SYNTHESIS GAS PRODUCTION FROM PEAT
USING A STEAM PLASMA

A

THESIS

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ABSTRACT

The present work describes a unique application of plasma technology being investigated at McGill University.

Steam plasma was used to transform peat into a synthesis gas suitable for methanol production. Fourteen runs were made, in which the effects of temperature and carbon/steam molar ratio on the product gas composition and on the carbon conversion were investigated. A stainless steel reactor of 20 cm diameter and 120 cm length was used. Finely ground peat (mean particle size 63 microns, moisture content 15.5%) was fed continuously into the reactor top, and exposed to mean reaction temperatures ranging from 1250 K to 1420 K. A carbon conversion of 89% and a hydrogen/carbon monoxide molar ratio of 1.8 in the product gas were achieved.

The trends in the data were investigated, and models derived to reflect the results. They indicated that 90% conversion and a hydrogen/carbon monoxide molar ratio of 2.0 could be attained with the appropriate operating conditions. A new reactor geometry is proposed to achieve this objective.

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RESUME

Cette thèse décrit une nouvelle application dans un domaine de la technologie des plasmas dans lequel le département de Génie Chimique de McGill s'est spécialisé.

Un plasma de vapeur d'eau a été employé pour gazifier de la tourbe pulvérisée et produire un gaz de synthèse qui se prêterait à la production du méthanol. Quatorze expériences ont été faites au cours desquelles les effets de la température et du rapport molaire carbone/vapeur sur la composition des gaz produits ont été examinées. Le réacteur consistait d'un cylindre en acier inoxydable de 20 cm de diamètre interne et de 120 cm de haut. La tourbe, sous la forme d'une poudre fine (diamètre moyen de 63 microns et 15.5% d'humidité) était alimentée d'une façon continue en haut du réacteur, et exposée à des températures moyenne entre 1250 K et 1420 K. Une conversion de 89% du carbone contenu dans la tourbe en un gaz avec un rapport hydrogène/monoxide de carbone de 1.8 a été atteinte.

Des modèles, basés sur les résultats expérimentaux, sont proposé. Ils indiquent qu'une conversion de 90% et un rapport hydrogène/monoxide de carbone de 2.0 peuvent certainement être obtenus en utilisant des conditions d'opération appropriées. Une nouvelle géométrie de réacteur est proposée pour atteindre cet objectif.

ACKNOWLEDGEMENTS

There are many people the author wishes to express his gratitude to, only some of whom are mentioned here. In particular, the author would like to thank:

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SECTION I:

GENERAL INTRODUCTION

GENERAL INTRODUCTION

One might question the investment of research dollars to examine the transformation of peat to synthesis gas for methanol production, using a steam plasma. In the Province of Quebec, special circumstances justify this expense.

The use of peat as a feedstock might appear unwise. The gas, oil, and coal reserves in Quebec are too small to be of any consequence. Peat is the only fossil fuel available in the province for production of organic chemicals. Table I, from assessments by Ketcheson and Jeglum (1972), Simard (1972), Hunter (1975), and Monenco (1977), shows that Quebec has only 2.5% of Canada's total peat resources. As reported at the Symposium on Energy from Biomass in Montreal (1980), even though there exists a large difference in the peat resources reported by Ontario and Quebec, much of the Ontario resource is located in the James Bay and Hudson Bay regions bordering Quebec. It is "quite possible that Quebec also possesses vast peatland areas in similar frontier regions". Unfortunately, Quebec has not fully assessed its resources yet.

Another report by Monenco (1978), cites Statistics Canada figures which show Quebec accounted for about 41.1% of the peat actually produced in Canada in 1977 (see Figure 1). This peat was produced mainly for agricultural purposes by small family-owned businesses. Canada has 30.2% of the world's peat resources, but only about 0.5% of its production.

The electrical generation of the high-temperature steam reactant in the form of plasma is questionable. Electrical methods are the most convenient way of maintaining temperatures in excess off 1200 Celsius, but electrical energy is usually expensive. In the Province of Quebec, there exists a surplus of hydro-electric power, which is likely to persist for many years to come. Indeed, due to the problems of storing electrical

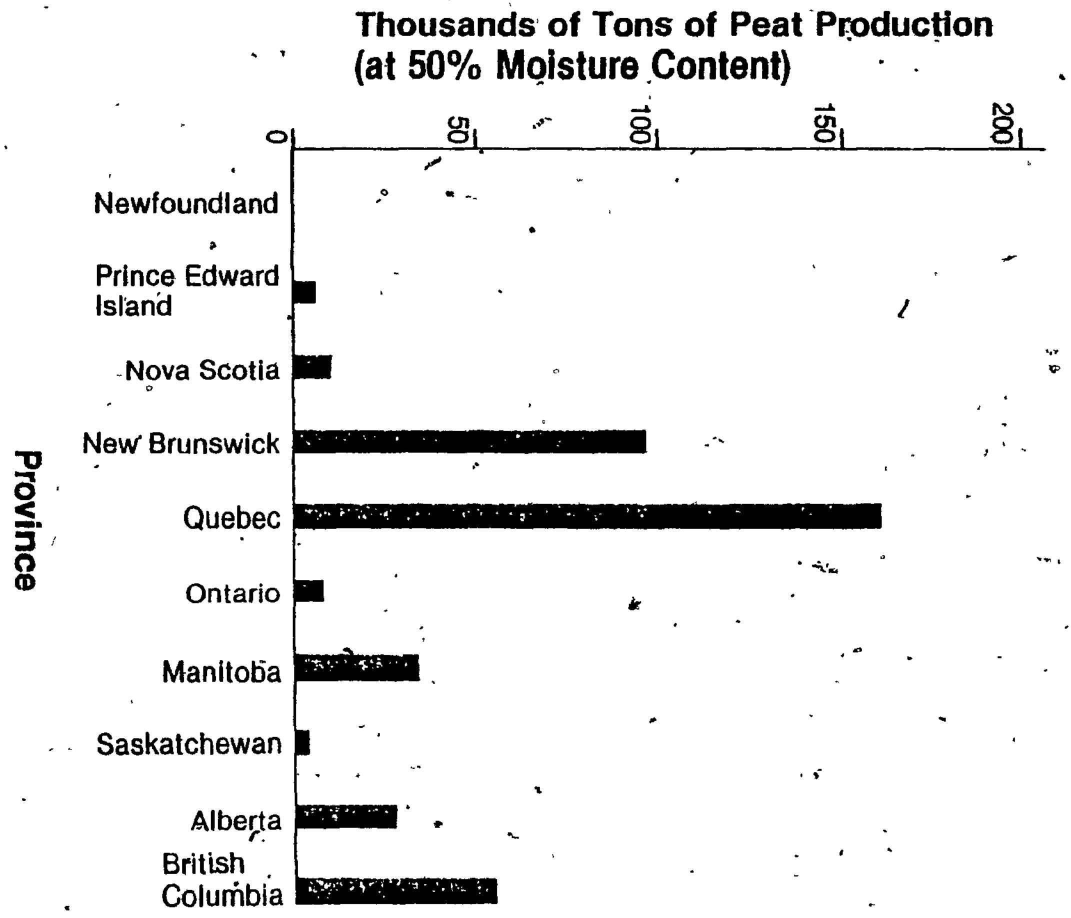
Table I
Peat Resources by Province(c)

Province	Peat Resources (10^6 tonnes)(a) (b)
Ontario	43,823
Alberta	17,405
Saskatchewan	15,664
Newfoundland	3,481
British Columbia	3,128
Quebec	2,176
Manitoba	227
New Brunswick	106
Nova Scotia	8
Prince Edward Island	4
Total	86,022

(a) estimated resources based on surveyed areas
(b) assumes 50% moisture
(c) Anon., "The Scope of Peat in the Canadian Energy Context", from assessments by Ketcheson and Jeglum (1972), Simard (1972), Hunter (1975), and Monenco (1977).

FIGURE 1:

PEAT PRODUCTION BY PROVINCE (1977)


Thousands of Tons of Peat Production
(at 50% Moisture Content)
0
50
100
150
200
Province
Newfoundland
Prince Edward Island
Nova Scotia
New Brunswick
Quebec
Ontario
Manitoba
Saskatchewan
Alberta
British Columbia

energy, generators must be shut-down evenings and weekends. Hydro-Quebec has the responsibility of supplying power to all sectors in the province. The Annual Report of Hydro-Quebec (1982) indicates that the overall demand for electricity actually dropped 3.1% in 1982, and this downward trend is expected to persist. The Chairman of the Board stated that "in the short run, the volume of electricity sales outside the province will be limited by the capacity of our interconnecting lines (with the rest of Canada and the United States), and so the utility must look to domestic markets to dispose of its surpluses". With this strategy of promoting the use of electricity in domestic sectors, hydro-electric power is available in Quebec at some of the cheapest rates in the world. Industrial elecricity in 1982 was available for an average of 2.38 cents per kilowatt-hour, although depending on the consumption levels, rates as low as 1.7 cents were possible. This means many plasma applications are a viable option in Quebec, where they might not be elsewhere in many areas of the industrial world.

The Research Institute of Hydro-Quebec, IREQ, has clearly stated a committment to the development of plasma technology, and has shown some interest in the present work.

The MONTHLY ENERGY REVIEW (June 1983) states that the average industrial electricity cost in the United States was 4.95 cents per kilowatt-hour in 1982. Little of this energy is produced by hydro-electricity. Table II shows that generation of electricity by

Table II
Primary Energies Consumed to Produce Electricity in the United States[a]

Primary Energy Source	March 1983 Production (10^9 kwh)	% of Total Production	% Change in Production over Year
1. Coal	95.6	52.5	- 2.1
2. Hydroelectricity	30.3	16.6	+ 1.4
3. Nuclear	23.9	13.1	+ 5.0
4. Natural Gas	19.7	10.8	- 16.6
5. Petroleum	12.6	6.9	- 7.0
Total	182.1	100.0	- 2.8

(a) Anon., MONTHLY ENERGY REVIEW prepared by the U.S. Department of Energy (D.O.E.) (June 1983).

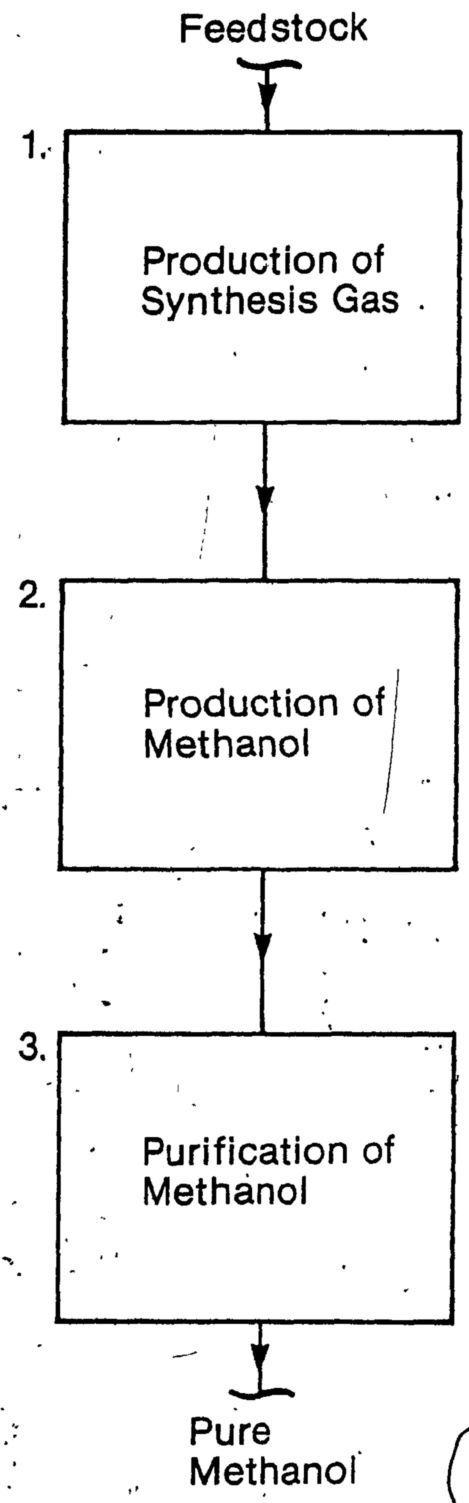
hydro-electric means has increased, but total production of electricity in the United States has decreased (as in Quebec).

Considerable expertise exists in plasma technology in Quebec. As far back as the early 1960's, Gauvin and Gravel (1962) conceived the conversion of carbon-containing material in an Atomized Suspension Technique Reactor (ASTR) using plasma. Expertise has been gained in many areas of plasma engineering within the Plasma Technology Group at McGill University. Gauvin et al. (1983) discussed a preliminary investigation of peat conversion using superheated steam, which provided a good basis for the design of this work. While the steam plasma in the present work was produced by reacting hydrogen with oxygen, the Plasma Technology Group is presently committed in conjunction with IREQ to developing a steam plasma torch for chemical applications.

Finally, there are several good reasons to produce a synthesis gas for methanol production. A schematic of the major steps involved in the latter is given in Figure 2. The technology being developed in this work would replace the first step. From a technical standpoint, a plasma-based system offers several advantages over a conventional process. First, liquid water fed to a steam plasma torch may be pressurized, and the ASTR operated at the pressure of the methanol-synthesis step. This avoids expensive but otherwise necessary gas compression. Second, no oxygen is required to burn a (conventional) natural gas feedstock to generate reaction temperatures. Finally, conditions are controlled easily in the

FIGURE 2:

MAJOR PRODUCTION STEPS IN METHANOL SYNTHESIS

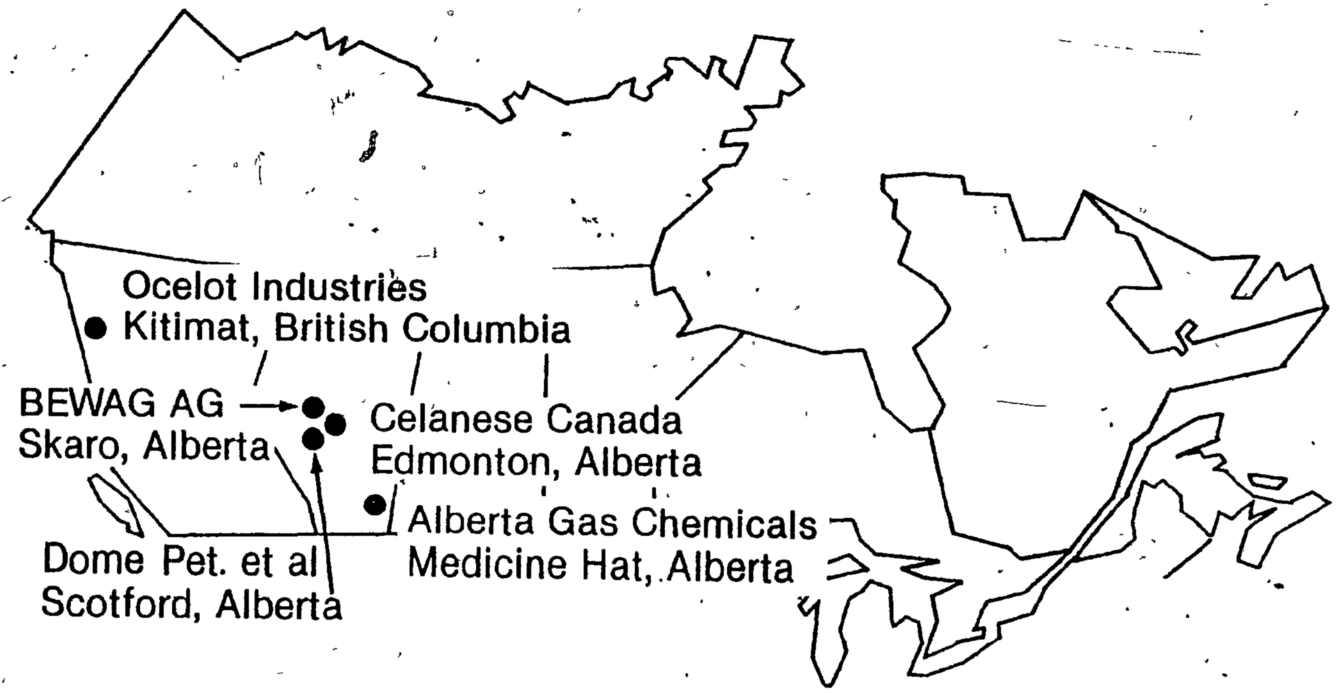

Feedstock
1.
Production of Synthesis Gas
2.
Production of Methanol
3.
Purification of Methanol
Pure Methanol

plasma-based system. In this way a synthesis gas can be produced with the desired composition (one with a hydrogen-to-carbon monoxide ratio of two), while minimizing unwanted by-products. No separate water-gas shift plant is thus required as in the conventional system.

Canada's western provinces, rich in oil and natural gas, are responsible for all the methanol production in Canada. Since late 1981, when the federal government began to ease their National Energy Program (NEP), industrial development in the west has accelerated. As reported by Kohn (1981), methanol plants were being considered by Celanese Canada (1982), BEWAG (1984), and Dome Petroleum/Alberta Gas/Alberta Energy (1984). The combined capacity of these three plants was expected to be 3.3 million metric tonnes per year, of which much will be exported to the United States. OIL WEEK (Sept. 19 1983), reports the present production of petrochemicals in Canada. Methanol is produced by Alberta Gas Chemicals (720,000 tonnes per year), Ocelot Industries (448,000 tonnes per year) and Celanese has started its production (690,000 tonnes per year). This information is summarized in Figure 3. The large increase in methanol production anticipates a rapidly expanding market in the late 1980's. As reported by Kieschnick (1983), methanol offers potential as a transport fuel. The October 3, 1983 CHEMICAL ENGINEERING discusses the ongoing methanol-car tests, and how California is "one step closer to full commercialization of methanol as a replacement for petroleum fuels".

FIGURE 3:

METHANOL PRODUCTION PLANTS IN CANADA


Ocelot Industries
Kitimat, British Columbia
BEWAG AG
Skaro, Alberta
Celanese Canada
Edmonton, Alberta
Alberta Gas Chemicals
Medicine Hat, Alberta
Dome Pet. et al
Scotford, Alberta

A strong demand for methanol, with proven production technology, would justify a methanol installation in Quebec.

The general objectives of the present research project can now be outlined. The simulated steam plasma was developed, and an ASTR-based system built. Reaction conditions were explored to determine whether the desired synthesis gas could be produced while minimizing by-products. Maximizing carbon conversion in the peat was also explored. Simple models were developed, and the data was fit to the models to see how the independent variables would affect the system. Lastly, recommendations for future improvements were developed.

The gasification of peat using plasma is a unique idea being explored by the Plasma Technology Group at McGill University. The type of steam plasma used in this work is novel. A model has never been developed to reflect the effect of physical variables for this steam/peat system. Finally, it is encouraging to note that the data reported are promising with respect to further development of the process.

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SECTION II

LITERATURE REVIEW

LITERATURE REVIEW

A. INTRODUCTION

The body of literature dealing with plasma technology has grown to the point where it is difficult to cover all aspects in detail. Theses from the Plasma Technology Group at McGill University have discussed the developments of plasma engineering fairly comprehensively. These works will be referred to, but this literature review will be restricted to pertinent references.

A general discussion of plasma is first presented. It is defined, and the method used to generate plasma is explained. The physical variables affecting plasma characteristics are noted. Finally, the method of steam plasma production used in this work and some of its properties are discussed, including current plasma applications.

The next section introduces the reader to peat and peatlands in a general way, and characterizes peat physically and chemically. The transformations of peat and the resulting products are summarized.

Before dealing with methanol production, a summary of related work is given. Experimental work involving peat conversion without plasma is discussed. Then, carbon conversion using plasma is reviewed. These reviews are specific, with an emphasis on recent work described in the literature. Grosdidier de Matons' (1983) results are reviewed in detail since they provide the basis for the present work.

Finally, the economics of methanol production for a plasma-based process using peat are considered. This section is based largely on a study by Gauvin and Duncan (1982).

B. PLASMA CONSIDERATIONS

Introduction

There are three types of plasmas, illustrated in Figure 1. High-temperature plasmas are obtained by nuclear fusion, in which atomic particles become so energized they overcome their electrical repulsion, then collide and fuse. This releases energy to the plasma, and the process becomes self-sustaining. These plasmas are typically at temperatures over one million K, and require electromagnetic devices such as the Tokamak to contain them. Thermal plasmas are produced by electric arcs or electro-magnetic coupling. They are gas mixtures in quasi-equilibrium, usually at temperatures between three thousand and twenty thousand K. These temperatures are easier to contain, and consequently thermal plasmas lend themselves to chemical processing. A thermal plasma is used in the present work. Cold Plasmas are generated under vacuum conditions, producing an ionized gas mixture which is not in thermal equilibrium. The electron temperatures are in the order of ten to one hundred times the bulk temperature of the gas. Gas temperatures near ambient are possible with this type of plasma.

What is a thermal plasma? Doolittle (1977) describes the simple case "when hydrogen is heated up to a very high temperature... it becomes ionized, with the electrons being driven off and the positively charged

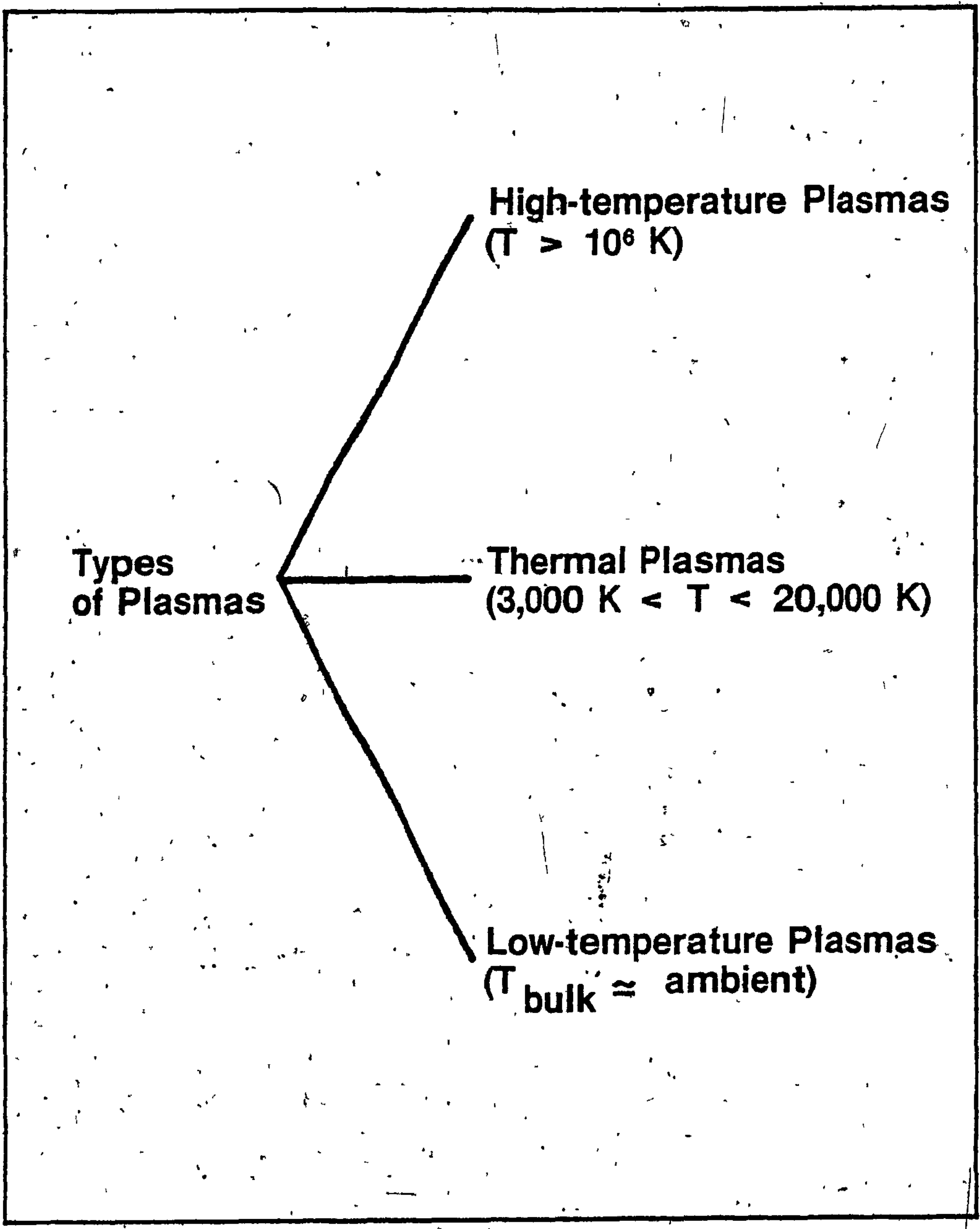

Types of Plasmas
High-temperature Plasmas
(T > 10^6 K)
Thermal Plasmas
(3,000 K < T < 20,000 K)
Low-temperature Plasmas
(T_{bulk} ≈ ambient)

FIGURE 1:

TYPES OF PLASMAS

nuclei left behind. The combination of the free electrons and positively charged nuclei constitute what is called a plasma". The mixture is electrically conducting, but electrically neutral on a macroscopic scale.

Thermal plasmas are produced in several ways, illustrated in Figure 2. The four types of thermal plasma generation devices are used by the Plasma Technology Group at McGill University. The induction plasma torch is described by Munz (1974) and the transferred-arc torch by Gauvin et al. (1981). The third type of torch, the DC-jet plasma torch, was employed in this research. The torch has been used extensively in the Plasma Technology Group by Chevalier and Kubanek (July 1970), Lewis (1973), Katta (1973), Grosdidier de Matons (1983), and Amelot (1983). Finally, a plasma torch consisting of hollow tubular electrodes separated by a narrow gap is now under investigation. It will be used to generate a steam plasma.

Requirements for Plasma Generation

A DC-jet plasma generating system consists of three main components: utilities (including the power supply), the control console, and the torch. These are shown in Figure 3. The utilities required for this plasma system are cooling water, DC current, and a suitable plasma gas. They are monitored by the control console, and then fed to the torch.

FIGURE 2:

METHODS OF PRODUCING THERMAL PLASMAS

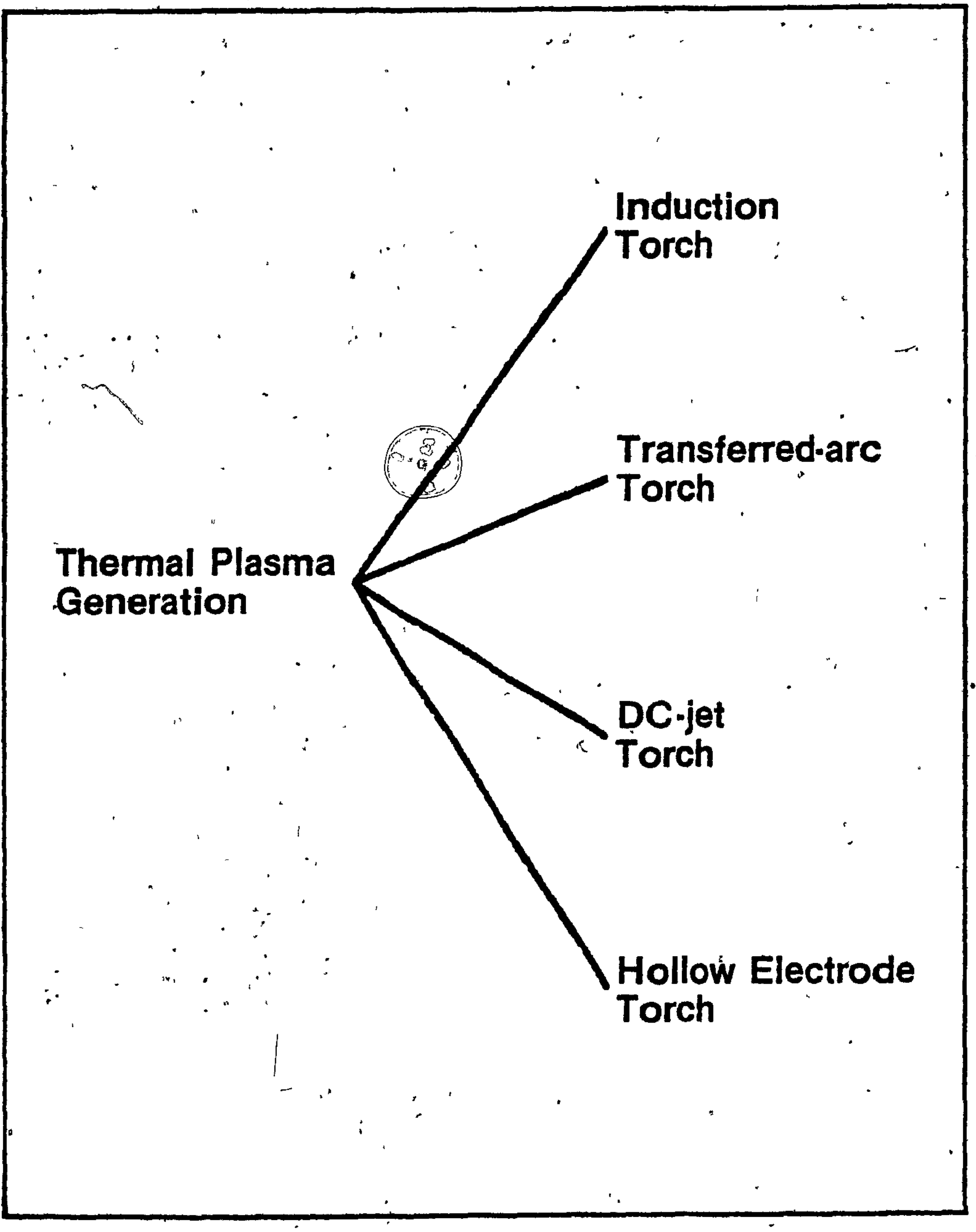
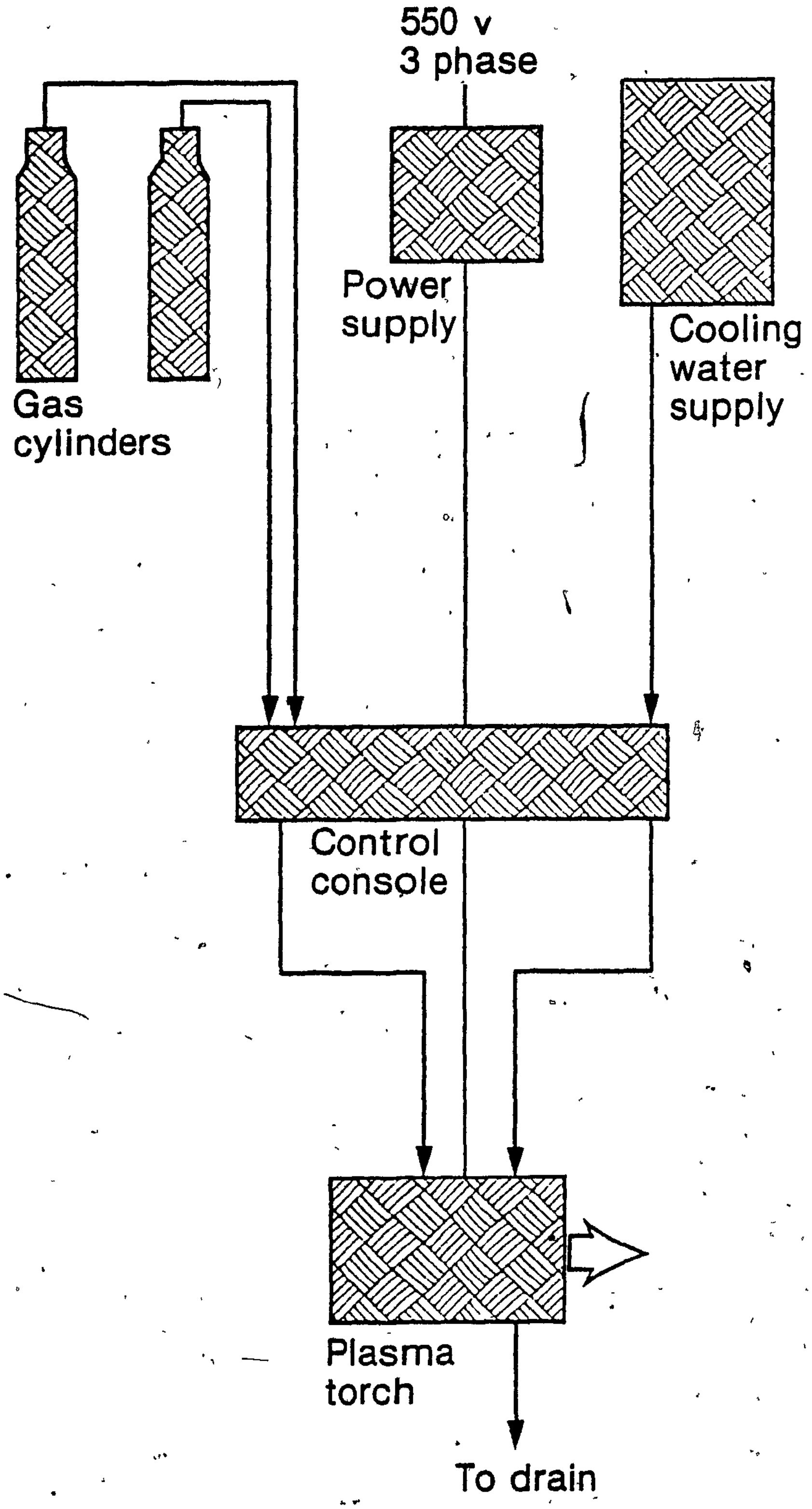

Thermal Plasma Generation
Induction Torch
Transferred-arc Torch
DC-jet Torch
Hollow Electrode Torch

FIGURE 3:

DC-JET PLASMA GENERATION SYSTEM


550 v
3 phase
Gas
cylinders
Power
supply
Cooling
water
supply
Control
console
Plasma
torch
To drain

A photograph of the torch is given in Figure 4. A hydrogen plasma from this torch is shown in Figure 5. Figure 6 gives a drawing of the bottom segment of the torch where the plasma forms. The cathode is made of thoriated tungsten, and is cone-shaped. The anode, made of copper, surrounds the cathode tip. The two electrodes form an annulus, through which the plasma gas passes. Both electrodes are water-cooled. Gas may be injected into the base of the anode before the plasma tail-flame exits the nozzle.

