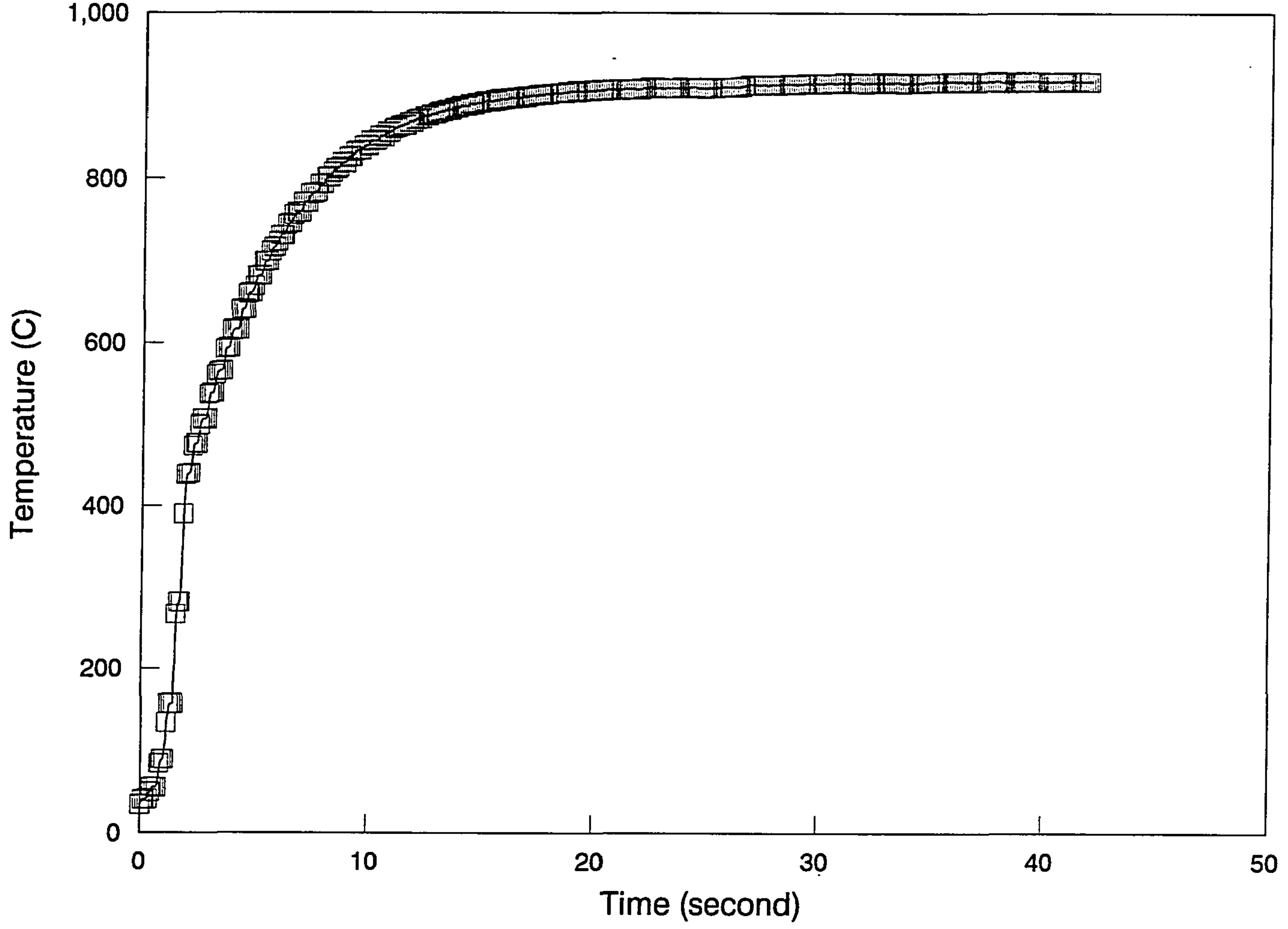

Figure 4.3: Coal Surface Heating Rate at 1000 watt Power

Section B. Rapid Hydropyrolysis of Bituminous Coal

The effect of several experimental variables on rapid hydropyrolysis of Kentucky no. 9 high volatile bituminous coal was investigated in this study. The experimental variables that were studied included 15 to 60 seconds exposure time, 650 to 900 °C peak temperature, 68 to 774 micrometer average coal particle size, and reaction atmospheres (hydrogen and helium). Peak temperature of a coal sample is defined as that measured temperature which remains almost constant with time of exposure. Total coal conversion (weight loss) and the amount of liquid hydrocarbons (acetone soluble) and gas produced were reported as a function of these variables.

Effect of Exposure Time on Bituminous Coal Hydropyrolysis. The effect of exposure time on the Kentucky no. 9 high volatile bituminous coal hydropyrolysis was studied in the time range 15 to 60 seconds. In all the experiments, the peak temperature was maintained at 900 °C, coal particle size of 63 to 74 micrometer, and hydrogen atmosphere was used. In each run, the total amount of coal sample used was about 0.012 gram (in four crucibles in a thin layer). The effect of exposure time on high volatile bituminous coal as measured by the amount of weight loss and liquid hydrocarbons collected are presented in Table 4.3. All percent conversions are calculated on moisture and ash free (maf) basis. The results are on the conservative side since all the coal particles might not have been fully exposed to the radiant beam.

The effect of exposure time on the hydropyrolysis of high volatile bituminous coal is also shown in Figure 4.4. It can be seen that the total coal conversion (production of

Table 4.3

Effect of Exposure Time on Bituminous Coal Hydropyrolysis

Experimental variables:

Peak temperature: 900 °C

Coal particle size: 63 to 74 micrometer

Atmosphere: hydrogen

Serial Number	Exposure Time (seconds)	Percent Total Coal Conversion	Percent Liquid	Percent Gas
1	15	16.4	6.7	9.7
2	22	26.8	10.2	16.6
3	30	38.5	16.3	22.2
4	45	42.1	17.5	24.6
5	60	44.8	17.8	27.0

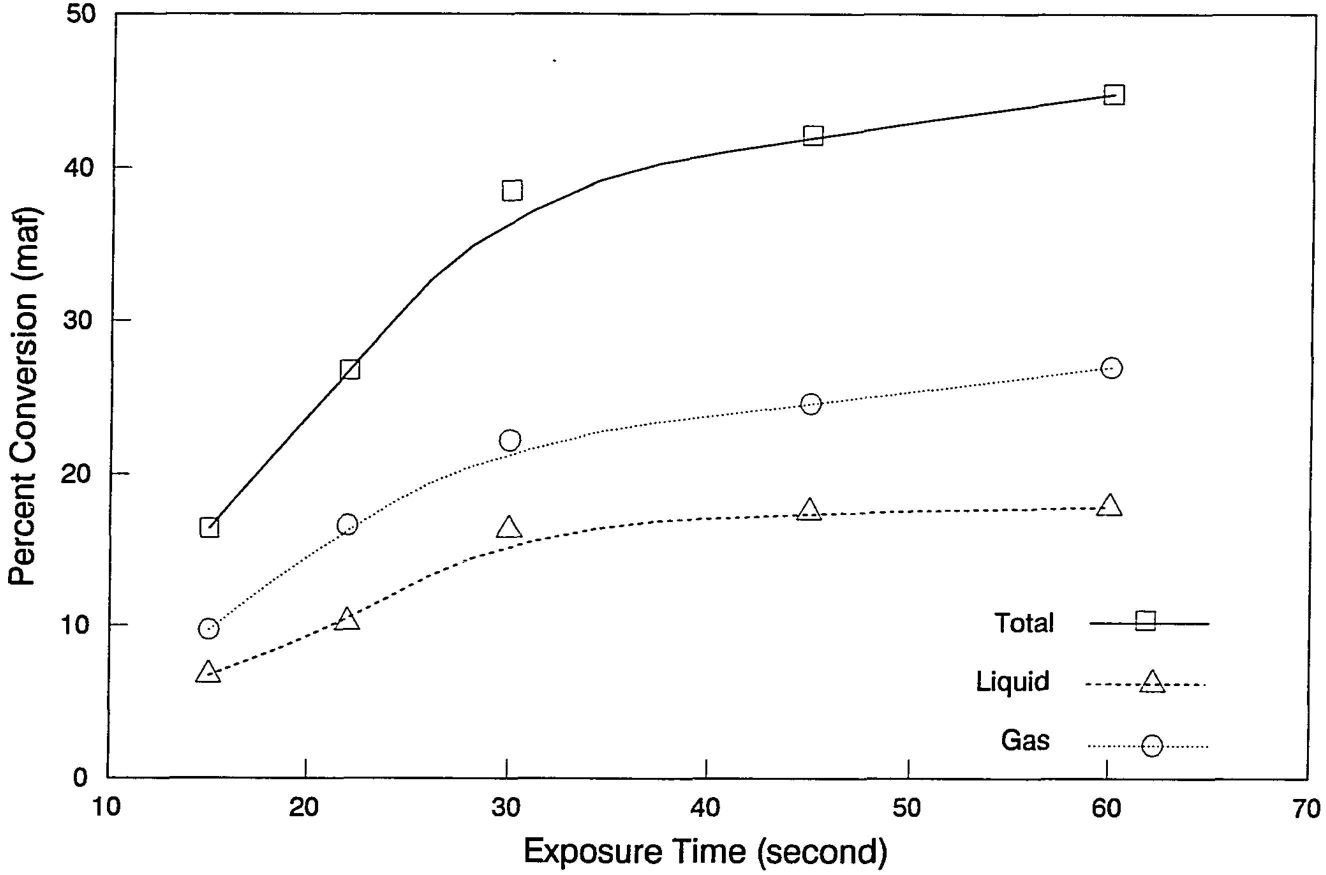

Figure 4.4: Coal Conversion Versus Exposure Time

liquid hydrocarbons and gas) increased from 16.4% at 15 seconds to 38.5% at 30 seconds of exposure time. The liquid hydrocarbons yield also increased significantly from 6.7% to 16.3% at 15 and 30 seconds, respectively. A further increase in the exposure time up to 60 seconds showed no significant enhancement in the total coal conversion and the production of the liquid hydrocarbons. The total coal conversion increased from 38.5% at 30 seconds to 44.8% at 60 seconds and the production of liquid hydrocarbons increased from 16.3% to 17.8%. The most suitable exposure time for the high volatile bituminous coal hydropyrolysis was thus found to be 30 seconds for which the total coal conversion and the liquid hydrocarbons yield were found to be 38.5% and 16.3%, respectively. A gaseous product analysis showed that the gas sample was rich in hydrogen indicating that the amount of hydrogen was adequate for the hydropyrolysis of the coal sample.

The total coal conversion was then compared to the volatile matter content of the high volatile bituminous coal from a proximate analysis. The amount of volatile matter in a coal sample is determined by ASTM method D3175-89a. In this method, volatile matter is measured by establishing the loss in weight resulting from heating a coal sample for seven minutes in a furnace chamber maintained at a temperature of 950 °C. The percentage loss of weight minus the percentage moisture equals the volatile matter. The volatile matter for Kentucky no. 9 high volatile bituminous coal was reported to be 46.93% on the moisture and ash free basis. The amount of volatile released (total coal conversion) from this study at 900 °C and 60 seconds was found to be 44.8% which was close to the total amount of volatile matter contained in the high volatile bituminous coal.

Effect of Peak Temperature on Bituminous Coal Hydropyrolysis. The effect of peak temperature on the hydropyrolysis of high volatile bituminous coal was studied in the temperature range of 650 °C to 900 °C. The coal particle size used was 63 to 74 micrometer. The exposure time used was 30 seconds as it was found to be the most suitable condition.

The results showing the effect of peak temperature on the hydropyrolysis of coal sample are presented in Table 4.4 and shown in Figure 4.5. The peak temperature was varied from 650 °C to 900 °C. The total coal conversion to liquid hydrocarbons (acetone soluble) and gas increased steadily from 19.6% at 650 °C to about 38.5% at 900 °C peak temperature. The production of liquid hydrocarbons increased from 2.8% at 650 °C to 16.3% at 900 °C. The effect of peak temperature was studied only in this range due to the limitations of the power source. The peak temperature of 900 °C and exposure time of 30 seconds were used to study the effect of coal particle size, as discussed later.

Effect of Particle Size on Bituminous Coal Hydropyrolysis. The effect of particle size on the hydropyrolysis of high volatile bituminous coal was studied using three different coal particle size ranges. These included 63 to 74 micrometer (68 micrometer average size), 354 to 420 (387 micrometer average size), and 797 to 841 micrometer (774 micrometer average size). The exposure time and peak temperature were kept constant at 30 seconds and 900 °C, respectively. Results of the effect of particle size on

Table 4.4

Effect of Peak Temperature on Bituminous Coal Hydropyrolysis

Experimental variables:

Exposure time: 30 seconds

Coal particle size: 63 to 74 micrometer

Atmosphere: hydrogen

Serial Number	Peak Temperature (°C)	Percent Total Coal Conversion	Percent Liquid	Percent Gas
1	650	19.6	2.8	16.8
2	710	26.5	7.8	18.7
3	810	33.3	13.0	20.3
4	900	38.5	16.3	22.2

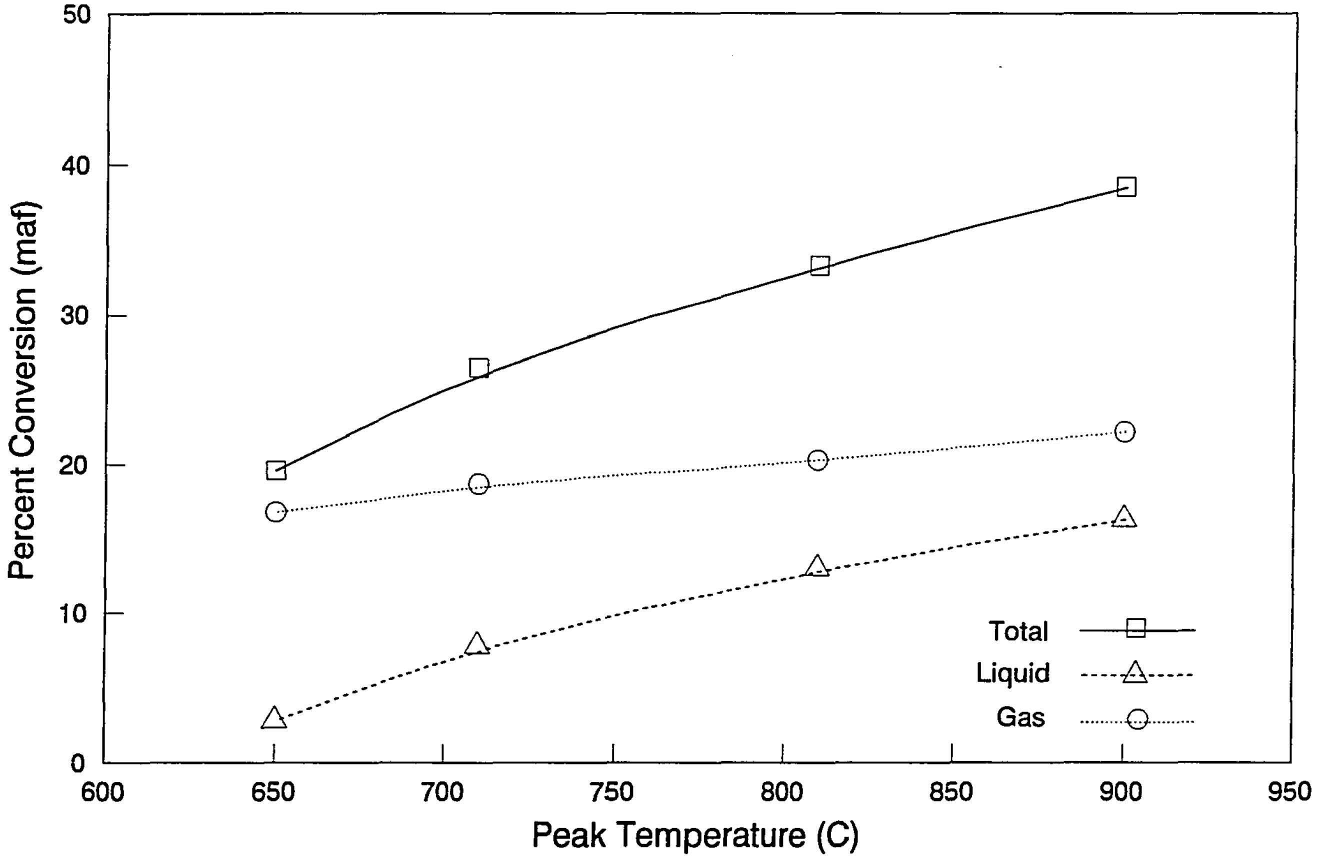

Figure 4.5: Coal Conversion Versus Peak Temperature

the hydropyrolysis of the high volatile bituminous coal are presented in Table 4.5 and also shown in Figure 4.6. It was found that the total coal conversion decreased slightly from 38.5% for coal of average particle size of 68 micrometer to 36.4% and 35.4% for coal particle size of 387 and 774 micrometer, respectively. The liquid product also decreased slightly from 16.3% for coal of average particle size of 68 micrometer to 14.0% and 12.4% for coal average particle size of 387 and 774 micrometer, respectively.

These small decreases were considered due to the decrease in surface area when larger coal particles were used. Overall, the yield was not found to be strongly dependent on the coal particle sizes studied. Sugawara et al. (1990) also concluded that coal particle sizes less than 500 micrometer had a negligible effect on the total volatile yields in their rapid coal hydropyrolysis study. The yield of liquid hydrocarbons also decreased with an increase in coal particle size.

From these results, a coal sample with particles in the range of 63 to 74 micrometer (68 micrometer average particle size) was chosen to study the effect of reaction atmospheres on rapid coal hydropyrolysis.