Figure 7 gives the mechanical components of the plasma torch. The ceramic gas distributor and protective seating plate allow gas to flow uniformly around the water-cooled cathode. The anode fits tightly into the anode holder, and is held in place by the retaining nut.

A high-frequency discharge is produced between the anode and cathode to initially strike the arc. This causes ionization of the gas flowing between the electrodes, and subsequent acceleration of charged particles in the electric field. Further collision and ionization increases the kinetic energy and temperature of the gas. In this way, a high temperature plasma results.

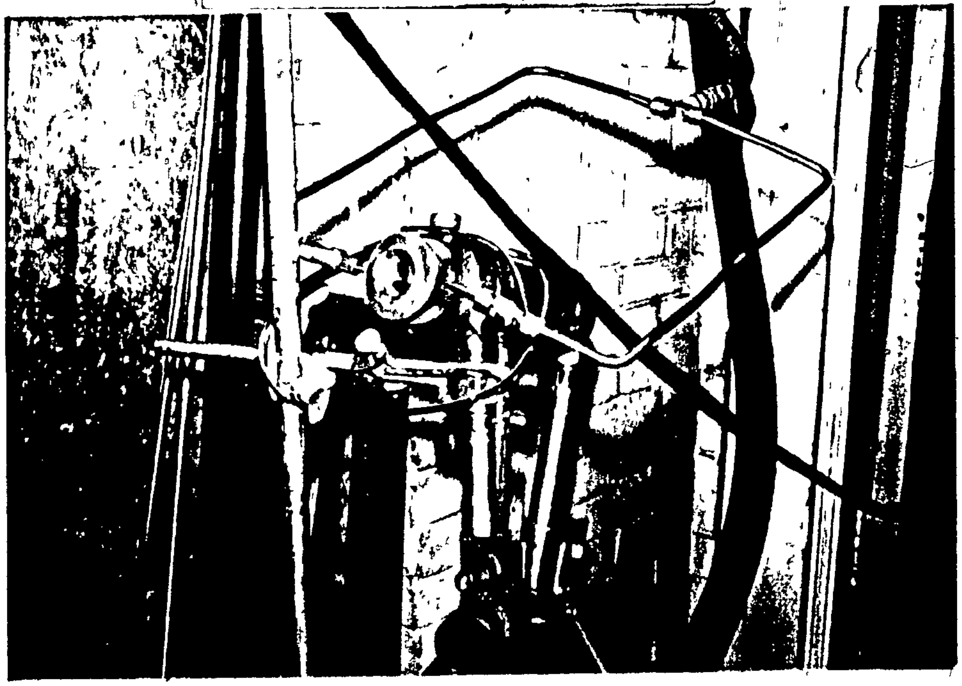
FIGURE 4:

PHOTOGRAPH OF DC-JET PLASMA TORCH

FIGURE 5:

PHOTOGRAPH OF A HYDROGEN PLASMA

COLOURED PICTURES
Images en couleur



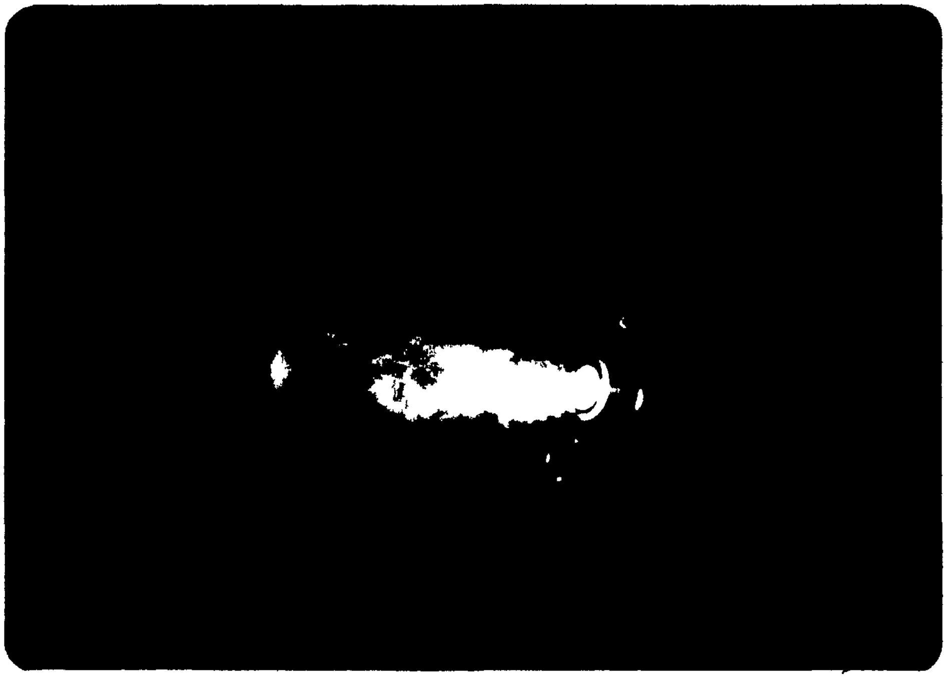
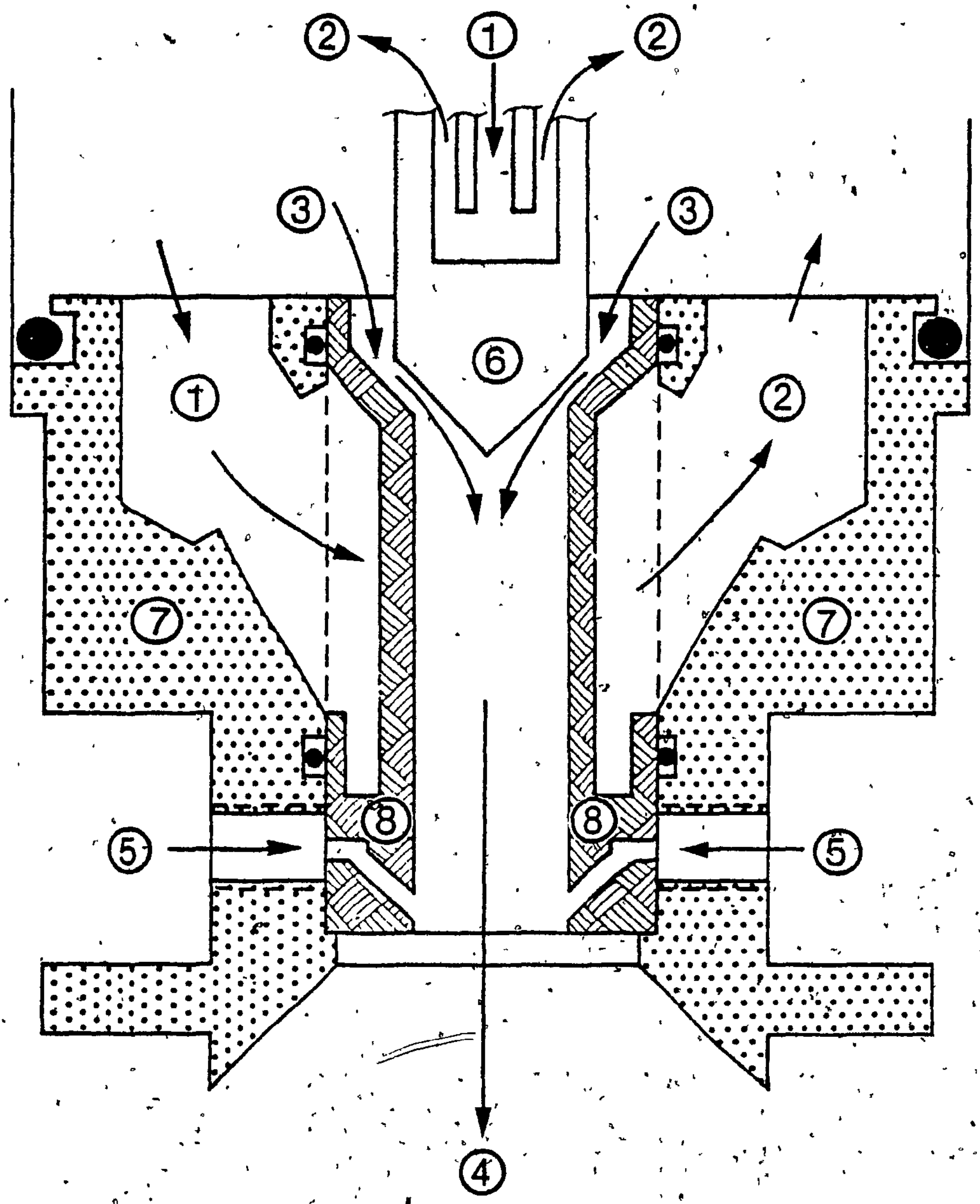


FIGURE 6:

BOTTOM OF DC-JET PLASMA TORCH

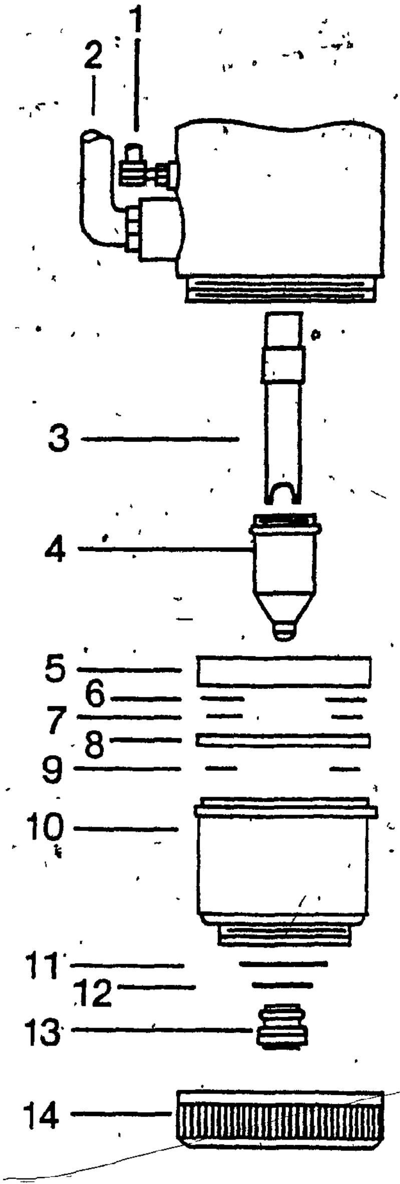


1. Cooling water in
2. Cooling water out
3. Plasma gas in
4. Plasma gas out
5. Auxiliary gas injection
6. Cathode
7. Anode holder
8. Anode

FIGURE 7:

MECHANICAL COMPONENTS OF LOWER TORCH

1 Gas Entry
2 Cooling Water Entry
3 Water Tube
4 Cathode
5 Gas Distributor
6 Brass Washer
7 O-ring
8 Seating Plate
9 O-ring
10 Anode Holder
11 O-ring
12 O-ring
13 Anode
14 Retaining Nut



Following breakdown and ionization of the plasma gas, an electric arc is formed between the cathode and the anode. The electric arc is intermittent, re-igniting and travelling between the electrodes thousands of times per second, as reported by Wheaton and Dean (1961). The voltage drop across the annulus is characteristic for a given gas and flow rate.

Plasma Operating Conditions

The parameters affecting the stability and efficiency of a DC-jet plasma torch are important in determining the operating conditions for experimentation. Efficiency is defined as the ratio:

$$\frac{\text{energy absorbed by the plasma gas}}{\text{total electrical energy provided}}$$

Bokhari and Boulos (1980) describe many of the basic parameters affecting the torch operation. The type of plasma gas, gas flow rate (velocity), current, and spacing of electrodes all affect torch efficiency and stability. These are now discussed.

Ibberson and Thring (1969) give the current/voltage characteristics of several plasma gases. At constant gas flow rates, the voltage drop in the torch is unchanged for changing currents above 350 amperes. A high current is used to produce a high plasma gas temperature. It has been found that decreasing current increases torch efficiency. This may be explained by the fact that less energy is transferred to each unit mass of gas with a lower current, resulting in a lower gas temperature and hence less energy loss by radiation to the anode. The lower limit of current is determined simply by arc stability.

With increased plasma gas flow rate, the characteristic voltage drop across the electrodes increases. It has been determined that this is due to the electric arc being pushed further down the anode tube, and the corresponding increase in arc length results in increased voltage drop. Also, the greater gas flow cools the plasma arc: this lowers the exit temperature of the plasma gas, lowering its electrical conductivity, and raising the potential drop across the electrodes. The lower arc temperature again results in increased efficiency. The lower limit of gas flow is set by anode degradation: inadequate gas flow results in extremely high temperatures and subsequent melting of the anode. On the other hand, if the gas flow is too high, the arc will blow out.

Anode length and electrode spacing are crucial parameters. Since most of the energy losses are attributable to the cooling of the anode, reducing anode size increases efficiency. Often, adequate cooling for short anodes is not possible, resulting in the melting of the anode. Electrode spacing is set by operating experience. Varying the spacing varies the arc length and hence the torch stability.

Steam Plasma Production

In this work, steam plasma is the gasifying medium. Steam plasma torches, while they do exist, are expensive and have limited availability. The only steam plasma torch which may be purchased is made by Alusuisse in Switzerland, developed for the production of fine silica. Sheer et al. (1979) produced a plasma of steam mixed with other gases, in work described later. The present study uses a steam plasma generated by injecting oxygen into a hydrogen plasma. The extremely turbulent plasma promotes very effective mixing. The explosion kinetics, investigated by Aiken (1982), results in a near-equilibrium state within a fraction of a second.

In order to understand more fully the reacting medium of steam plasma, calculations were made by the author to establish the properties of steam at different temperatures. These were done by minimizing the free energy of a system containing ionic and nonionic (hydrogen- and oxygen-containing) species. The data required for calculations are available in the Janaf Tables (1970). The system, then, was assumed to be made of ideal gases at equilibrium, and at atmospheric pressure. All ionic species, and many nonionic species are of negligible concentrations at temperatures up to six thousand K. The mole fractions of the significant species are shown in Figure 8. When comparing the data to that by Ihara (1977), good agreement is obtained. The steam plasma dissociates into atomic species, with only negligible dissociation until two thousand K:

FIGURE 8:

EQUILIBRIUM SPECIES FROM WATER DECOMPOSITION VERSUS TEMPERATURE

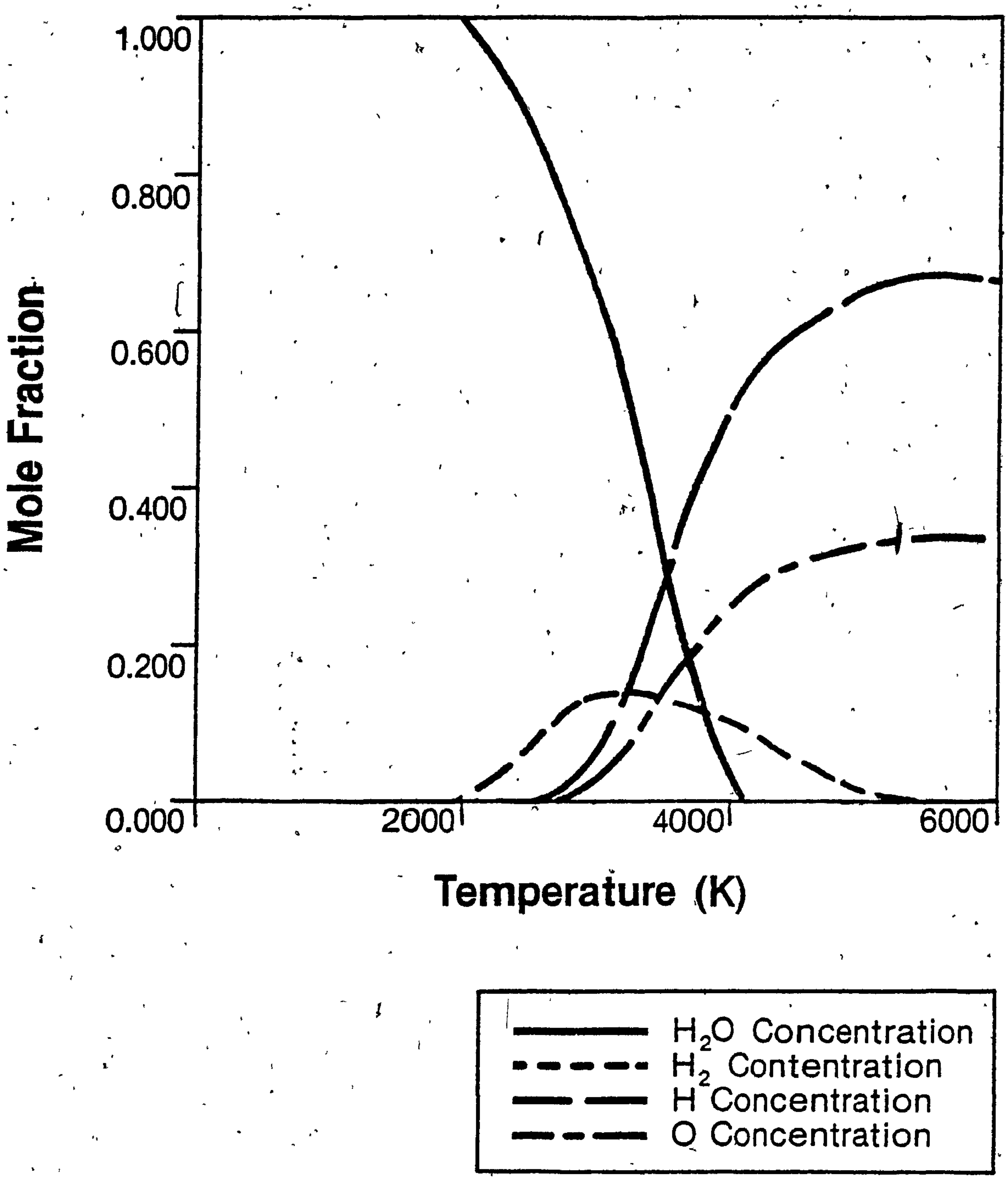

1.000
0.800
0.600
0.400
0.200
0.000
Mole Fraction
2000
4000
6000
Temperature (K)
H_2O Concentration
H_2 Contentration
H Concentration
O Concentration

Figure 9 gives the temperature of steam versus electrical energy, as calculated using a computer program by Bale et al. (1979). The equilibrium temperature from the energy of the hydrogen/oxygen combustion is slightly over 3000 K. The steam is beginning to dissociate at this temperature, causing the levelling of the curve. Large quantities of energy are required to raise the temperature of dissociating steam. This information is important in estimating the condition of the steam plasma in contact with the peat.

Uses of Plasma

Thermal plasmas provide a number of potential advantages for the chemical industry. Ettlinger et al. (1980) list a number of processes for which they appear to be particularly well-suited:

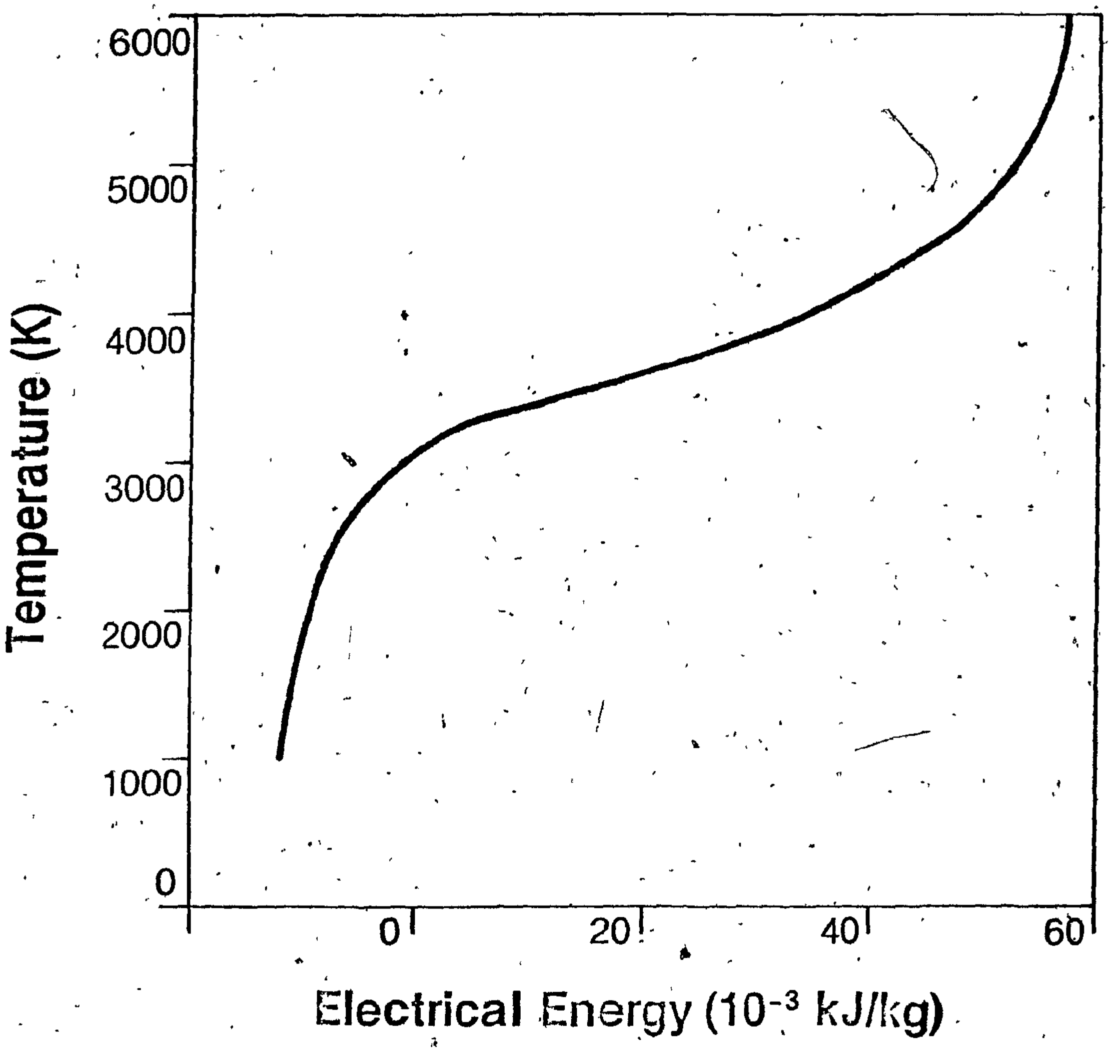
1. processes involving highly endothermic reactions;
2. processes requiring high temperatures to obtain reasonable reaction rates;
3. processes with reactions needing excited species to obtain reasonable reaction rates;
4. processes needing gases of high energy, without dilution by combustion gases and;
5. processes requiring phase changes of materials with high melting or boiling points.

This work uses advantages 1, 2, and 4.

FIGURE 9:

TEMPERATURE VERSUS ELECTRICAL

ENERGY INPUT FOR STEAM


Temperature (K)
6000
5000
4000
3000
2000
1000
0
0
20
40
60
Electrical Energy (10^{-3} kJ/kg)

Using the ASTR system eliminates the likelihood of advantage 3. The temperature of the plasma drops quickly on exit from the plasma torch as reported by Lewis and Gauvin (1973), to levels where excited species are no longer present in any significant quantities. Using Figure 9, one may estimate the maximum temperature of the steam plasma at the torch. But, reaction temperatures are low enough at the steam/peat mixing location to be measured with chromel-alumel thermocouples (less than 1500 K). Figure 8 shows that water does not dissociate at these temperatures.

Advantage 5 is used in applications such as spray-coating with high melting point materials (for example ceramics).

There is a growing spectrum of plasma applications in extractive metallurgy, organic and inorganic reactions, and heat treatment of materials. The most widely-used applications of thermal plasmas lie in the last category, including:

1. cutting and welding of metals;
2. spray-coating of materials;
3. particle processing (spheroidization);
4. reduction of mineral oxides;
5. production of acetylene and ethylene;
6. smelting of metals;
7. production of ferro-alloys and;
8. production of refractory metals (titanium etc.).

C. PEAT PROPERTIES AND USES

Introduction

Peat is a soil covered entirely by plant material, and composed of organic residues. It is formed by the anaerobic decomposition of dead plant material. The extent of decomposition depends upon several factors including depth of burial and water drainage. Peat is a non-renewable resource since peat bogs grow at the rate of only two to three millimeters in depth per year in Canadian climatic conditions.

Peatlands are classified according to their geological relationship with the main groundwater system. Peatlands are called "low-moor" if they are continuous with the main groundwater system, and "high-moor" if they are not. The peatlands from which the peat for this work was obtained were "high-moor". Water in these deposits comes from rain or snow, and therefore the mineral content of the water is low. "High-moor" peatland is characterized by its content of mosses. Sphagnum mosses, of several varieties, are common in these regions.

Many classification schemes exist for peat. The most widely used is the von Post system. This system groups different types of peat into ten categories according to their degree of humification (decomposition). The categories, H1 to H10, are based upon a qualitative analysis of the peat, and are discussed in detail by Fuchsman (1980). H1 peats are completely undecomposed, with the plant material in it easily discernable. The H10 classification refers to completely decomposed peat with no visible plant structure. The peat used in this work has an H5/H6 classification.

In a peat bog, a variety of different peats are observable. It is difficult to assess its classification. Indeed, some peat is so humified that it would appear to have no organic content at all. Other peats encountered in the same bog are so slightly decomposed that the leaves, roots and stems may be identified. For this reason, a more common peat classification will be used for qualitative considerations, with the von Post scheme used only for more exact classifications. Tibbetts and Fraser (1978) define two distinct peat types:

(1) Peat Moss: A peat of very little humification. It subsequently has a distinct plant structure, is light in colour, and has a low bulk density.

(2) Fuel Peat: A peat of significant humification. The plant structure is difficult to discern, and the peat is muddy and dark in colour. Fuel peat was used in this work.

More quantitative classification schemes are proposed in the literature, but none are universally accepted. The associations primarily responsible for these developments are the International Peat Society (IPS) and the American Society for Testing and Materials (ASTM).

Two photographs are included to illustrate the definitions presented above. The peatlands from which the peat was taken is shown in Figure 10. It is located in the county of Lobiniere, near Quebec City, on the south shore of the St. Lawrence River. Note the short trees present in this bog. The ground is not firm enough to support large trees. The untouched ground is portrayed in Figure 11. The entire area is covered mainly by Sphagnum, which through time is covered, decomposing into a more energetic (humified) type of peat.

Chemical and Physical Properties

Peat may be considered a geologically young coal. Proximate analyses and heating values of peat and various other fuels are given in Table I, as compiled by Monenco (1981). The series of wood/peat/lignite coal/subbituminous coal shows a gradual change in composition and physical properties. With increasing geological age, carbon content increases and volatiles content decreases. Increasing compression results in a higher density for coals. An important result of these transformations is the increasing heating value of the fuels.

The properties of different peats also change with increasing decomposition. Table II summarizes chemical properties of different peat types. As previously stated, the peat used in this work is in the H5/H6 classification of the von Post Scale. This peat is fairly decomposed, with an indistinct plant growth. It was obtained underneath the top growth

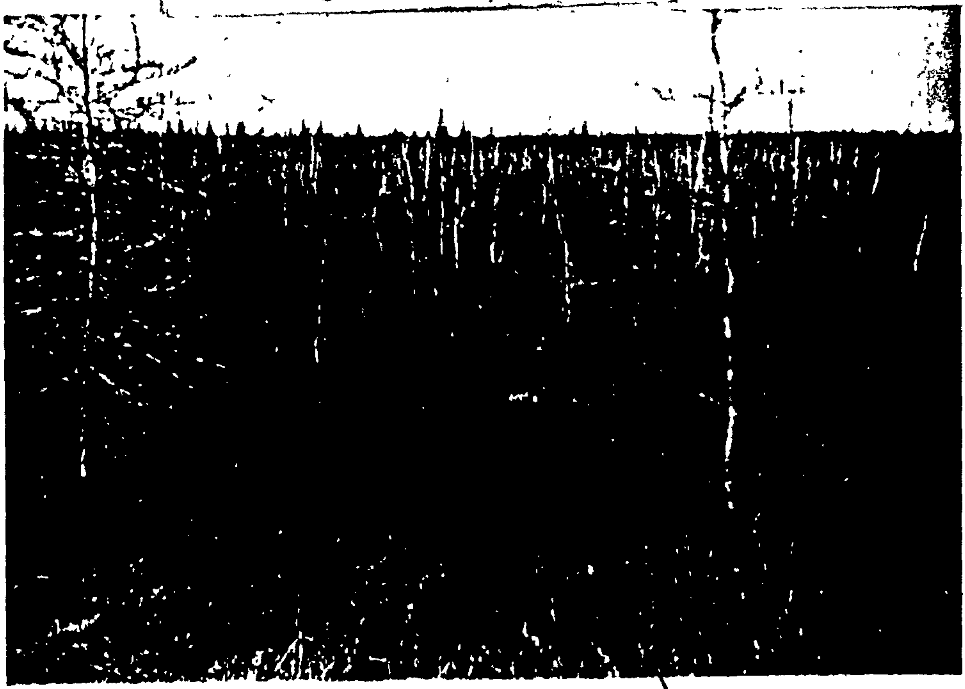
FIGURE 10:

PHOTOGRAPH OF PEATLANDS

FIGURE 11:

PHOTOGRAPH OF UNTOUCHED PEAT

COLOURED PICTURES
Images en couleur



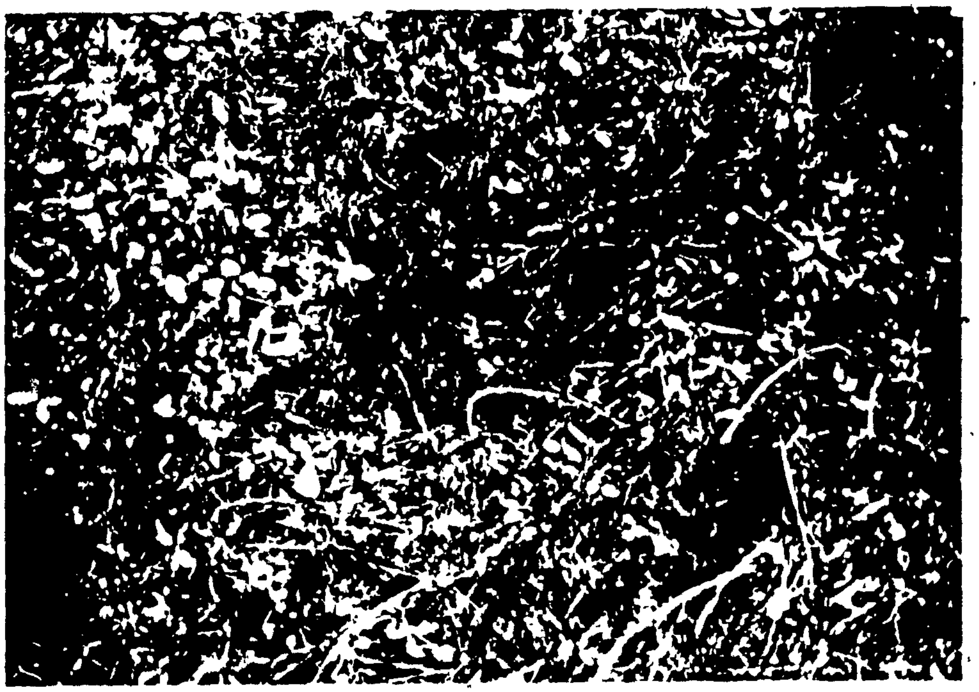


Table I
Properties of Peat and Related Fuels(d)

Property	Fuel			
	Wood	Peat	Lignite Coal	Bituminous Coal
% Carbon(c)	48–50	50–60	65–75	76–87
% Hydrogen	6.0–6.5	5.0–6.5	4.5–5.5	3.5–5.0
% Oxygen	38–42	30–40	20–30	2.8–11.3
% Nitrogen	0.5–2.3	1.0–2.5	1–2	0.8–1.2
% Sulfur	–	0.1–0.2	1–3	1–3
% Ash	0.4–0.6	2–10	6–10	4–10
% Volatiles	75–85	60–70	50–60	10–50
% Moisture	30–55	40–60	40–60	3–8
Specific Gravity(a) (Kg/m³)	320–420	300–400	650–780	720–880
Heat Value(b) (Kcal/Kg)	4400–4600	4700–5100	4800–5800	6800–7900

(a) Assuming average % moisture
(b) Assuming dry basis
(c) All values are mass percentages
(d) Anon., "Evaluation of the Potential of Peat in Ontario: Energy and Non-Energy Uses", prepared by the Montreal Engineering Company (Monenco) (1981)

Table II
Elemental Compositions of Different Types of Peat[a][b]

Element	Peat Type - Von Post Scale		
	H1/H2	H5/H6	H9/H10
% Carbon	48–53	56–58	59–63
% Hydrogen	5.0–6.1	5.5–6.1	5.5–7.0
% Oxygen	40–46	34–39	31–34
% Nitrogen	0.5–1.0	0.8–1.1	0.9–1.9
% Sulfur	0.1–0.2	0.1–0.3	0.2–0.5

(a) Considers organic matter only

(b) Anon., "Evaluation of the Potential of Peat in Ontario: Energy and Non-Energy Uses", prepared by the Montreal Engineering Company (Monenco) (1981) (shown in Figure 11). When squeezing the peat, the plant structure becomes more evident. About one-third of the peat passes through the fingers in an amorphous form as muddy water.

The ash content, or inorganics, varies considerably in peat. The quantity and composition depend on geological environment and type of peatland. The ash content may range between 2% and 22%, with the mean content about 7% by mass. Fuel peat has a higher ash content than peat moss. Table III gives an ash composition from a peatland in the Eastern Townships of Quebec. The main components are silicon dioxide (silica) and calcium oxide.

Peat has a very high porosity. All peats, as harvested, contain over 80% water by volume. Water retention in peat is an important parameter. Peat moss often contains over 95% water, but loses 50% to 80% of this when drained. Fuel peat has a smaller water content when in place, but with drainage retains much more of this than the peat moss.

Table III
ASH Composition in a Quebec Peat(a)

Compound	Mass Percent
SiO_2	39.36
Al_2O_3	12.40
Fe_2O_3	13.74
TiO_2	0.54
CaO	26.77
MgO	3.08
K_2O	1.29
Na_2O	1.38
MnO	0.21
P_2O_5	1.11

(a) Anon., "The Scope of Peat in the Canadian Energy Context", a paper presented at the Symposium on Energy from Biomass, Montreal (1980)

Peat Conversion Processes

A study prepared by Monenco (1978) classifies types of possible transformations according to Figure 12. The three basic categories (pyrolysis, reduction, and oxidation) may each be subdivided. It should be noted that these transformations are all occurring simultaneously in a reacting system such as that used in this work. By varying reaction conditions, specific transformations may be favoured.

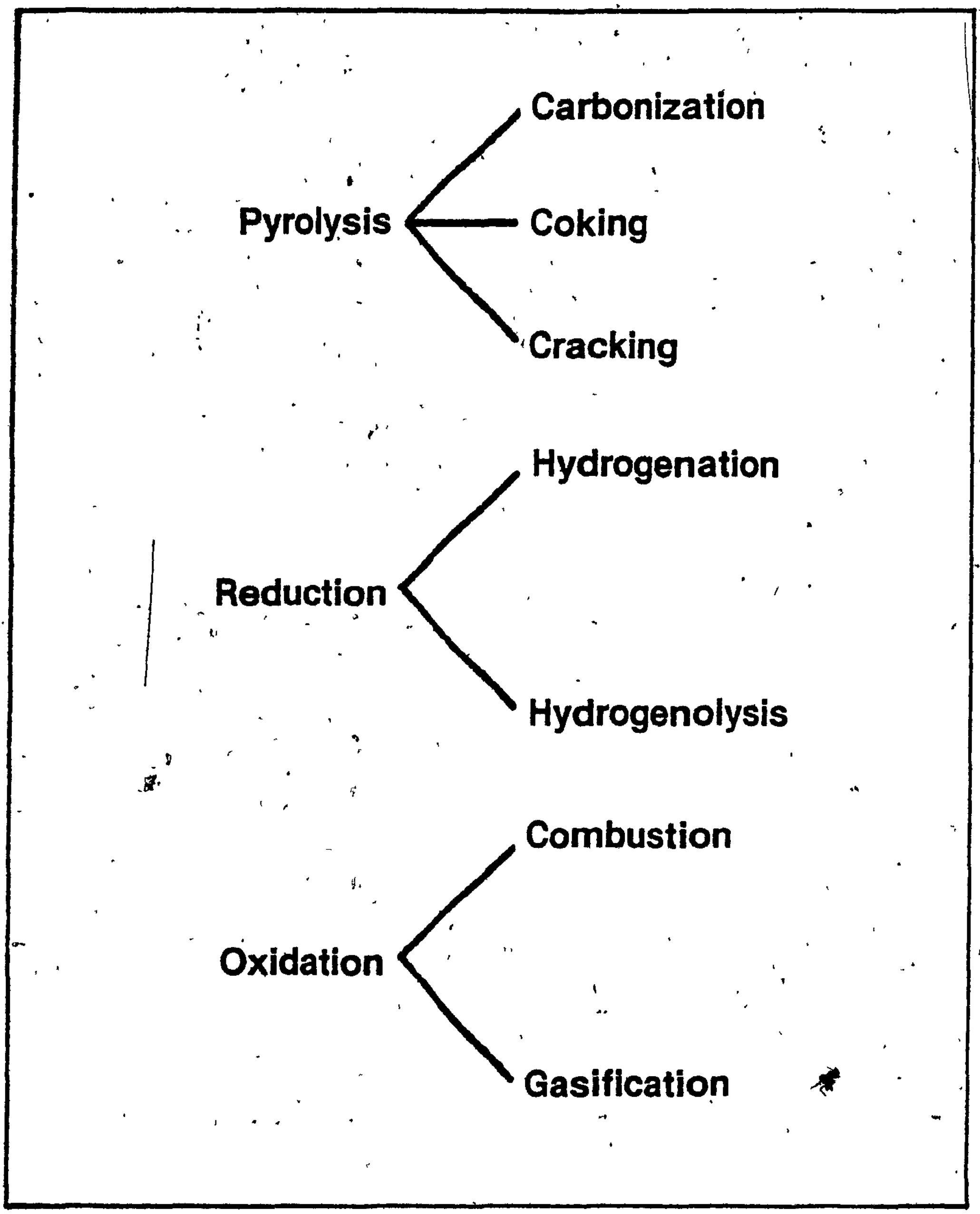
Pyrolysis of peat is it's physical decomposition due to the application of heat. This causes the volatile components of the peat to evolve. These components, according to Fuchsman (1980) include carbon monoxide, carbon dioxide, moisture, and low molecular weight organic compounds. This type of transformation occurs at lower temperatures than oxidation and reduction.

Peat reduction is the class of reactions which occur between hydrogen in a free or combined state and peat.

Oxidation is subdivided into two distinct types of transformations: combustion and gasification.

FIGURE 12:

TYPES OF PEAT TRANSFORMATION


Pyrolysis
Carbonization
Coking
Cracking
Reduction
Hydrogenation
Hydrogenolysis
Oxidation
Combustion
Gasification

Oxidation by combustion of peat occurs when oxygen is present. The reaction is highly exothermic and produces large quantities of carbon dioxide:

$$C\,(\text{fixed}) + O_2 \rightarrow CO_2$$

It is due to the high exothermicity of this reaction that it predominates in conditions for electrical power generation from peat.

Oxidation by gasification is the general term for a variety of reactions. It is the chemical transformation of peat into gaseous products in the absence of oxygen. By providing a high temperature environment and by minimizing oxygen in a system, it is possible to have gasification reactions predominate.

Potential Uses of Peat

Peat resources and peat production in the world are given by Monenco (1981), and are summarized in Table IV. The countries are ranked according to the magnitude of their resources. Canada has the largest peat resources in the world, and yet exploits a very small amount of this resource. Countries noted for their peat production such as Finland and Ireland have only a fraction of Canada's resources.

Table IV
World Peat Resources and Peat Production(b)

Country	Ranking in Peat Resources	Peat Production(a) (10^9 tonnes)		
		fuel peat	peat moss	total
Canada	1	-	488	488
Soviet Union	2	80,000	120,000	200,000
United States	3	-	800	800
Indonesia	4	-	-	-
Finland	5	3100	500	3600
Norway	8	1	83	84
United Kingdom	10	50	500	550
Ireland	12	5570	380	5950
West Germany	13	250	2000	2250
Total		90,000	130,000	220,000

(a) moisture % not given in reference

(b) Anon., "Evaluation of the Potential of Peat in Ontario: Energy and Non-Energy Uses", prepared by Montreal Engineering Company (Monenco) from an assessment by Kivinen and Pakarinen (1980).

As Lang (1979) discusses, it is mainly peat moss (H1 to H3) which is currently produced in Canada. It is used as a soil fertilizer in horticulture, and as packing material for fruit. Fuel peat has a higher heat value, and has long been used in the Soviet Union, Finland, and Ireland as a fuel.

The gaseous products formed from peat transformation may be:

1. burned directly as a fuel;
2. upgraded to higher quality fuels or;
3. used as a feedstock.

Pyrolysis results in a low-Btu gas and a solid product of high carbon content. If an atmosphere of oxygen rather than air is used, a medium-Btu gas may be produced, owing to a lesser content of nitrogen. Reduction produces a high-Btu gas composed mainly of methane, and a bitumen which may be further upgraded to lighter hydrocarbons. Oxidation by gasification yields a medium-Btu gas, or a synthesis gas which may be used to produce ammonia or methanol. Oxidation by combustion of peat as an energy source is a well-established technology. Because of the already low cost of hydro-electric power in Quebec and Canada, this transformation will be economically unattractive for some time.

Brief Thermodynamic Review

A thermodynamic simulation of the reacting system was done to obtain some insight into the range of variables which should be used. To do this, an interactive computing program available on MUSIC (McGill University System for Interactive Computing) called F*A*C*T (Facility for the Analysis of Chemical Thermodynamics) was used. The EQUILIB program on F*A*C*T, described by Bale et al. (1979), determines the equilibrium concentration of chemical species, when specified compounds react. It computes the most stable mixture of products, and calculates changes in the extensive thermochemical functions (such as enthalpy and volume).

The most important assumptions made for the modelling are summarized:

1. Peat is treated as a mixture of carbon, hydrogen, oxygen, nitrogen and water. This results in inaccurate enthalpy data.
2. All activity and fugacity coefficients are unity.
3. Equilibrium is obtained in the experimental system.

It was found that the model reflected the trends in gas compositions accurately for different temperatures and carbon-to-steam ratios. The degree of carbon conversion from the solid peat into the gaseous phase was not well predicted.

Some results of the analysis are presented in Figures 13 and 14. Figure 13 gives the mole fractions of the product gases versus temperature, for Grosdidier de Matons' carbon-to-steam ratio in the feed of 1.65. It is evident that at temperatures below 1200 K, product gas composition is quite sensitive to temperature variations. Temperatures above this level are required to minimize undesirable by-products such as carbon dioxide and methane. It is also apparent that further reaction with steam becomes insignificant with increasing temperatures. The hydrogen-to-carbon monoxide ratio at temperatures above 1200 K is less than two.

Lower carbon-to-steam ratios in the feed produce more desirable results, as shown in Figure 14. Hydrogen-to-carbon monoxide ratios for different temperatures and varying carbon-to-steam ratios are shown. The desired ratio of two is marked on the graph. For the present work, it was decided to generate temperatures in excess of 1200 K, and use carbon-to-steam ratios less than 0.6. Experimental conditions had to be more aggressive than those predicted in this analysis to promote carbon conversion.

FIGURE 13:

EQUILIBRIUM MOLE PERCENTAGES OF GASEOUS PRODUCTS FROM CARBON CONVERSION, VERSUS TEMPERATURE, FOR A CARBON-TO-STEAM MOLAR RATIO OF 1.65

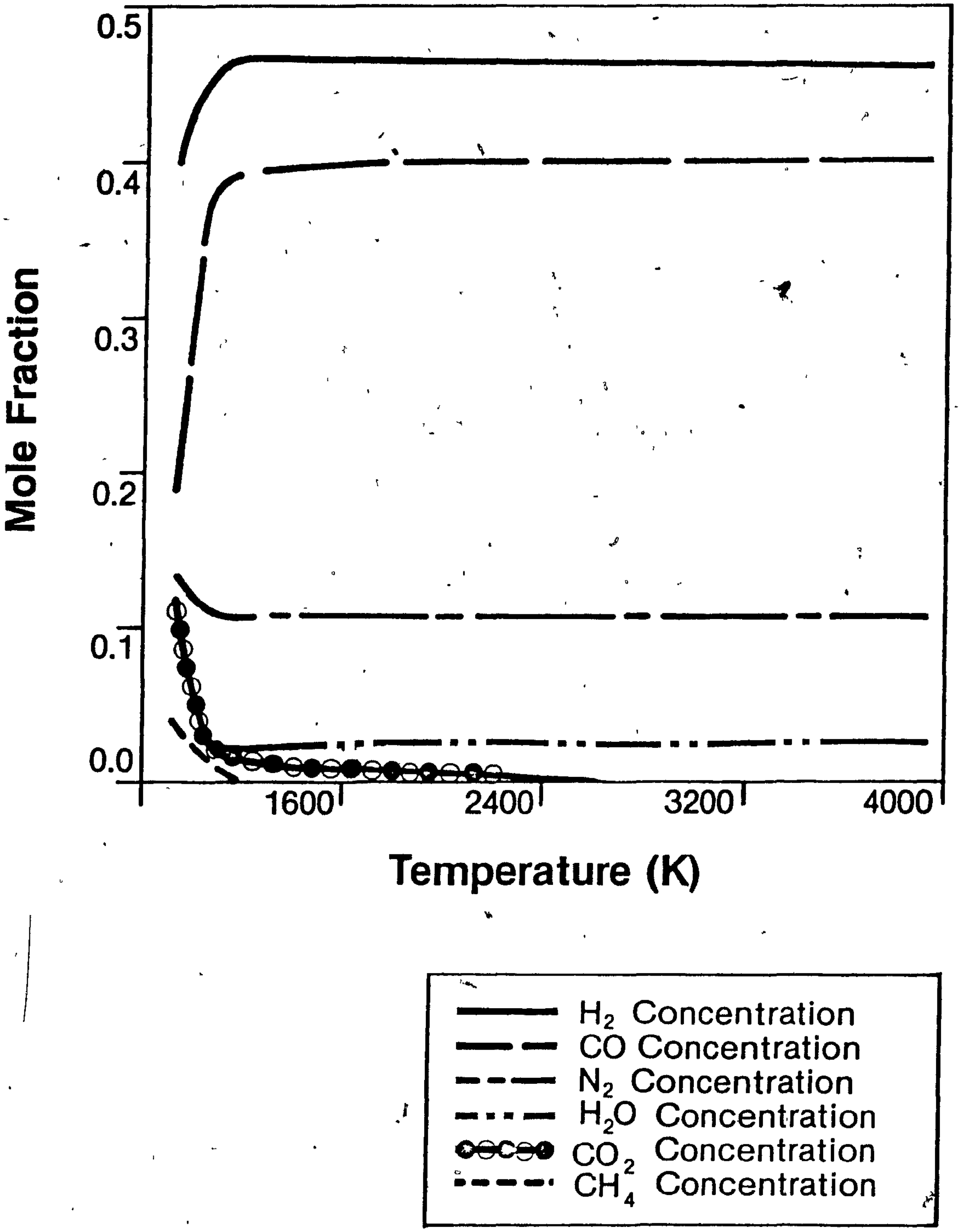
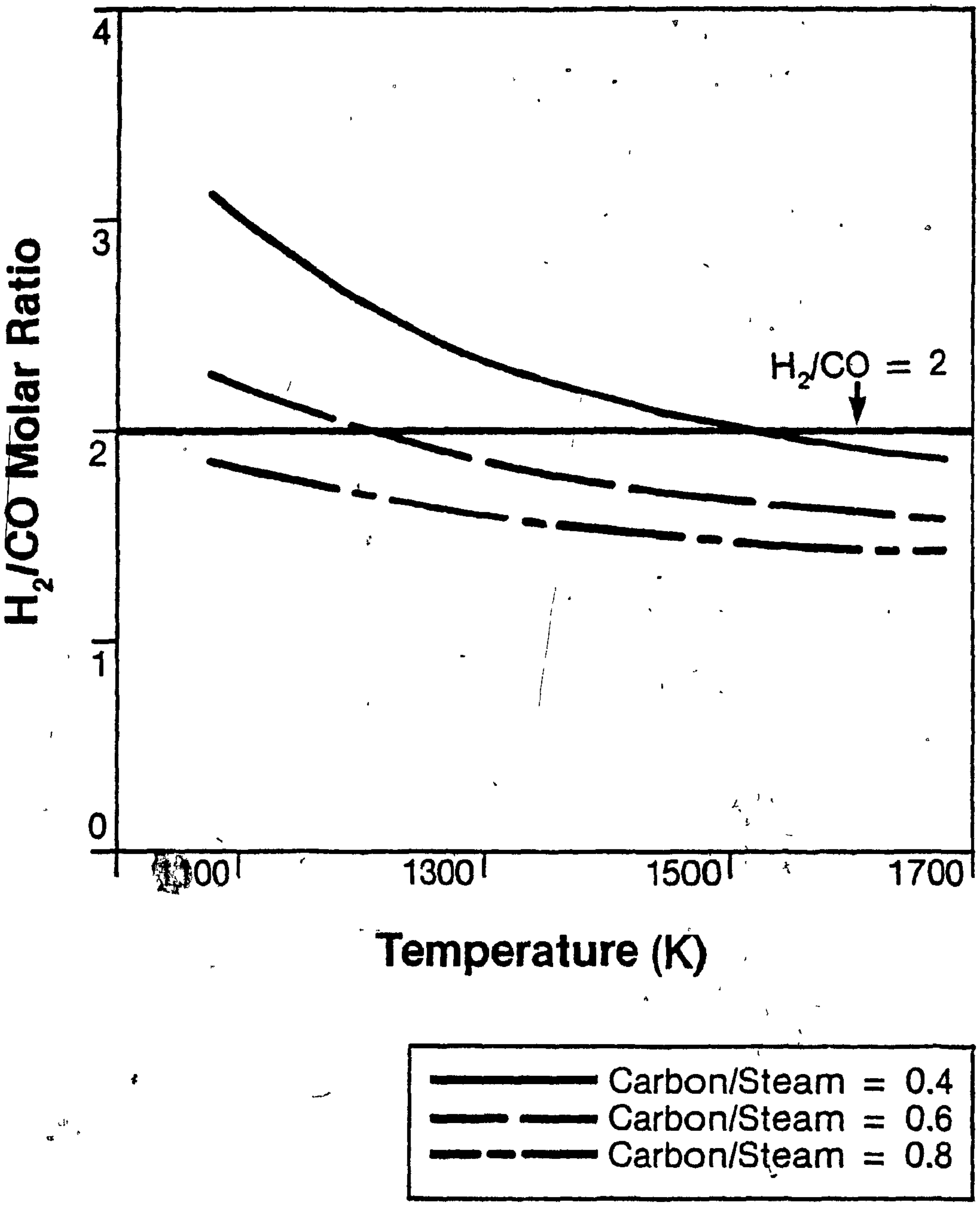

Mole Fraction
0.5
0.4
0.3
0.2
0.1
0.0
1600
2400
3200
4000
Temperature (K)
H_2 Concentration
CO Concentration
N_2 Concentration
H_2O Concentration
CO_2 Concentration
CH_4 Concentration

FIGURE 14:

HYDROGEN-TO-CARBON MONOXIDE MOLAR RATIO AT EQUILIBRIUM IN PRODUCT GAS FROM CARBON CONVERSION VERSUS TEMPERATURE, FOR VARYING CARBON-TO-STEAM MOLAR RATIOS


4
3
2
1
0
H₂/CO Molar Ratio
H₂/CO = 2
1100
1300
1500
1700
Temperature (K)
Carbon/Steam = 0.4
Carbon/Steam = 0.6
Carbon/Steam = 0.8

D. RELATED EXPERIMENTAL WORK

Introduction

While unaware of any other research done in peat conversion using plasma outside of McGill University's Plasma Technology Group, related work is reviewed in two sections:

1. the conversion of peat using non-plasma technologies and;
2. the conversion of carbon using plasmas.

Following these two reviews, the work of Grosdidier de Matons (1983) is described.

Peat Conversion Without Plasma

Interest in the use of peat as a chemical feedstock or as an alternative fuel is growing as a result of the increasing cost of fossil fuels. A similar interest is mounting over the possible use of wood and biomass. There are no commercial operations based on a peat feedstock to date, but several are being evaluated. Supporting technologies for the harvesting and preparing of peat are also being developed.

The term "biomass" refers to a plant material which might have value as a fuel or chemical feedstock. Since 1975, the technologies for converting biomass have developed, to the point that in 1981 biomass contributed about as much energy as hydro-electricity in the United States. Clements et al. (1983), discuss the production of industrial chemicals from biomass. Technologies considered are anaerobic digestion, fermentation, and thermochemical conversion. Thermochemical conversion to synthesis gas such as that produced in the present work, appears to be the most economically feasible.

Under the "biomass" technologies, wood gasification appears to be the most likely to succeed. Graham (1982) reviews the most recent technologies for wood gasification. He concludes that while there are many processes that may be used to generate synthesis gas from wood, most of the systems have not been adequately demonstrated. Research into wood gasification using plasma is being investigated by TASC (USA) and Resorption Canada. A joint venture between Canertech, Nouveler, and the Department of Energy, Mines and Resources Canada was announced by The Biomass Energy Institute (1982), for the gasification of wood. Large funds are to be invested in the development of a pilot plant gasifying ten tons of wood per hour. The gasifier is based on the Omnifuel Gasification scheme. It has a fluidized-bed design, and can employ both air and oxygen as the reactant.

A commercial operation involving the gasification of peat, scheduled for completion in early 1986, may start-up. Pope (1983) reveals that an American consortium called Peat Methanol Associates (PMA) has financial backing to build a plant to convert about 113 million cubic metres of peat into about 6.8 billion litres of high-grade methanol. The biomass gasifier is to be built jointly by Koppers Company and Babcox and Wilcox.

The many systems available for peat gasification are reviewed fairly comprehensively by Leppamaki et al. (1976). Commercial systems for coal gasification have been modified for peat conversion including the Lurgi, Koppers-Totzek, and Winkler systems. Experimental systems developed especially for peat gasification but unproven on a commercial scale, are producing the most encouraging results. The technology with perhaps the greatest potential is being developed by the Institute of Gas Technology (IGT) (Punwani et al., 1979). It is called the PEATGAS Process for reducing peat to synthetic natural gas (SNG).

The most developed technology related to peat gasification is coal gasification. There are many commercial processes available for this conversion, to produce synthetic fuels. Most of these projects, in view of the economic times, are having difficulty finding adequate financial backing. Ryser (1983) discusses a facility funded by Allis-Chalmers Corporation, which should eventually operate at full-capacity. The plant is producing low-Btu gas from high-sulphur coal. Another plant apparently headed to commercialization is being built by Great Plains Gasification

Associates, as described in CHEMICAL ENGINEERING (Oct. 18 1982). They will use lignite coal, the type of coal closest to peat chemically, and produce synthesis gas for methanol production. A Lurgi gasifier system will be used.

Carbon Conversion Using Plasma

The use of plasma to convert carbon-containing fuels is currently being investigated by several concerns. Notable among the firms are Amoco Chemicals Corporation of the United States (Kovenor, 1983), Chemische Werke Huels AG of Germany (Muller and Peuckert, 1983), and SKF Steel Engineering AB of Sweden (Santen, 1983). In addition, there are several universities examining the use of plasma for carbon conversion. The work being investigated varies:

1. The type of plasma used varies. It might be generated by any of the available plasma torches, using any plasma gas. Both induction torches and DC-jet plasma torches have been used. Hydrogen (as a reactant), argon (simply for heat), or methane (as a feedstock), have been used as plasma gases.

2. The type of feedstock varies. Different grades of coal, heavy oil, mixtures of liquid hydrocarbons, methane, and carbon dioxide have all been reacted.

3. The type of desired product varies. Conditions have been used to maximize production of activated carbon, acetylene, synthesis gas, synthetic natural gas, ethylene, hydrogen, and lighter hydrocarbons.

The decision to work on a given system is dependent on economic variables, available material resources, and available expertise. The unique aspects of this work, when taken in view of the general state-of-the-art research, are now noted. Pure steam plasma has never been used as a gasifying medium, and peat has never served as feedstock in a plasma system to the author's knowledge.

Perhaps the most relevent work done with respect to this research was carried-out by Sheer, Korman, and Dougherty (1979) at Columbia University in New York. They investigated the arc gasification of coal using plasma mixtures of nitrogen, argon, and steam. Some of the coal was injected into the plasma arc, and then further reacted using superheated steam. They report the production of gas mixtures near to synthesis gas composition. Only forty to fifty percent conversions were obtained. The solid product was considered for its use as a finely divided, highly reactive carbon source. These results can be explained by the short residence time of the coal in a high-temperature environment, followed by a longer residence time (about one second) in a lower temperature zone. Pyrolysis of the coal occurred, resulting in a synthesis gas composition of high hydrogen content. The lower temperature zone was in the order of 1300 K, which is not adequate for high carbon conversion. The coal composition is not given for carbon-to-steam molar ratio calculations, but the coal-to-steam mass ratio of 1.35 could not result in high conversion. This ratio was presumably lower in the high temperature zone. It should be noted that it was not their objective to obtain a high carbon conversion. The analysis of their conditions is helpful insofar as this experimentation is concerned.

Work of Grosdidier de Matons

Grosdidier de Matons' experiments were designed to determine whether peat could be reacted effectively in a plasma-based system. While his results certainly achieved that goal, there were some limitations in his work that were considered in the design of the present study:

1. The materials used were readily available. Consequently, the reactor was not designed specifically for peat conversion, but rather it was obtained from another project. The large diameter of the reactor limited the success of his results.

2. Steam was injected into a nitrogen plasma, limiting temperatures and diluting the reacting system.

3. Carbon-to-steam ratios used in the work were too high for ideal gasification conditions.

Grosdidier de Matons' experimental conditions are presented in Table V and his results in Table VI. These tables may be used to determine the effect of temperature, mean peat particle size, and the carbon (contained in the peat)-to-steam ratio. It is desirable to have a hydrogen-to-carbon monoxide molar ratio of two in the product gas, and a high carbon conversion.

By comparing Experiments 1 and 4, the effect of changing temperature may be observed. Both the hydrogen-to-carbon monoxide ratio and the conversion improve with increased temperature. Experiments 2 and 6 show that decreased particle size has a significant effect on the carbon conversion. In the present work, peat was ground to obtain a small particle size. Experiments 5 and 6 show the need for more steam to be present in the reacting mixture, to generate a higher conversion and a better hydrogen-to-carbon monoxide ratio in the product gas.

While the operating conditions used in the experiments done by Grosdidier de Matons gave generally poor gas compositions and conversions, they gave insight into the effects of the physical variables of the process.