Effect of Surrounding Atmosphere on Bituminous Coal Hydropyrolysis. In order to study the effect of surrounding atmosphere on high volatile coal hydropyrolysis, experiments were also conducted in a helium atmosphere. The experimental variables were maintained at 30 seconds exposure time, 900 °C peak temperature, and 63 to 74 micrometer coal particle size. The total conversion of coal in helium (pyrolysis) was about 34.9% and the amount of liquid product produced was about 13.2% as shown in

Table 4.5

Effect of Coal Particle Size on Bituminous Coal Hydropyrolysis

Experimental variables:

Exposure time: 30 seconds

Peak Temperature: 900 °C

Atmosphere: hydrogen

Serial Number	Particle Size (micrometer)	Percent Total Coal Conversion	Percent Liquid	Percent Gas
1	63 to 74	38.5	16.3	22.2
2	354 to 420	36.4	14.0	22.4
3	707 to 841	35.4	12.4	23.0

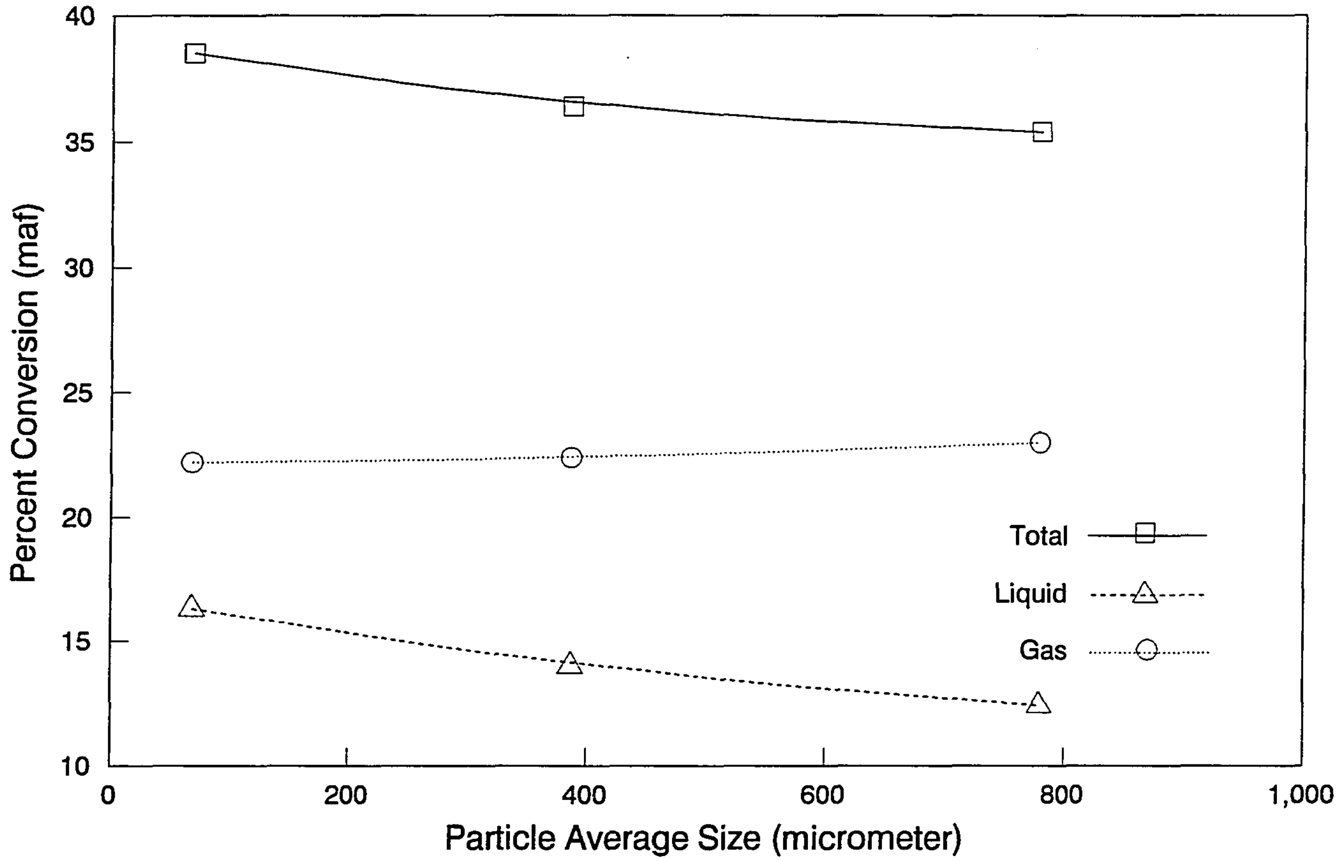

Figure 4.6: Coal Conversion Versus Particle Size

Table 4.6. These values were slightly lower than the values obtained from the experiment conducted in hydrogen atmosphere (hydropyrolysis) which were 38.5% and 16.3%, respectively.

Simulated distillation data for liquid product from the rapid pyrolysis experiment (helium atmosphere, Table 4.6, S.N. 3) were found to be very different from those for liquid product from rapid hydropyrolysis experiment (hydrogen atmosphere, Table 4.6, S.N. 1) as shown in Table 4.7. The liquid product collected from rapid pyrolysis experiment (helium atmosphere) had only about 3.1% of the distillate with boiling point lower than 200 °C whereas the liquid product collected from rapid hydropyrolysis experiment had about 25.4 % of distillate with boiling point lower than 200 °C (gasoline boiling range which includes light straight run gasoline and naphtha). Furthermore, the liquid product collected from rapid pyrolysis experiment had only 23% of the total distillate with boiling point lower than 300 °C (gasoline and kerosine range) which is much lower compared to 65.4% liquid product collected from the rapid hydropyrolysis experiment. From these results, it is evident that rapid hydropyrolysis has an advantage over rapid pyrolysis is the quality of the liquid hydrocarbons produced. Liquid product (acetone soluble) from rapid hydropyrolysis experiment (Table 4.6, S.N. 1) contained about 25.4% of distillate in the gasoline boiling range (32 to 200 °C) as compared to only 3.1% in the liquid hydrocarbons collected from rapid pyrolysis experiment (Table 4.6, S.N. 3). The details of the gas chromatographic simulated distillation technique are discussed later.

Table 4.6

Effect of Surrounding Atmosphere on Bituminous Coal Hydropyrolysis

Experimental variables:

Exposure time: 30 seconds

Peak Temperature: 900 °C

Coal particle size: 63 to 74 micrometer

Serial Number	Atmosphere	Percent Total Coal Conversion	Percent Liquid	Percent Gas
1	hydrogen	38.5	16.3	22.2
2	hydrogen	37.7	16.0	22.6
3	helium	34.9	13.2	21.7

Table 4.7

Simulated Distillation Data for Liquid Products of Hydropyrolysis and Pyrolysis of Bituminous Coal

Boiling Range (°C)	Hydropyrolysis (percent)	Pyrolysis (percent)
< 150	0	0
150 to 200	25.4	3.1
200 to 250	21.9	6.6
250 to 300	18.1	12.8
300 to 350	33.0	0.3
350 to 400	1.6	77.2

The results indicate that the reaction mechanism plays an important role in the liquid product distribution. When coal is heated rapidly, its chemical structure is broken due to thermal cracking. The products formed are called primary volatiles which are made up of gases and low molecular weight liquid hydrocarbons. These primary volatiles are metastable (intermediate products) and usually in the free radical forms. The primary volatiles then travel through the coal particles before being released out. Once the primary volatiles are released, they follow several reaction paths before being stabilized. In an inert atmosphere such as helium these primary volatiles, in the free radical form, are stabilized through a repolymerization process. They recombine with each other to form high molecular weight compounds or tarry materials which were observed in the rapid pyrolysis experiments. However, in the presence of hydrogen, the primary volatiles are stabilized through reactions with hydrogen. The products from these reactions generally have lower molecular weights or boiling points than those produced by rapid pyrolysis (in inert atmosphere) since the repolymerization process is reduced significantly. As a result, liquid hydrocarbons produced from rapid hydropyrolysis are mostly made of lower boiling point compounds compared to those produced from rapid pyrolysis. The details of the rapid coal hydropyrolysis mechanism are discussed later. In view of these results, all subsequent experimental runs conducted in this study were in hydrogen atmosphere (hydropyrolysis).

Simulated Distillation of Coal Hydropyrolysis Liquid Product. One of the most important parts of this study was the characterization of the liquid and gaseous products.

Therefore, the discussion of the analytical techniques used to characterize the products has been included in the body of the thesis rather than presented in an appendix. In practice, ASTM D86-78 is normally used to determine the boiling point distribution of liquid hydrocarbons in the petroleum industry. However, this technique could not be used in this study since the amounts of liquid hydrocarbons collected were very small. Instead, the liquid product has been subjected to ASTM D2887-89 standard test method for boiling range distribution of petroleum fractions by gas chromatography. This method is also known as a gas chromatographic simulated distillation technique.

The liquid product sample for gas chromatographic simulated distillation for this illustration was collected from the experimental run (Table 4.6, S.N. 1) conducted at 30 seconds of exposure time, 900 °C peak temperature, 63 to 74 micrometer particle size, and atmospheric hydrogen pressure. The total amount of dry coal used for the run was about 0.012 gram. The total amount of coal converted to liquid and gaseous products was found to be 0.004 gram (38.5% on moisture ash free basis) and the amount of liquid product (acetone soluble) collected was 0.0017 gram (16.3% on moisture ash free basis). The gas chromatographic simulated distillation analytical technique was conducted in two parts. The first part was to generate data curve (calibration curve) to plot retention time versus the normal boiling point of known hydrocarbons which are presented in Table 4.8 and also shown in Figure 4.7.

The liquid product sample from the chosen experimental run (Table 4.6, S.N. 1) was then subjected to the gas chromatographic simulated distillation technique and the data are presented in Table 4.9. About 25.4% of the distillate is in gasoline boiling range

Table 4.8

Gas Chromatographic Boiling Point Calibration Curve

Carbon Number	Chemical	Boiling Point (°C)	Retention Time (minutes)
5	pentane	36	0.879
	acetone	56	0.926
6	hexane	69	1.648
8	octane	126	4.791
10	decane	174	8.210
11	undecane	196	10.139
12	dodecane	216	11.984
14	tetradecane	254	15.381
15	pentadecane	271	16.921
16	hexadecane	287	18.385
18	octadecane	316	21.104
22	docosane	369	25.768
28	octacosane	431	31.464

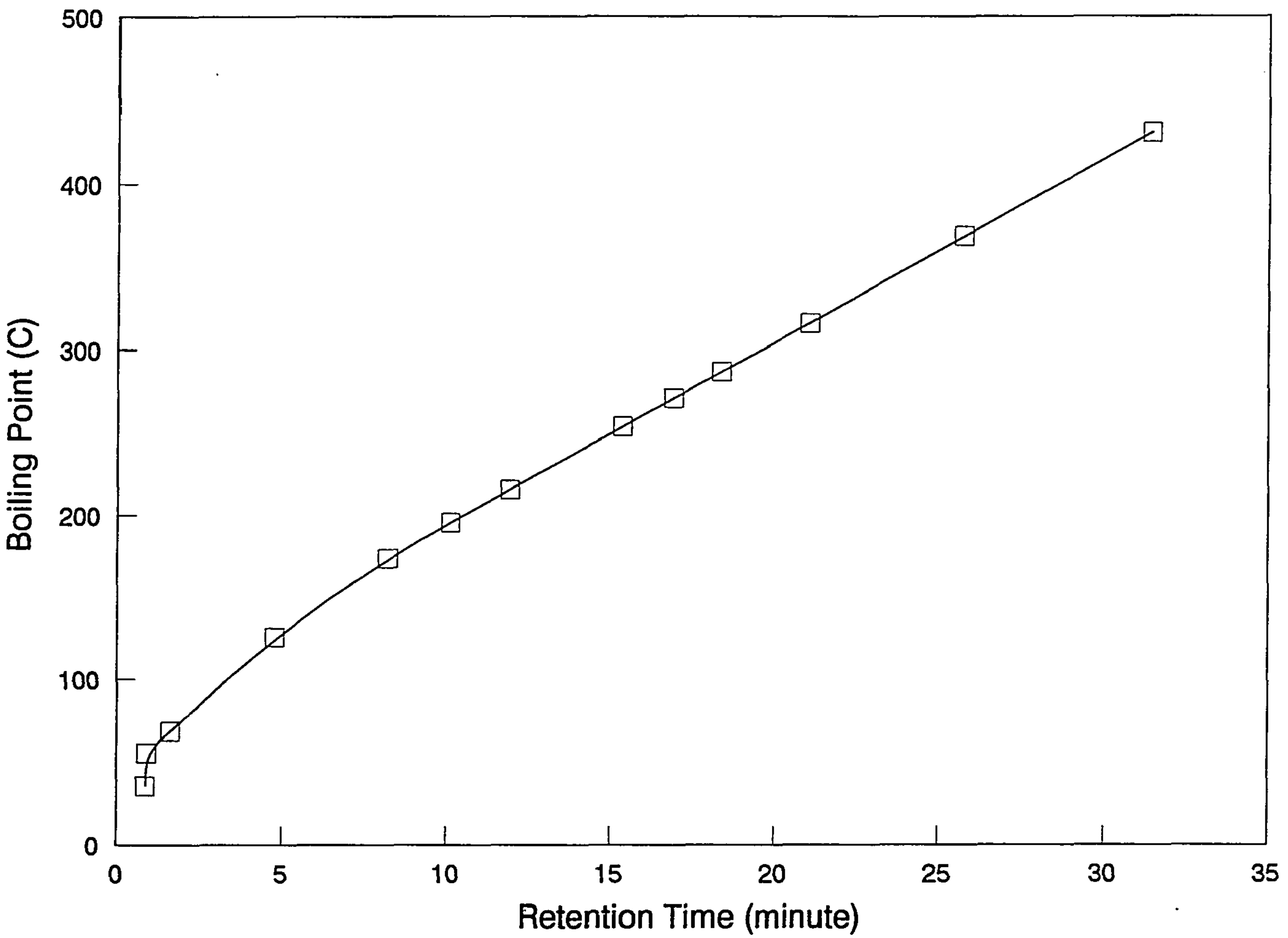

Figure 4.7: Normal Boiling Point of Hydrocarbons Versus Retention Time

Table 4.9

Gas Chromatographic Simulated Distillation of Liquid Product of Bituminous Coal Hydropyrolysis

Boiling Range (°C)	Amount of Distillate (percent)
< 150	0
150 to 200	25.4
200 to 250	21.9
250 to 300	18.1
300 to 350	33.0
350 to 400	1.6

(32 to 200 °C) (ASTM distillation cut) which includes light straight-run gasoline and naphtha. The data also show that about 65.4% of this liquid is in boiling range of gasoline and kerosine (< 300 °C).

Gas Chromatographic Analysis of Gaseous Product. The gaseous product sample for gas chromatography analysis for this illustration was collected from the same experimental run (Table 4.6, S.N. 1). The gas chromatography analytical technique to determine the gaseous product composition was again conducted in two parts. The first part was to develop the procedure to assign anticipated gases that may be produced during hydropyrolysis with their retention times. The quantitative amount of gas was determined using a standard mixture with known composition. Result of the gases present versus retention time is presented in Table 4.10.

The result of the gas chromatographic analysis is presented in Table 4.11 which shows that the gas sample is rich in hydrogen gas (about 98% of the total composition) indicating that the amount of hydrogen is adequate for the hydropyrolysis of the coal sample. The hydrogen free gas composition is also presented in Table 4.11 which shows that the gaseous product mainly consists of carbon monoxide and carbon dioxide. About 92.6% of the volatiles released in the gaseous form were carbon monoxide and carbon dioxide. Methane made up the rest of the gas composition (about 7.4%). In the pyrolysis experiment (in helium atmosphere, Table 4.6, S.N. 3) hydrogen was not detected in the gas analysis as presented in Table 4.12. Other gases such as ethane, acetylene, and ethylene were also not detected.

Table 4.10

Gaseous Product Versus Retention Time

Gas	Retention Time (minutes)
hydrogen	1.5
oxygen	5.6
nitrogen	6.0
carbon monoxide	7.7
methane	11.4
carbon dioxide	13.7
acetylene	16.5
ethylene	19.2
ethane	21.9

Table 4.11

Gas Composition of Hydropyrolysis Product

Gas	Total (mol %)	Hydrogen Free (mol %)
hydrogen	98.13	
carbon monoxide	1.67	89.45
methane	0.14	7.34
carbon dioxide	0.06	3.21

Table 4.12

Gas Composition of Pyrolysis Product

Gas	Total (mol %)
hydrogen	0.0
carbon monoxide	97.3
methane	1.7
carbon dioxide	1.0

Carbon Conversional Balance of Bituminous Coal. The carbon conversion of the bituminous coal to various products was also estimated. Carbon, hydrogen, and nitrogen analysis was used to determine the contents of the products (char plus ash and liquid). The carbon content of the coal was obtained from the coal ultimate analysis. The experiment at the most suitable conditions of the coal rapid hydropyrolysis (Table 4.6, S.N. 1) was chosen for the carbon conversion calculations. This is a representative sample of the rapid coal hydropyrolysis experiments conducted in this study. The conversions based on carbon content of coal are as follows:

Total carbon conversion: 32.56%

Carbon conversion into liquid product (acetone soluble): 14.28%

Carbon conversion into gases: 18.28%

The carbon balance of the bituminous coal is also shown in Figure 4.8.

Section C. Hydropyrolysis of Low Rank Coals

Hydropyrolysis experiments were also conducted using lignite and subbituminous coals. North Dakota Beulah lignite and Montana Rosebud subbituminous coals were used in this study. The total amount of coals converted to liquid hydrocarbons and gaseous products, the amount of liquid hydrocarbons produced, and the product distribution in the liquid hydrocarbons collected were compared for the three coals: bituminous, subbituminous, and lignite.