Table V
Grosdidier de Matons' Experimental Conditions(e)

Experiment Number	Reactor Temperature (Kelvin)(a)	Peat Flow (kg/h)(b)	Mean Particle Diameter (10^{-6} m)(c)	Carbon-to-Steam Molar Ratio(d)
1	1110	8.5	48	1.54
2	1190	8.5	48	6.02
3	1190	8.5	48	2.63
4	1165	8.5	48	1.59
5	1235	7.0	30	1.37
6	1205	7.2	30	6.02

(a) maximum temperature measured 18 centimeters from the reactor top

(b) calibrated under atmospheric pressure conditions

(c) using lowest particle sizes in size categories

(d) steam injected at 105 Celcius into the torch anode and into a port 30.5 centimeters from the reactor top

(e) Grosdidier de Matons, P., "Peat Gasification in a Plasma-Heated Cocurrent Reactor", M. Eng. Thesis, McGill University (1983).

Table VI
Grosdidier de Matons' Experimental Results[c]

Experiment Number	Carbon Conversion (%)[a][b]	Hydrogen-to-Carbon Monoxide Molar Ratio[b]
1	53.0	0.94
2	54.0	0.75
3	60.6	0.74
4	63.4	1.04
5	79.9	0.91
6	63.8	0.75

(a) based on the carbon in the product gas
(b) mean of results obtained in samples
(c) Grosdidier de Matons, P., "Peat Gasification in a Plasma-Heated Cocurrent Reactor", M. Eng. Thesis, McGill University (1983).

The present work builds upon Grosdidier de Matons' investigation:

1) The reactor was designed after completing the thermodynamic study briefly discussed. This gave some insight into the experimental conditions likely to give the desired results.
2) More experiments were carried out over the designed experimental area.
3) The steam used was produced from a plasma of hydrogen mixed with oxygen, rather than injecting steam into a nitrogen plasma as in the work of Grosdidier de Matons.
4) The data collection was more complete. Representative samples of the gases and solids produced were analyzed, allowing for overspecification (hence verification) of mass balances. Complete temperature profiles were obtained over the entire reactor.

E. ECONOMICS OF METHANOL PRODUCTION

Introduction

Fuchsman (1980) summarizes the basic types of peat usage in countries that consume peat commercially. In the Soviet Union, Ireland, and Finland where peat is consumed in significant amounts, it is used primarily as a fuel. In Canada, Germany, and the United States, peat is used almost exclusively for horticultural purposes. There is little use of peat as a feedstock for production of chemicals, except in a few instances:

1. in Germany and Finland, peat coke is being produced for the metallurgical industry;
2. Ireland uses peat to produce activated carbon and;
3. the Soviet Union uses peat to produce a variety of chemical products, including waxes and sugars.

This work concentrates on the production of synthesis gas, used primarily in the production of methanol:

$$2\,H_2 + CO \rightarrow CH_3OH$$

By reacting peat with steam in the absence of oxygen, the peat is chemically transformed by pyrolysis, reduction, and oxidation by gasification.

Why produce methanol from peat? An economic pre-feasibility study prepared by Intergroup Consulting Economists (1976) on a large-scale methanol fuel production process from wood, concludes that when methanol becomes competitive as a fuel, it will first be used in gas turbines. The report states that once the technical problems are solved, pure methanol or methanol/water mixtures may be used as an automotive fuel. Higher efficiency and lower toxic emissions result when the use of methanol is compared to that of gasoline. Problems with the technology include conversion of existing vehicles, and corrosion. Othmer (1981) states that methanol will power automobiles and diesel trucks at a lower cost than gasoline does currently. Examples of this technology being developed to the point of commercial importance are described in the literature: Parkinson (1982), Kaplan (1982), Kieschnick (1983), OIL & GAS JOURNAL (Aug. 15 1983), and CHEMICAL ENGINEERING (June 23 1983 and Oct. 3 1983), to name but a few. CANADIAN CHEMICAL PROCESSING (Nov. 1982) states that fuel applications of methanol, which were responsible for 3.5% of total methanol use in 1979, will increase to over 30% of total methanol use by 1990.

Aside from the potentially huge market considered above, methanol is already among the top twenty chemicals produced worldwide, as shown in Table VII and discussed by Webber (1983). It is now used in the producion of acetic acid, formaldehyde, engineering plastics, dyes, solvents, and methyl tertiary butyl ether (MTBE). The Stanford Research Institute (1981) states that in 1978 Canada had 4% of the world production. This is

Table VII
Selected Chemicals' Production Worldwide[(a)]

Chemical	Rank (1982)	Average Annual Growth (%)	
		1977-1982	1972-1982
Sulfuric Acid	1	-3.1	0.4
Nitrogen	2	7.8	9.5
Ammonia	3	-2.5	0.2
Oxygen	4	-2.1	0.0
Ethylene	6	-0.6	1.7
Benzene	17	-7.0	-1.6
Methanol	19	2.3	1.8
Hydrochloric Acid	25	-1.8	0.6
Formaldehyde	27	-5.0	-1.9
Acetic Acid	31	1.4	2.1
Acetone	40	-4.6	0.1
Ethanol	50	-5.3	-5.8

(a) Anon., "Basic Chemical Output Fell Third Year in a Row", C&EN, pp. 10-12 (May 2 1983).

expected to increase to 10% during the 1980's.

Conventional Methanol Production

There are three basic types of methanol synthesis processes available: the high pressure (30,000 kPa or 300 atm.), low pressure (5000 kPa or 50 atm.), and intermediate pressure (10,000 kPa or 100 atm.) routes. High pressure plants have not been built since the early 1970's. The intermediate process is used in new installations, and gives the best economy. There are two widely-used intermediate pressure processes for methanol production: the ICI process and the Lurgi process. While the two processes are similar, the ICI process is used almost exclusively in North America.

The ICI process can be represented simply by the three stages shown in Figure 15. In the first stage, the feedstock is reacted to produce synthesis gas. Feedstocks may include naphtha, coal, or (usually) natural gas. It is this stage that could be replaced with a plasma process, using peat as the feedstock.

The synthesis gas production stage is represented in greater detail in Figure 16 for a natural gas feedstock. The natural gas enters the process and is separated in an approximately 4:1 ratio by a stream divider. The larger stream is heated in a carbon absorber to reduce the sulphur content in the natural gas. The gas is mixed with three volumes of

FIGURE 15:

MAJOR PRODUCTION STEPS IN METHANOL SYNTHESIS

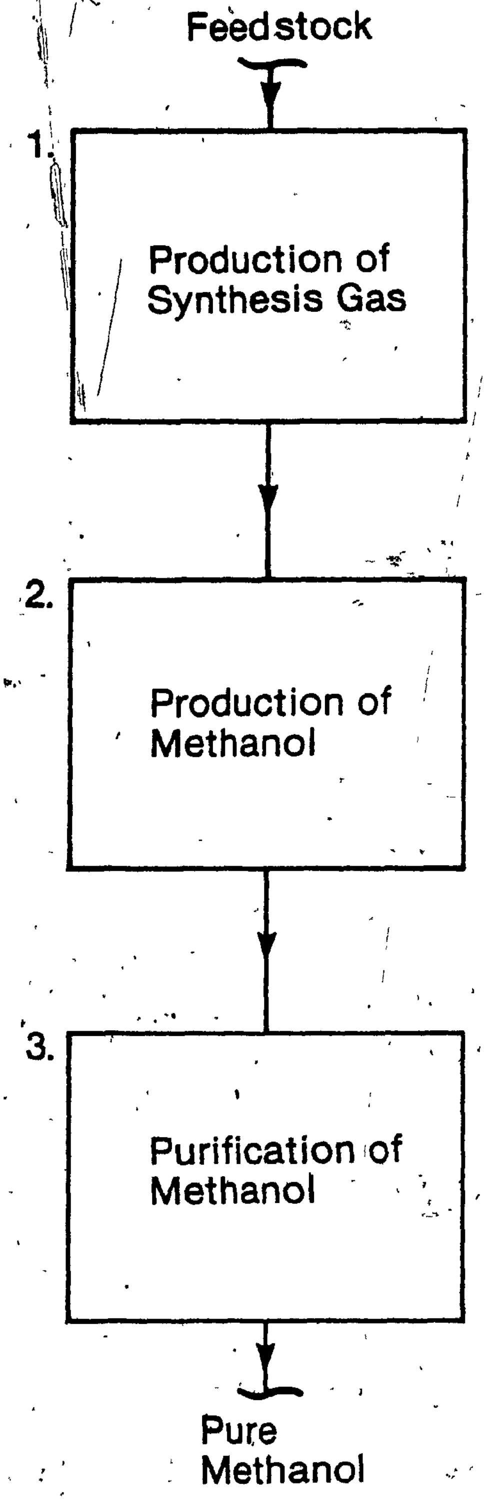
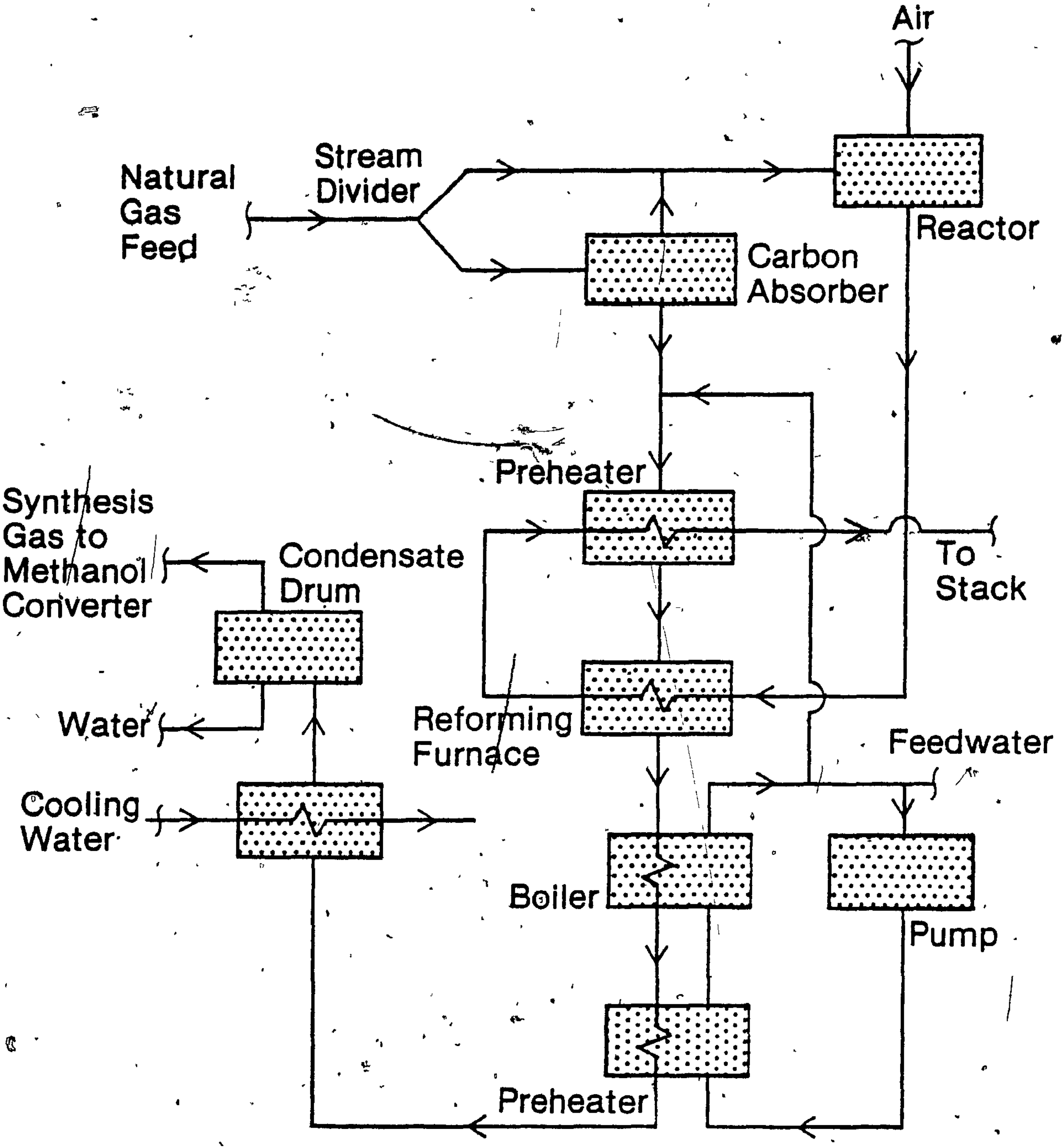

Feedstock
1.
Production of Synthesis Gas
2.
Production of Methanol
3.
Purification of Methanol
Pure Methanol

FIGURE 16:

SYNTHESIS GAS PRODUCTION FOR ICI PROCESS


Air
Natural Gas Feed
Stream Divider
Reactor
Carbon Absorber
Preheater
To Stack
Synthesis Gas to Methanol Converter
Condensate Drum
Reforming Furnace
Water
Feedwater
Cooling Water
Boiler
Pump
Preheater

steam, preheated to 870 Celcius, and reacted in the reformer to produce synthesis gas. The gas contains significant carbon dioxide and some methane and nitrogen. It leaves the reformer at 870 Celcius and 2000 kPa (290 psia), to be compressed for the methanol synthesis, to a pressure of 10,000 kPa (100 atm.). The smaller stream of natural gas is combined with the purge gases from the carbon absorber, and the sulphur-rich mixture is burned with air. The flue gas is used to heat the reforming furnace and to preheat the reacting natural gas. It is then vented to the atmosphere.

In the second stage, the methanol production from the synthesis gas occurs in a catalytic methanol converter. The resulting crude methanol is then purified by distillation in the third stage.

The Plasma Process

The plasma process involves the reaction of peat with a steam plasma to generate synthesis gas. There are several advantages associated with a plasma-based system:

1) The peat gasification may be effected at the pressure of the methanol synthesis. To do this, it is only necessary to pressurize the feed to the gasifier (water and peat). The conventional method requires the compression of the synthesis gas, which is a more expensive process than pressurizing liquid water and the gas transporting the solid feed.

2) None of the feedstock used in the process is burned for heat as in the conventional process, since the heat is provided by electrical energy

in the plasma generation.

3) The reaction conditions in the system are more easily controlled than in the conventional process reformer. With the plasma route, the synthesis gas produced may have the desired hydrogen-to-carbon monoxide ratio of two, and very little by-products. No water-gas shift plant is then required.

4) The energy from the spent stream in the reactor is used completely in a heat exchanger to preheat the steam required for reaction.

5) The equipment size and capital costs will be reduced from the conventional process due to operation at higher pressure.

6) Peat lends itself to this type of chemical processing. It is in abundance, has a low sulphur content, is very reactive, and is relatively easy to harvest, dry, and grind to the required size.

Gauvin and Duncan (1982) completed a preliminary economic feasibility study on the production of methanol from peat using plasma-generated steam. The process was considered in terms of feed preparation, peat gasification, heat recovery, and synthesis gas purification. The results of this study are presented in Table VIII. The conventional process, using a reformer to produce synthesis gas, has a production cost of 0.796 dollar per imperial gallon of methanol ($Cdn, 1982). With the plasma process, the production cost is estimated at 0.597 dollar per imperial gallon of methanol ($Cdn, 1982). It should be noted that the plasma calculations assume a ratio of two for hydrogen-to-carbon monoxide, and a carbon conversion of ninety-five percent.

Table VIII
Comparison of Methanol Production Costs(e)

Type of Cost	Conventional Cost ($ per imperial gallon)(a)(b)	Plasma Process Cost ($ per imperial gallon)(a)(c)
Total production cost(d)	0.796	0.597

(a) in August 1982 Canadian dollars
(b) for a large plant producing 2500 tons methanol per day
(c) for a smaller plant producing 1200 tons methanol per day
(d) considers utilities cost and capital cost in estimation
(e) Gauvin, W.H., and Duncan, S.R., "Methanol from Peat Using Plasma-Generated Superheated Steam", Centre de Recherche Noranda (1982).

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SECTION III:

EXPERIMENTAL

EXPERIMENTAL SECTION

A. INTRODUCTION TO EXPERIMENTAL

Literature Review

Applications of plasma technology to chemical and metallurgical processes are rapidly increasing in conventional fields such as high-temperature metal extraction and refining, petrochemicals production, and waste treatment. As the fundamental understanding of the principles of operation of these various processes improves, new and imaginative concepts derived from this experience begin to suggest themselves. This opens new and challenging possibilities in yet other fields.

One such concept, developed by the Plasma Technology Group at McGill University, concerns the use of water vapour as a plasma gas. Application of this plasma to drying operations appears to be very promising indeed (Amelot, 1983). A second application, to gasify peat for the production of synthesis gas, was undertaken shortly thereafter with equally encouraging results (Grosdidier de Matons, 1983). An Atomized Suspension Technique Reactor (ASTR) was used to effect the transformation of peat to hydrogen and carbon monoxide. Since that time, a preliminary economic study (Gauvin and Duncan, 1982) has shown that a methanol process based on the plasma technology would be economic. From these results, further studies were warranted to develop the technology.

The objective of the present study, stated briefly, was to explore further the transformation of peat into synthesis gas for methanol production.

A thermal steam plasma generated by a DC-jet torch was used. The steam plasma was produced by injecting oxygen into a hydrogen plasma. Dried and ground peat of an H5/H6 classification on the von Post scale was mixed with the steam plasma. No oxygen was added to the reacting system so as to promote pyrolysis and gasification reactions: heat generated by combustion reactions was not necessary, and would have produced large quantities of undesired carbon dioxide. The synthesis gas obtained was for methanol production, so the desired hydrogen-to-carbon monoxide molar ratio in the product gas was two.

Based on a thermodynamic study and analysis of related work, especially that of Grosdidier de Matons (1983), it was decided to use reaction temperatures in excess of 1200 K and carbon-to-steam molar ratios in the feed of less than 0.6. Careful design of the ASTR-based system was necessary to obtain reasonable results.

Objectives of Work

The objectives for this work can be summarized as:

1. to design and build a second-generation reactor capable of reacting peat with steam plasma;
2. to investigate the effect of temperature and the carbon-to-steam ratio in the feed on the carbon conversion and the hydrogen-to-carbon monoxide ratio in the product gas;
3. to analyze the results and derive models which reflect the data;
4. to determine the optimum operating conditions of the system for synthesis gas production and;
5. to identify areas in which further research is required.

First, a review of all the resources and equipment used in the research is made. The gathering and preparation of peat, and its measured properties are discussed. The commissioning experiments required to develop the steam plasma are mentioned. A brief description of the equipment and some of the constraints in its use are given. Details of the apparatus are contained in Appendix I.

Experimental procedure and details on the subsequent solids and gas analyses are then given. The latter item is important to establish the credibility of the results. The actual experimental conditions and results are summarized in the same section.

The development of the different analyses is given. Direct analysis of the experimental results is first considered, including the discussion of temperature profiles and mass balances. Analysis of the gas and solids results shows that the data provided credible results. The model of the physical variables is then developed. Brief sections are included on the special experiments done, and on the economics of this system.

Finally, the conclusions and recommendations for future work are presented.

B. PEAT CHARACTERISTICS

The peat for this work was obtained in the County of Lobiniere in the Province of Quebec. It was dug from fairly loose ground and transported in garbage cans to McGill University. The wet peat resembled mud, but contained a significant quantity of decomposing wood and roots. Even though the top layer of Sphagnum had been discarded, some undecomposed material was still discernable.

Initial drying of the peat took place outdoors on plastic sheets. Shelter from wind was necessary, because as the peat dried and became less dense, it tended to blow away. Even summer weather did not provide enough consecutive dry days to allow drying of the peat to ambient moisture, so it was transported inside. This may be an important consideration in a commercial process.

The moisture content of the peat was determined to be 15.5%. This measurement was repeated for each assessment, and found to be constant for assessments taken one week apart. Once taken to the laboratory, eight days of drying were required before the equilibrium moisture content was attained. The determination was made by placing the peat sample in an oven overnight at a temperature of 95 Celsius, and weighing the dried sample immediately after removal. Any lower boiling point volatiles would also evolve during this process.

The peat was ground in a Sprout-Waldron grinder, located at the Noranda Research Centre in Montreal. The dried peat was simple to comminute, although peat fines in the air necessitated the use of filter masks.

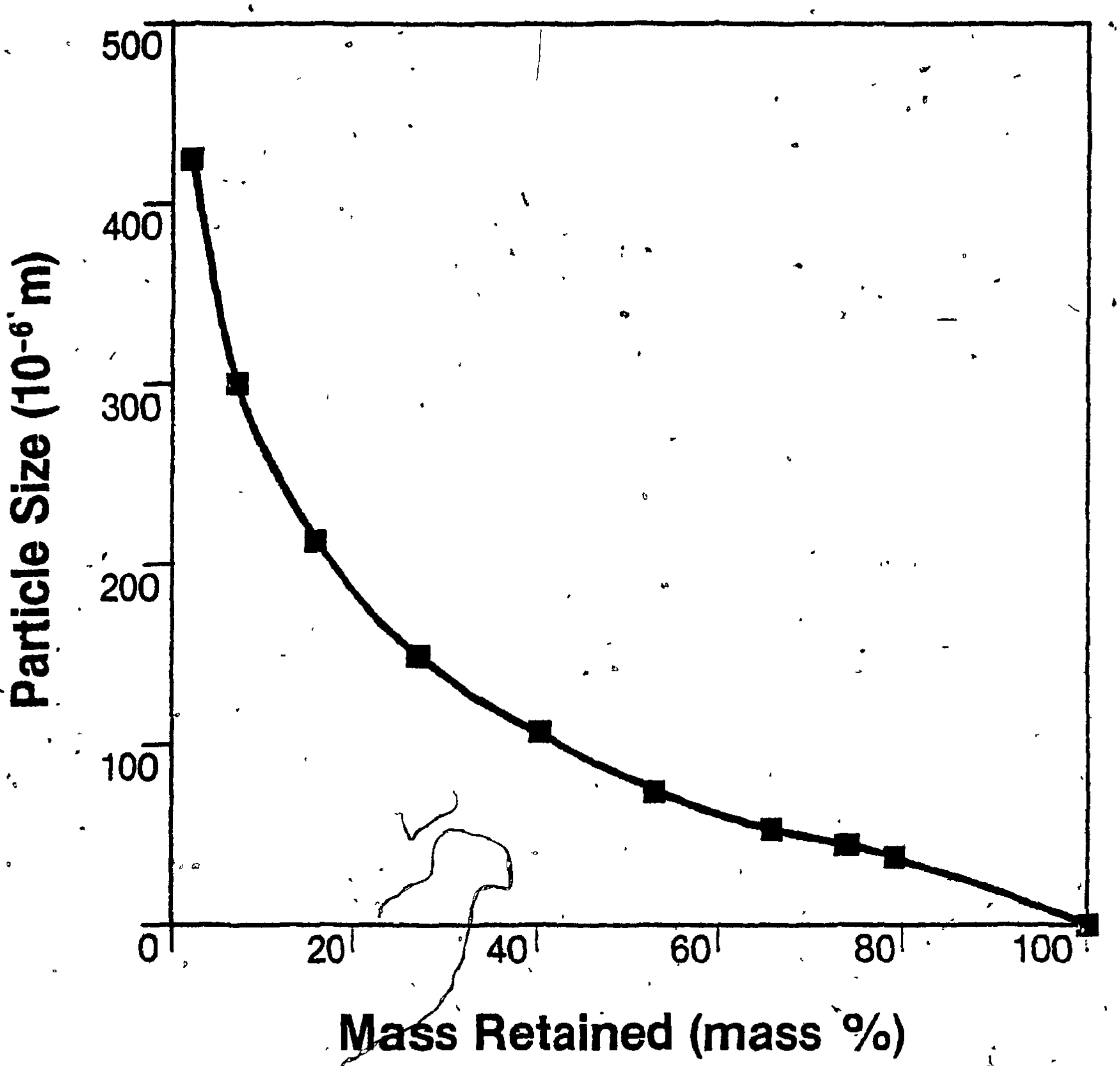
The peat size distribution was obtained using a Tyler screen shaker. The results of the test are given in Figure 1. The technique used for this sieve analysis was important for consistent, reproducable data:

1. A small sample of between nine and ten grams was used in each determination to prevent "blinding" or clogging of the screens.
2. It was found that if the separation shaking time was allowed to continue, more and more peat would fall to the smallest size categories. This was due to attrition of the peat as the test continued. Twenty minutes of shaking time was used in all analyses, and the determination repeated several times.

Grosdidier de Matons established that a small peat size distribution resulted in better carbon conversion. This was obtained by sieving the peat, and discarding the large particle size fraction. Grosdidier de Matons used peat of particle sizes less than 106 microns. This work used peat of particle sizes less than 149 microns, resulting in the size distribution given in Table I. The extra size category increases the mass of the retained peat by about 18%. From Figure 1, it may be seen that even

FIGURE 1:

CUMULATIVE PERCENTAGE OF MASS RETAINED VERSUS PARTICLE SIZE, FOR A SIEVE ANALYSIS OF THE GROUND PEAT



Particle Size (10^{-6} m)
500
400
300
200
100
0
20
40
60
80
100
Mass Retained (mass %)

Table I
Size Distribution of the Retained Peat[a]

Mesh	Mesh Screen Size (10^{-6} m)	Amount on Each Plate, Xi (%)	Cumulative Amount (%)	Average Particle Size in Class, d_i (10^{-6} m)
100	149	discarded	0	
140	106	18.0	18.0	127.5
200	74	17.5	35.5	90
270	53	17.0	52.5	63.5
325	44	11.4	63.9	48.5
400	37	7.4	71.3	40.5
pan	0	28.7	100.0	18.5

Average Particle Size $= \sum_i x_i d_i = 63.3 \star 10^{-6}$ m

(a) using a sample of 9 to 10 grams and 20 minutes of separation time.

with the extra size class, about 27% of the peat is discarded. To discard more of the peat was impractical, in view of the quantity of peat required for experimentation. A larger, more efficient Sweco screen was used to separate the peat. The weighted mean peat particle diameter was 63.3 microns.

The ultimate composition of the peat was analyzed by Dr. C. Daessle of Organic Microanalyses in Montreal. The measurement was performed for two peat samples taken at different times over the course of experimentation. The results were consistent, with the mean values given in Table II. They do not add to 100% due to experimental error, and the presence of small amounts of sulphur. The adjusted values which were used in the mass balances are shown. Dr. B. Patterson of Concordia University in Montreal made an ultimate determination of sulphur in the peat of 0.22%.

Table II
Ultimate Composition of the Retained Peat

Species	Content in Peat (mass%)[a][b]	Adjusted Content (mass%)[c]
Carbon	44.61	45.11
Hydrogen	5.84	5.90
Oxygen	41.13	41.59
Nitrogen	2.21	2.24
Ash	5.10	5.16
Total	98.89	100.00

(a) determination made by Dr. C. Daessle, Organic Microanalyses, Montreal

(b) values have been corrected to be on a dry basis

(c) proportionally adjusted

C. EQUIPMENT

Commissioning Experiments

Prior to experimentation, the steam plasma had to be characterized. It was necessary to perform experiments in the open, so that stable operating conditions could be established. The reactor was not capable of containing the plasma at higher energy levels, so operating conditions near minimum energy levels were required. Even the addition of peat to the reactor did not cause a significant fall in temperature levels: most of the energy was lost by radiation to the surroundings, and only a small amount was consumed in the endothermic reaction.

To produce the steam plasma, oxygen was added to a hydrogen plasma. The following experimental procedure was used:

1. The torch was started-up with argon gas. Argon has a much lower break-down potential than hydrogen; the characteristic voltage (with the torch configuration used) was about 25 volts with argon, and about 130 volts with hydrogen.

2. Transfer to hydrogen was effected by maintaining the argon flow, while increasing the hydrogen flow to the desired level. Then, the argon flow was removed. The hydrogen flow had to be readjusted: the pressure drop into the torch reduced with argon removal, resulting in increased hydrogen flow.

3. Oxygen was added to the base of the anode, to stoichiometric levels for steam production. This addition did not affect the electrical characteristics of the hydrogen plasma. It was found that an excess of oxygen resulted in rapid degradation of the copper anode. A slightly reducing (hydrogen-rich) mixture resulted in longer anode life. Stoichiometric conditions were used for this work.

The resulting steam plasma is shown in Figure 2. Note the split of the plasma. This might be due to either the difference in velocities between the (expanded) hydrogen plasma and the oxygen gas, or the difference in temperatures between the two gases. This split was important when the plasma was confined in the reactor. It resulted in "hot spots": areas of the reactor wall at significantly higher temperatures than others. The split also produced asymmetrical temperature and flow profiles in the reactor. The turbulent nature of the plasma flame can also be seen in Figure 2. This promotes good mixing in the reactor.

The important results of the commissioning experiments are now discussed. Figure 3 shows the voltage drop across the anode for changing gas flows. The current was kept constant at 250 amperes for all data points. Note that the voltage decreases by only 8 volts (6%) for a steam plasma flow decrease of 103 litres per minute (38%). Below the lowest flow of 164 liters per minute, the plasma became unstable, and shut-down was required. A second important experiment showed the effect of current on

FIGURE 2:

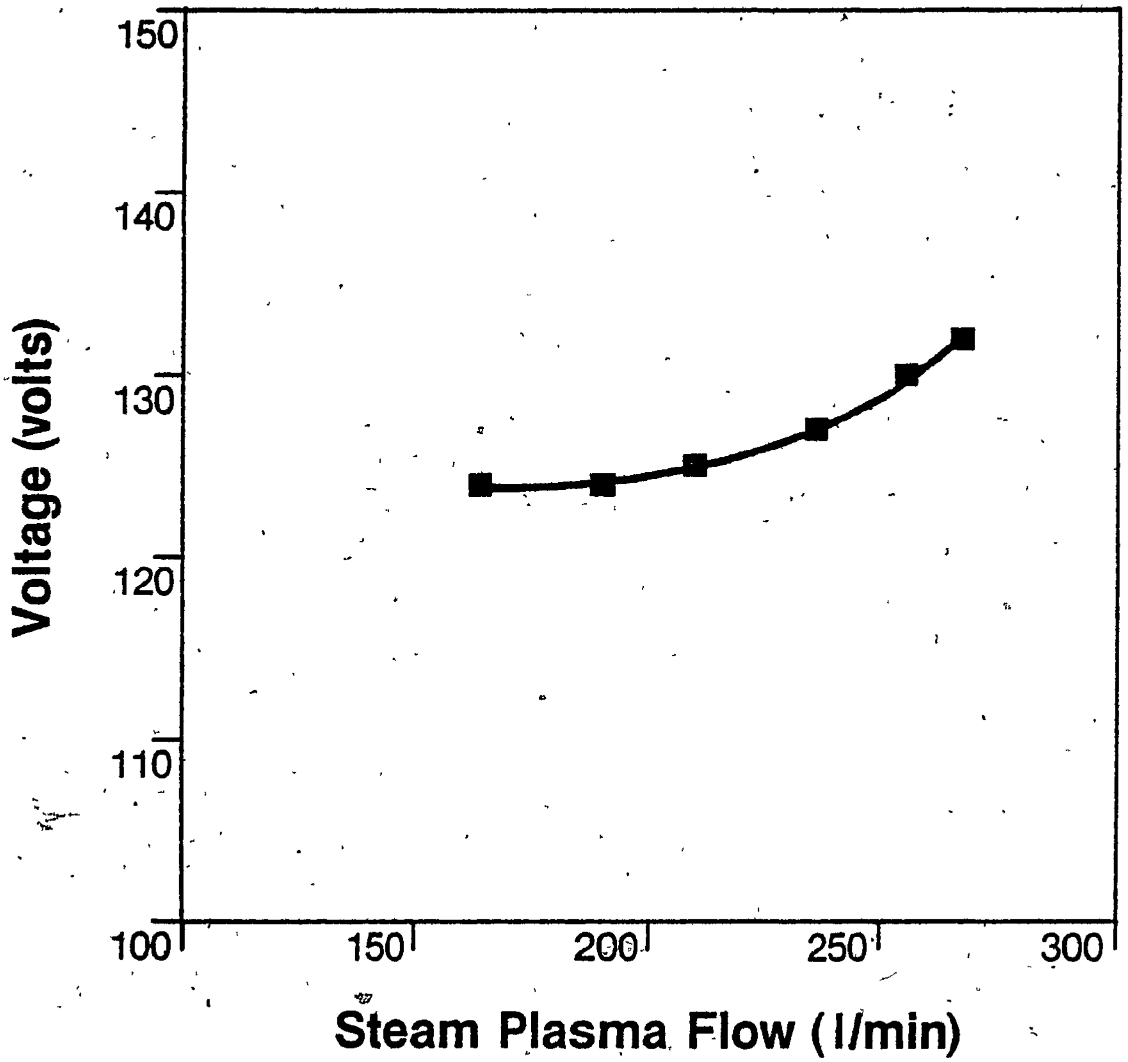
PHOTOGRAPH OF STEAM PLASMA

COLOURED PAPER
PAPIER DE COULEUR

FIGURE 3:

VOLTAGE VERSUS STEAM PLASMA FLOW,

AT A CURRENT OF 250 AMPERES



Voltage (volts)
150
140
130
120
110
100
150
200
250
300
Steam Plasma Flow (l/min)

the stability of the plasma, at fixed plasma gas flows. Smaller currents are possible with higher gas flows. It was found that only currents of 220 amperes were attainable for gas flows of 190 liters per minute. Increasing the flow to 210 liters per minute allowed currents as low as 130 amperes. All volumes reported were at room temperature and atmospheric pressure.

The total energy imparted to the plasma is from two sources:

1. Chemical energy from the exothermic hydrogen/oxygen reaction. This energy increases with increased gas flow. A change in gas flow affects the electrical characteristics of the plasma only slightly.

2. Electrical energy due to the DC-plasma jet generation. This energy input can be increased by increasing the power to the plasma. Since the voltage for a hydrogen plasma varies very little with current, increasing current effectively increases power input.

To obtain a "minimum-energy" plasma so that the reactor did not melt, the above two effects were considered. Operation at 210 liters per minute and 130 amperes was used during most of the experiments. With these conditions, about three quarters of the total energy was provided by the chemical reaction. It should be noted that the total energy input for each experiment varied slightly even when using the same currents and gas flows, because the characteristic voltage of the plasma changed slightly. Except in certain experiments, current was held constant at 130 amperes.

Brief Description of Apparatus

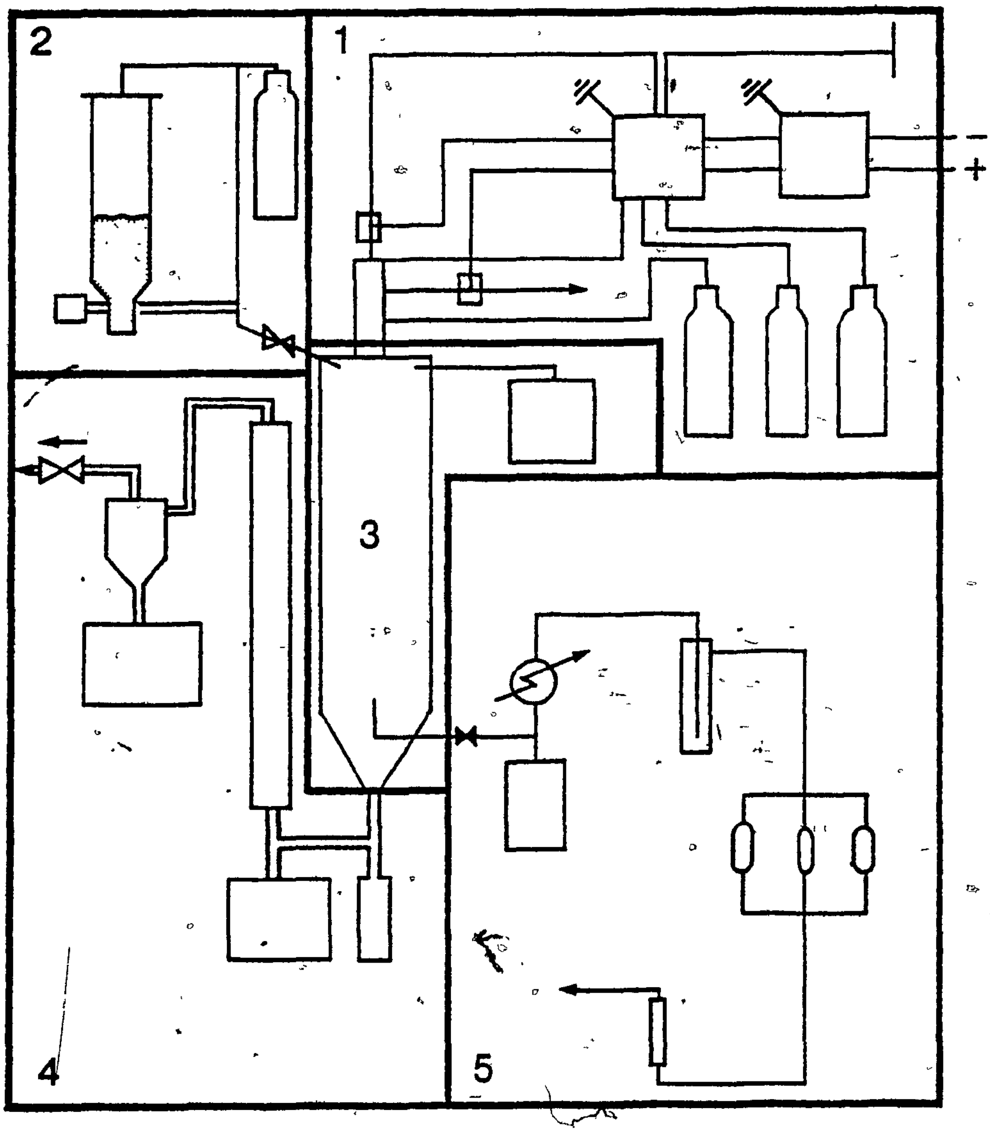
A description of the experimental apparatus is given below; mechanical details are available in Appendix I. Figure 4 shows the system broken down into five sections:

1. the plasma feeding system;
2. the peat feeding system;
3. the reactor;
4. the effluent system and;
5. the sample train.

The plasma generation system produced the steam plasma as a jet into the centre of the reactor top. The flow of gases, flow of cooling water, and the electrical current were controlled by one operator at the control console. The peat feeding system screw-conveyed peat from a hopper into a nitrogen line. The nitrogen blew the peat into the top of the reactor, where the peat and steam plasma mixed. Tangentially fed steam was added to lower the temperature of the system. The cylindrical reactor was 120 cm long and 20 cm in diameter. It contained a viewing window, wall thermocouples, and insertable thermocouples. The effluent from the reactor passed through two collectors, a 180 cm long condenser, a cyclone, and a one-way valve before being purged to the atmosphere. The gas sampling train was made-up of a condenser and collector, a drying column, three sample bottles in parallel, and a rotameter.

FIGURE 4:

EXPERIMENTAL SYSTEM


2
1
3
4
5
−
+

The laboratory space measured 9.6 by 3.1 meters. Four people were required to run an experiment: the plasma operator, data collector, data recorder, and temperature monitor.

Constraints In Equipment Use

The experimental system made use of high electrical powers, high gas pressures, explosive gas mixtures, and high temperatures. Precautions had to be taken in view of these factors. The main considerations for safe and effective experimentation can be summarized as:

1. temperature limitations of the reactor;
2. explosion limits of the reacting mixture;
3. shut-down precautions;
4. pressure increase considerations and;
5. pressure fluctuations.

These considerations are now discussed.

The temperature variation constraint was a result of the plasma being:

1. unstable at low gas flows and/or electrical powers and;
2. too energetic (hot) at high gas flows and/or electrical powers. As previously described, this problem was compounded by the asymmetry of the plasma flame.

The reactor was uncooled (except for the top flange), and made of type 304 stainless steel to minimize thermal inertia for a rapid approach to thermal steady state. The reactor was not insulated on the outside to allow maximum heat loss by radiation and natural convection. It should be remembered that the wall temperatures of the reactor are lower than the gas temperatures inside.

The properties of type 304 stainless steel are summarized by Allegheny Ludlum Steel Corporation (1959), and presented in Table III. It begins to melt at a temperature of 1400 Celsius (2550 Fahrenheit), but the maximum allowable temperature for intermittant operation is 870 Celcius (1600 Farenheit). While the outside wall temperature frequently was in excess of this latter value, there was no degradation of the reactor walls (inside or outside) on visual inspection. The increase in height of the reactor during an experiment reflected the mean coefficient of thermal expansion: about 0.3 cm or 1/8 in.

Auxiliary steam addition reduced the temperature of the "hot zone". The "hot zone" was the top 50 cm of the reactor which became bright red in colour during experimentation. A strip chart recorder gave the wall and insertable thermocouple readings. Also, one operator monitored the wall temperature of the reactor continuously using a Leeds and Northrup Company optical pyrometer. If the temperature exceeded the maximum operating levels, and thermal equilibrium was not close, shut-down occurred. This usually happened when the plasma flame was not

Table III
Stainless Stell Type 304 Properties(a)

	Property	Value (British units)	Value (SI units)
1.	Melting Range	2550-2650°F	1400-1455°C
2.	Density	0.29 lb/in.^{3}	8.03 g/cm^3
3.	Coefficient of Thermal Expansion	9.20 in/in/°F (68°F-212°F)	16.56 cm/cm/°C (20°-100°C)
4.	Coefficient of Thermal Expansion	11.0 in/in/°F (68°F-1600°F)	19.8 cm/cm/°C (20°C-870°C)
5.	Maximum Operating Temperature	1600°F (intermittent use)	870°C
6.	Maximum Operating Temperature	1700°F (continuous use)	930°C

(a) Anon., "Stainless Steel Handbook", Allegheny Ludlum Steel Corporation (1959).

well-centered.

Due to the production of large amounts of hydrogen in the enclosed reactor, a potentially explosive mixture was present. Sax (1979) gives data on explosive mixtures, summarized in Table IV. The two main products from the gasification reactions are carbon monoxide and hydrogen. Even though these gases are diluted with nitrogen (conveying) gas and excess steam, precautions were taken to minimize the leakage of air into the system. The system was periodically pressure tested to 70 kPa (10 psig) between experiments. Also, experiments were preceded and followed by a purge of the reactor with argon gas. With a gas flowrate of 100 liters per minute, it takes:

1. 31 seconds to purge the reactor assuming plug flow (PF) and;
2. 72 seconds to reduce gas concentrations to 10% of their initial value assuming a continuously-stirred tank reactor (CSTR).

The argon flow was held at 100 liters per minute for several minutes at the beginning and end of experiments.

As is inevitable with such a complex system, emergency shut-downs occurred. In this event, the reactor contained an explosive mixture. The problem was compounded by the rapid cooling of the gases, causing them to contract and generate a vacuum in the reactor. Air influx through the effluent lines could have resulted in an explosion. A safety system was developed to handle this problem, as shown in Figure 5. It involved a

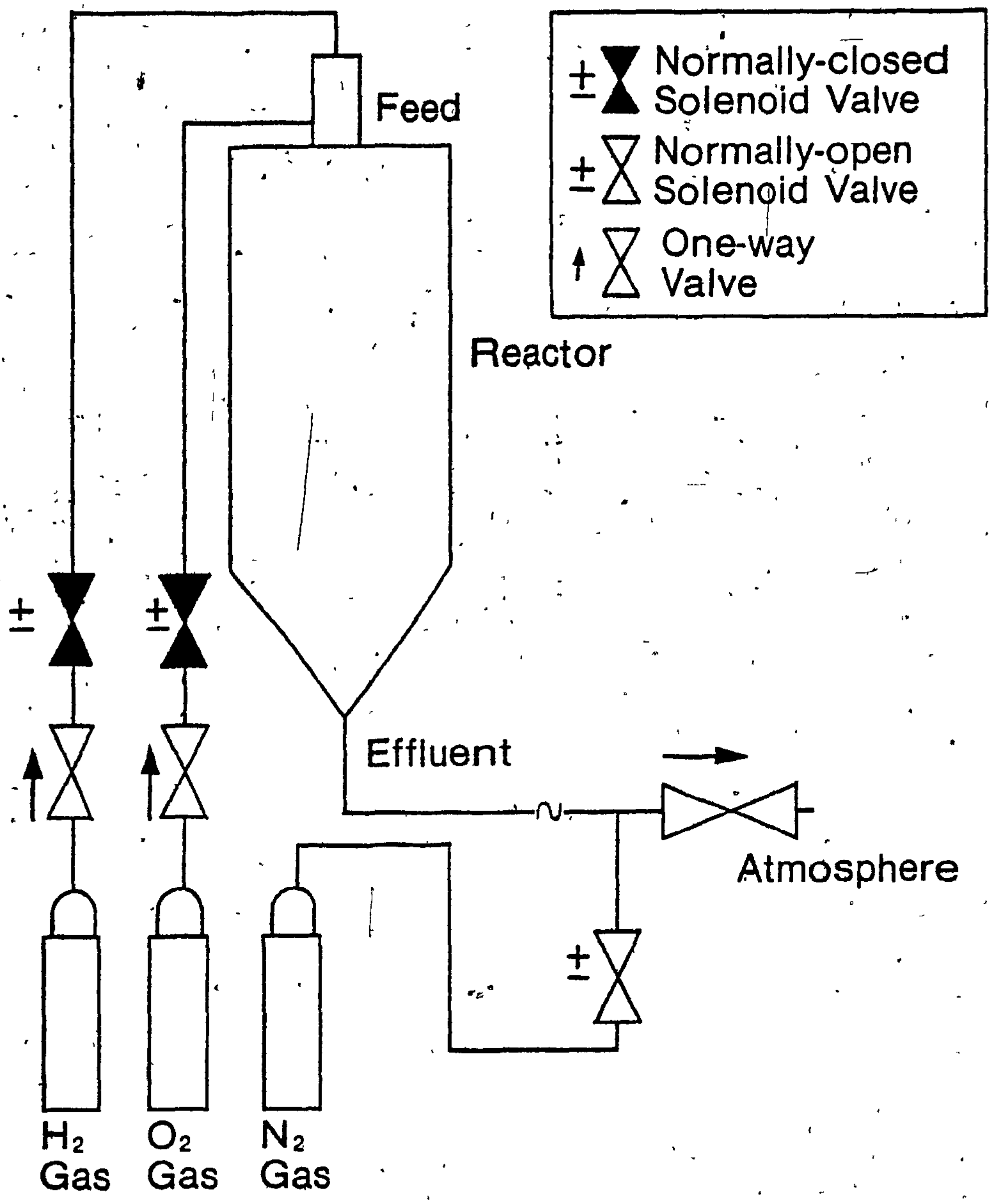
Table IV
Explosive Limits of Hydrogen and Carbon Monoxide in Air[a]

Gas	Upper Explosive Limit	Lower Explosive Limit
Hydrogen	74.2%	4.1%
Carbon Monoxide	74.2%	12.5%

(a) Sax, N.I., "Dangerous Properties of Industrial Materials", Van Nostrand Reinhold Company, fifth edition (1979).

FIGURE 5:

SAFETY SYSTEM


Normally-closed Solenoid Valve
Normally-open Solenoid Valve
One-way Valve
Feed
Reactor
Effluent
Atmosphere
±
H_2 Gas
O_2 Gas
N_2 Gas

system of normally-off and normally-on solenoid valves, coupled with one-way valves. Solenoid valves were used on the oxygen, hydrogen, and nitrogen gas lines. On emergency shut-down:

1. The power to the torch was cut-off, causing the normally-closed valves to shut. One-way valves on the oxygen and hydrogen cylinders were precautions against valve leakage.

2. The normally-open solenoid opened, causing nitrogen to flood the system. This had the effect of diluting the gas mixture at the effluent exit, as well as allowing reactor pressures to reach atmospheric levels with the inert nitrogen. The large one-way valve at the exit prevented large back-flow of air into the hot system. It had some bubble leak since a strong shutting spring could not be used, which would have resulted with an increased backpressure to the system.

The <u>maximum allowable pressure</u> in the system was over 70 kPa (10 psig), as this was the level to which the system was pressure-tested. However the plasma gases entered the reactor with a backpressure of 550 kPa (80 psig), and the possibility of plugging lines existed with the long effluent lines. Higher peat feeding rates produced a pressure rise in the reactor. As a precautionary measure, during experimental runs with high peat feeds, the vycor viewing window was covered with a metal plate. A safety release valve was also on the reactor.

The pressures generated with higher peat flow rates were accompanied by pressure fluctuations, with frequencies about 1 Hz. Pressures could suddenly develop to as high as 70 to 80 kPa (10 to 12 psig) in the course of an experiment. Whenever this phenomena occurred, the experiment was shut-down and the results considered invalid. Small pressure fluctuations of in. of water were present in all runs, having frequencies in the order of milliseconds.

D. PROCEDURE

General Procedure

Due to the complexity of the experimental system, and the possibility of an error resulting in explosion, a detailed and precise experimental procedure was followed. An entire experiment, including initial checks and excluding delays, would take about one hour. While the thirteen pages of procedures are not included here, they are outlined:

1. A preliminary check of the utilities and safety systems was carried out by (at least) two people.

2. The plasma torch was started on argon. The system and sample bottles were purged, and instruments were checked.

3. The hydrogen plasma and auxiliary steam flow were started. This was followed by removal of argon and addition of oxygen. It was not until oxygen addition occurred that high temperatures developed (due to the hydrogen/oxygen combustion reaction). From this point, pressures and temperatures were monitored continuously in the reactor.

4. Thermal equilibrium with steam plasma was approached after approximately one minute, then the ball valve on the nitrogen conveyor line was opened and the peat feeding screw activated.

5. The ball valve to the sample line was opened, and (about) two minutes allowed to elapse so as to ensure that the reactor and sample line were purged.

6. The gas samples were taken, and the point in time was marked on the strip chart recorder (which was monitoring the thermocouples).

7. After the samples were collected, extra data were obtained. This data included gas temperature profiles using the insertable thermocouples. These were usually situated at the reactor centerline, and withdrawing them allowed radial temperature profiles to be measured.

8. Turn-over to argon plasma occurred, followed by a purge time of several minutes.

9. The gas samples were analyzed immediately, then the solids samples gathered from the various collectors afterwards.

10. A "between experiments" check list was followed prior to the next experiment, to ensure that no major problem had developed.

Gas Analysis

The gas analysis was done using a Hewlett-Packard gas chromatograph. A Spherocarb carbon molecular sieve from Chromatographic Specialties was installed in the gas chromatograph. The column was conditioned, then calibrated for each gas present in the gas mixtures: hydrogen, oxygen, nitrogen, carbon monoxide, methane, and carbon dioxide. The gas sample contained no solids or steam by virtue of the condenser and drying column/filter in the sample line, prior to the sample bottles. The specifications for the gas chromatograph operating conditions are given in Table V.

The gas samples were contained in sample bottles such as the one shown in Figure 6. The end ports were connected to the sample line stream, and each sample bottle was flushed. After at least 30 seconds purge time, the sample was taken. The stopcock at the "outside" end of the bottle was

Table V
Operating Conditions for the Gas Chromatograph[a]

1. Column Packing: Spherocarb 80/100 mesh
2. Column Size: 180 cm length, 0.32 cm diameter
   (6 ft. length, 1/8 inch diameter)

3. Column Temperature

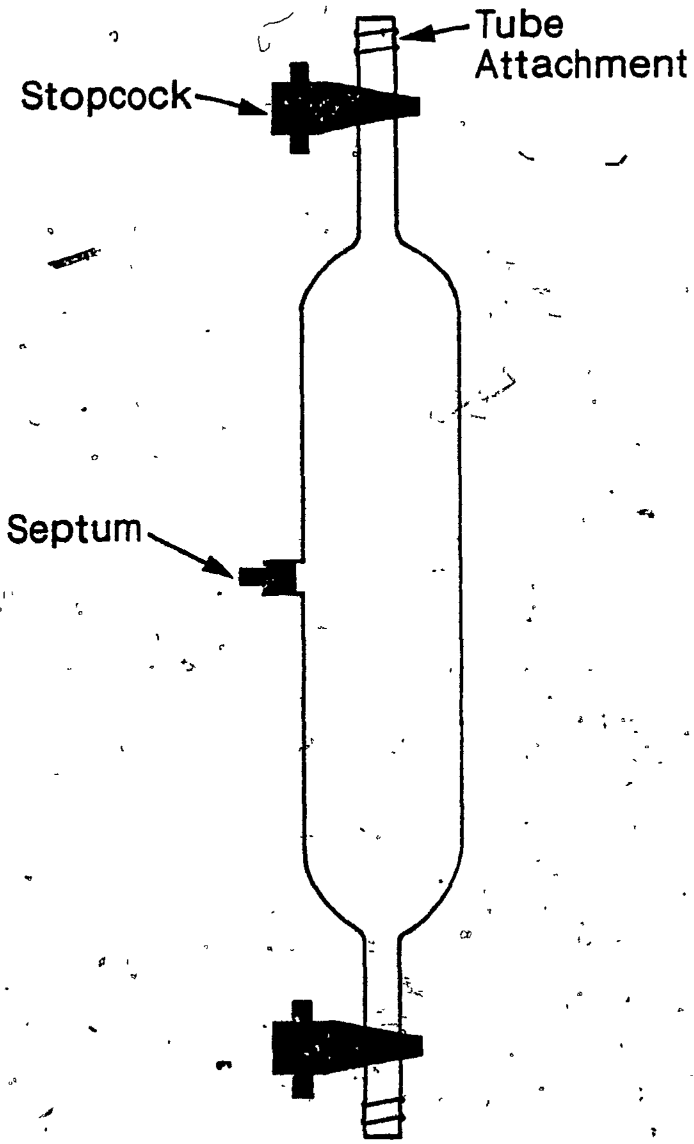
Temperature (°C)	Rate of Temperature Rise (°C/min.)	Time (min.)
30	–	4
–	32	2
100	–	8

4. Injector Temperature: 200°C
5. Detector Temperature: 300°C
6. Carrier Gas and Flow: Helium, 40 ml/min
7. Detector: thermal conductivity
8. Order of Gas Appearance:
   Hydrogen
   Oxygen
   Nitrogen
   Carbon Monoxide
   Methane
   Carbon Dioxide

(a) Private Communication with Paul C. Cheung, Chromatographic Specialties Limited.

FIGURE 6:

SAMPLE BOTTLE


Tube
Attachment
Stopcock
Septum

first closed, followed by the "reactor" end stopcock. This allowed a positive pressure to build in the sample bottle, and minimized air entry. The gas stream was then diverted to another bottle for subsequent sampling.

After the experiment, the bottles were transported immediately to the gas chromatograph. The hydrogen in the samples leaked fairly rapidly (in the order of hours), and so it was necessary to do the gas analysis "in-house".

A 0.5 milliliter sample was withdrawn from the bottle by injecting a syringe into the septum arm. The gas mixture from each of the sample bottles was run in the gas chromatograph three times. Some points are worth noting with regards to the gas analyses:

1. the calculation of peak areas had some uncertainty. This uncertainty was reduced by running each sample three times, and averaging the areas calculated from each run.

2. The septums degraded slowly. They eventually leaked gas rapidly enough so that after a few hours the sample bottle pressure equalized with the atmosphere, and air leaked in. This effect was measured by re-running a sample several hours (three to six) after the experiment. If oxygen appeared in the sample, the septum was changed. A new septum leaked slowly enough so that no oxygen would be present after this time period.

3. The gas chromatograph is very sensitive, and a change of operating conditions results in a change of calibration. Two calibration points were rechecked towards the end of the experimentation period, using nitrogen and methane. The points on the calibration curves were within 0.01 milliliters in a volume of 0.20 milliliters.

4. A thermal conductivity detector was used in the gas chromatograph. The hydrogen peaks were very small, since the thermal conductivity of hydrogen is near to that of the carrier gas, helium. As a result, the area of a peak only gave an order of magnitude indication of the quantity of hydrogen gas in the sample . A hydrogen peak from an injection of 0.25 milliliters, typical for an experiment, resulted in an area of about six square millimeters on the strip chart recorder paper. The hydrogen concentrations reported in the results were obtained by difference.

Solids Analysis

The solids samples were collected throughout the apparatus: in the two collectors immediately after the reactor and in the collector below the cyclone. Most solids accumulated in the cyclone. The samples were stored in glass jars and allowed to settle. After two to three days, the liquid fraction was decanted and discarded. Three portions were withdrawn, saved in small glass vials, and their contents dried thoroughly. One was sent for analysis, one used for an ash determination, and another saved.

The above preparation method was found to give the most representative solids samples, noting:

1. The decanted liquid (when vacuum filtered) yielded a very small mass of solids, which was contaminated by the paper filter. It was thus discarded.

2. While there was virtually no solids accumulation in the reactor over the course of all the experiments, there was some accumulation in the effluent piping.

3. Some solids (the fines) would go straight through the effluent lines and not be caught in the cyclone. This small amount was apparent on visual observation of the effluent purge to the atmosphere.

All solids analyses were done by Dr. C. Daessle of Organic Microanalyses in Montreal. The methods used are outlined by Pregl and Grant (1951). The solids sample is burned in an oven using a catalyst to oxidize the sample completely. The gas is then conveyed over columns of absorbing material, and the oxidized gases are selectively removed from the mixture. Determining the weight gain of the column allows the mass fractions of elements in the solids to be calculated. The conditions and catalysts used in the analyses are summarized in Table VI.

Table VI
Conditions for Solids Analysis

1. Element(s) Tested for	Catalyst for Combustion	Time of Combustion (min.)	Temperature of Combustion (°C)	Combustion Product(s)
Carbon Hydrogen	CuO (wire)	17	600	CO_2 H_2O
Nitrogen	CuO (wire)	17	800	N_2
Oxygen	C (graphite) (granular)	20	1100	O_2

2. Combustion Product	Absorbing Material in Column
CO_2	soda asbestos (14 to 22 mesh)
H_2O	anhydrone (magnesium perchlorate)
N_2	volumetric method
O_2	I_2O_5 (granular)

Since the solids analysis could not be done "in house", a first-hand knowledge of the errors is not available. Discussion with Dr. Daessle revealed the following:

1. The mass fraction of ash was determined by weighing the residue from the oxidized sample. The balance was accurate to ± 2 micrograms. The sample sometimes splattered in the extreme conditions of the oven, though, and unusual ash fractions were sometimes obtained.

2. Solid samples must be thoroughly dried, and the analysis performed soon afterwards. The samples can pick-up moisture which appears as hydrogen and oxygen in the determination.

3. The solids sample must be carefully chosen. The mass of solids used for the analyses was in the order of a few milligrams. A non-homogeneous choice of solids sample would produce unrepresentative results.

The accuracy of the analysis was checked and shown to be good. Repeat samples were submitted, without prior knowledge of the analyzer, and consistent results were obtained. Different samples from the same experiment were also analyzed, and the sample was proven to be homogeneous. Moisture determinations of the peat were done (with the method previously described) at McGill University upon retrieval of the samples, and this moisture content was incorporated into the mass balances. Also, the mass fraction of ash was verified by burning samples overnight at a temperature of 700 Celsius, and the residue weighed immediately after removal from the oven.

It is important to note a difference in the nature of the solids samples versus the gas samples. The three gas samples were taken at different points in time. The solids samples accumulated throughout the experiment. Results of some experiments had to be disregarded if an unscheduled shut-down occurred, even if good gas samples had been collected, because the solids were still unrepresentative.

E. EXPERIMENTAL CONDITIONS AND RESULTS

Introduction

Before discussing the conditions and results, the nature of the experimental variables must be discussed. There exists only one experimental replicate in temperature and carbon-to-steam molar ratio. The reason for this is that some of the experimental "conditions" were only known after the experiment was done. The two primary variables were established in the following ways:

1. The carbon-to-steam molar ratio in the feed was altered by changing the peat feed rate. An approximate feed rate was set by changing the speed of the motor which turned the auger of the screw conveyor. Even at a constant motor speed, however, the feed rate could vary. The small pressure fluctuations (previously described) caused an oscillating gas flow in and out of the hopper, conveying peat in excess of that which was

carried by the screw alone. If the magnitude of the pressure fluctuations increased slightly, the feed rate increased slightly. The mean peat feed rate was determined after the experiment by measuring the mass fed from the hopper, and timing the interval over which it was fed.

2. The temperature of the system, for the "same" power settings and feed rates, changed from one experiment to another. In order to use the same power, the same current flow is required. Even though a constant current was used for most experiments, fluctuations in the voltage between experiments resulted in different powers. The temperatures in the reactor were obtained by the thermocouple readings on the strip chart recorder. The measured temperatures deviated from the "effective" temperatures for reasons about to be described.

The two primary variables are affected by parameters which cannot be directly measured. These parameters cannot all be known, but some of the obvious ones are:

1. The flame geometry changes from experiment to experiment. This affects many things, most importantly the temperature profiles. The peat would react to different degrees depending on its environment. The high degree of turbulence in the upper part of the reactor minimized this problem.

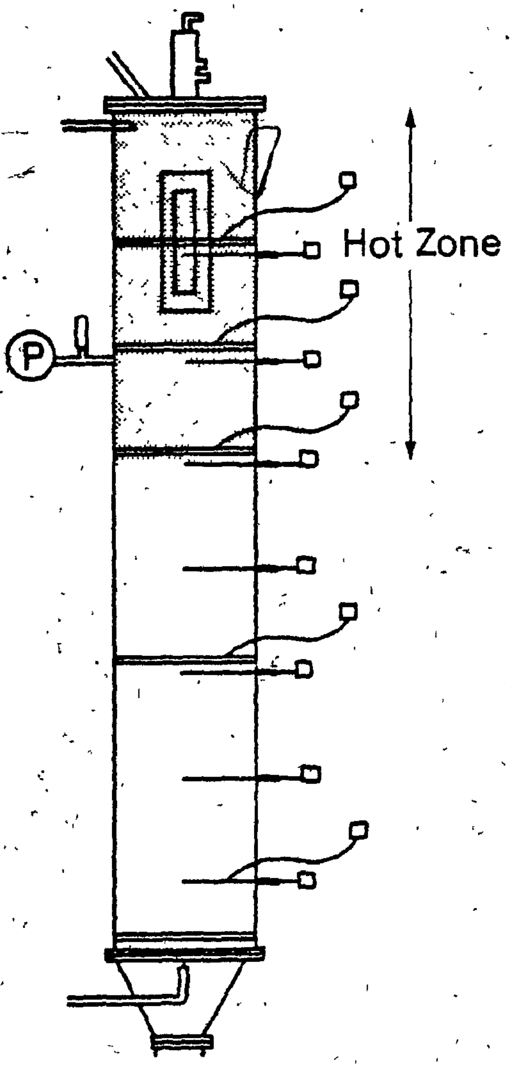
2. The mixing efficiency between the peat and steam varied between experiments. This is a function of variables such as the peat-to-nitrogen conveyor gas ratio and flame geometry.