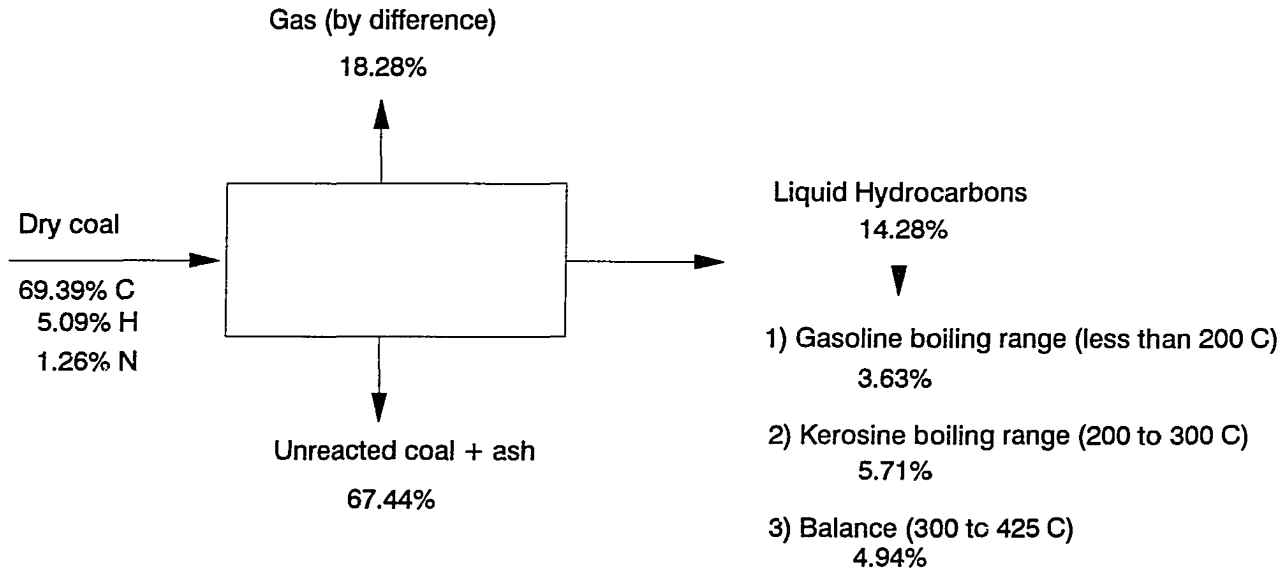

Figure 4.8: Carbon Conversional Balance for Rapid Hydropyrolysis of Kentucky no. 9 Coal

The experimental variables studied for the hydropyrolysis of the subbituminous and lignite coals were exposure time, peak temperature, particle size, and reaction atmosphere. The experimental results for rapid hydropyrolysis of subbituminous and lignite coals are presented in Appendix A. The most suitable condition for both subbituminous coal and lignite were also found to be 30 seconds exposure time, 900 °C peak temperature, 63 to 74 micrometer particle size, and hydrogen atmosphere. The total amount of dry coals used for each run was about 0.012 gram. The total coal conversion and the amount of liquid hydrocarbons and gas produced for each coal are presented in Table 4.13.

The total amount of coal converted to liquid and gaseous products decreased with the coal rank. The total amount of coal converted to liquid and gaseous products for bituminous coal was found to be 38.5% and decreased to 33.6% for subbituminous coal and to 32.2% for lignite. The production of liquid hydrocarbons also decreased from 16.3% for bituminous to 8.8% for subbituminous and 3.5% for lignite coal. From these results, it can be observed that although the total conversion of coals did not decrease that much, the amount of liquid hydrocarbons collected was reduced significantly from bituminous to lignite coal. The lignite and subbituminous coals which have higher oxygen content than the bituminous coal, produced larger quantities of oxygenated volatiles, while the bituminous coal volatiles were dominated by hydrocarbons. The oxygenated volatiles were mostly in the gaseous form such as carbon dioxide and carbon monoxide while the hydrocarbons were mostly in the liquid form. Consequently, significant amount

Table 4.13

Effect of Coal Rank on Hydropyrolysis

Experimental variables:

Exposure time: 30 seconds

Peak Temperature: 900 °C

Coal particle size: 63 to 74 micrometer

Atmosphere: hydrogen

Serial Number	Coal Rank	Percent Total Coal Conversion	Percent Liquid	Percent Gas
1	bituminous	38.5	16.3	22.2
2	subbituminous	33.6	8.8	24.8
3	lignite	32.2	3.5	28.7

of the subbituminous and lignite coals were converted to gaseous product as compared to the bituminous coal.

The product distribution of the liquid hydrocarbons for various ranks of coal were also determined using the gas chromatographic simulated distillation technique. The results from these analyses are presented in Table 4.14. The amount of low boiling distillate in the liquid product decreased with the coal rank. The amount of distillate with boiling point lower than 200 °C (gasoline boiling range) was about 25.4% for bituminous coal. This fraction was not detected in liquid products collected from rapid hydropyrolysis of subbituminous and lignite coals. The total amount of distillate with boiling point lower than 300 °C (gasoline and kerosine range) from rapid hydropyrolysis of bituminous coal was about 65.4%. The amount of distillate below 300 °C collected from subbituminous and lignite coals were about 36.0% and 21.0%, respectively.

The gaseous products from rapid hydropyrolysis of the three type of coals were also analyzed using gas chromatography and the results are presented in Table 4.15. The composition of the gaseous products in each case was mostly made-up of carbon monoxide and carbon dioxide, and the total amount of these two gases was 90% or more in each of the three cases. However, it was observed that there was an increase in carbon dioxide content from bituminous to lignite coal. It increased from 3.2% for bituminous to 27.1% for subbituminous and to 28.7% for lignite coal. This increase is due to the fact that subbituminous and lignite coals have a greater oxygen content. The ultimate analyses of bituminous, subbituminous, and lignite show percent oxygen contents of 8.9, 15.2, and 20.6, respectively, on a moisture and ash free basis (maf). The high oxygen

Table 4.14

Boiling Point Distribution of Liquid Product of Hydropyrolysis of Various Coal Ranks

Boiling Range (°C)	Bituminous (percent)	Subbituminous (percent)	Lignite (percent)
< 150	0	0	0
150 to 200	25.4	0	0
200 to 250	21.9	7.6	9.2
250 to 300	18.1	28.4	11.8
300 to 350	33.0	1.7	3.5
350 to 400	1.6	62.3	75.5

Table 4.15

Gas Composition of Hydropyrolysis of Various Coal Ranks

(Hydrogen Free Composition)

Gas	Bituminous (mol %)	Subbituminous (mol %)	Lignite (mol %)
carbon monoxide	89.45	63.07	59.38
methane	7.34	9.82	11.88
carbon dioxide	3.21	27.11	28.74

content in the subbituminous and lignite coals produced greater amounts of oxygenated volatiles which included carbon dioxide and carbon monoxide. Methane made-up the rest of the composition which varied from about 7.3% for bituminous to 9.8% and 11.9% for subbituminous and lignite coals, respectively. Other hydrocarbon gases such as ethane, acetylene, and ethylene were not detected in the three gaseous analyses.

Section D. Proposed Mechanism and Mathematical Correlations for Rapid Coal Hydropyrolysis

Mechanism and mathematical correlations are important in understanding a reaction in greater depth. Mechanism helps to explain how a reaction takes place. On the other hand, mathematical correlations are important in predicting the effect of experimental conditions on the product yields for a given reaction.

Mechanism of Rapid Coal Hydropyrolysis and Pyrolysis. The results of this study indicate that the reaction mechanism plays an important role in the liquid product distribution. The following mechanism is proposed for coal hydropyrolysis and pyrolysis reactions.

$$\text{Coal} \xrightarrow{\text{thermal cracking}} \text{Metastable Products} \tag{4.1}$$

$$\text{Metastable Products} \xrightarrow{\text{secondary cracking}} \text{Gas} \tag{4.2}$$

$$\text{Metastable Products} \xrightarrow{\text{repolymerize}} \text{High B.P. Liquids} \tag{4.3}$$

$$\text{Metastable Products} + H_2 \text{ -------> Low B.P. Liquids} \qquad (4.4)$$

When coal is heated rapidly, its chemical structure is broken down into lower molecular weight hydrocarbons known as metastable products due to thermal cracking as shown by equation [4.1]. The rate of thermal cracking is dependent of the reaction temperature. The higher the temperature, the greater the amount of products. The products formed are called primary volatiles and are made up of gases and low molecular weight liquid hydrocarbons. These primary volatiles are metastable (intermediate products) and usually in the free radical forms. The primary volatiles then travel through the coal particles before being released out. In larger coal particles, the primary coal volatiles spend a longer period of time in regions of high temperature due to the increase in path length the primary volatiles have to travel, thereby resulting in an increased exposure time. As a consequence, the primary volatiles go through secondary reactions thereby cracking into gaseous molecules as shown by equation [4.2]. Consequently, less liquid hydrocarbons and more gaseous products are produced from larger coal particles.

Once the primary volatiles are released, they could follow several reaction paths before being stabilized. In an inert atmosphere such as helium these primary volatiles, in the free radical form, are stabilized through a repolymerization process as shown by equation [4.3]. They recombine with each other to form high molecular weight compounds or tarry materials which is observed in the rapid pyrolysis experiments. However, in the presence of hydrogen, the primary volatiles are stabilized through reactions with hydrogen as shown by equation [4.4]. The products from these reactions generally have lower molecular weights or boiling points than those produced by rapid pyrolysis (in inert atmosphere) since repolymerization process is reduced significantly. As a result, liquid hydrocarbons produced from rapid hydropyrolysis are mostly made of lower boiling point compounds compared to those produced from rapid pyrolysis.

Mathematical Correlations of Coal Rapid Hydropyrolysis. Models compounds, which are usually pure chemicals, have been used to study coal thermal reactions. Mechanisms of various thermal reactions during pyrolysis have been proposed from these studies. However, the kinetics of coal pyrolysis, hydropyrolysis, and other thermal reactions are more complicated due to the fact that numerous functional groups that are present in the coal react simultaneously. Since the reactions of coal pyrolysis are not completely understood, chemical modelling has not been very successful in predicting the products of actual coal pyrolysis and hydropyrolysis reactions. The nature of coal pyrolysis and hydropyrolysis, lack of complete knowledge of the reaction mechanism, and the lack of sufficiently accurate values for rate parameters have all made it difficult to characterize coal with a simple chemical compound. The results of previous investigations indicate that no one model compound can accurately represent coal to study the kinetics of coal pyrolysis and hydropyrolysis. The value of frequency factor could be several orders of magnitude off for those model compounds.

A number of mathematical models and correlations have been developed based on data obtained from coal pyrolysis and hydropyrolysis studies. These models predict with sufficient accuracy the product yields and distribution. Several mathematical models and correlations have been developed to determine products of coal pyrolysis and hydropyrolysis in entrained flow reactors. These correlations and mathematical models are limited to specified operating conditions and cannot be applied to processes where other heating techniques are used. Finally, all the mathematical correlations are for high pressure and cannot be applied for low pressure conditions used in this study.

In this investigation a statistical correlation for the formation of products is proposed. Statistical treatment of the data from all the hydropyrolysis experimental runs is used to determine which of the experimental variables such as exposure time, peak temperature, and coal particle size are important in affecting the product distributions. A multiple regression technique (LOTUS 123 VERSION 3.1) is used to perform multiple linear regression analysis. The results of the regression is expressed in the form of a linear equation:

$$y = b_o + b_1x_1 + b_2x_2 + \dots\dots + b_nx_n$$

where $x_1, x_2, \dots, x_n$ are the independent variables (experimental parameters) and y is the dependent variable (product yield). The following equations and correlation coefficients are obtained:

Total fraction of coal converted (maf)

$$X_T = \exp\left[0.7056\ ln\ t + 0.000171\ d_p - \frac{1705.71}{T} + 2.5177\right] \qquad (4.5)$$

with r= 0.926

Fraction of coal converted to liquid hydrocarbons (maf)

$$X_L = \exp\left[0.7112\ ln\ t - 9.3x10^{-5}\ d_p - \frac{5376.32}{T} + 4.7805\right] \tag{4.6}$$

with r= 0.915

Fraction of coal converted to gases (maf)

$$X_G = \exp\left[0.701\ ln\ t + 0.000313\ d_p - \frac{306.15}{T} + 0.7997\right] \tag{4.7}$$

with r= 0.931

where,

t = exposure time in seconds

T = peak temperature in °K

d_p = average particle size in micrometer

X_T = total fraction of coal converted (percent maf)

X_L = fraction of coal converted to liquid hydrocarbons (percent maf)

X_G = fraction of coal converted to gases

Results from the multiple regression analysis indicate that exposure time and peak temperature have a significant effect on the product yields. Particle size does not have a significant effect on the product yields. The experimental results and the predicted values of product yields from the proposed correlations are tabulated in Tables 16, 17, and 18. The predictions are obtained by substituting the operating data from the present

Table 4.16

Experimental and Predicted Total Coal Conversion from Proposed Correlation

Time (Sec.)	Size (microns)	Temperature (°K)	Experimental (% maf)	Prediction (% maf)
15	68	1173	16.4	19.8
22	68	1173	26.8	26.0
30	68	1173	38.5	32.3
45	68	1173	42.1	43.0
60	68	1173	44.8	52.7
30	387	1173	36.4	34.1
30	774	1173	35.4	36.4
30	68	1083	33.3	28.6
30	68	983	26.5	24.4
30	68	923	19.6	21.8

AAPD = 10.22%

Table 4.17

Experimental and Predicted Coal Conversion

to Liquid Hydrocarbons from Proposed Correlation

Time (Sec.)	Size (microns)	Temperature (°K)	Experimental (% maf)	Prediction (% maf)
15	68	1173	6.7	8.3
22	68	1173	10.2	10.9
30	68	1173	16.3	13.6
45	68	1173	17.5	18.1
60	68	1173	17.8	22.3
30	387	1173	14.0	13.2
30	774	1173	12.4	12.7
30	68	1083	13.0	9.3
30	68	983	7.8	5.6
30	68	923	2.8	3.9

AAPD = 18.16%

Table 4.18

Experimental and Predicted Coal Conversion to Gases from Proposed Correlation

Time (Sec.)	Size (microns)	Temperature (°K)	Experimental (% maf)	Prediction (% maf)
15	68	1173	9.7	11.7
22	68	1173	16.6	15.3
30	68	1173	22.2	19.0
45	68	1173	24.6	25.2
60	68	1173	27.0	30.9
30	387	1173	22.4	21.0
30	774	1173	23.0	23.7
30	68	1083	20.3	18.6
30	68	983	18.7	18.1
30	68	923	16.8	17.7

AAPD = 8.63%

study into each of the correlations. The Absolute Average Percentage Deviation (AAPD) is defined as:

$$AAPD = \frac{1}{n}\sum_{i=1}^{n}\left(\frac{|X_{exp} - X_{pre}|}{X_{exp}}\right) 100\%$$

With the proposed correlations, the predicted product yields show an AAPD of 10.22%, 18.16%, and 8.63% for the total fraction of coal converted, fraction of coal converted to liquid hydrocarbons, and fraction of coal converted to gases, respectively. These results show that satisfactory predictions of the product yields are achieved with the proposed correlations for rapid hydropyrolysis of coal conducted at atmospheric pressure. These are the only correlations available for rapid hydropyrolysis of coal at atmospheric pressure.

Section E. Comparison of Coal Conversion Processes

The results for the rapid hydropyrolysis and pyrolysis of the high volatile bituminous coal in this study were compared to the results reported for several coal conversion studies which include:

1) Coal carbonization process

2) Rapid coal hydrogenation or hydropyrolysis process

3) Catalytic hydrogenation process

4) Rapid coal pyrolysis using lasers

Coal Carbonization Process. Carbonization is a process in which coal is heated in a large oven at a slow rate at a high temperature to produce metallurgical coke. The oven temperature typically ranges from 500 to as high as 1000 °C. Davis (1945) reported that the carbonization time can vary from 30 hours when operated at 500 °C to seven hours at 900 °C. The heating rate is very slow since only the oven walls are heated and large amount of coal is carbonized at a time. Therefore, the temperature increase within the fresh coal is very slow and as a result the coal carbon matrix is not changed. Seglin and Bresler (1981) reported that a typical heating rate in a carbonization process is less than 5.5 °C / minute (0.092 °C / second).

Since the heating rate of these two processes is very different, the product yields and their characteristics are also expected to be different. Results from a typical coal carbonization process are presented in Table 4.19 as reported by Davis (1945). The data were taken from the carbonization of several high volatile bituminous coals in a 13 in. retort oven operated at 900 °C for about seven hours. About 30% by weight of the coal (maf) was converted to liquid and gaseous products. Almost half of the volatile matter released was in the gaseous form (14.6% of the coal weight (maf)). The yield of liquid hydrocarbons was reported to be only about 8% of the coal weight (maf). These values are compared with the results from rapid pyrolysis of bituminous coal that was conducted in helium atmosphere (Table 4.6, S.N. 3). The total amount of coal converted to liquid and gaseous products from rapid pyrolysis was 34.9% of the coal weight (maf). The amount of coal converted to liquid hydrocarbons was 13.2%. The results show that rapid

Table 4.19

Yield of Carbonization Products at 900 °C

Product	Amount (% of coal, maf)
coke	70.2
gas	14.6
tar	6.8
light oils	1.07
free ammonia	0.168
liquor	6.0

pyrolysis converts a greater amount of coal and produces more liquid hydrocarbons than a slow heating pyrolysis process such as carbonization.

However, the conversions from carbonization process are far lower compared to the total coal conversion and liquid hydrocarbons obtained from rapid hydropyrolysis of bituminous coal (in hydrogen atmosphere) conducted at 900 °C in this study (Table 4.6, S.N. 1) which were 38.5% and 16.3%, respectively of the coal (maf).

The product distribution of the liquid product collected from the carbonization process and rapid hydropyrolysis conducted in this study are also different. The product distribution of liquid from a carbonization process was mostly made up of high boiling point hydrocarbons. Rhodes (1945) reported the composition as presented in Table 4.20. There was only 2.6% distillate having a boiling point below 200 °C which is in gasoline boiling range (32 to 200 °C). The amount of distillate with boiling point lower than 300 °C (gasoline and kerosine boiling range) was about 29% of the total liquid product collected from this process. These values are comparable to the boiling range distribution of liquid product collected from rapid pyrolysis conducted in helium (Table 4.6, S.N. 3). The amount of distillate with boiling point lower than 200 °C (gasoline boiling range) was about 3.1% of the total liquid hydrocarbons collected.