3. The magnitude of the pressure fluctuations changed from experiment to experiment. While the period of a fluctuation was in the order of milliseconds, giving essentially constant flow, there was probably a slight pulsing of the peat feeding.

None of the above effects were measured, but they were certainly important, and caused some uncertainty in the data. The temperature measurement is especially vulnerable to these effects. The reaction temperature has been defined as the mean value of the uppermost and third thermocouple. The third thermocouple corresponds to the bottom of the "hot zone", which is shown in Figure 7. This is probably a representative temperature, because it is at this temperature that gasification will take place: pyrolysis occurs in the order of milliseconds, and gasification reactions require longer times (in the order of a second). Residence time calculations were made for the "hot zone", and found to be about 3/4 of a second. Below the zone, temperatures were too low for further gasification.

FIGURE 7:

ILLUSTRATION OF "HOT ZONE"


Hot Zone
P

Summary of Experimental Conditions

The conditions for the experiments, and some directly calculated parameters, are given in Tables VII and VIII. The first nine experiments used a constant current and almost constant power input, and the last five experiments were ones in which special parameters changed. Although an attempt was made to maintain the peat feed constant for these last five experiments, it did vary somewhat. In experiments ten to twelve, power was increased by increasing current. In experiment fourteen, power was increased by increasing the hydrogen and oxygen flows. The last experiment was at normal power, but the reactor was insulated using fiberglass over the bottom 70 cm, specifically the area below the "hot zone".

The peat and steam flows are given in Table VII, followed by the calculated carbon (in the peat)-to-steam molar ratio. The steam flow is constant except for experiment fourteen.

Current, voltage, and power are given in the first three columns of Table VIII. Current was set by the operator, and the voltage was characteristic for a given set of conditions. The power was calculated taking into account heat losses to the cooling water. A power-to-peat ratio may be calculated directly from the experimental conditions. The temperatures did not reflect the power to peat ratios as much as was expected, mainly due to the "unmeasured parameters" already mentioned. The graph of temperature versus power-to-peat ratio is given in Figure 8 to

Table VII
Experimental Conditions: Feeds

Experiment Number	Special Condition	Peat Flow (kg/h)[(a)]	Carbon-to-Steam Molar Ratio[(b)]
1		3.33	0.16
2		3.65	0.17
3		4.88	0.23
4		5.01	0.23
5		5.12	0.24
6		6.59	0.30
7		6.94	0.32
8		10.65	0.47
9		24.13	0.95
10	I = 150 A.	5.62	0.26
11	I = 200 A.	5.42	0.25
12	I = 250 A.	5.82	0.27
14	higher plasma	4.08	0.18
15	insulation	5.82	0.29

(a) measured by mass of feed and (divided by) the time of feed
(b) steam mainly from steam plasma, with some auxiliary steam at 107 °C

Table VIII
Experimental Conditions: Temperatures

Experiment Number	Plasma Current (amperes)	Plasma Voltage (volts)	Electric Power (kw)(a)	Power-to-Peat Ratio (kwh/kg)(b)	Temperature (K)(c)
1	130	150	14.20	16.53	1333
2	130	165	15.62	15.47	1300
3	130	155	14.67	11.38	1275
4	130	135	12.78	10.70	1275
5	130	155	14.67	10.85	1323
6	130	155	14.67	8.43	1265
7	130	150	14.20	7.94	1330
8	130	170	16.09	5.35	1328
9	130	160	15.14	2.51	1223
10	150	155	16.93	10.28	1383
11	200	150	21.84	11.58	1338
12	250	130	23.66	11.09	1418
14	130	157	14.86	14.29	1398
15	130	150	14.20	9.45	1251

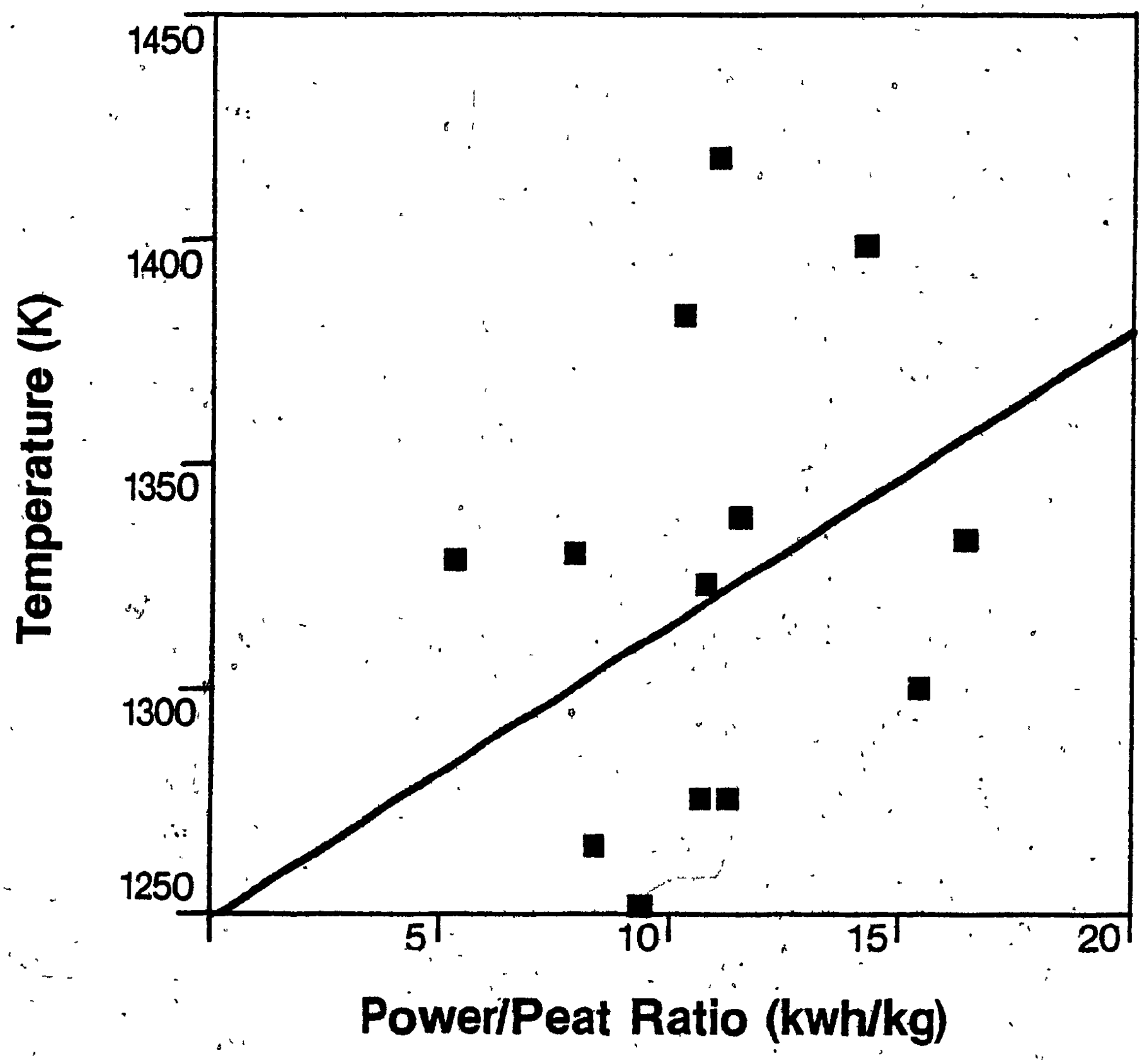
(a) calculated from P = IV, and corrected for heat losses to cooling water

(b) considers electrical and chemical power

(c) mean of two thermocouples at points 20 centimeters and 50 centimeters from the reactor top.

FIGURE 8:

TEMPERATURE IN REACTOR VERSUS POWER-TO-PEAT RATIO


1450
1400
1350
1300
1250
Temperature (K)
5
10
15
20
Power/Peat Ratio (kwh/kg)

confirm this.

The experimental region examined is given in Figure 9. An experimental design using data at the extreme points of the experimental region and replicates at the center could not be executed due to the nature of the variables. The grid area is well covered over the low carbon-to-steam ratio area. The single point at a ratio of 0.95, even though it produced bad results, is important since it is outside the experimental region of "high density".

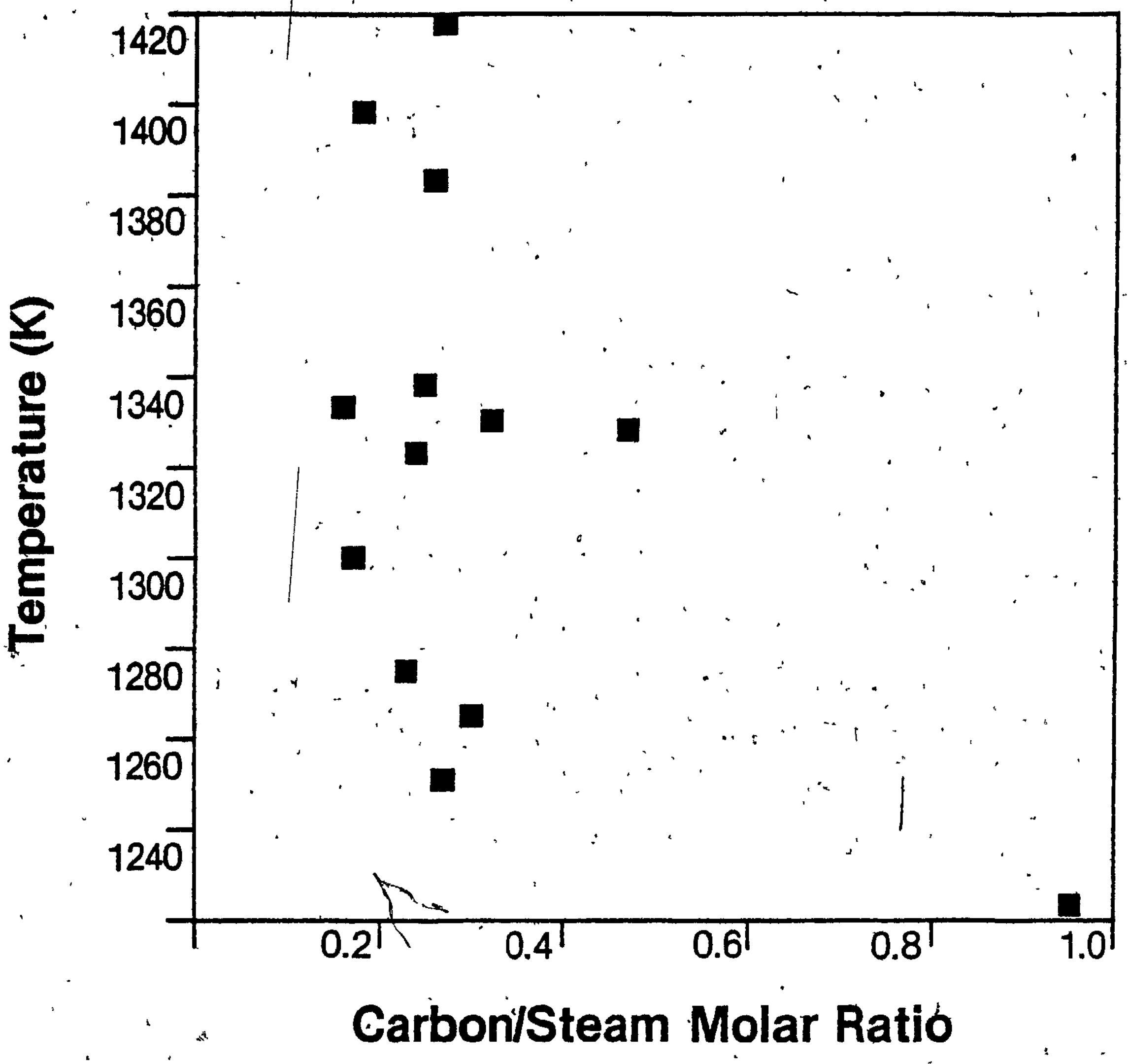
Carbon-to-steam ratios varied from 0.16 to 0.95 i.e. severalfold, while temperatures varied only between 1223 and 1418 K i.e. over a much smaller range. This is due to the temperature limitations of the apparatus mentioned.

Summary of Experimental Results

The experimental results are the gas and solids analyses. These data are included in Appendix II.

FIGURE 9:

GRID OF EXPERIMENTAL REGION


1420
1400
1380
1360
1340
1320
1300
1280
1260
1240
Temperature (K)
0.2
0.4
0.6
0.8
1.0
Carbon/Steam Molar Ratio

F. DISCUSSION OF RESULTS

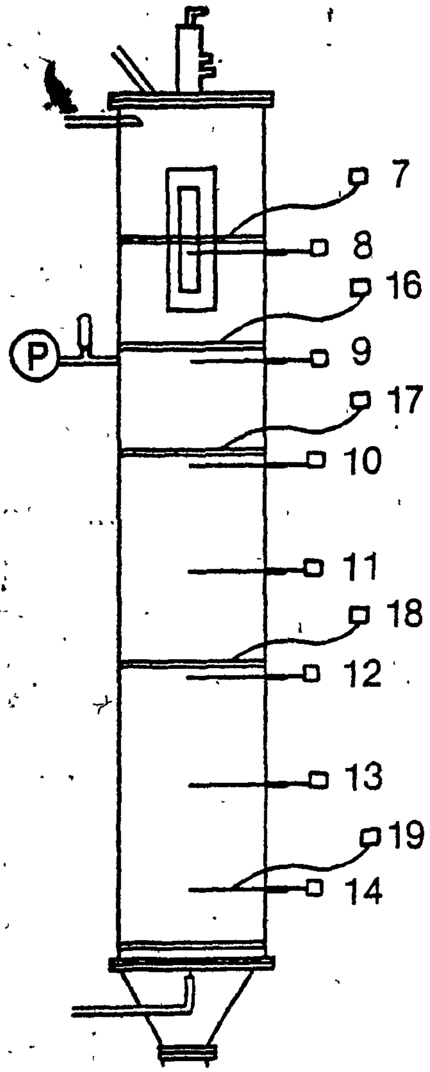
Temperature Profiles

Thermocouples were used throughout the experimental system. The temperatures measured by the thermocouples were recorded on a Thermoelectric strip chart recorder during the course of every experiment. Temperature measurements were required for the inlet and outlet cooling water to the torch for efficiency calculations. In the (heated) auxiliary steam line, temperatures were required to ensure that the steam was slightly superheated.

The thermocouples on the reactor were as shown in Figure 10. Thermocouples 7, 16, 17, 18 and 19 were strapped to the outside wall of the reactor. Thermocouples 8 to 14 were "insertable" thermocouples. They were contained in a 0.32 cm (1/8 in.) sheath, which were held tightly in the reactor by Swagelock tube fittings. By welding tubes onto the reactor to hold part of the thermocouple, teflon tube fittings could be used without melting. Teflon fittings allow repeated tightening and loosening, so the degree of thermocouple entry could be adjusted during an experiment. The insertable thermocouples were usually left at the reactor centerline. Thermocouple 8, at the highest position, had to be replaced due to melting after several experiments. All thermocouples were type "K", or chromel-alumel. A stainless steel sheath was used.

FIGURE 10:

THERMOCOUPLES ON REACTOR


7
8
16
P
9
17
10
11
18
12
13
19
14

Temperature measurements are presented:

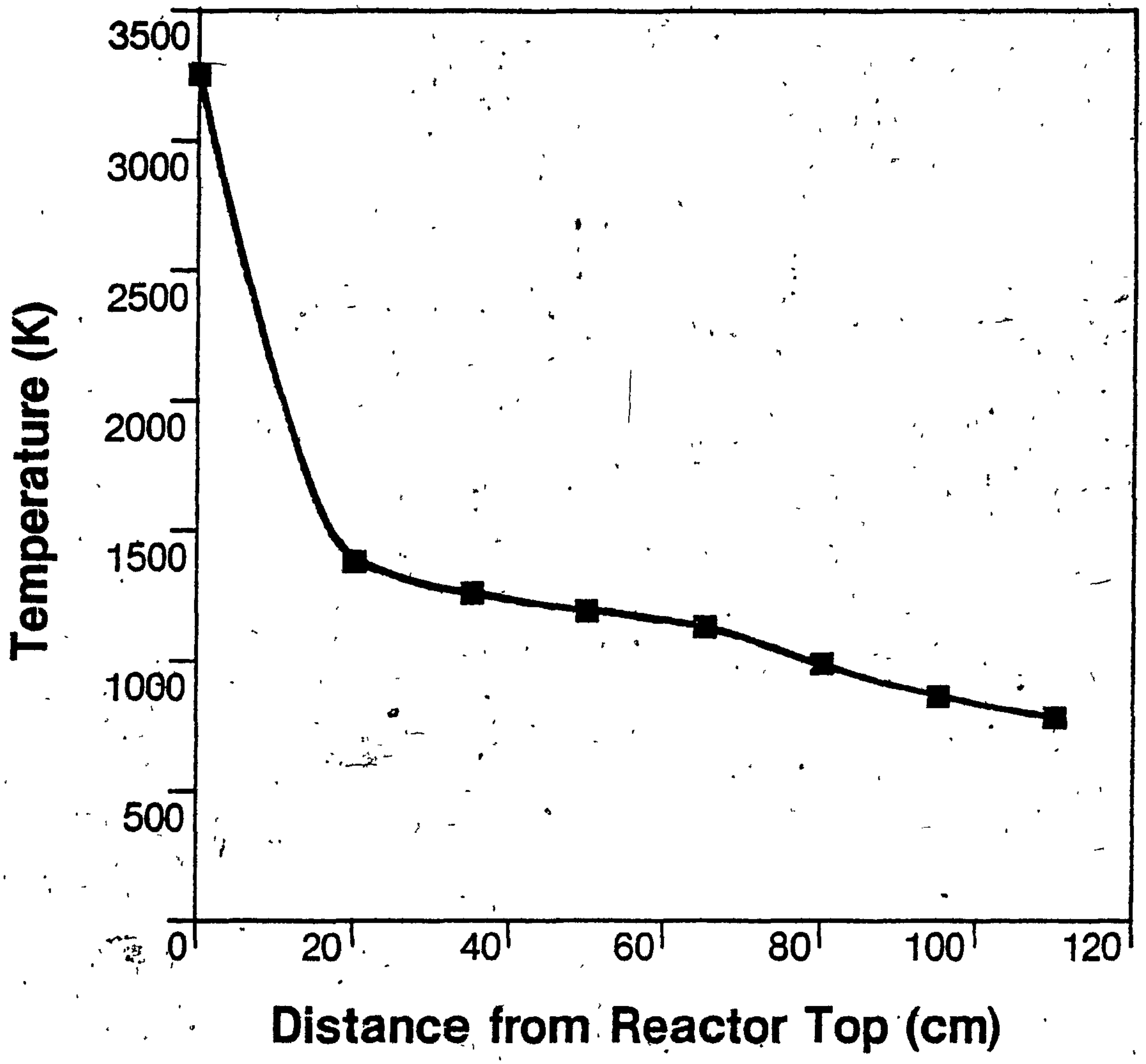
1. along the reactor centerline at steady state;
2. over reactor radii at steady state and;
3. at different locations for transient measurements through time.

The results for chosen cases are shown in Figures 11 to 14. Radiation and conduction corrections should be applied to the temperature data obtained from the thermocouples. Katta (1972) outlines the use of appropriate corrections that can be used for thorough calculations. The temperature analyses use data in an uncorrected form.

Figure 11 shows a plot of temperature along the centerline of the reactor versus reactor length. The first data point on the graph is calculated using steam enthalpy calculations, with the electrical and feed data for the experiment. The next seven points on the graph correspond to the insertable thermocouples going down the reactor. The initial gradient is steep up to a temperature in the range of 1200 to 1500 K. Then, the temperature falls slowly for the first three thermocouple readings, and slightly faster afterwards. The first three thermocouples cover the top 50 cm of the reactor, or the area previously described as the "hot zone". The exit temperature from the reactor is almost 700 K.

FIGURE 11:

AXIAL TEMPERATURE PROFILE



Temperature (K)
3500
3000
2500
2000
1500
1000
500
0
20
40
60
80
100
120
Distance from Reactor Top (cm)

FIGURE 12:

RADIAL TEMPERATURE PROFILES AT VARIOUS REACTOR HEIGHTS

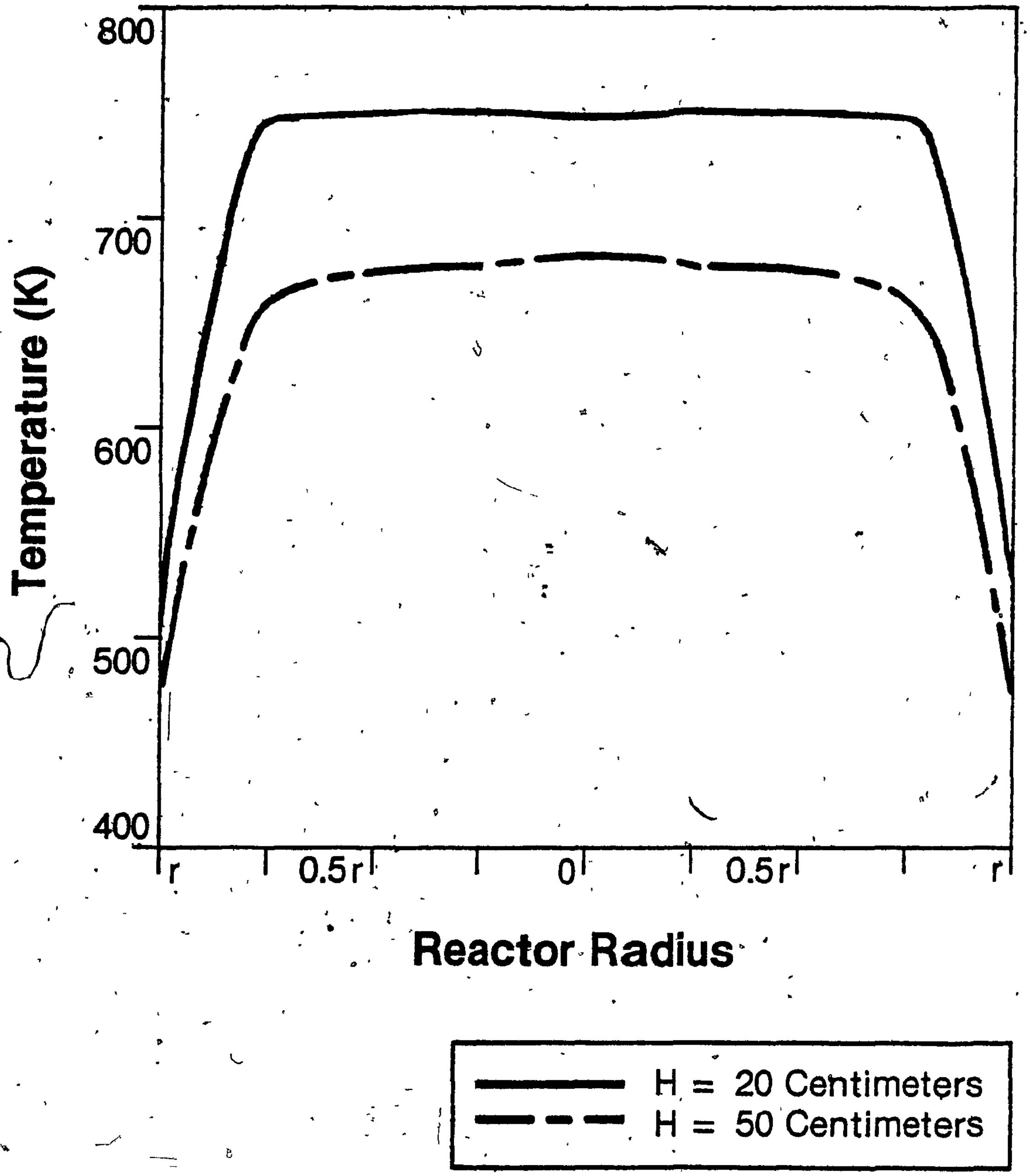
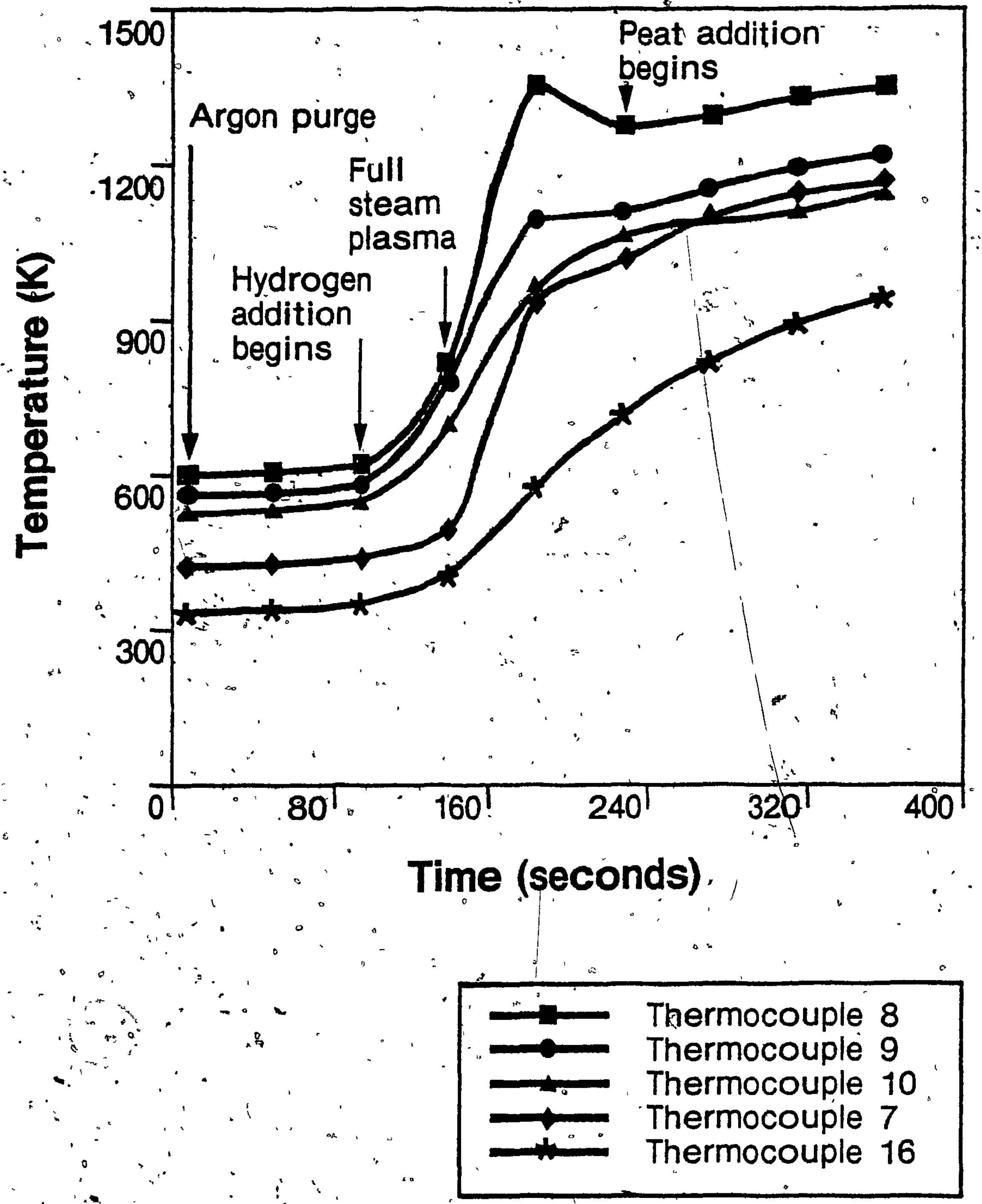

Temperature (K)
800
700
600
500
400
r
0.5r
0
0.5r
r
Reactor Radius
H = 20 Centimeters
H = 50 Centimeters

FIGURE 13:

TEMPERATURE VERSUS TIME, FOR THE UPPER PART OF THE REACTOR



1500
1200
900
600
300
Temperature (K)
0
80
160
240
320
400
Time (seconds)
Argon purge
Hydrogen addition begins
Full steam plasma
Peat addition begins
Thermocouple 8
Thermocouple 9
Thermocouple 10
Thermocouple 7
Thermocouple 16

FIGURE 14:

TEMPERATURE VERSUS TIME, FOR THE

LOWER PART OF THE REACTOR

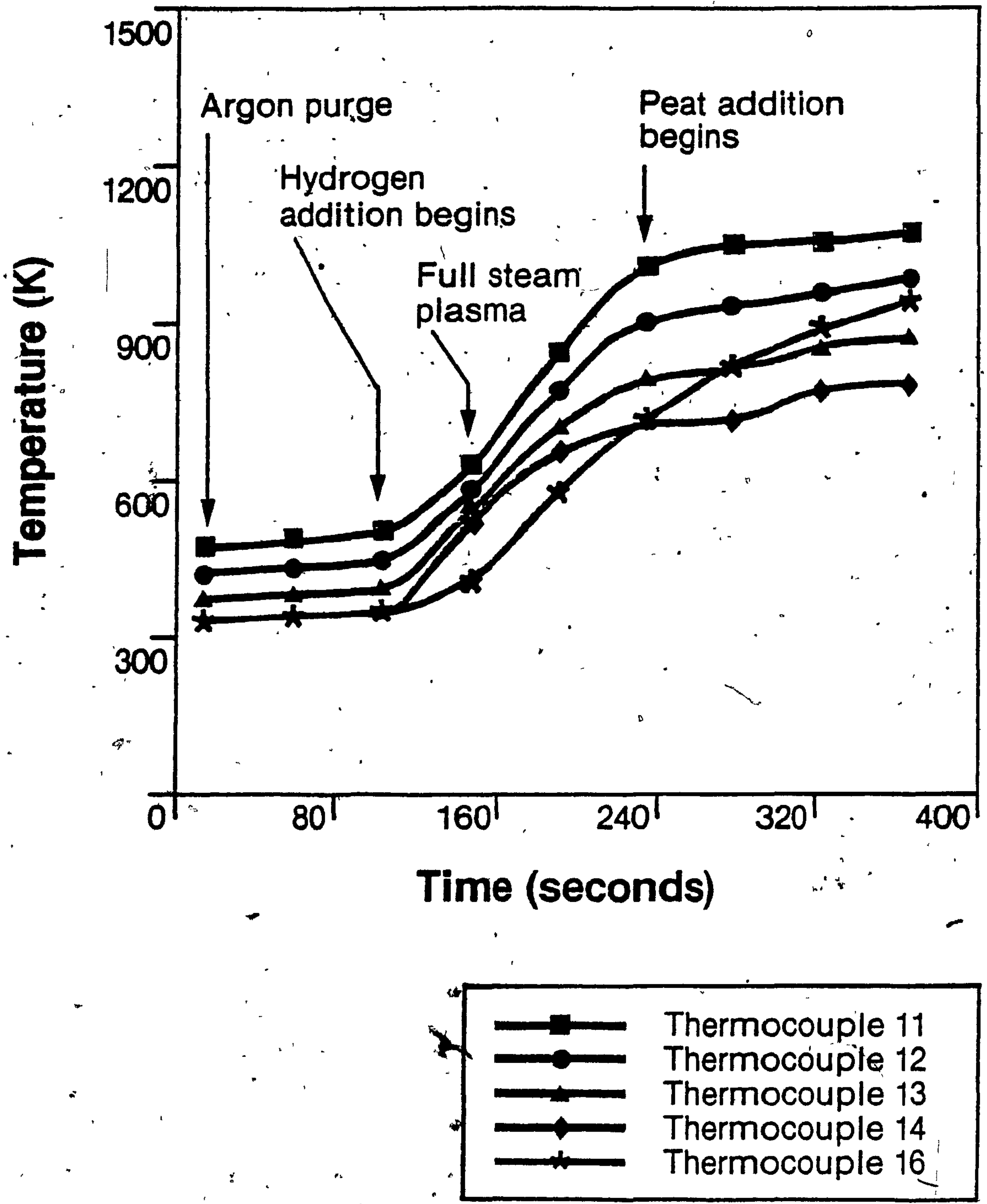
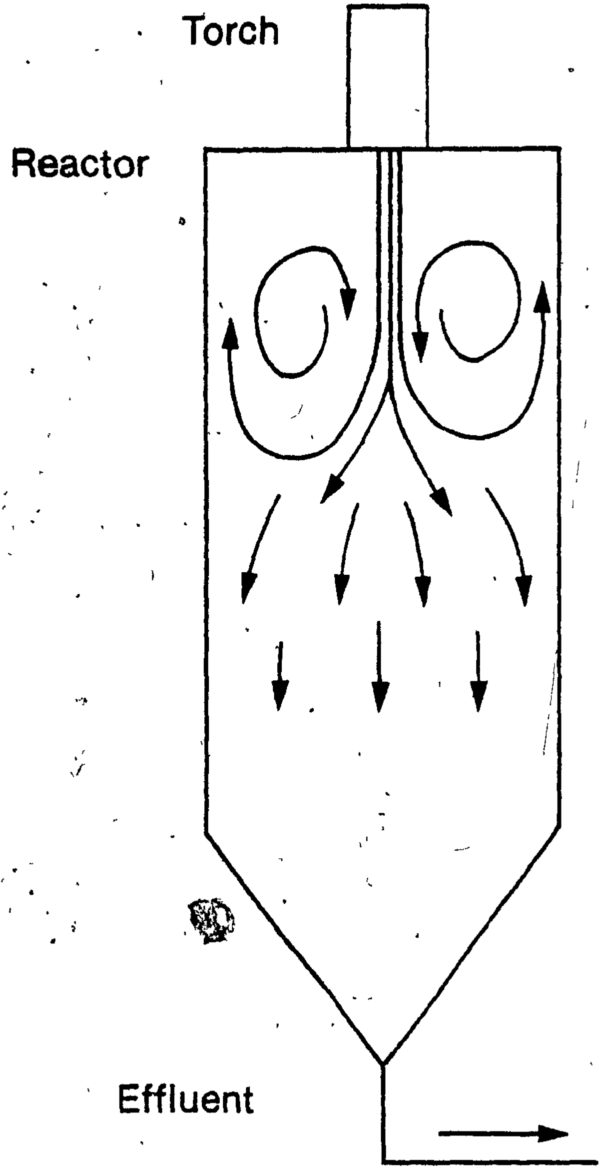

1500
1200
900
600
300
0
80
160
240
320
400
Temperature (K)
Time (seconds)
Argon purge
Hydrogen addition begins
Full steam plasma
Peat addition begins
Thermocouple 11
Thermocouple 12
Thermocouple 13
Thermocouple 14
Thermocouple 16

Figure 12 gives the radial temperature profiles at the first and third thermocouples, using an argon plasma. Axial symmetry was assumed for the profiles, although this was not strictly true for a steam plasma. The temperatures and gas flow rates are lower with the argon plasma than in the experiments, but approximately the same profile shapes are expected. Argon data was used because the gathering of temperatures in the radial direction was too time consuming to be obtained during experimental conditions. At the top thermocouple, 20 cm below the reactor top, a nearly flat temperature profile exists. The thermocouple 35 cm from the reactor top gave an unusual profile (not shown), thought to be disturbed by asymmetry. The third thermocouple shows a flat profile. These data are explained by the gas flow patterns in the reactor.