However, the product distribution of liquid hydrocarbons from carbonization process are much different compared to those of liquid product collected from rapid hydropyrolysis of coal conducted in this study (Table 4.6, S.N. 1). The liquid product collected in this study in gasoline boiling range is 25.4% and the amount of distillate in both kerosine and the gasoline boiling range (< 300 °C) is 65.4%.

Table 4.20

Boiling Point Distribution of Liquid Product (cumulative) from Carbonization Process

Boiling Range (°C)	Amount of Distillate (weight percent)
> 170	1.2
to 200	2.6
to 210	4.0
to 235	11.4
to 270	21.2
to 300	28.8

These results validate the advantage rapid hydropyrolysis has over a slow heating rate process such as carbonization to produce high value hydrocarbon liquids. The rapid heating technique in a hydrogen atmosphere not only produced greater amount of liquid product (high value chemicals) but also produced better quality (lower boiling point distillate) of liquid product.

Rapid Coal Hydrogenation or Hydropyrolysis Process. A process has been developed by the Cities Service to produce liquid hydrocarbons from coal called Short Residence Time (CS-SRT) Hydropyrolysis Process (Rosen et al. 1976, Greene, 1978, Ladelfa et al. 1978). The process is based on a very short residence times (0.02 to 2 seconds) which include a) rapid heat up to reaction temperature by mixing the coal with preheated hydrogen, and b) rapid quenching. The reactor is operated at about 850 °C with no catalyst. The key features of this process are short residence time, rapid heat up, and rapid quench to produce high quality fuels and chemicals.

The results for rapid hydropyrolysis of bituminous coal operated at 760 °C, 1500 psi reactor pressure (hydrogen), and less than 0.5 second residence time are presented in Table 4.21. The total coal conversion was reported to be about 55.4% of the coal weight (maf). However, about 33.2% of the coal was converted to gases which included methane, ethane, carbon dioxide, and carbon monoxide. About 13.3% of the coal weight (maf) was converted to liquid products which included benzene, toluene, xylene (BTX), and light oils. This conversion was comparable to the amount of liquid hydrocarbons

Table 4.21

CS-SRT Process: Typical Process Yields

Product	Yields (wt. % of coal)
methane + ethane	24.9
CO_x	8.3
BTX	9.8
light oils	3.5
tar	trace
liquor + H_2S + NH_3	14.4
total coal conversion	55.4

produced in this study (13.0% at 800 °C) even though the total conversion was higher in the CS-SRT process.

The gas composition from the CS-SRT process mostly consisted of methane and ethane. Since hydrogen was consumed to produce these gases, the process was less attractive because hydrogen has higher economic value than hydrocarbon gases. As a comparison, methane made up less than 10% of the total gas produced from rapid hydropyrolysis conducted in this study. Evidently, hydrogen was not used as much to produce less valuable hydrocarbon gases and therefore, the technique used in this study was more attractive economically. The composition of light oils produced in the CS-SRT process was not reported.

Catalytic Hydrogenation Process. The Schroeder process is one of the catalytic hydrogenation technique which involves the rapid hydrogenation of pulverized coal at high temperature and pressure with the benefit of a molybdenum catalyst (Seglin and Bresler, 1981). The difference between this process and the Cities Service Short Residence Time Process is that it operates at longer residence time (about 20 seconds) and uses a catalyst.

The Schroeder Process when using bituminous coal and operating at conditions of 900 °C, 3000 psig hydrogen pressure, five minutes total heating time, and 1% molybdenum catalyst loading on moisture ash free basis was reported to give high coal conversion. About 83.7% of the coal weight (maf) was converted to liquid hydrocarbons and gases. However, only 17.4% of the coal was converted to liquid hydrocarbons while

46.3% of the coal was converted to hydrocarbon gases. The amount of liquid hydrocarbons produced from the Schroeder Process was comparable to the amount of liquid produced in this study which was 16.3% of the coal weight (maf). However, the coal conversion technique used in this study has several advantages over the Schroeder Process. This technique did not use a catalyst or high pressure and did not consume as much hydrogen to produce hydrocarbon gases. The compositions of the liquid hydrocarbons and gases produced from the Schroeder Process were not reported.

Coal Pyrolysis Using Laser. The results of coal pyrolysis using a laser beam as heating source were also compared with the results of this study. Karn et al. (1971) used a pulsed ruby laser with a focused beam that gave an energy concentration of 55,000 watt / cm^2 which produced 53% solids residue and 47% gas from pyrolysis of high volatile bituminous coal. The product gas mixture was high in hydrogen, carbon monoxide, and acetylene. Coal pyrolysis using a carbon dioxide laser was also conducted which produced 71% solids residue and 29% gas. Only traces of liquid hydrocarbons were observed. Results from the pyrolysis experiment (Table 4.6, S.N. 3) showed about 13.2% of the coal weight (maf) was converted to liquid hydrocarbons (acetone soluble). Therefore, the results of this study were much better compared to the results obtained from a typical coal pyrolysis using a laser beam.

From these comparisons it can be concluded that the method used in this study has several advantages over the coal conversion processes discussed earlier. The rapid hydropyrolysis technique used in this investigation is conducted at atmospheric pressure, at a relatively shorter exposure time (less than one minute), and in the absence of a catalyst. The economics of this technique thus are more attractive. A shorter period of heating time used reduces secondary reactions of the liquid hydrocarbons significantly. As a result, reduced amounts of gases are produced as compared to that obtained from other similar coal conversion processes.

This rapid heating technique also produces relatively a better quality liquid product. The heating rate plays a major role in determining the amount of liquid hydrocarbon produced. A low heating rate method such as carbonization produces relatively lesser amounts of liquid hydrocarbons than this technique. On the other hand a much higher heating rate technique such as a laser beam also produces much less amount of liquid hydrocarbons. Most of the products were solids and gases. The finding that heating rate is critical in determining the amount of liquid hydrocarbons produced will be of great assistance to future research workers in this area. Finally, the hydrogen consumption to produce lower value hydrocarbon gases such as methane, ethane, ethylene, and acetylene was observed to be less than for other coal conversion processes. Hydrogen consumption is primarily responsible for keeping the cost of syn-fuels non-competitive with crude oil. The conceptual plant for rapid hydropyrolysis of coals is presented in Appendix C.

Repeatability

In each experimental run, variations in the coal hydropyrolysis experimental conditions will have an impact on the total coal conversion, production of liquid, and product distribution. These experimental conditions include the exposure time, peak temperature, particle size, and reaction atmosphere. In addition, the steps such as collecting and separating the products like washing and solvent removal could lead to variations in product quantity and quality. Weighing technique used in the experiments could lead to some degree of error.

Two experimental runs were performed under identical operating conditions (Table 4.6, S.N. 1 and 2). The total amounts of coal converted were found to be 38.5 and 37.7 weight percent on the moisture ash free basis. The percentage error of less than 5% indicates a good repeatability. The amounts of liquid hydrocarbons produced in the two experimental runs were found to be 16.3 and 16.0 weight percent. The percentage error was again less than 5% which suggests a good repeatability.

CHAPTER V

CONCLUSIONS

The conclusions of this study are as follows:

1) A novel process for the rapid hydropyrolysis of coals for the production of liquid hydrocarbons has been investigated. The experimental set-up consists of targeting a coal sample with a high intensity xenon light beam for a short period of time in the absence of a catalyst. The technique was successful in conducting rapid hydropyrolysis of bituminous, subbituminous, and lignite coals.

2) The total conversion of 38.5% (maf) for bituminous coal was obtained at 900 °C, thirty seconds exposure time, and 68 micrometer of average particle size in a hydrogen atmosphere. The conversions for subbituminous and lignite coals were found to be 33.6% and 32.2%, respectively.

3) The production of liquid hydrocarbons at 900 °C, thirty seconds exposure time, and 68 micrometer of average particle size and in a hydrogen atmosphere were 16.3%, 8.8%, and 3.5% for bituminous, subbituminous, and lignite coal, respectively.

4) Since the amount of liquid hydrocarbons obtained in the experimental runs were very small, a gas chromatographic simulated distillation technique was successfully carried out for estimating product distribution.

5) The boiling point distribution of the liquid hydrocarbons produced differs extensively for the three coals. The amount of distillate with boiling point lower than 200 °C (gasoline range) was about 25.4% for bituminous coal. The fraction in this boiling range was not detected in liquid products collected for rapid hydropyrolysis of subbituminous and lignite coals. The total amount of distillate with boiling point lower than 300 °C (gasoline and kerosine range) for bituminous coal was about 65.4%. The amount of distillates in the same boiling range for subbituminous and lignite coals were about 36.0% and 21.0%, respectively.

6) The total coal conversion (production of liquid hydrocarbons and gas) for bituminous coal increased from 16.4% to 44.8% for an increase in exposure time from 15 to 60 seconds. The liquid hydrocarbons yield also increased significantly from 6.7% to 17.8% for the same increase in exposure time.

7) The total coal conversion of bituminous coal to liquid hydrocarbons and gas increased steadily from 19.6% at 650 °C to about 38.5% at 900 °C peak temperature. The production of liquid hydrocarbons increased from 2.8% at 650 °C to 16.3% at 900 °C.

8) The total coal conversion decreased slightly from 38.5% for coal of average particle size of 68 micrometer to 36.4% and 35.4% for particle size of 387 and 774 micrometer, respectively. The liquid product also decreased slightly from 16.3% for particle size of 68 micrometer to

14.0% and 12.4% for particle size of 387 and 774 micrometer, respectively.

9) The total conversion of bituminous coal in helium (pyrolysis) was about 34.9% and the liquid produced was about 13.2%. These values were slightly lower than the values obtained for hydropyrolysis which were 38.5% and 16.3%, respectively. The liquid product for pyrolysis experiment had only about 3.1% of the distillate with boiling point lower than 200 °C whereas the liquid from hydropyrolysis experiment had about 25.4 % of distillate boiling below 200 °C. Furthermore, the liquid product collected from the rapid pyrolysis experiment had only 23% of the total distillate boiling below 300 °C which is much lower when compared to 65.4% liquid product for the rapid hydropyrolysis under similar experimental conditions.

10) Results of rapid hydropyrolysis of coal show that it is an effective coal liquefaction technique and is superior in many respects to other coal conversion processes. It is conducted at atmospheric pressure, at a relatively shorter exposure time (less than one minute), and in the absence of any catalyst. The economics of this technique thus has potential to be more attractive.

CHAPTER VI

RECOMMENDATIONS

The following recommendations are made:

1) In this study the maximum operating conditions of 900 °C, 96 watt / cm^2 and 60 to 70 °C / second were used for the rapid hydropyrolysis of coal using a high intensity xenon light beam. Rapid hydropyrolysis of coal should be investigated using higher temperature, heat flux, and heating rate. These conditions can be achieved by other heat sources such as:
   i) Simultaneously using several high intensity beams.
   ii) Using a concentrated solar beam available at the National Renewable Energy Laboratory, CO. and other solar research facilities.
   iii) Using a combination of several high temperature emitter burners and parabolic concentrators.
2) The high temperature emitter burners have never been used for the rapid hydropyrolysis study. Research should be undertaken to investigate these burners for this purpose.
3) In this study, a shuttering mechanism was used to expose a coal sample in a batch mode to the high intensity light beam for a short period of time. The use of continuous reactors such as entrained bed or fluidized bed reactor should be investigated to eliminate the use of a shutter.

4) Production of inexpensive hydrogen is an important aspect of this process. Efforts should be made to investigate the steam-char reaction to produce hydrogen by the rapid heating technique.

5) An economic analysis of the proposed coal rapid hydropyrolysis process should made to determine its economic feasibility.

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APPENDIX A

Table A.1

Summary of Results on Rapid Hydropyrolysis of Lignite Coal

Time (Sec.)	Size (microns)	Temperature (°C)	Total (% maf)	Liquid (% maf)	Gas (% maf)
15	68	900	10.5	0.9	9.6
22	68	900	16.7	1.7	15.0
30	68	900	32.2	3.5	28.7
45	68	900	37.2	3.5	33.7
60	68	900	40.2	4.5	35.7
30	68	810	27.7	2.7	25.0
30	68	700	25.0	1.8	23.2
30	68	650	14.3	0.9	13.4
30	387	900	30.3	2.7	27.6
30	774	900	28.6	1.8	26.8

Table A.2

Summary of Results on Rapid Hydropyrolysis of Subbituminous Coal

Time (Sec.)	Size (microns)	Temperature (°C)	Total (% maf)	Liquid (% maf)	Gas (% maf)
15	68	900	14.8	2.8	12.0
22	68	900	25.0	4.6	20.4
30	68	900	33.6	8.8	24.8
45	68	900	38.0	9.3	28.7
60	68	900	42.6	10.2	32.4
30	68	810	30.6	7.4	23.2
30	68	700	20.4	5.5	14.9
30	68	650	15.7	3.7	12.0
30	387	900	30.6	6.5	24.1
30	774	900	29.6	4.6	25.0

APPENDIX B

Title : Rapid Hydropyrolysis of Resid Oil

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"Prepared for presentation at : The AIChE 1993 Spring National Meeting
Houston, TX.
March 28 - April 1, 1993
Symposium on Hydroprocessing of
Petroleum and Distillates

"Date : February 2, 1993"

"UNPUBLISHED"

Abstract

Production of transportation fuels from atmospheric or vacuum resid oil is becoming increasingly attractive to the petroleum industry due to the increased processing of heavy crude oil and poor demand for coke. Conventional techniques of hydrogenation of resid oil, though attractive, have been expensive due to hydrogen requirements, high pressure equipment, and high cost of commercial supported catalysts.

In this study, a novel rapid hydropyrolysis technique is being investigated. Samples of atmospheric and vacuum resid oil are targeted, in the absence of a catalyst, with a high intensity xenon light beam. A shuttering mechanism exposes an oil sample to the beam only for a few minutes at a time. This technique provides the best part of several processes: high heating rate of resid oil sample to achieve high carbon conversion, control of secondary reactions via low ambient gas temperature, and hydrogen rich atmosphere to achieve high yields of low boiling liquid hydrocarbons.

Experiments using atmospheric and vacuum resid oils have been conducted at a heat flux of 96 watt/cm^2, heating rate of 60 to 70 °C/sec, temperatures in the range of 700 - 940 °C, and exposure times in the range of one to six minutes in a hydrogen atmosphere (1 atm). Under these conditions, about 56% by weight of atmospheric resid oil and 48% by weight of the vacuum resid oil are converted to liquid products (acetone

soluble). A G.C. simulated distillation technique shows that about 17% and 13% of the liquid produced (acetone soluble) has a boiling point below 300°C for atmospheric and vacuum resid oil, respectively.

Rapid Hydropyrolysis of Resid Oil

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INTRODUCTION

In order to provide the industrialized world with sufficient inexpensive hydrocarbon fuels and chemical feedstocks, petroleum crude has to be utilized to its maximum. Hydrogenation of residual oil, obtained from a petroleum distillation unit, provides a product with an increased hydrogen content. However, to increase the hydrogen content of the product to the level necessary for transportation fuels or chemical feedstocks, catalysts which promote hydrogenation and hydrocracking must be employed. Catalytic reactions play an important role in residual oil hydrogenation yielding products of lower molecular weight with higher hydrogen to carbon ratio [1, 2]. The removal of S, N, and O heteroatoms and hydrogenation of the residual oil molecule is usually accomplished by using commercial catalysts containing various combinations of Co, Ni, Mo, and W on Al_2O_3 or Al_2O_3-SiO_2 support.

Catalyst deactivation is a major problem in the catalytic residual oil hydrogenation process. Coke formation decreases catalyst activity by blocking catalyst active sites, primarily through chocking the pore mouths. Deposits of nickel and vanadium deactivate the catalyst permanently by restricting diffusion paths of the reactant molecules. Even regeneration of commercial catalysts may not restore the original hydrogenation activity. Therefore, commercial supported catalysts used in residual oil hydrogenation are difficult to regenerate and have a short life. The usage and loss of expensive commercial catalysts are one of the major problems in this area.

Lopez et al. [3] listed the advantages of using a dispersed-phase water soluble catalyst over commercially used, supported catalysts. The water soluble catalyst is a highly active form of molybdenum sulfide. The results from the hydrogenation of residual oil using a dispersed-phase catalyst show that the catalyst gives a high degree of desulfurization and demetallation (nickel and vanadium removal). The small particle size of the catalyst provides two advantages. First, the catalyst is highly active due to a large specific surface area, and second, the catalyst is sufficiently small to be readily dispersed in the residual oil allowing the oil to be easily pumped. They also claim that moderate or relatively large amounts of nickel and vanadium can be deposited on the catalyst surface without reducing its activity. Moreover, the recycled catalyst can accommodate as much as 70 to 85 weight percent of nickel and vanadium without excessive loss of activity.

In previous studies [4, 5, 6], it has been shown that some of the ore concentrates can be directly used for coal hydrogenation reactions. Based on this premise, efforts have been made to use sulfide or oxide concentrate as a catalyst or a starting point for the preparation of dispersed molybdenum catalysts for residual oil hydrogenation reactions.

It is obvious that this procedure will result in cost reduction because of a significant saving in material and processing expenses.

Hydrogenation of residual oil using a dispersed water soluble ammonium molybdenum catalyst study was conducted by Mohamed and Mathur [7]. In this study, hydrogenation of atmospheric residual oil was carried out in the presence of a dispersed water soluble ammonium molybdate catalyst prepared from a molybdenum ore. This provided an effective economic alternative to the use of expensive commercial catalyst for the hydrogenation of residual oil. An ASTM distillation of the hydrogenated residual product gave 30 percent liquid boiling below 215 °C.

Rapid hydropyrolysis of coal using various heating techniques have been studied by several workers [8 - 15]. However, the rapid hydropyrolysis of atmospheric or vacuum residual oil has not been reported in the literature.