As first reported by Kubanek (1966), large gas recirculation occurs in an ASTR system. The flow patterns are represented in Figure 15. The top part of the reactor is assumed to behave as a continuously stirred tank reactor (CSTR). This helps to explain the temperature profile in Figure 11. The centerline temperature for the first three thermocouples is falling slowly. Thereafter, the reactor behaves in a plug flow (PF) manner, and the temperatures fall more rapidly.

FIGURE 15:

GAS RECIRCULATION PATTERN IN THE REACTOR


Torch
Reactor
Effluent

The "hot zone" is where the peat transformation occurs. This was further proven, with an experiment in which a sample was drawn from the thermocouple 10 port (the bottom of the hot zone) as well as at the bottom of the reactor. The gas samples from each location were found to have virtually the same composition.

Thermal equilibrium was approximated in less than two minutes after peat addition to the reactor, as portrayed in Figures 13 and 14. Figure 13 shows the temperatures measured by the thermocouples over the top half of the reactor. Thermocouples 8, 9, and 10 are at the centerline in the "hot zone". Thermocouples 7 and 16 are wall thermocouples in the "hot zone". Thermocouple 7 was placed near a "hot spot", or a position on the reactor wall which heated quickly due to the split of the steam plasma flame. Note that centerline temperatures at the reactor top are sensitive to peat addition or changes in the plasma. The quench due to peat addition is clearly seen in thermocouple 8. Once "steady state" was approached, temperatures at the top of the reactor still fluctuated by approximately 25 to 35 K, indicating that thermal "steady state" is never really obtained.

Steam Properties

The steam plasma was produced by injecting oxygen into a hydrogen plasma, and had a high enthalpy. But, relative to other thermal plasmas of the same enthalpy, the steam did not reach a high temperature. If the sum of the chemical and electrical energies are considered, the steam was absorbing between 50 and 65 kilowatts during the experiments. Most of this energy was provided by the exothermic reaction. Table IX summarizes the energy input to the gas from each source, and the maximum temperature of the steam in the torch.

Figure 11 illustrated the rapid fall in temperature of the plasma to levels well below 2000 K at the steam/peat mixing point. The hottest temperatures measured at the top thermocouple were about 1500 K (obtained in several experiments). At these temperatures, steam has no significant dissociation. The value of plasma in this work, then, was primarily as a heat source. There were no activated species generated by the plasma which were participating in the reaction (if the gas was in equilibrium).

Table IX
Maximum Steam Plasma Temperatures

Experiment Number	Chemical Power (kw)(a)	Electrical Power (kw)(b)	Total Power (kw)	Calculated Maximum Temperature (K)(c)
1	40.86	14.20	55.06	3703
2	40.86	15.62	56.48	3715
3	40.86	14.67	55.53	3707
4	40.86	12.78	53.64	3691
5	40.86	14.67	55.53	3707
6	40.86	14.67	55.53	3707
7	40.86	14.20	55.06	3703
8	40.86	16.09	56.95	3719
9	40.86	15.14	56.00	3711
10	40.86	16.93	57.79	3726
11	40.86	21.84	62.70	3767
12	40.86	23.66	64.52	3783
14	43.40	14.86	58.26	3701
15	40.86	14.20	55.06	3703

(a) assumes a constant heat of combustion of −57,798 cal/gmole

(b) corrected for heat losses to cooling water

(c) interpolating from Ihara, S., "Approximation of the Thermodynamic Properties of High-Temperature Dissociated Water Vapour", Electrotechnical Laboratory Bulletin, Tokyo (Feb. 1977)

Mass Balances

Mass balances were completed around the reactor in order to assess the consistency of the data, and to obtain carbon conversions for each experiment. The input to the reactor and output from the reactor are shown in Figure 16.

A simple algorithm of the computer program written to calculate the mass balances is given in Figure 17. The program listing is given in Appendix III. There are a few important points to note:

1. The liquid collected was assumed to have no light hydrocarbons present in it. Small quantities of an immiscible layer were sometimes discernable in the condensed liquid, but were negligible for the purposes of the balances.

2. The ash and nitrogen masses were assumed to be constant in the process, and were used as tracers. It is unlikely that nitrogen containing products formed. The production of nitrogen oxides was examined using F*A*C*T, described by Bale et al. (1979), and concentrations much less than the parts per billion range were predicted. The ash, on the other hand, might have contained some metals which changed their oxidation state.

3. The excess steam was calculated by difference for the oxygen and hydrogen balances. If error in the balances resulted in the calculated values not to be in exactly stoichiometric proportions, a mean value was used, and the mass differences were calculated.

FIGURE 16:

MATERIAL FLOWS THROUGH THE REACTOR

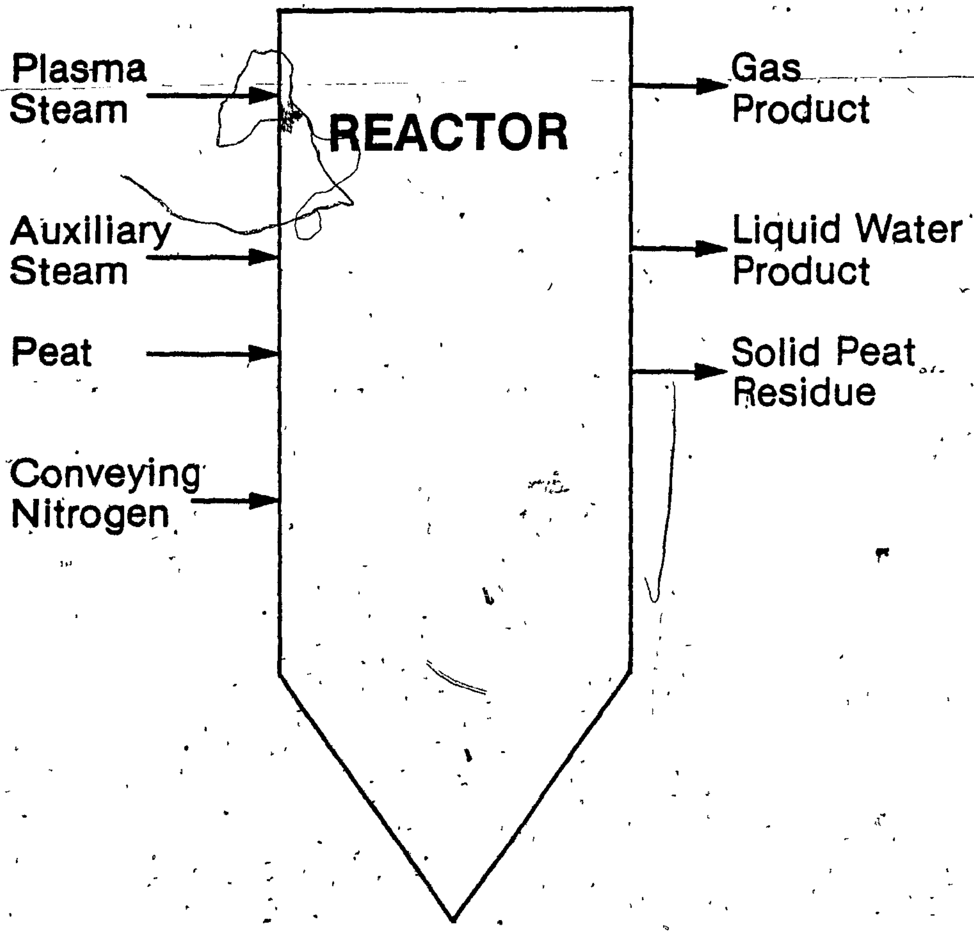
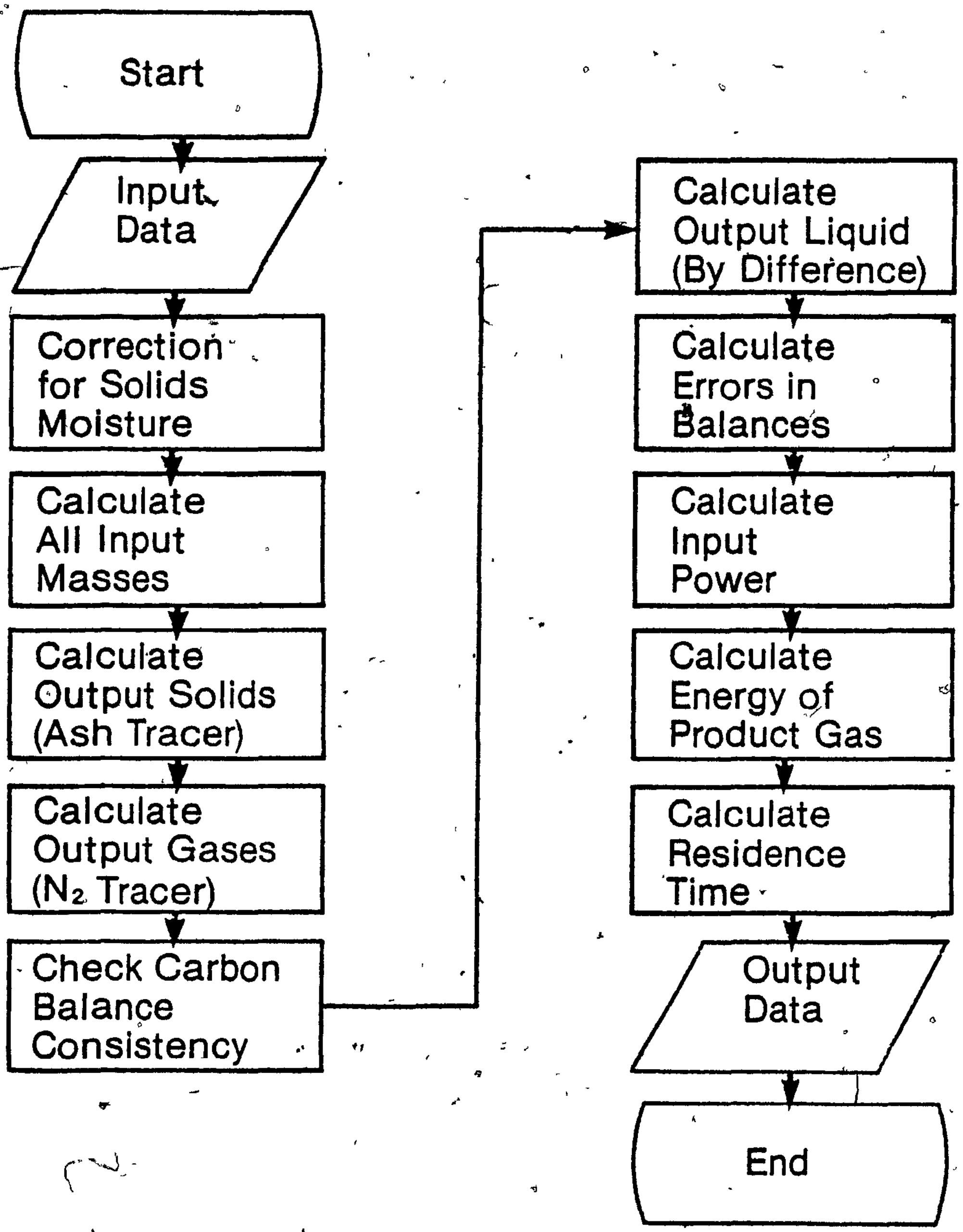

Plasma Steam
Auxiliary Steam
Peat
Conveying Nitrogen
REACTOR
Gas Product
Liquid Water Product
Solid Peat Residue

FIGURE 17:

ALGORITHM OF MASS BALANCE PROGRAM


Start
Input Data
Correction for Solids Moisture
Calculate All Input Masses
Calculate Output Solids (Ash Tracer)
Calculate Output Gases (N_2 Tracer)
Check Carbon Balance Consistency
Calculate Output Liquid (By Difference)
Calculate Errors in Balances
Calculate Input Power
Calculate Energy of Product Gas
Calculate Residence Time
Output Data
End

4. The carbon balance was completely specified, allowing a verification of the data. Only experiments for which the input carbon was within 15% of the output carbon were considered. Imprecise balances could be caused by obvious errors in experimental procedure, or by some other unperceived reason.

The results are given in Tables X and XI. The carbon balance conversion is defined as the weight gain of carbon in the outlet stream compared to the input stream. The values are positive and negative, and all are less than 15%. The carbon conversions are defined as the mass of carbon passed from the peat into the gas phase, divided by the mass of carbon in the unreacted peat. One conversion has been calculated based upon the mass of carbon in the gas phase, and one based upon the mass of carbon remaining in the solid residue. The average value is the final result. The residence time (tau) is calculated as the volume of the "hot zone", divided by the volumetric flow rate of the product gases at the temperature of the "hot zone". This assumes that the peat has the same residence time as the product gas, and plug flow conditions prevail. The lower heating value of the product gas is calculated using the heats of combustion for the gases in the mixture, on a steam-free and nitrogen-free basis. A low-Btu gas has a value of 100-250, medium-Btu gas has 250-550, and a high-Btu gas has near to 1000. The molar ratio of hydrogen-to-carbon monoxide should have a value of two for synthesis gas.

Table X
Results of Mass Balances

Experiment Number	Carbon Balance Conversion (%)[a]	Gas Carbon Conversion (%)	Solids Carbon Conversion (%)	Average Conversion (%)
1	2.39	79.90	77.52	78.71
2	13.33	95.71	82.38	89.04
3	10.73	74.91	64.18	69.54
4	-3.26	82.89	86.15	84.52
5	-3.55	71.95	75.50	73.72
6	-4.20	73.29	77.49	75.39
7	-11.73	71.21	82.94	77.08
8	-0.87	59.68	60.55	60.11
9	-5.73	33.28	39.01	36.14
10	-6.00	71.07	77.07	74.07
11	-4.13	65.98	70.12	68.05
12	-1.06	70.98	72.14	71.51
14	-0.97	69.04	70.00	69.52

(a) defined as the percentage increase in mass of carbon leaving the reactor, compared to the carbon entering the reactor

Table XI
Results of Mass Balances

Experiment Number	Residence Time, T (seconds)(a)	Energy of Product Gas (kJ/m³)(b)	Energy of Product Gas (Btu/ft³)(b)
1	0.735	10790	289.7
2	0.726	11220	301.2
3	0.592	12050	323.4
4	0.720	11140	299.0
5	0.692	11170	299.8
6	0.686	11700	314.0
7	0.640	12750	342.3
8	0.719	11640	312.3
9	0.547	12080	324.1
10	0.651	11390	305.8
11	0.681	11320	303.7
12	0.633	11460	307.7
14	0.670	11090	297.7
15	0.710	11400	306.0

(a) based on the volume of the top 50 centimeters of the reactor, for the product gas mixture at the mean temperature of this volume.

(b) on a steam-free and nitrogen-free basis

Average conversions varied from 36.14% in experiment 9 to 89.04% in experiment 2. The hydrogen-to carbon monoxide ratios varied from 1.15 in experiment 9 to 2.39 in experiment 1.

Sensitivity of Mass Balances

The success of the analysis depends upon the accuracy of the mass balances. To get an indication of how the mass balances are affected by different parameters, a sensitivity analysis was performed.

For the analysis, changes were made to the data to simulate experimental inaccuracy. The mass balance program was then run again, and the effect on the carbon balance was examined.

Two cases were considered:

1. Experiment 1 had a very low peat flow rate. The product gas analyzed was high in nitrogen content, since even with a high conversion there was not a large quantity of gas produced. Nitrogen was used as a tracer, and this experiment resulted in an accurate determination of the nitrogen mole fraction in the gas phase. On the other hand, the percentages of all the other gases were small (see experiment 1 gas analysis data in Appendix II).

2. Experiment 9 had a high peat feed rate. The opposite of case 1 was true: small nitrogen percentages in the product gas and larger percentages of other gases were found.

The results of the analysis are presented in Tables XII and XIII. The parameters examined were :

1. The nitrogen carrier gas flow rate was changed in value by one graduation on the rotameter, or a 10% difference in reading.

2. The nitrogen percentage in the product gas was changed by a reading of 2%. This change was determined by observing the fluctuation in data from the three different analyses for each of the gas samples obtained in experiments 1 and 9.

3. The peat mass fed to the system over the course of an experiment: the value of 50 grams corresponds to half of a graduated container which was used to fill the peat hopper.

4. The time of the feed: with quick start-up and shut-down of an experiment, this inaccuracy was estimated to be five seconds at most.

5. The plasma gas flow: a change of two graduations on the rotameter or 2% was used.

6. The ash percentage in the peat feed: this was determined outside McGill, so the change of 1% used was arbitrary.

7. The ash percentage in the residue: the change of 2% was used to reflect the larger values of ash in the residues, in comparison to the peat.

The results show that with a small peat flow (experiment 1), the peat mass affects the carbon conversion the most. A decrease in feed of one half of a graduated cylinder of peat resulted in an increase of carbon in the effluent of almost 27% in the mass balance calculations. The peat

Table XII
Mass Balance Sensitivity: Low Peat Flow[a]

Variable Investigated	Old Value of Variable	New Value of Variable	Change in Carbon Balance Conversion (%)
Nitrogen Carrier Gas Rotameter Reading (%)	150	160 140	3.08 -3.07
Nitrogen in Product Gas (volume %)	17.0	19.0 15.0	-1.59 1.72
Peat Mass Fed to Reactor (grams)	208.2	258.2 158.2	-11.97 26.56
Time of Peat Feed (seconds)	225	230 220	0.80 -0.80
Hydrogen Plasma Gas Rotameter Reading (%)	31	33 29	0 0
Peat Ash (mass %)	5.16	6.16 4.16	2.76 -2.75
Product Residue Ash (mass %)	25.47	27.47 23.47	-0.71 0.80

(a) the actual value of carbon balance conversion with the experimental values of variables is 2.39%, with an average conversion of 78.71%.

Table XIII
Mass Balance Sensitivity: High Peat Flow[(a)]

Variable Investigated	Old Value of Variable	New Value of Variable	Change in Carbon Balance Conversion (%)
Nitrogen Carrier Gas Rotameter Reading (%)	150	160	3.45
		140	-3.45
Nitrogen in Product Gas (volume %)	8.5	10.5	-15.22
		6.5	31.68
Peat Mass Fed to Reactor (grams)	683.6	733.6	-3.33
		633.6	3.68
Time of Peat Feed (seconds)	102	107	2.40
		97	-2.40
Hydrogen Plasma Gas Rotameter Reading (%)	31	33	0
		29	0
Peat Ash (mass %)	5.16	6.16	9.97
		4.16	-9.96
Product Residue Ash (mass %)	10.48	12.48	-8.24
		8.48	12.13

(a) the actual value of carbon balance conversion with the experimental values of variables is -5.73%, with an average conversion of 36.14%.

mass fed to the reactor was fairly accurate, although changes in peat density with respect to height in the graduated cylinder and peat hopper might have affected values slightly.

A decrease in the peat mass fed to the reactor, then, resulted in an increase in outlet carbon over inlet carbon. This can be explained mathematically. A change in peat flow does not alter the nitrogen fed to the system very much, since the peat contains only 2.24% of this element. Peat contains large quantities of carbon, and this causes a significant change in the carbon feed. The nearly unchanged nitrogen tracer calculates almost the same carbon mass out from the system with decreased peat feed, but the carbon into the system has decreased significantly.

With a higher peat feed rate, the mass balances become less sensitive to peat mass, and more sensitive to the ash tracer in the solids and the nitrogen percentage in the product gas. The ash in the peat and residue become important parameters. A change of 1% in peat ash results in a change of 10% in the carbon balance, and a decrease of 2% in the residue ash results in an increase of about 12% in the carbon balance. This reflects the importance of obtaining a representative solids sample. If the sample collected from the experiment was not a reasonable representation of the total solids, or if a non-homogeneous sample was chosen for analysis, the balances would be inaccurate. An accurate gas analysis is necessary, because a change of 2% in the nitrogen volume percent results in a change of almost 32% in the carbon balance conversion.

The change in the mass balances with the change in the ash contents can be explained mathematically. An increase in the percent of ash in the peat results in a greater mass of ash going into the reactor, and therefore coming out. Since ash is a tracer, this results in a calculated increase of carbon mass out of the reactor.

The change in the mass balance due to different nitrogen volume percentages in the product gas can also be explained. The amount of nitrogen in the product gas is small relative to the sum of the carbon-containing gas components. An increase in nitrogen is magnified in the mass balances, because nitrogen is the tracer used to calculate the absolute masses of all the other gases.

In conclusion, this analysis showed that the mass balances were most sensitive to:

1. the mass of peat fed to the reactor or;
2. the ash content in the solids and the nitrogen in the gas product.

The rate of peat feed determined which of these two was the most important factor. Small changes in the values of these parameters altered the conversion of the mass balances significantly. To have carbon balances consistent to within 15% is a fairly stringent criterion for this system.

Analysis of Gas Compositions

Prior to the analysis of the gas compositions, a qualitative discussion of the major reactions occurring in the system is made. Leppamaki et al. (1979) summarize the ten most significant reactions which occur in carbon conversion, given in Table XIV. The heats of reaction are also provided.

The first transformation to occur in the system is pyrolysis. This is a physical transformation involving the evolution of volatiles from the peat, and not represented in the table. The first reaction represents the breaking-up of the volatiles from pyrolysis, into smaller molecules. Reactions 2,3, and 4 involve oxygen. These are exothermic reactions, and would be referred to as "oxidation by combustion" reactions using the previously described classifications. By minimizing oxygen and maintaining high temperatures in the system, these three reactions do not occur to any great extent. Reaction 5 is the desired reaction for the experiments. By providing a large excess of steam and high temperatures, the equilibrium should shift to the right. Reaction 6 is the "gas-shift" reaction. The production of carbon dioxide in the product gas is due primarily to this. Increasing temperature results in more reaction, and therefore less steam is present in the system. Also, reaction 7 is favoured more, resulting in a decrease of carbon dioxide. Reactions 8,9, and 10 are responsible for small amounts of methane forming at lower temperatures. The gas composition data in Appendix II show that methane rarely forms with the

Table XIV
Important Reactions in the Experimental System(b)

Reaction Number	Reaction(a)	H_{298} (kJ/gmole)
1	volatile matter $\rightleftharpoons CH_4 + C$	slightly exothermic
2	$C + 1/2\, O_2 \rightleftharpoons CO$	-111
3	$CO + 1/2\, O_2 \rightleftharpoons CO_2$	-254
4	$H_2 + 1/2\, O_2 \rightleftharpoons H_2O$	-242
5	$C + H_2O \rightleftharpoons CO + H_2$	131
6	$CO + H_2O \rightleftharpoons CO_2 + H_2$	-41
7	$C + CO_2 \rightleftharpoons 2\, CO$	172
8	$C + 2\, H_2 \rightleftharpoons CH_4$	-75
9	$CO + 3\, H_2 \rightleftharpoons CH_4 + H_2O$	-206
10	$CO_2 + 4\, H_2 \rightleftharpoons CH_4 + 2\, H_2O$	-165

(a) all the carbon in these reactions is graphite, and all the H_2O is in a gaseous state

(b) Leppamaki, E., Asplund, D. and Ekman, E., "Gasification of Peat: A Literature Review", Technical Research Centre of Finland (1976) reaction conditions in this work.

Innumerable reactions occur simultaneously in the system. The best way to represent the product mixture is by minimizing Gibbs free energy. The F*A*C*T program was used for these calculations. It was discussed previously how this type of analysis represents gas mixtures quite well, but not solids conversions. The present analysis of the gas mixtures is done in two ways:

1. Since gas compositions are represented quite well with F*A*C*T, a product-gas mixture is considered without the presence of any solids. With this situation, the gas composition is a function of temperature, but not of the carbon-to-steam molar ratio. The "equilibrium" temperature for each gas in a given mixture is assessed.

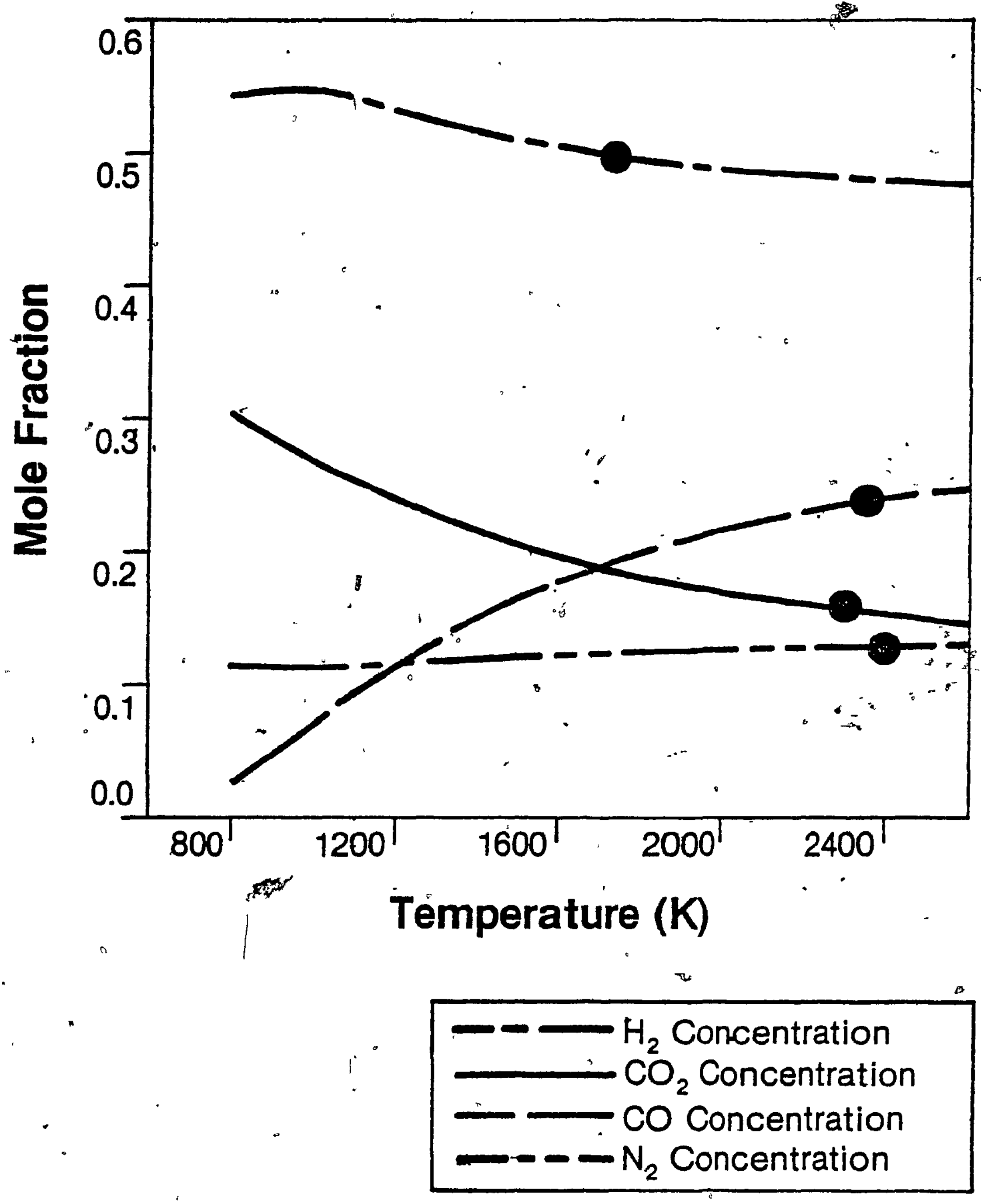
2. The gas composition is calculated when taking into account the complete mass input to the system. The carbon-to-steam molar ratio is now a parameter as well as temperature. The trends with changing conditions are explored, and these compared to experimental data.