An alternative for hydrogenation of residual oil is to conduct the process without the use of a catalyst. In this study, a novel technique known as rapid hydropyrolysis is investigated as a way to hydrogenate residual oil. The advantages of this technique are the absence of a catalyst and high pressure equipment.

EXPERIMENTAL EQUIPMENT AND PROCEDURE

Rapid resid oil hydropyrolysis experiments are conducted in a batch system. The major materials used consist of atmospheric and vacuum resid oil, hydrogen and helium gases, acetone, and tetrahydrofuran. Analyses of resid oils are presented in Table I.

Table I

Analysis of Arabian Light Atmospheric Resid oil And Vacuum Resid Oil.

Percentage	Atmospheric	Vacuum
Carbon	85.10	83.58
Nitrogen	0.22	0.40
Hydrogen	10.76	10.54

Experimental Set-up

A pyrex reactor with a quartz cover plate, high intensity light equipment (power supply, lamp housing and 1000 watt lamp), gas chromatograph, asymptotic calorimeter, three axis manipulator, type K thermocouple with digital thermometer, gas pump, safety bag, pressure gauge, and analytical balance capable of weighing to the nearest 0.0001 gram are the major equipment used during the course of this study. The rapid resid oil hydropyrolysis experiments are carried out in an experimental set-up as shown in Figure 1. The experimental set-up consists of a pyrex reactor, gas supply equipment, and a high intensity light assembly with a shuttering arrangement. Hydrogen and helium gases are supplied from high pressure (2500 psig) cylinders. Hydrogen gas is passed through several safety devices before entering the reactor as a precaution : (i) a flame arrestor is used to stop gas supply if a flashback occurs and to extinguish the flame before it reaches the gas supply and (ii) a check valve to prevent any back-mixing. A pressure gauge is used to check for any leak in the system before each experiment is conducted for safety consideration. A teflon safety bag is used to prevent any pressure buildup during the experiment. Finally, a gas pump is used to purge the system with helium and hydrogen before each experiment.

High intensity Light Assembly With Shuttering Arrangement. The high intensity light beam is produced by a xenon light equipment. The light source equipment consists of two units: power supply and lamp housing. The power supply (LPS 1000) is designed to operate with high pressure xenon, mercury, or xenon-mercury arc lamps in the range

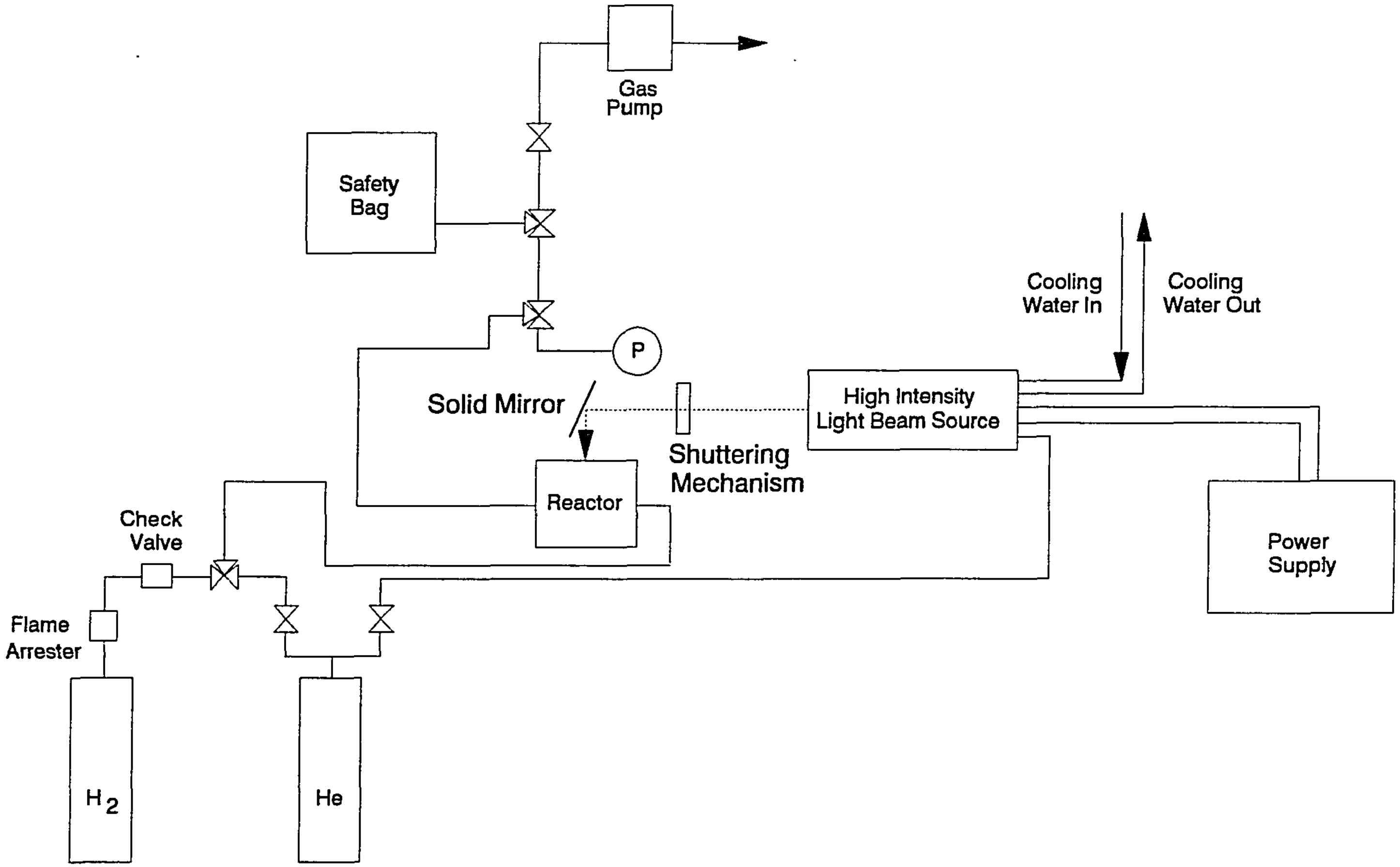

Figure 1: Schematic Diagram of the Experimental Set-up

of 100 to 1000 watts and is capable of delivering 100 watt/cm^2 flux. The appropriate voltage for the lamp is automatically selected and the power of the lamp is adjusted by varying the current. The instrument is also equipped with a low operating circuit, in which case the lamp current can be reduced to as low as 20 % of the normal value. Voltage and current are displayed during each operation. The power supply is air cooled.

The arc lamp housing is designed to accommodate selected xenon, mercury, or mercury-xenon arc lamp with power rating up to 1000 watts. The housing uses an f/4 elliptical reflector, which gives a high reflection efficiency. With the f/4 reflector, a horizontal beam of light is focused at a distance 407.1 mm from the front window. The front window is made of quartz so that wavelengths of light greater than 250 nanometers (nm) can pass through. The lamp housing is water cooled and sealed, so that a venting system is not required. Also, it is designed for nitrogen or helium purging to prevent the production of ozone.

The light source, a 1000 watt xenon arc lamp with a spectral emission in the range of 250 nm to 2500 nm, is assembled in the lamp housing. Xenon lamp is used in this study because its spectral emission is similar to that of sunlight. The lamp can be operated at various power levels and is capable of delivering up to 100 watt/cm^2 flux beam at 1000 watts power level.

A shuttering mechanism is designed and incorporated between the window and the reflective solid mirror to expose the resid oil sample for a few minutes at a time. A 45 degree reflective solid mirror is used to change the orientation of the high intensity light beam from horizontal to vertical. The reflective solid mirror is coated with magnesium fluoride to achieve maximum reflectance. The solid mirror is cooled by forced air to avoid the loss of the magnesium fluoride coating.

Reactor Design. The resid oil hydropyrolysis reactor is designed and constructed to have several characteristics that make this investigation unique. With this reactor, rapid heating rates of resid oil and quenching of the resid oil volatiles and products in a relatively cool surrounding gases and reactor wall are possible.

The hydropyrolysis reactions are conducted in a cylindrical pyrex reactor. The details of the hydropyrolysis reactor are shown in Figure 2. The reactor is 74 millimeters (mm) i.d., 80 mm o.d., and 122.1 mm high with a thicker wall at the top of the reactor to accommodate a 75 mm o-ring to provide a gas seal. A quartz cover plate at the top of the reactor opening allows the high intensity light to pass through. The dimensions of the quartz plate are 101.6 mm diameter and 3.2 mm thick. The inlet and outlet tubing to the reactor are located at the bottom and top of the reactor, respectively. A gas sampling port is also located at the top of the reactor on the opposite side of the reactor outlet. The light beam from the high intensity light equipment moves horizontally. The beam is deflected at 90° by a reflective solid mirror and enters the reactor from the top through the quartz plate which serves as a lid as well as a window for the entering beam. A resid oil sample is placed in a low wide-form crucible. The dimensions of the crucible are 18 mm diameter at the top and 12 mm high. About 0.08 gram of resid oil is placed in the crucible which is placed on a perforated aluminum sheet of about 1 mm thick, which acts as a support. The resid oil sample is exposed to the radiant heat by

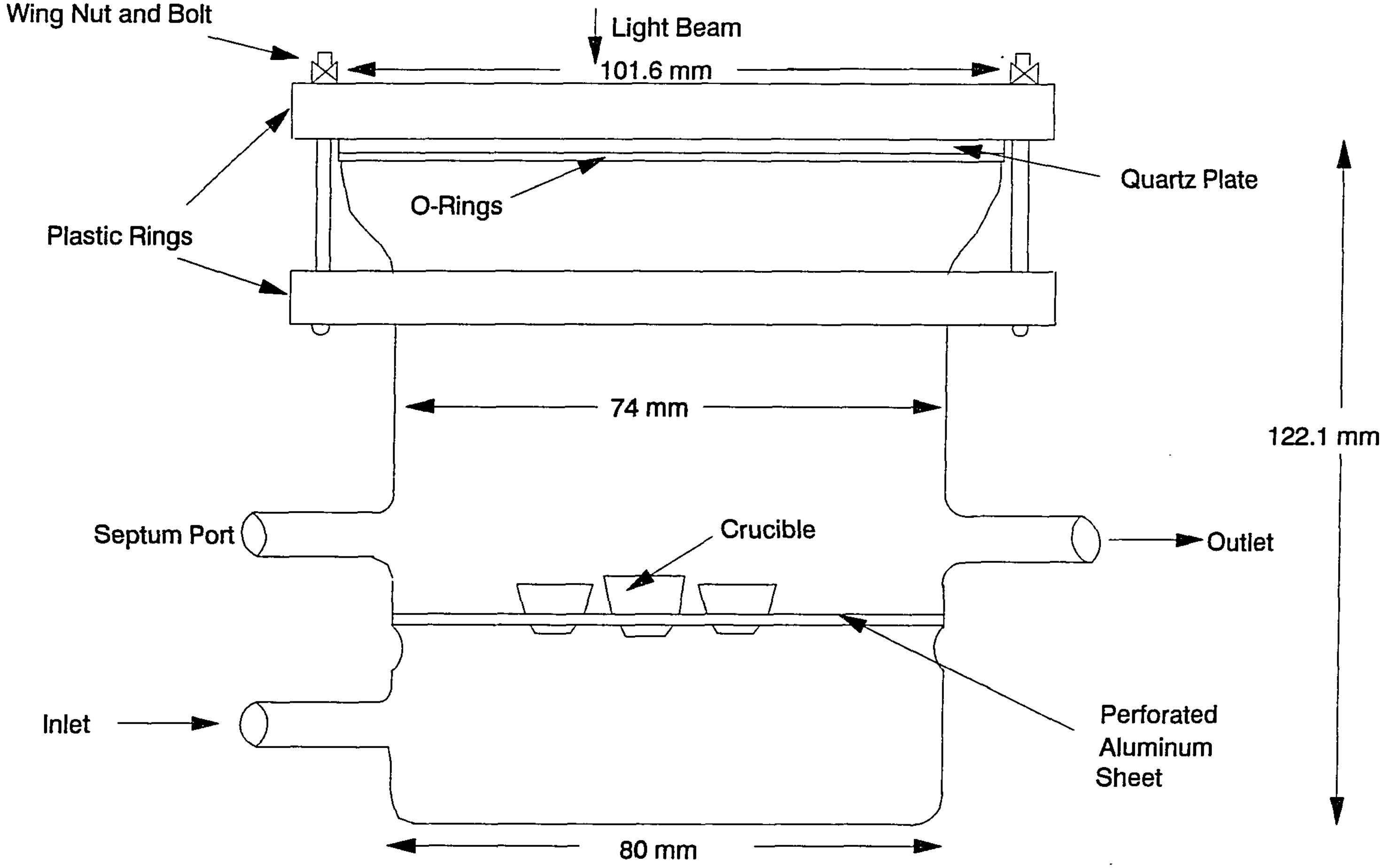

Figure 2: Structural Details of Hydropyrolysis Reactor

positioning the sample at the focal point of the beam. A gaseous product analysis shows that the gas sample is rich in hydrogen indicating that the amount of hydrogen is adequate for the hydropyrolysis of the resid oil sample.

Hydrogen and helium atmospheres are used for the resid oil hydropyrolysis and pyrolysis, respectively. Helium is used for several reasons. First, the thermal conductivity of helium matches with that of hydrogen in the temperature range of interest. Second, it is inert and is used for conducting pyrolysis experiments as a comparison to those in hydrogen atmosphere. Finally, it is used to purge the reactor several times to remove all the air before hydrogen is passed through. This is to avoid the mixing of air and hydrogen which can lead to explosion.

<u>Heat Flux and Temperature Measurements.</u> An asymptotic water cooled calorimeter is used to measure the heat flux of the high intensity beam at the focal point where sample is to be located. The asymptotic calorimeter is made of a solid copper with the front surface coated with carbon black. The diameter of the calorimeter is about 25 mm. The meter is mounted on a three axis manipulator and positioned to intercept the concentrated high intensity light beam at its focal point. The output from the calorimeter is sent to a volt meter which is used to determine the amount of heat flux absorbed by the resid oil sample.

A Digital Thermocouple Thermometer is used with type K (Chromel - Alumel) thermocouple to determine the temperature of the high intensity light beam at the focal point. The voltage output from the Digital Thermometer is sent to a personal computer using a data acquisition program called LABTECH NOTEBOOK. The output is continuously recorded by the computer. Throughout this study, the gaseous and liquid samples are characterized using a gas chromatograph. Details of the analytical procedure are provided later.

Experimental Procedure

A resid oil sample weighing about 0.08 gram is placed in a porcelain crucible which is placed on a perforated aluminum sheet acting as a support in the reactor. The quartz plate lid is then clamped to the reactor. This assembly is then connected to the rest of the system.

The system is then purged with helium three or four times to expel any air and keep the contents of the reactor in a total helium atmosphere. The system is then purged with hydrogen to keep the reactor contents in hydrogen. This procedure is adopted to prevent any mixing of air with hydrogen which can lead to an explosion. The inlet and outlet to and from the reactor are then closed so that the resid oil rapid hydropyrolysis reaction can be carried out in a batch system. A pressure gauge is used to check for any leaks.

The light beam equipment is then turned on while the shutter is closed. The power is adjusted to a low level (less than 100 watts). The shutter is then opened to allow the beam to pass enabling the sample to be positioned at the beam focal point. The shutter is closed again and the power is adjusted to a desired level. The shutter is then opened to expose the sample to rapid heating for a given period of time. The duration of light beam exposure is controlled by the shutter.

After the sample has been exposed, the reactor and its contents are allowed to cool down and a gas sample is taken through the septum port (before the quartz plate is removed). The gas sample is analyzed using the gas chromatograph. The quartz plate is then removed. Both the reactor and the quartz lid are then washed with analytical grade acetone. The acetone soluble product oil is then transferred into a sample bottle and is analyzed later. This is referred as low boiling point product. The reactor and the quartz lid are then washed with analytical grade tetrahydrofuran before another experimental run is conducted.

The liquid product sample (acetone soluble) is subjected to ASTM D2887-89 standard test method for determining boiling point range distribution of various hydrocarbon fractions by a gas chromatograph. This procedure is also known as gas chromatographic simulated distillation technique for boiling point measurements. The gas is also analyzed using the gas chromatograph with a different column.

After the simulated distillation of the acetone soluble product, acetone is evaporated from the sample using helium. The product oil is then weighed, labeled, and stored. The crucible with carbon residue and ash are also weighed, labeled, and stored.

Percent Resid Oil Conversion (Liquid Hydrocarbons + Gas)

The percent resid oil conversion (total yield) is calculated as :

$$\% \text{ Total conversion} = \frac{\text{initial weight of resid oil - weight of residue}}{\text{initial weight of resid oil}} \times 100$$

The percent resid oil converted to low boiling point liquid product (acetone soluble, b.p. < 425 °C) is calculated as:

$$\% \text{ Low b.p. liquid} = \frac{\text{weight of liquid (acetone soluble)}}{\text{weight of resid oil}} \times 100$$

The percent resid oil converted to high boiling point liquid product (tetrahydrofuran soluble, b.p. > 425 °C) is calculated as:

$$\% \text{ High b.p. liquid} = \frac{\text{weight of liquid (THF soluble)}}{\text{weight of resid oil}} \times 100$$

The percent of resid oil converted to gaseous product is calculated as :

$$\% \text{ Gases} = \% \text{ Total conversion} - \% \text{ Low b.p. liquid} - \% \text{ High b.p. liquid}$$

RESULTS AND DISCUSSIONS

The objective of this investigation was to study the rapid hydropyrolysis of Arabian Light atmospheric resid oil and vacuum resid oil for the production of light distillates. The results of this study have been divided into the effect of exposure time, temperature, and gaseous atmosphere. The heat flux used was in the range of 70 to about 97 watt / cm^2. The results from ASTM simulated distillation of the hydrogenated oil obtained at various experimental conditions are also presented.

Effect of Exposure Time

The effect of exposure time on the rapid hydropyrolysis of atmospheric and vacuum resid oils was studied in the range of one to six minutes at a constant temperature 940 °C. This was the highest temperature which could be obtained in our equipment. A hydrogen atmosphere was maintained above the samples. The results are shown in Figure 3. As can be seen the total conversion for atmospheric resid oil begins at 40.5% for one minute, reaching a value of 84.4% at three minutes and then remaining almost constant. Similar results are seen for low boiling point products (acetone soluble) which reach a value of 56.4% at three minutes exposure time with no appreciable increase with further increase in exposure time.

In another set of experiments, vacuum resid oil was subjected to rapid hydropyrolysis under similar experimental conditions. The results are shown in Figure 4. The total conversion is 78.4% with a yield of low boiling point products of 47.5% when the sample is subjected to three minutes of hydropyrolysis. The conversions of the vacuum resid oil are less, as expected, due to the asphaltic nature of the resid oil with no volatile matter below 560 °C. However, these conversions at atmospheric pressure with no catalyst usage are very attractive.

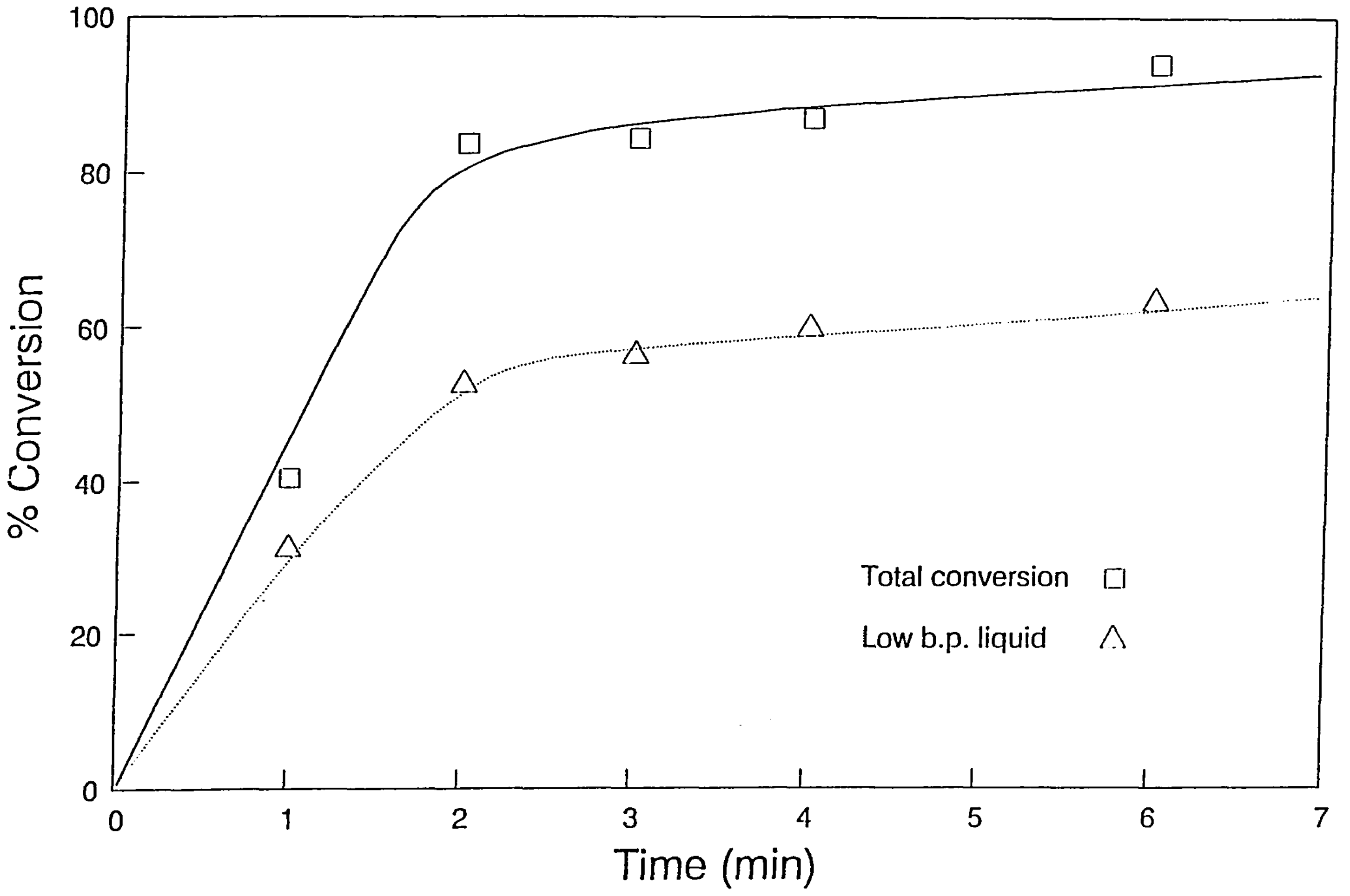

Figure 3 : Percentage Conversions of Atmospheric Residual Oil versus Time of Exposure at 940°C

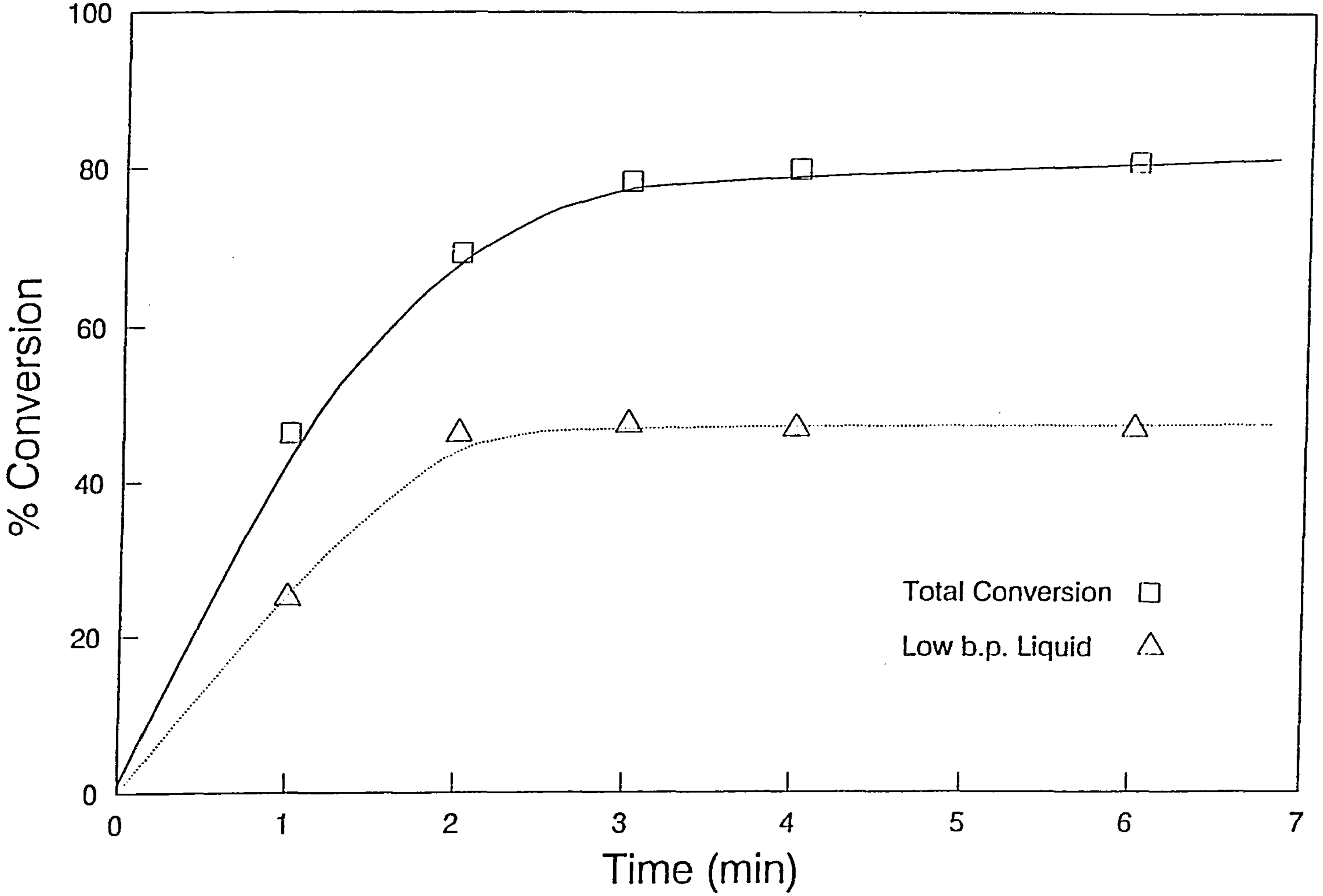

Figure 4 : Percentage Conversions of Vacuum Residual Oil versus Time of Exposure at 940°C

Production of Low Boiling Point Products (Acetone Soluble). In the rapid hydropyrolysis, the sudden increase in temperature causes primary thermal cracking reactions. Because of the low temperature of resid oil surroundings, the molecules do not go through secondary cracking but react with hydrogen to produce low boiling point molecules. However, if the exposure time is increased, the surrounding environment gets heated and causes secondary cracking. A product distribution in Figure 5 shows that for atmospheric resid oil, the low boiling point fraction (less than 300 °C) is about 14.3% at one minute exposure time, increases to 17.3% at three minutes, and then reduces to 7.5% at six minutes. The low amount of low boiling point fraction at one minute is because of the inadequate time available for thermal cracking. Similar results are observed for vacuum resid oil providing 13.4% of low boiling point fraction in the kerosine range (less than 300 °C) at three minutes of exposure time (Figure 6).

Effect of Temperature

Both atmospheric and vacuum resid oils were subjected to rapid hydropyrolysis in the temperature range of 700 to 940 °C (see Figures 7 and 8) keeping the exposure time constant at three minutes. The total conversion and conversion to low boiling point products for both resid oils are found to be highest at 940 °C. Low values at 700°C are due to inadequate primary thermal cracking reactions.

Table II shows the boiling point product distribution for the rapid hydropyrolysis of the two resid oils at 700 and 940 °C. The atmospheric resid oil produces low boiling fractions (less than 300°C and 300 - 350 °C) in higher amounts than obtained from

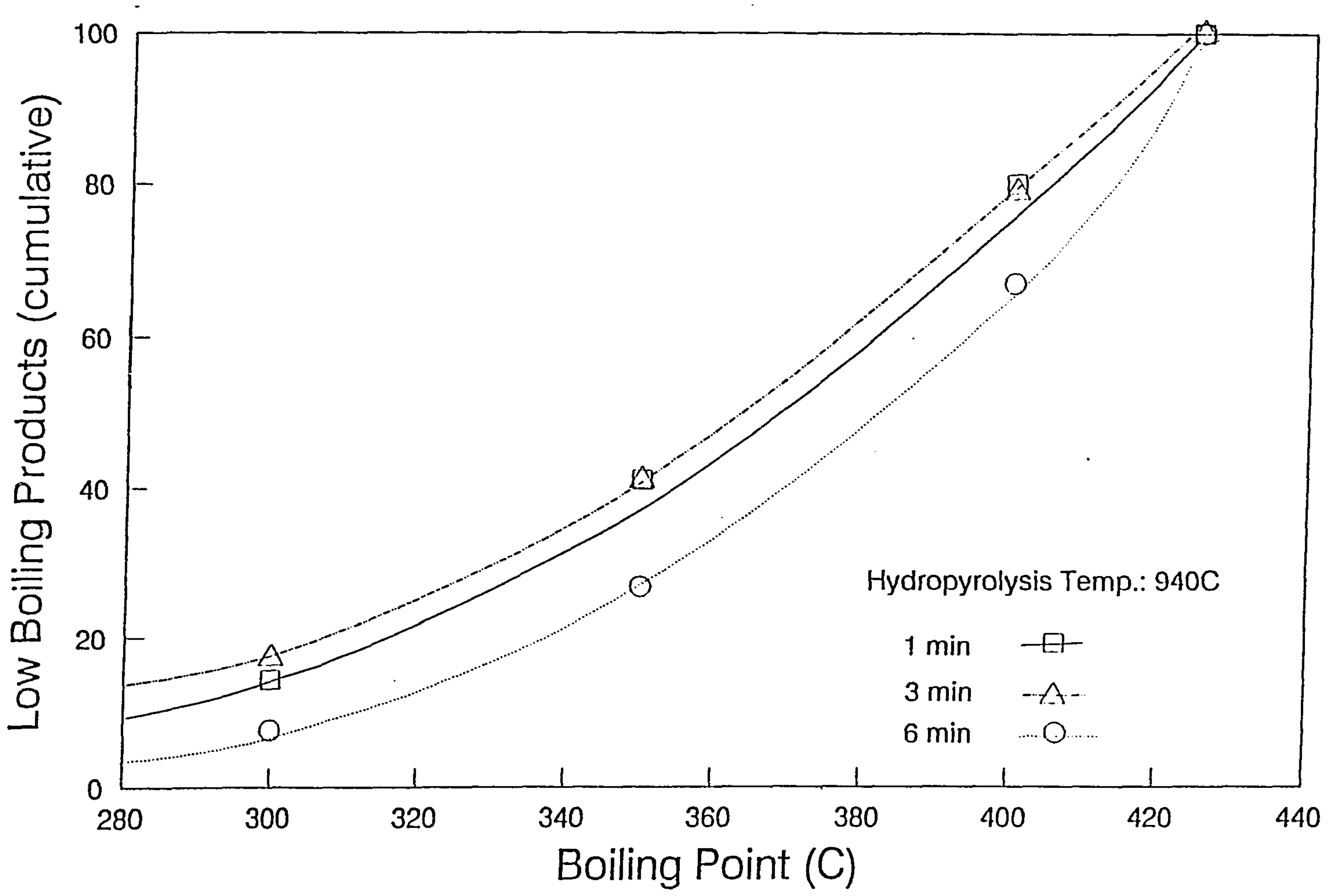

Figure 5 : Low Boiling Products Distribution (cumulative) of Atmospheric Residual Oil at Residence Time of 1,3 and 6 minutes

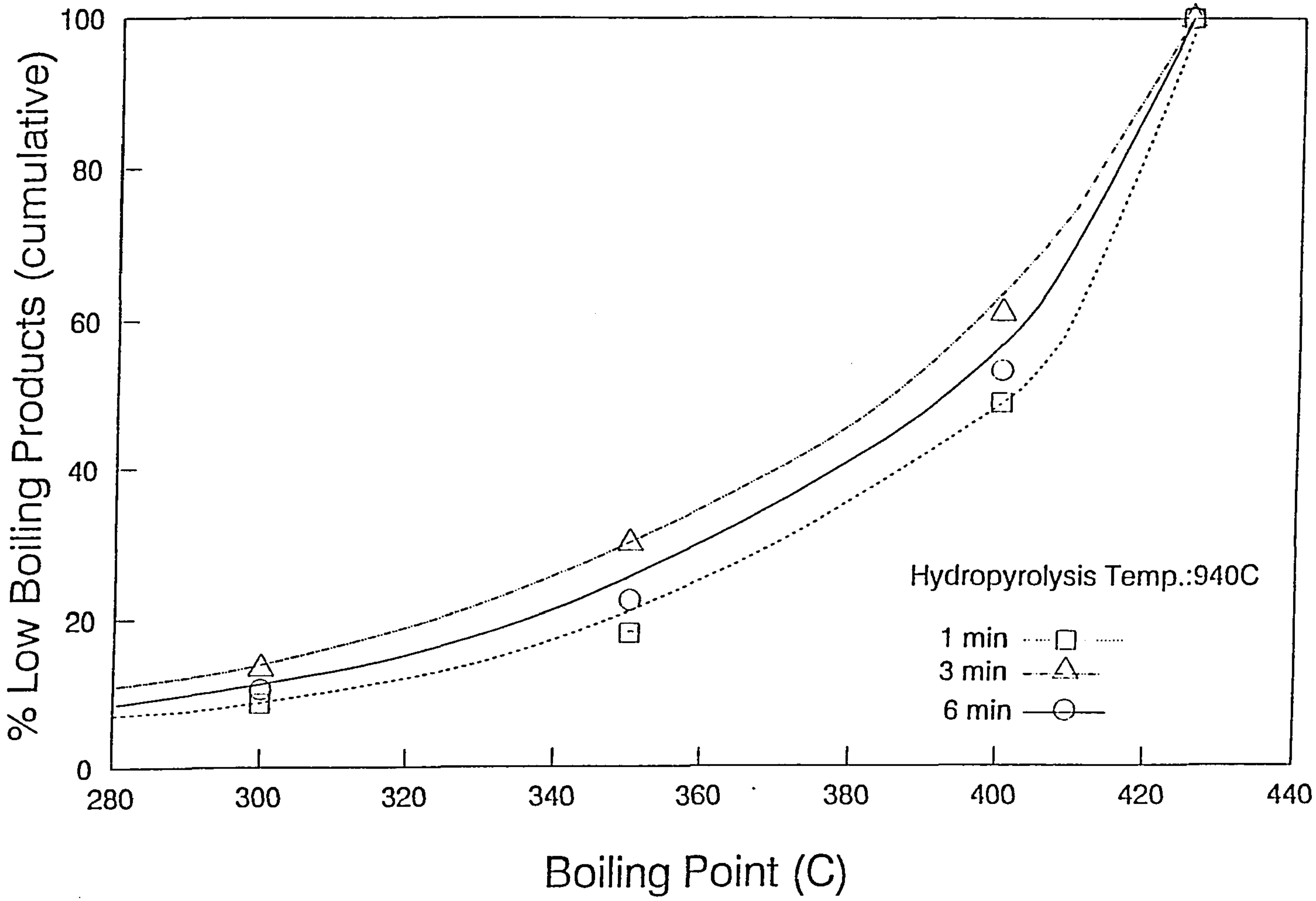

Figure 6 : Low Boiling Products Distribution (cumulative) of Vacuum Residual Oil at Residence Time of 1,3 and 6 minutes

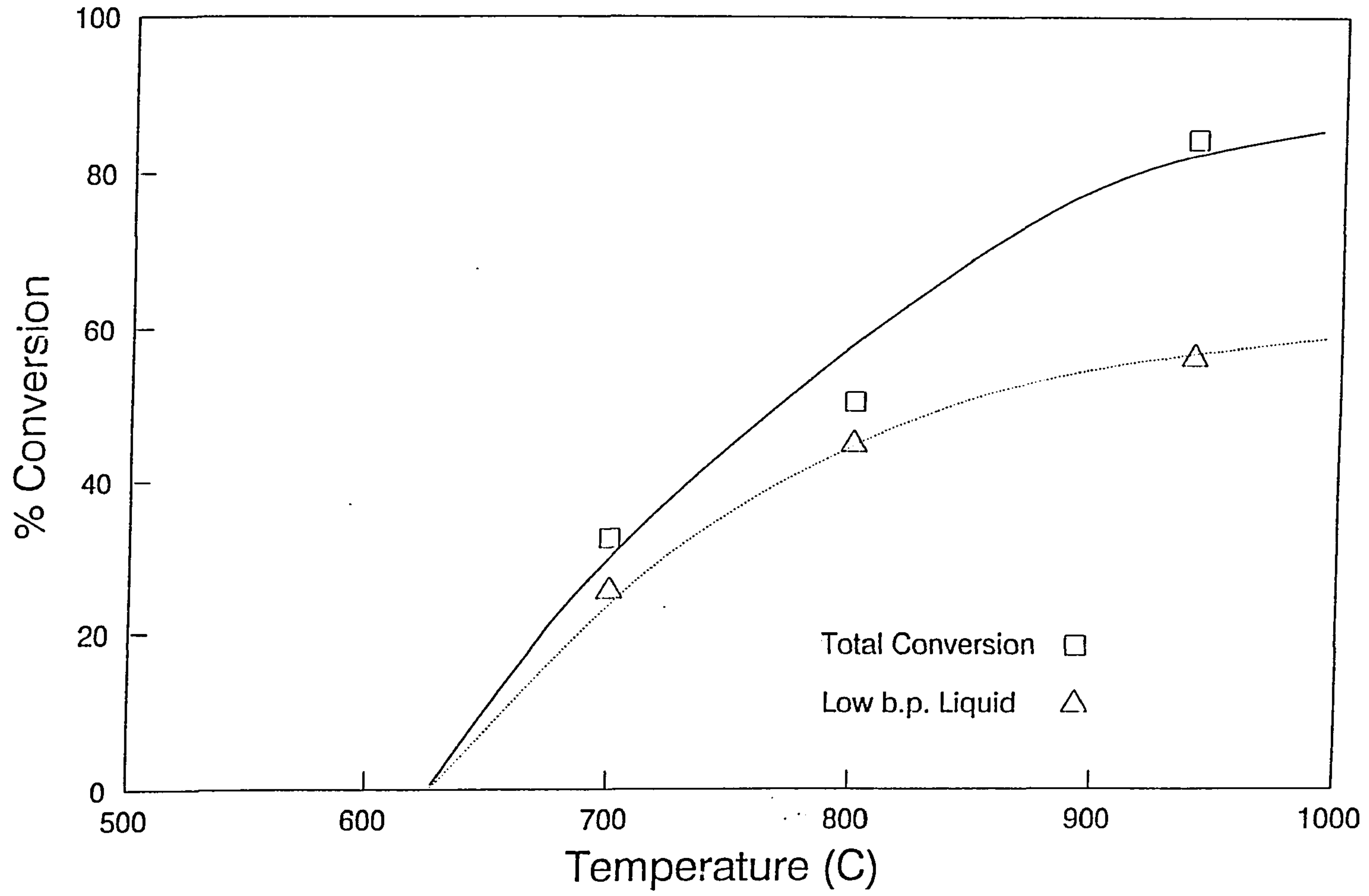

Figure 7 : Percentage Conversions of Atmospheric Residual Oil versus Temperature at Exposure Time of Three Minutes

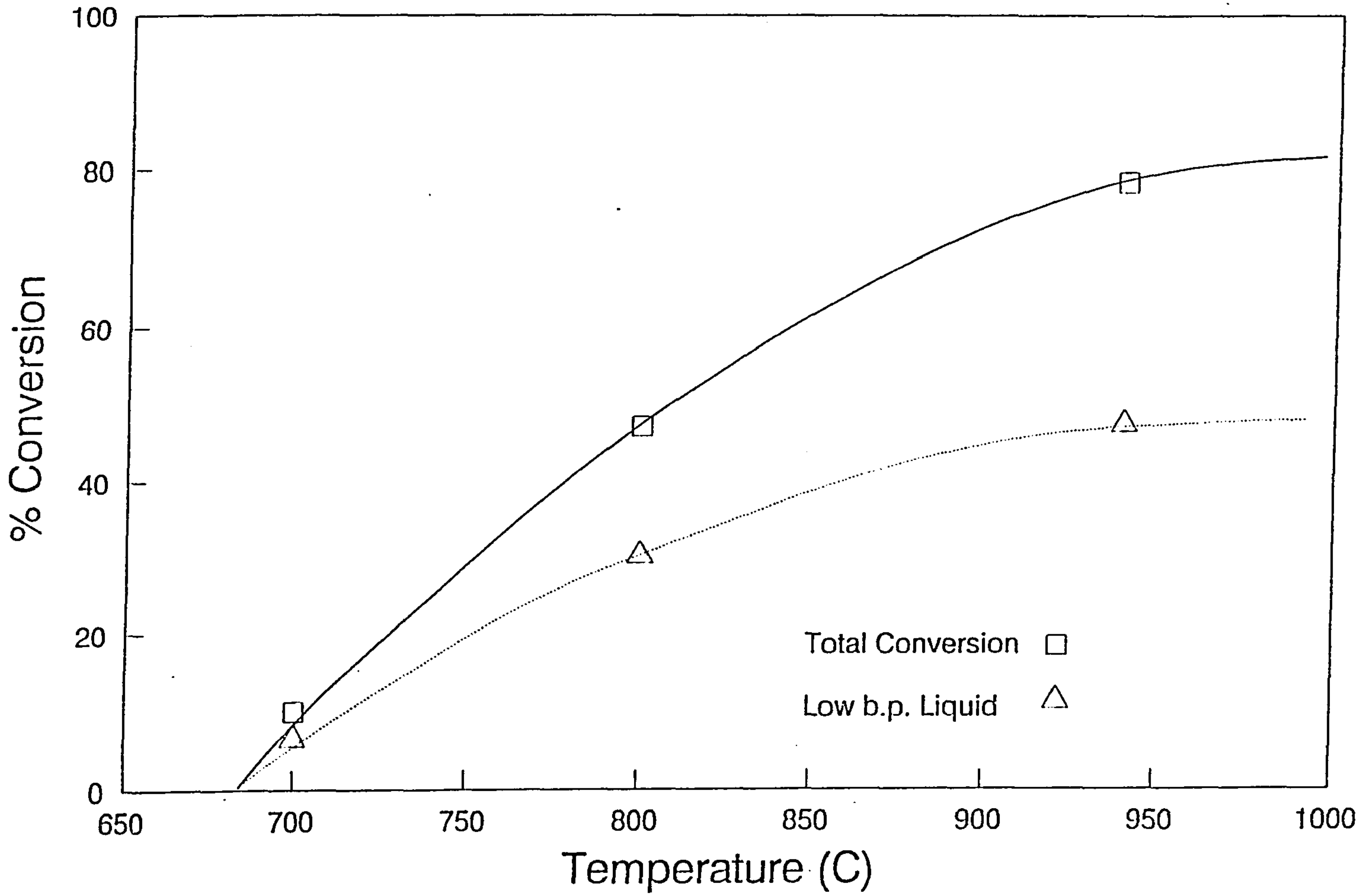

Figure 8 : Percentage Conversions of Vacuum Residual Oil versus Temperature at Exposure Time of Three Minutes

Table II

Percentage Conversion of Resid Oils Versus Time of Exposure at 940°C in hydrogen atmosphere.

	Percentage of conversion of			
	Atm. resid oil		Vacuum resid oil	
	overall	low bp. liq.prod	overall	low.bp.liq prod
Duration : 1 minute	40.5	31.1	46.4	25.0
Duration : 2 minutes	83.7	52.7	69.4	46.3
Duration : 3 minutes	92.1	56.4	78.4	47.5
Duration : 4 minutes	93.1	57.1	80.0	47.0
Duration : 6 minutes	94.0	63.5	81.0	47.1

vacuum resid oil. However, a production of 13.4% in the kerosine boiling range (less than 300 °C) from vacuum resid without the use of high pressure equipment or a catalyst is very attractive.

Effect of Helium and Hydrogen Atmosphere

Experiments were conducted on atmospheric and vacuum resid oils at 940 °C for three minutes exposure time in helium and hydrogen atmosphere. Results from these experiments are shown in Table III. The total conversion for the atmospheric resid oil in hydrogen was found to be 84.4% with 56.4% hydrogenated to low boiling point products. On the other hand, when similar experiments were conducted in helium the total conversion was about 88.8% with conversion to low boiling point products of only 44.7%. Similarly for vacuum resid oil, percent total conversion and conversion to low boiling point products were found to be 78.4 % and 47.5%, respectively in hydrogen. The conversions were reduced to 77.7% and 32.0% in helium atmosphere. Almost the same percent total conversion is observed for both resid oils in hydrogen and helium atmospheres which is considered to be due to equal primary cracking. In a hydrogen atmosphere, the products from the primary thermal cracking are stabilized by hydrogen yielding a higher amount of low boiling point products. However, in helium atmosphere the primary products repolymerize with each other to produce higher boiling point products. The low boiling point product distribution for the two resid oils in hydrogen and helium atmospheres are presented in Table IV.

Table III

Low Boiling Products Distribution of Hydropyrolized Resid Oils at 940°C for different exposure time.

	Atmospheric resid oil			Vacuum resid oil		
	1 minutes	3 minutes	6 munites	1 minutes	3 minutes	6 minutes
Boiling Point						
< 300°C	14.3	17.3	7.5	8.6	13.4	10.5
300 - 350°C	26.8	23.7	19.3	9.5	16.6	11.9
350 - 400°C	39.0	38.1	40.4	30.8	31.0	30.9
400 - 425°C	19.9	20.9	32.8	51.1	39.0	46.7

Table IV

Percentage Conversion of Resid Oils Versus Temperature at exposure time of three minutes in hydrogen atmosphere.

	Percentage of conversion of			
	Atm. resid oil		Vacuum resid oil	
	overall	low bp. liq.prod	overall	low.bp.liq prod
Hydrogen atmosphere Duration : 3 minutes				
Temp : 940 C	92.1	56.4	78.4	47.5
Temp : 800 C	50.6	45.0	47.2	30.4
Temp : 700 C	32.5	25.5	9.8	6.4

CONCLUSIONS

The following conclusions can be made:

1) The experimental set-up successfully conducted rapid hydropyrolysis of atmospheric and vacuum resid oils.

2) For the atmospheric resid oil, the percentage total conversion of 84.4% and percent conversion of 56.4% to low boiling point products are obtained at 940 °C and three minutes exposure time in hydrogen atmosphere.

3) For the vacuum resid oil, the percentage total conversion of 78.4% and percent conversion of 47.5% to low boiling point products are obtained at 940 °C and three minutes exposure time in hydrogen atmosphere.

4) The maximum amount of low boiling point liquid products in the kerosine boiling range (b.p. less than 300 °C) is 17.3% for atmospheric resid oil and is obtained at 940 °C and three minutes exposure time in hydrogen atmosphere.

5) The maximum amount of low boiling point liquid products in kerosine boiling range (b.p. less than 300 °C) is 13.4% for vacuum resid oil and is obtained at 940 °C and three minutes exposure time in hydrogen atmosphere.

6) The rapid hydropyrolysis of atmospheric and vacuum resid oils can result in high percentage total conversion and conversion to low boiling point products without the use of high pressure and catalyst.

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Appendix C

CONCEPTUAL PLANT FOR RAPID HYDROPYROLYSIS OF COALS

The proposed plant is based on our finding that fine particles of coal when heated in the presence of hydrogen at high heating rates of 60 to 70 °C / second and higher to about 900 °C can produce high yields of liquid products in the gasoline and kerosine range. Further, this process could utilize the advance High Heat Flux (HHF) technology made possible by the availability of high temperature emitter burners and concentrated solar radiation capable of heating coal rapidly to the required temperatures.

The HHF energy can be generated from either emitter burners or a high temperature beam of concentrated solar energy. This energy is delivered directly to the surface of a pyrolyzing coal particle to drive primary reactions to break down the coal matrix. The temperature of the surrounding environment can be effectively decoupled from the temperature at the coal particle surface, allowing a significant temperature difference to exist. This temperature difference, along with control of the composition of the gaseous environment, would limit the secondary cracking of the products of the initial surface decomposition reactions. This combination of reaction conditions would also allow production of a substantially greater fraction of liquids than obtained using other coal processing concepts. It is considered that there is enough flexibility to maximize the production of valuable low boiling liquid fractions while minimizing the production of tars (high molecular products), char and gases. These tars, chars and gases can be recycled within the process.

In this study a concentrated light beam generated by an electrical lamp was used as a radiative heat source. However, two novel radiative heat sources have been considered for the proposed plant. One heat source can be the use of emitter burners. The development of these burners is based on the old technology of gas mantle (incandescent lamp), made of rayon impregnated with metal salts, which were used in kerosine lanterns for illumination purposes. Recently, highly selective, rare earth oxide fibrous emitters operating at relatively high temperatures of 1500-1700 °C, using conventional fuels such as methane, butane, propane etc; have been developed. It is proposed to use these emitter burners to produce high intensity radiation to conduct rapid hydropyrolysis of coal. In essence, we would be burning methane to generate high intensity radiations to conduct rapid hydropyrolysis to obtain increased yield of low boiling point liquid hydrocarbons. Most of the methane used will be produced in the process itself. It is indeed a combination of two developing technologies to produce liquid fuels. The details of the emitter burner technology are discussed later.

Another novel source of radiative heat is concentrated solar energy. This concept has been proposed in details by researchers at the National Renewable Energy Laboratory, CO. (Nix et al., 1985; Hewett, 1986; Hewett et al., 1986; and Glatzmaier et al., 1988). A beam of concentrated solar radiation is attractive because it can be targeted directly on the absorptive solid such as coal. This is a viable way of converting solar energy which is a stationary energy source into a clean and easily transportable form of fuel. Moreover, sunlight is a non-polluting, abundant, and renewable source of energy.

The HHF hydropyrolysis process is unique. This includes the HHF generator which uses gas emitter burners or concentrated sunlight to produce the radiative heat for the conversion process. The high radiant heat fluxes converts coal, in a hydrogen atmosphere, to liquids, with some gases and char. The gases are separated and char is processed to produce hydrogen for use in the hydropyrolysis reactor. The concept may also represent a possible technique to convert coal to a clean burning fuel by the effective removal of sulfur.

Innovative Concept of Rapid Pyrolysis Using High Heat Flux

The proposed HHF conversion process combines the best parts of several processes: high heating rate of the coal particles to achieve high carbon conversion, control of secondary reactions via ambient gas temperature (low), and a hydrogen rich atmosphere to potentially achieve high yields of liquid hydrocarbons. This combination of process conditions effectively decouple the reactions which produce the primary volatiles at the surface of the coal particles and the secondary gas phase reactions of the primary volatiles. The HHF process would operate at low pressures (0 - 5 psig). Because of the hydrogen atmosphere, it is conceivable that any sulfur present in the coal will be converted to hydrogen sulfide, which would be removed in the purge gas stream and later processed to produce elemental sulfur.

Rapid Hydropyrolysis of Coal System

Figure 1 is a schematic of a conceptual process for the HHF hydropyrolysis of coal for the preferential production of high value liquid hydrocarbons (Hewett, 1986). It consists of two HHF process reactors. The first is the coal hydropyrolysis reactor which rapidly heats bituminous coal from ambient temperature to 900 °C at a heating rate of 60 to 70 °C / second to produce a high yield of liquid hydrocarbons (about 16.3 % for bituminous coal). The second is a char processing reactor operating at about 850 °C to 1000 °C , which is used for steam-char reaction for hydrogen production. Both reactors use the carbon-containing solids to accept the high heat flux directly.

The HHF coal hydropyrolysis reactor (Reactor 1) combines the bituminous coal and high heat flux in the presence of hydrogen. The coal, dried and ground to a particle size of about 63 to 74 micrometer diameter is not preheated. This assures that it will remain free-flowing throughout processing. The reactor must be designed specifically so that the coal is not heated until it is exposed to the high heat flux. Otherwise, it will become sticky and will agglomerate, probably into a non-processable form. The hydropyrolysis reactor would yield a mixture of light and heavy liquids, some gases (chiefly carbon monoxide and carbon dioxide), and a solid residue of char and ash. The fluid phases are transported to a separator where the separate streams are subsequently sent for further processing. The gas stream would contain some recycled hydrogen-rich gases as well.

For the use of this plant hydrogen will be produced from the char, a by product from Reactor 1. A review of the literature reveals that char, deprived of volatiles, is

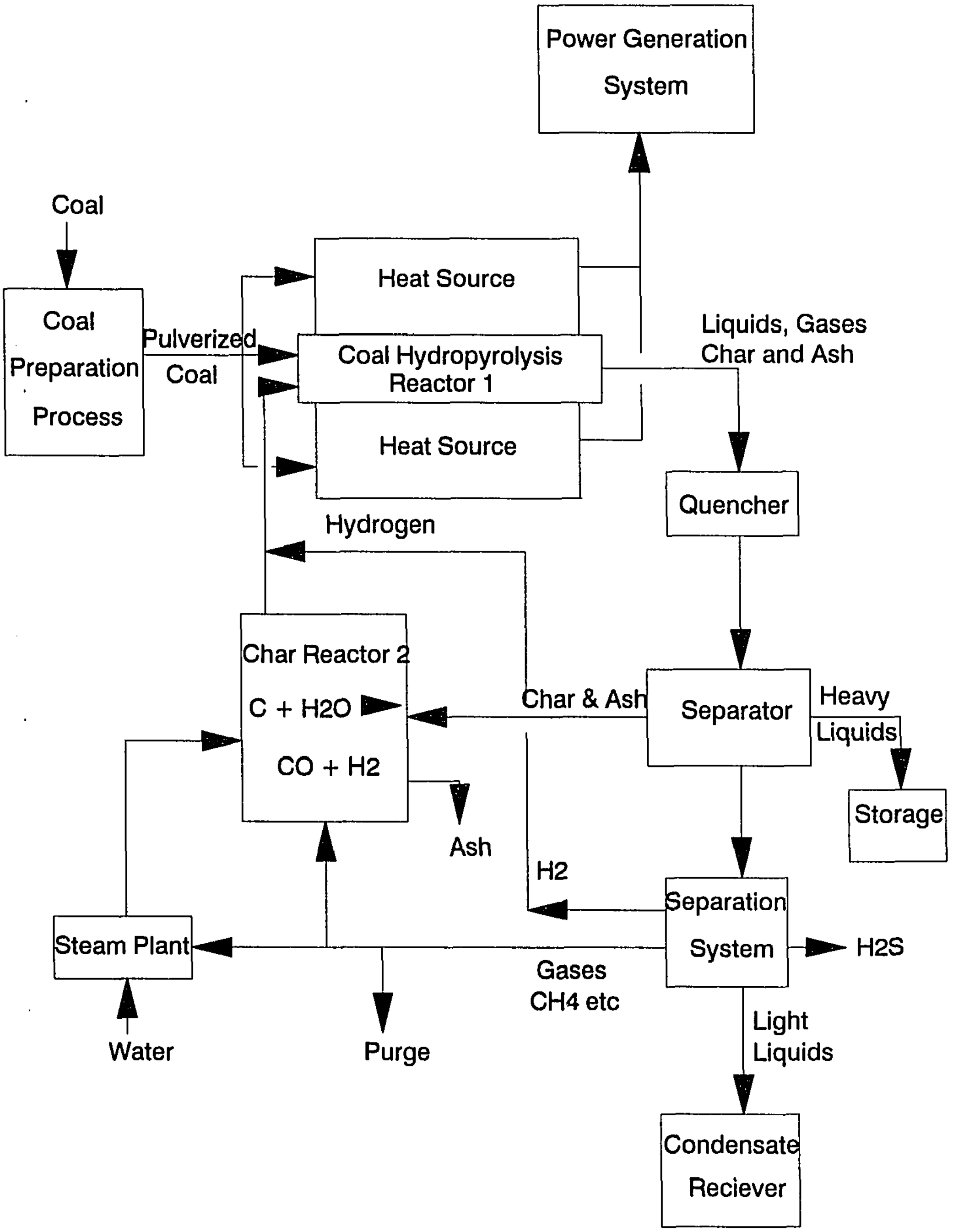

Figure 1: Schematic of a Rapid Hydropyrolysis Plant

(i) A Pyrolysis Reactor to Pyrolyze Coal in the Presence of Hyrogen and

(ii) A Char Reactor in which Char and Steam React to Produce Hydrogen-Rich Gas difficult to react efficiently or economically. The HHF coal hydropyrolysis concept being proposed has the potential to resolve the above-mentioned problem which may contribute significantly to reducing capital costs. Char, heated by the HHF technique in the presence of steam can react chemically to produce the hydrogen needed for the hydropyrolysis reactions. The HHF provides the required endothermic heat in Reactor 2 without producing CO_2.

Char can also be burned to generate steam (not shown in Figure 1) for various steps in the purification of process streams. The char burnout reactor can utilize the HHF radiation to oxidize the volatile-poor char with air. This is also a unique and valuable means of using the radiation since, ordinarily, the char is very difficult to burn. It is believed that HHF-assisted char burnout will allow combustion of char with air, possibly without ash agglomeration problems.

The physical design of the two reactors is subject to research and development, and must consider the tendency of coal to agglomerate over a very wide temperature range. The reactors must achieve good separation of solids from the vapors and gases. The optical density of the coal / gas mixture is also important in determining the efficiency of the reactors. The heating system for Reactor 2 is not shown in Figure 1. The char reactor can be of conventional design using a proven technology.

Emitter Burners. One of the radiative heat sources proposed for the rapid coal hydropyrolysis process is the use of high temperature emitter burners. This burner technology is based on the incandescent gas mantles technology developed almost a century ago for outdoor lighting. In the early 1900 these mantles were installed in gas lanterns and used for illumination purposes. Now, gas lanterns are mostly used for outdoor activities such as in boats and campgrounds as well as in homes remote from electric supplies. The mantles use various type of gases and liquid fuels which include propane, butane, or kerosine. Mantles using either liquid or gaseous fuels are made of knitted rayon or a similar fibre. The fabric is impregnated with a concentrated solution of thorium nitrate, containing cerous nitrate and other minor additives. The impregnated material is then treated with gaseous or liquid ammonia to avoid brown fumes on burning to oxide. One widely used commercial formula for lantern mantles is 99.1% ThO_2, 0.6% CeO_2, and 0.3% MgO. These oxides which include cerium, yttrium, or zirconium oxides when added to the thorium oxide excite it to give a high illumination power (Welsbach, 1896; Callow 1966 and 1967; Addison 1985).

Recent advances have been made in improving these incandescent gas mantles for other applications such as in thermo-photovoltaic energy conversion. The rayon fiber used for the conventional gas mantle has been replaced with other inert ceramic fibrous materials which can withstand high temperature operation. These fibers, impregnated with rare earth oxides which include ytterbium oxide, can act as emitters when heated at high temperatures. The emitters are thermally energized when heated to about 1700 °C and emit radiation within a very narrow wavelength. These burner / emitter system are also called 'Selective Emitter Burners' due to their unique characteristic of emitting selective wavelength radiation. The wavelength band radiated by the emitters depends on the type of rare earth oxide metal impregnated on the mantle. Ytterbium oxide for example, emits a concentrated radiated flux over the 400 to 2500 nanometer wavelength range. These selective emitter burners can be operated with conventional fuels such as methane, butane, propane etc (Goldstein et al., 1990; Nelson, 1991). The amount of liquid produced from rapid hydropyrolysis of coal does not depend on the wavelength but on the heat flux and the temperature the light beam can generate (Beattie et al., 1983). Therefore, the use of selective emitter burner is not necessary in rapid hydropyrolysis of coals. It is sufficient to use an emitter burner that can generate the required temperature and heat flux. The heat flux can also be enhanced by the use of a series of emitter burners-reflector combinations. It is proposed to use these emitter burners to provide radiant heat for conducting rapid hydropyrolysis of coal.

Rapid Hydropyrolysis Reactor - Emitter Burners Set-up. The basis of this technique is the result of the work conducted on HHF coal hydropyrolysis using a high intensity light beam targeting on a coal sample. The equipment for producing this beam (using 1000 watt lamp) was manufactured by Photon Technology International. In our experiments as mentioned earlier, the beam has been targeted on a coal sample in presence of hydrogen. The results from the study indicate that about 16.3% (maf) of liquid hydrocarbons can be produced when bituminous coal is rapidly heated (60 to 70 °C / second) to a relatively high temperature (900 °C). However this technique of producing high heat flux does not have any commercial potentialities if electrical lamps are used as a heat source. Therefore, it is proposed to use emitter burners or concentrated solar radiation and a quartz reactor where coal particles are rapidly hydropyrolized for this conceptual plant.

The emitter burner / concentrator system consists of a parabolic trough concentrator and emitter burner. The emitter will operate at high temperatures and will radiate through the quartz window onto a parabolic trough as shown in Figure 2. The trough will concentrate the radiant flux to levels high enough to produce the desired reactions in the reactor. The coal and hydrogen will flow through the reactor in a co-current fashion. The reactor made of quartz will be fed with coal at the top using a feeder. The high heat flux will rapidly heat the coal by radiation. The product vapors and hydrogen will be heated primarily by convection ie. contact with the hot particles. Therefore, sufficient circulating gas needs to be present, such that the bulk gas is not heated and it can serve as an adequate heat sink to prevent secondary thermal cracking.

Concentrated Solar Flux. Another emerging technology that can provide a radiative heat source is a concentrated solar flux system. Recent advances, in solar thermal technology convert the sun's radiation into useful products such as process heat or electricity by concentrating the sun's radiation. The solar thermal energy considered for the coal rapid hydropyrolysis process is far beyond the common perception of sunlight as used for low temperature heating of houses or to directly power photovoltaic cells. It would involve central receiver technology, where multiple mirrors reflect sunlight to a common focus. The radiant flux is directly proportional to the number of mirrors aimed at any target. These mirrors or solar concentrators are also known as heliostats. Heat flux in the range of 200 watt / cm^2 and higher can be easily achieved by this technique. Such systems have been designed and tested at the National Renewable

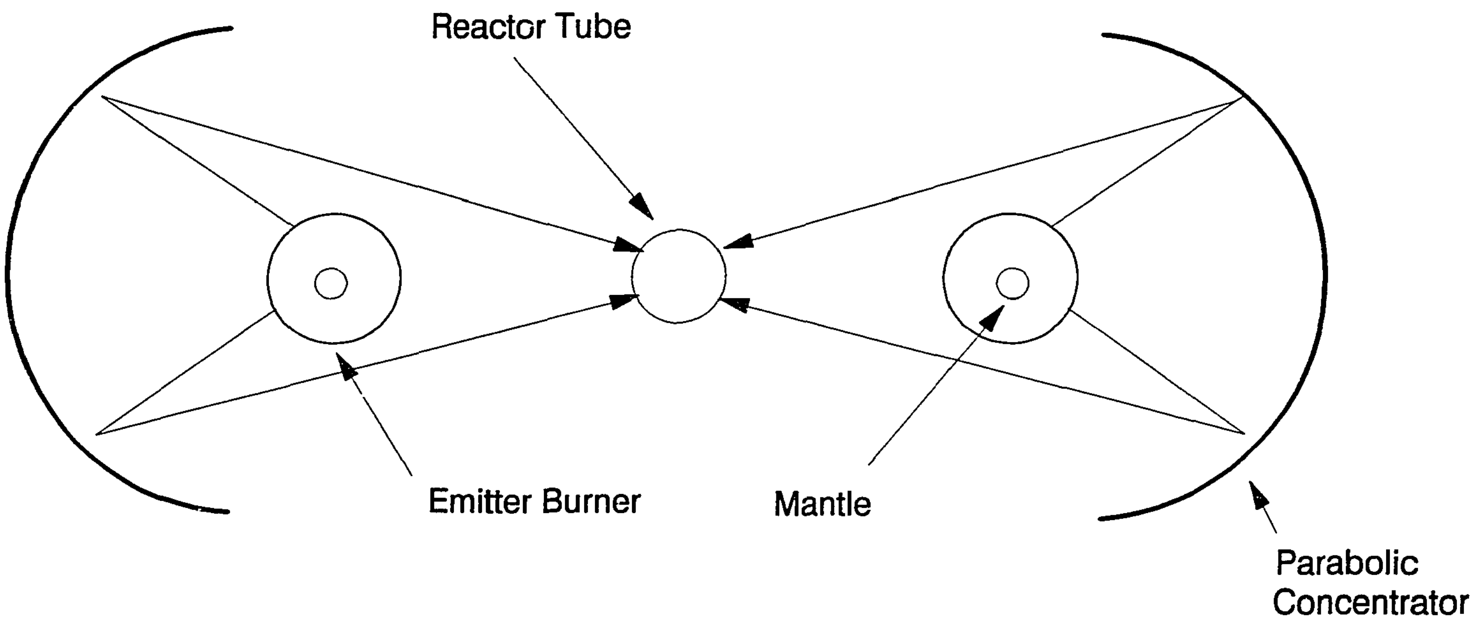

Figure 2: Rapid Hydropyrolysis Reactor - Emitter Burners Set-up

Energy Laboratory, CO. and other national laboratories for different applications of concentrated solar thermal energy. These includes destruction of hazardous wastes such as dioxin and the manufacture of chemicals such as silicon carbide at temperatures greater than 2000 °C.

Rapid Hydropyrolysis Reactor - Concentrated Sunlight Set-up. A reactor set-up can be used for rapid hydropyrolysis of coal using concentrated solar energy. Multiple mirrors will be used with parabolic concentrator to reflect the sunlight and focus the beam on to the quartz reactor. The coal and hydrogen will be fed into the reactor as discussed earlier. A possible way to hydropyrolize coal using concentrated sunlight is shown in Figure 3 (Glatzmaier, 1988). In this process, powdered coal is transported to the top of receiving tower where it can be exposed to concentrated solar radiation for a short period of time.

Potential Advantages of the Rapid HHF Coal hydropyrolysis Process

The proposed rapid HHF coal hydropyrolysis system offers the following advantages.

(a) The energy for hydropyrolyzing the coal can not only be placed directly onto the coal (in the presence of hydrogen) but also at a high heating rate (60 to 70 °C \ second) to achieve a high temperature (900 °C).

(b) The high heating rate available in the reactor can be used to maximize the yields of the more valuable liquid products at the expense of the lower value gaseous products.

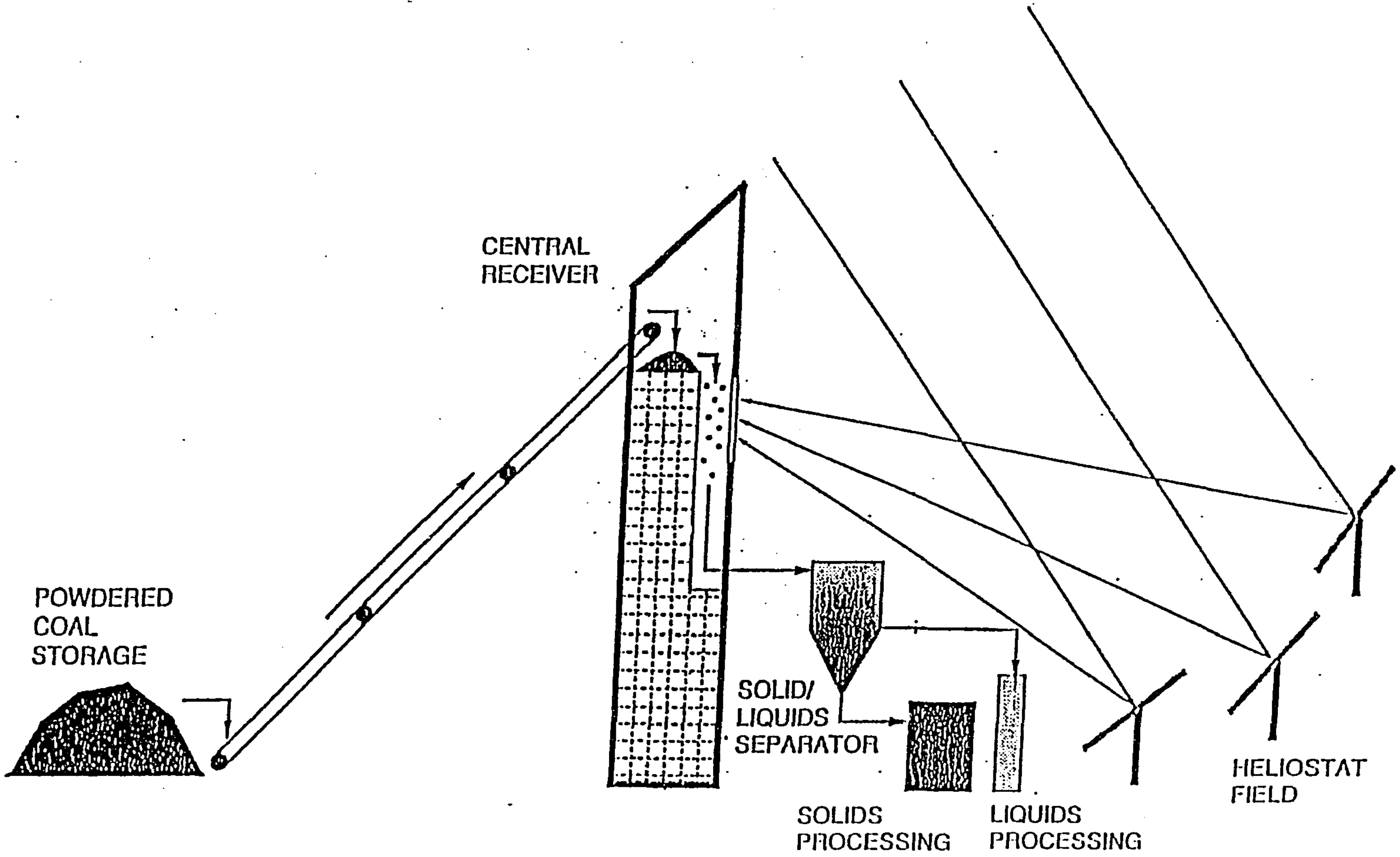

Figure 3: Conceptual Plant for Solar Rapid Hydropyrolysis of Coals

The yield of liquid hydrocarbons in the range of gasoline and kerosine from rapid hydropyrolysis of bituminous coal would be about 16.3% maf.

(c) HHF can be utilized to process the byproduct char in either of the following ways:

(i) to drive a chemical reaction involving char and steam to produce the hydrogen needed for the hydropyrolysis process.

(ii) to burn the char in the presence of air to generate steam for power generation.

(d) High temperature exhaust in the generation of HHF by emitter burners can be used to produce steam or electricity for use inside the plant and/or for sale to a utility.

(e) The emitter burners use fuel gas which can be pipeline gas, refinery gas or obtained as a by-product (at least some amount) from the process itself. Since the gas is inexpensive and burns efficiently to produce radiant heat, the energy economics of the process is expected to be better than that of conventional direct or indirect coal liquefaction techniques.

(f) Technology for concentrated solar energy has been proven and can be utilized for this process.

(g) There will be a minimal of environmental pollution because fuel gas and concentrated solar energy are used as the energy source.