The results of the first analysis are presented in Figure 18. The gas composition in experiment 6 was determined, including the steam which affects the equilibrium reactions dramatically. Steam accounted for just over 65% of the product gas by volume. The dry product gas equilibrium composition versus temperature is shown in Figure 18. The experimental results are represented by the circles on the curves. The carbon dioxide, carbon monoxide, and nitrogen mole fractions all have equilibrium

FIGURE 18:

EXPERIMENT 6 GAS MIXTURE AT

EQUILIBRIUM VERSUS TEMPERATURE



Mole Fraction
0.6
0.5
0.4
0.3
0.2
0.1
0.0
800
1200
1600
2000
2400
Temperature (K)
H_2 Concentration
CO_2 Concentration
CO Concentration
N_2 Concentration

temperatures between 2300 K and 2400 K. The hydrogen equilibrium temperature is just below 1800 K. These high equilibrium temperatures for the gas composition were unexpected. They are explained, in part, by the "true" temperatures being higher than the thermocouple measurements.

In the second analysis, the gas compositions resulting from changes in the carbon-to-steam molar ratio and temperature, and comparison with experimental results, are considered. The trends, rather than the absolute values of the gas compositions are examined because:

1. the equilibrium temperatures of the gas have been shown to be much higher than the experimentally measured temperatures and;
2. the carbon conversion is complete at equilibrium but not with the experimental conditions.

The results of the analysis are given in Figures 19 to 26:

1. Figures 19 to 22 show the change of mole fractions in the gas phase with carbon-to-steam molar ratio. The temperature was maintained at a constant value of 1325 K for all the equilibrium calculations, which are represented by the smooth curves. This temperature was chosen because it is the mean of the temperatures to which the data are compared. Experiments 1, 2, 5, 7, 8, and 11 have temperatures between 1300 K and 1338 K.

2. Figures 23 to 26 show the change of mole fractions of the different gases with temperature. The carbon-to-steam molar ratio was

FIGURE 19:

CARBON DIOXIDE MOLE FRACTION VERSUS CARBON/STEAM MOLAR RATIO, INCLUDING SOME EXPERIMENTAL RESULTS

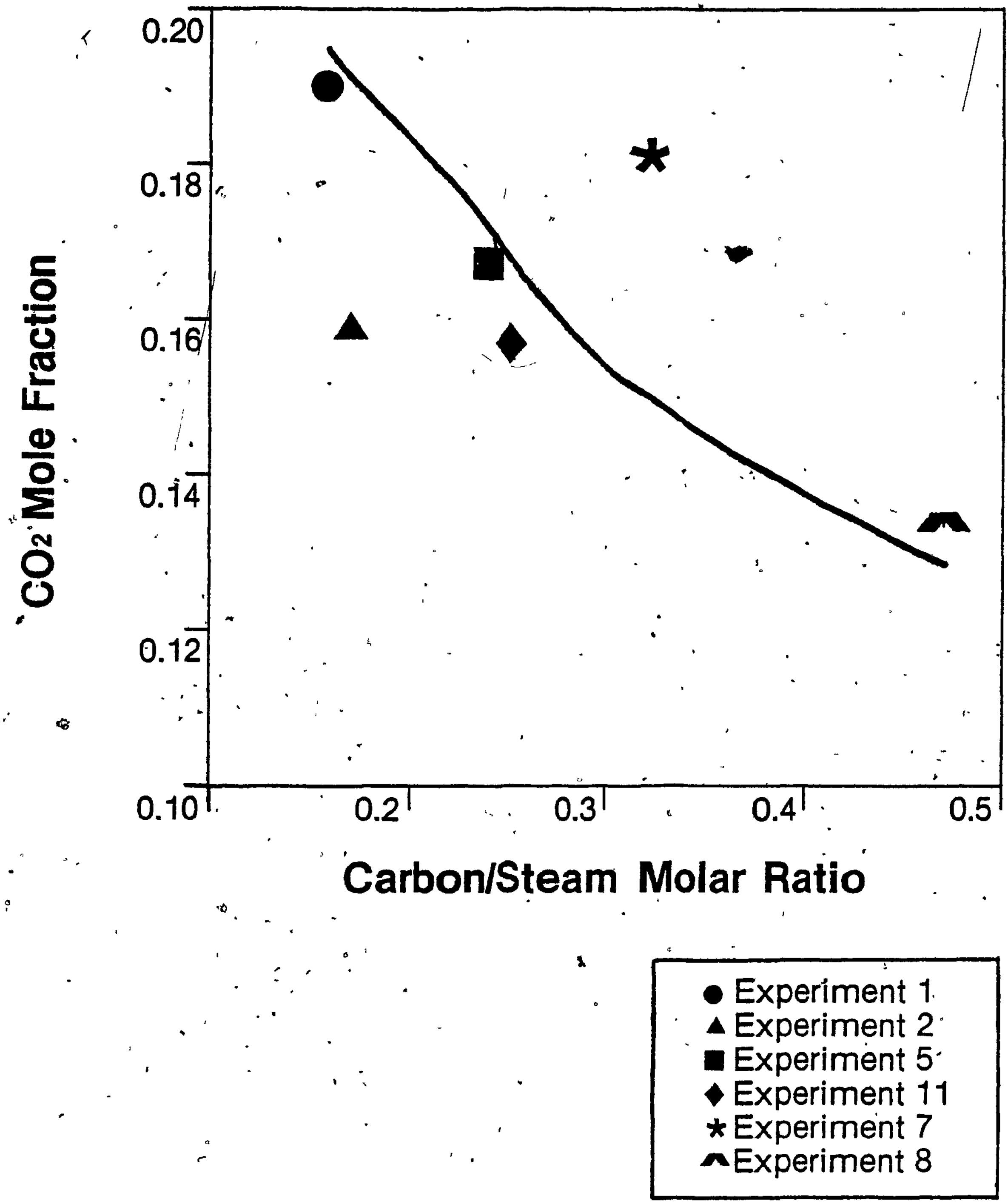

0.20
0.18
0.16
0.14
0.12
0.10
0.2
0.3
0.4
0.5
CO_2 Mole Fraction
Carbon/Steam Molar Ratio
● Experiment 1
▲ Experiment 2
■ Experiment 5
◆ Experiment 11
* Experiment 7
^ Experiment 8

FIGURE 20:

CARBON MONOXIDE MOLE FRACTION VERSUS CARBON/STEAM MOLAR FRACTION, INCLUDING SOME EXPERIMENTAL RESULTS

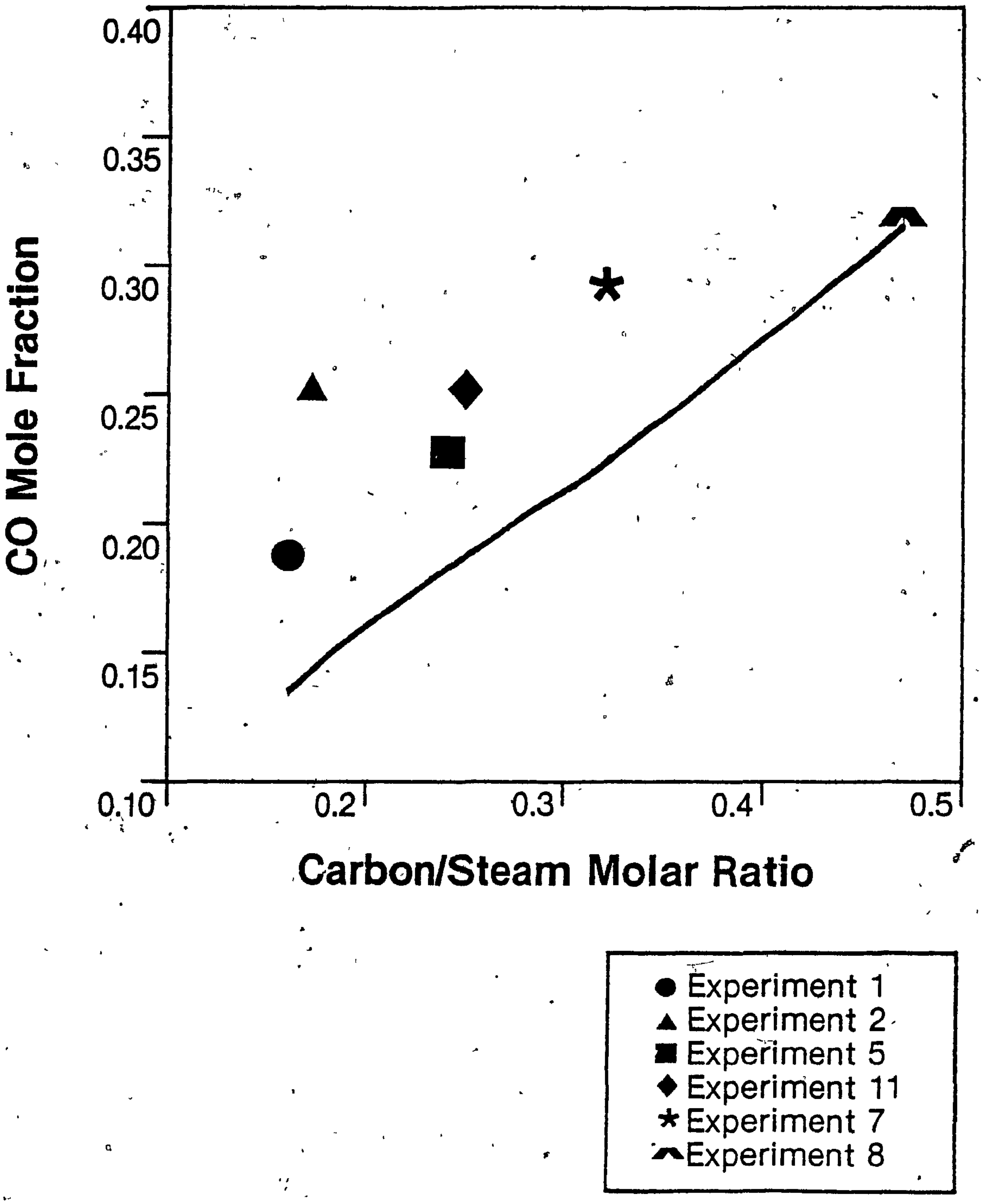

CO Mole Fraction
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.2
0.3
0.4
0.5
Carbon/Steam Molar Ratio
● Experiment 1
▲ Experiment 2
■ Experiment 5
◆ Experiment 11
* Experiment 7
Experiment 8

FIGURE 21:

HYDROGEN MOLE FRACTION VERSUS CARBON/STEAM MOLAR RATIO, INCLUDING SOME EXPERIMENTAL RESULTS

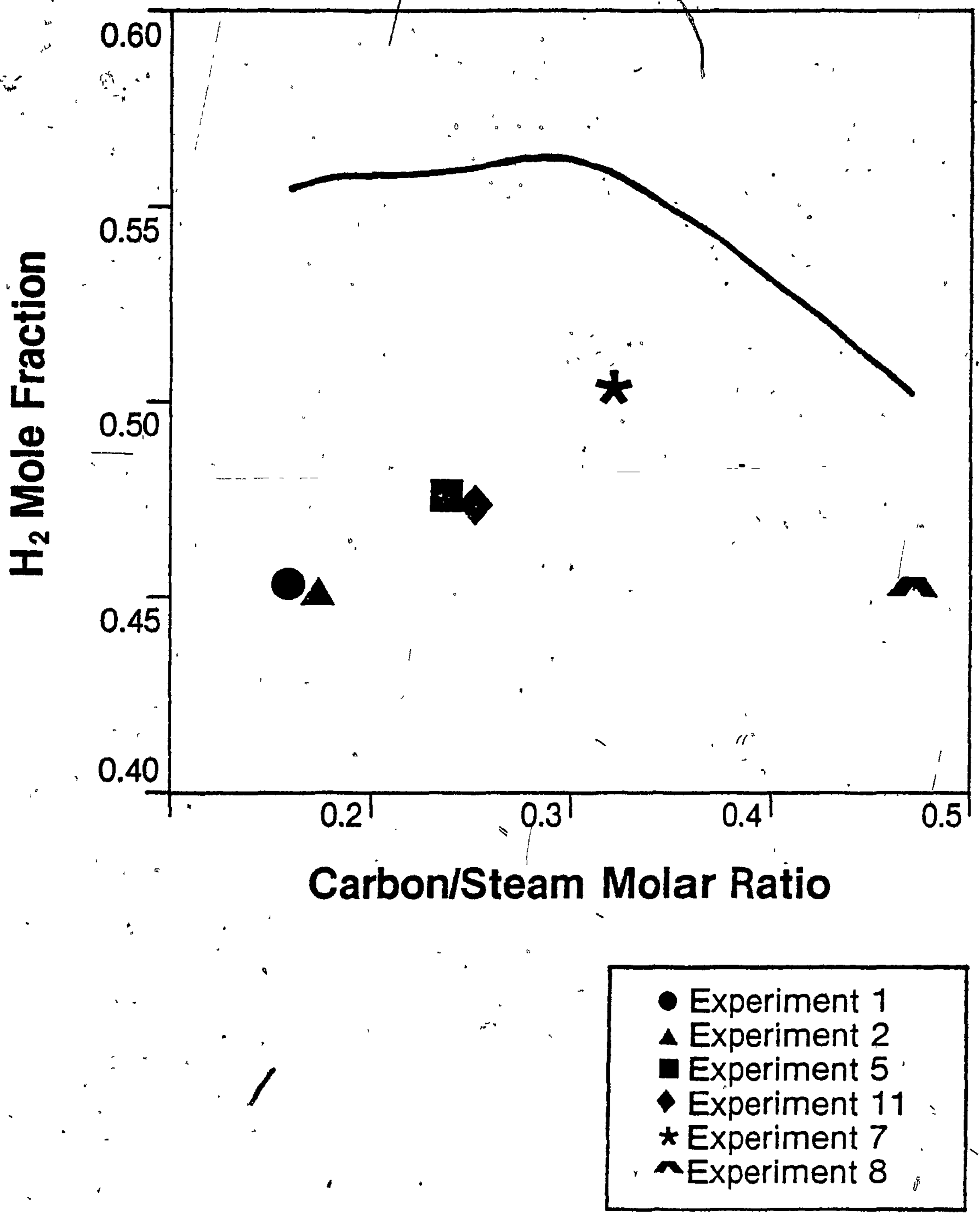

H$_2$ Mole Fraction
0.60
0.55
0.50
0.45
0.40
0.2
0.3
0.4
0.5
Carbon/Steam Molar Ratio
● Experiment 1
▲ Experiment 2
■ Experiment 5
◆ Experiment 11
* Experiment 7
^ Experiment 8

FIGURE 22:

NITROGEN MOLE FRACTION VERSUS
CARBON/STEAM MOLAR RATIO, INCLUDING
SOME EXPERIMENTAL RESULTS

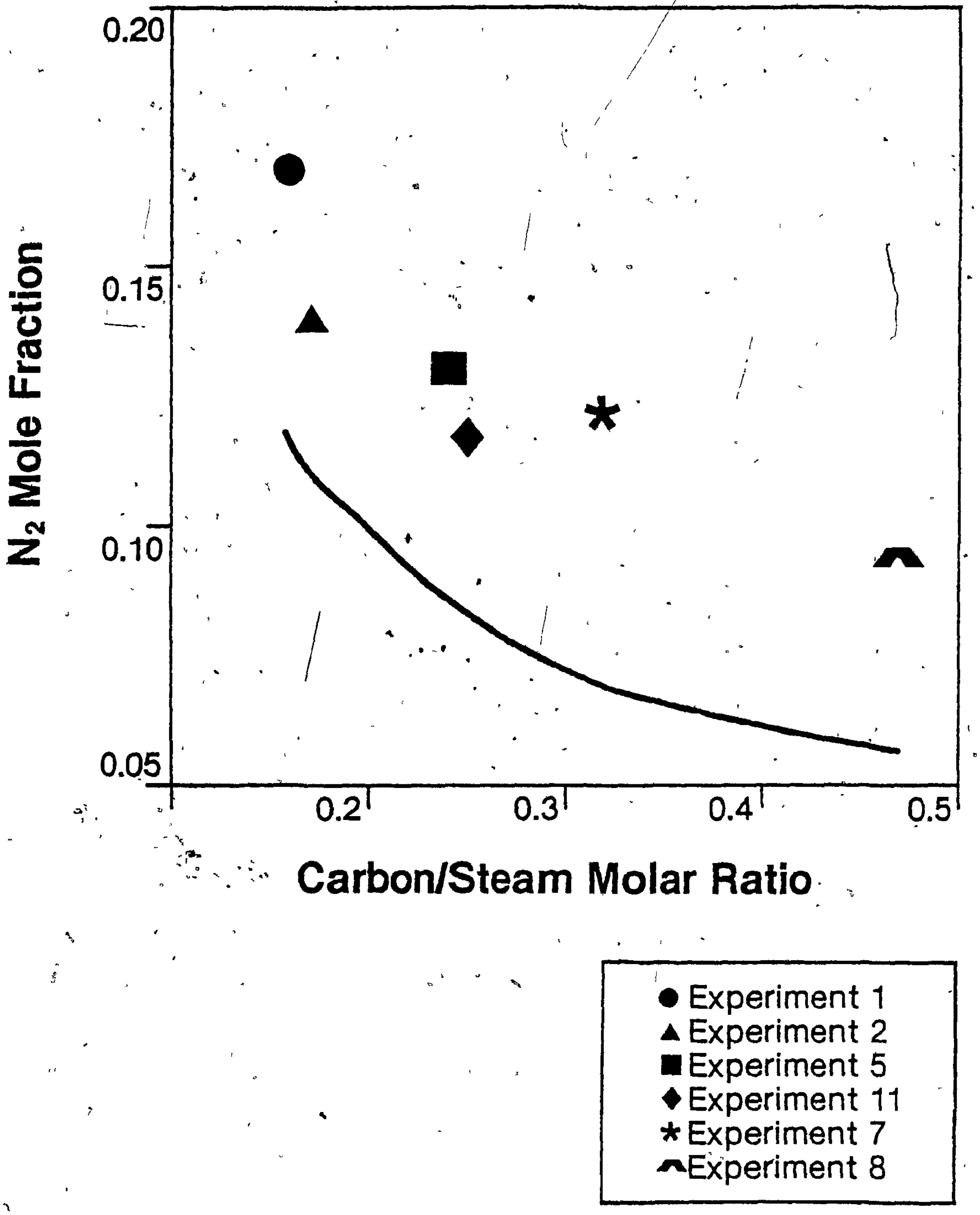

0.20
0.15
0.10
0.05
N_2 Mole Fraction
0.2
0.3
0.4
0.5
Carbon/Steam Molar Ratio
● Experiment 1
▲ Experiment 2
■ Experiment 5
◆ Experiment 11
* Experiment 7
^ Experiment 8

FIGURE 23:

CARBON DIOXIDE MOLE FRACTION VERSUS
TEMPERATURE, INCLUDING SOME
EXPERIMENTAL RESULTS

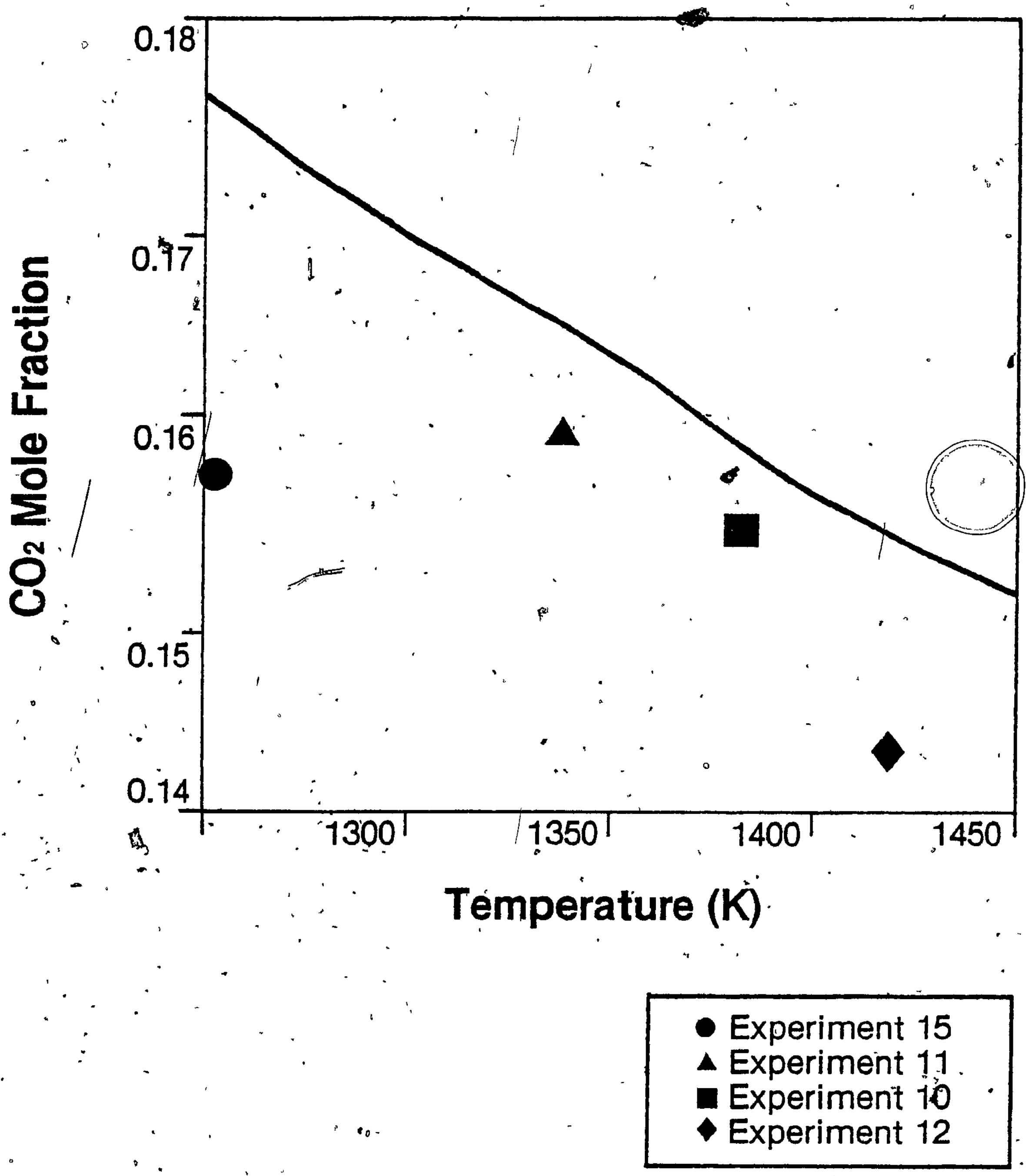
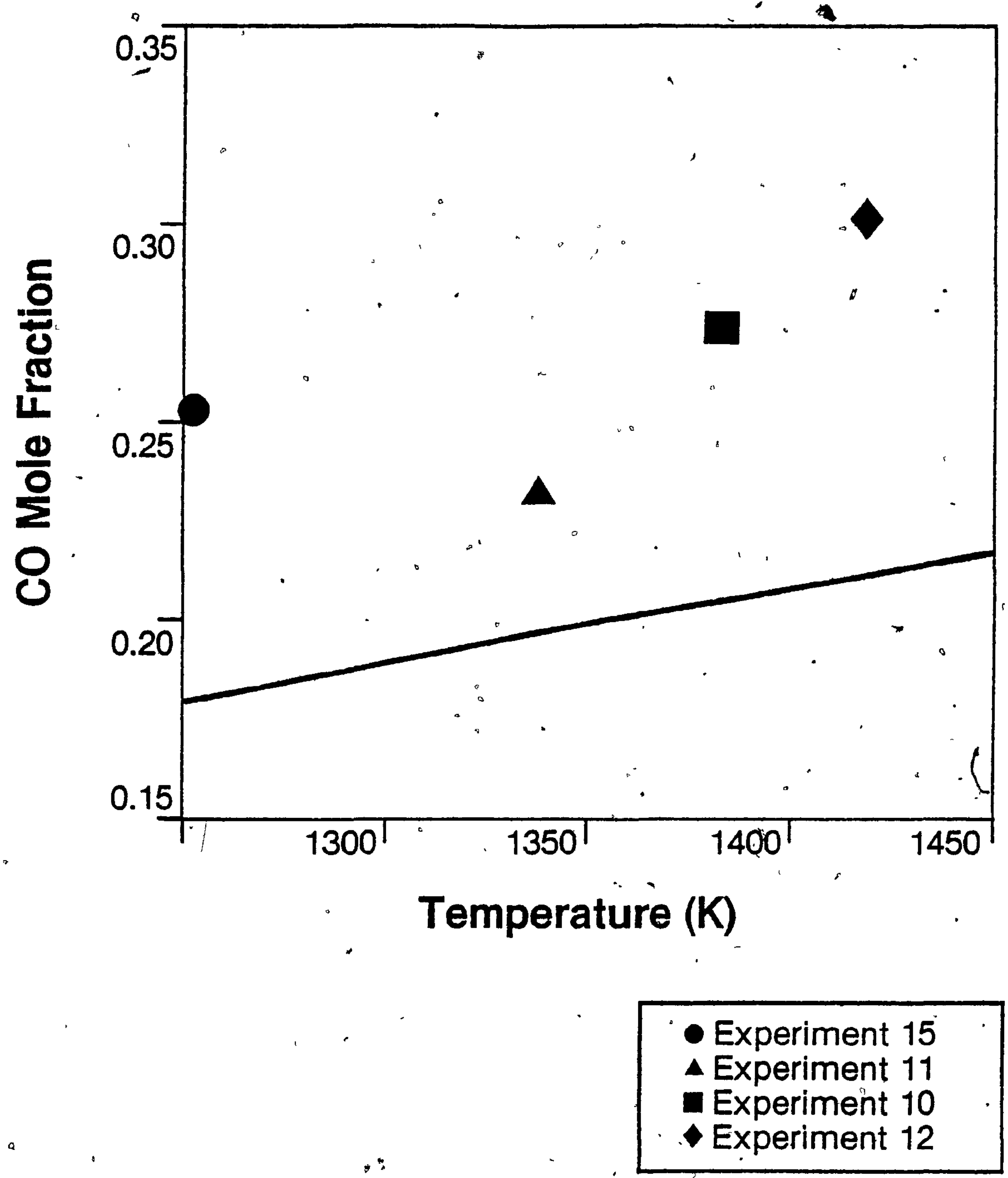

0.18
0.17
0.16
0.15
0.14
CO₂ Mole Fraction
1300
1350
1400
1450
Temperature (K)
● Experiment 15
▲ Experiment 11
■ Experiment 10
◆ Experiment 12

FIGURE 24:

CARBON MONOXIDE MOLE FRACTION VERSUS
TEMPERATURE, INCLUDING SOME
EXPERIMENTAL RESULTS



CO Mole Fraction
0.35
0.30
0.25
0.20
0.15
1300
1350
1400
1450
Temperature (K)
● Experiment 15
▲ Experiment 11
■ Experiment 10
◆ Experiment 12

FIGURE 25:

HYDROGEN MOLE FRACTION VERSUS TEMPERATURE, INCLUDING SOME EXPERIMENTAL RESULTS

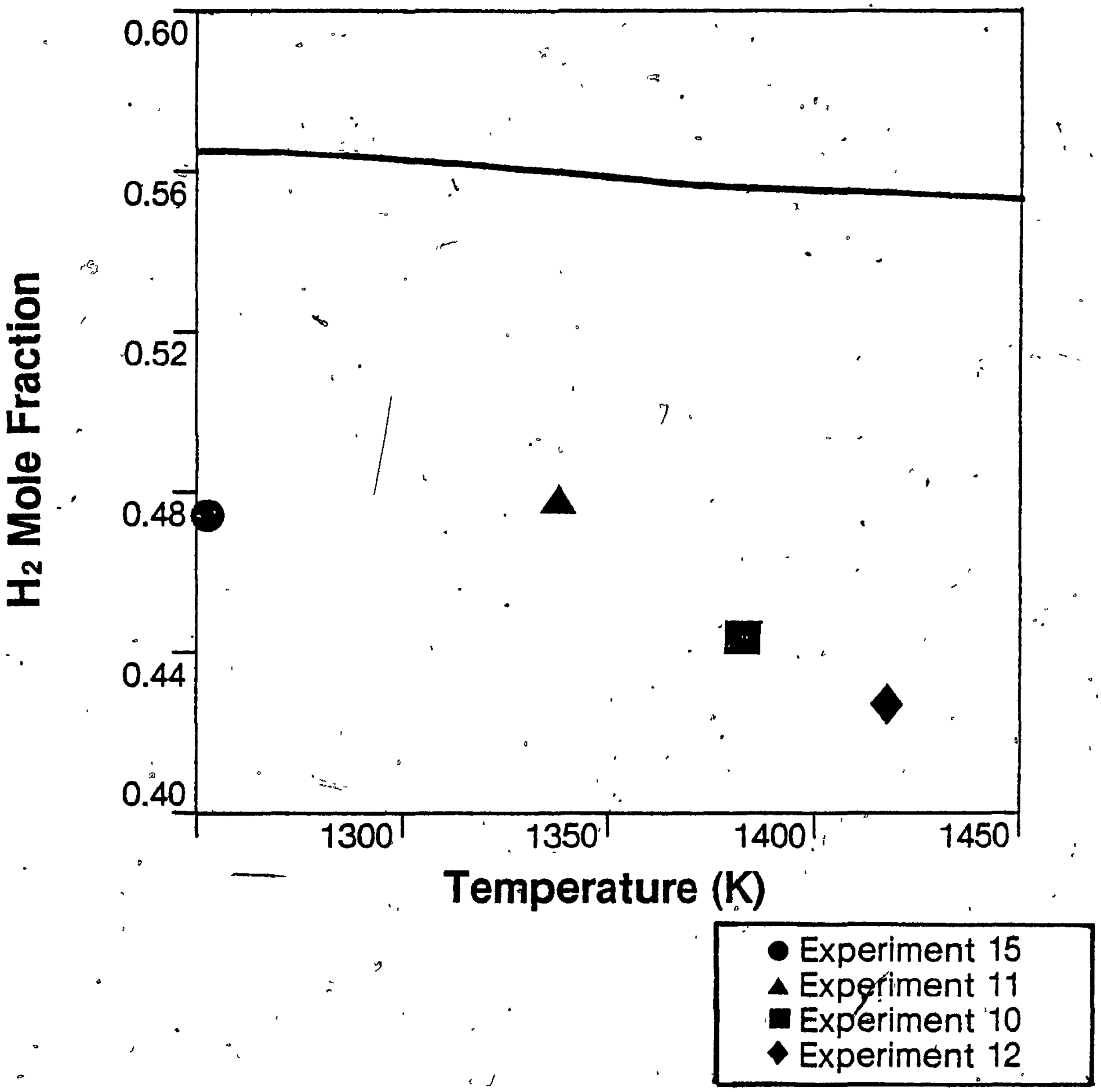
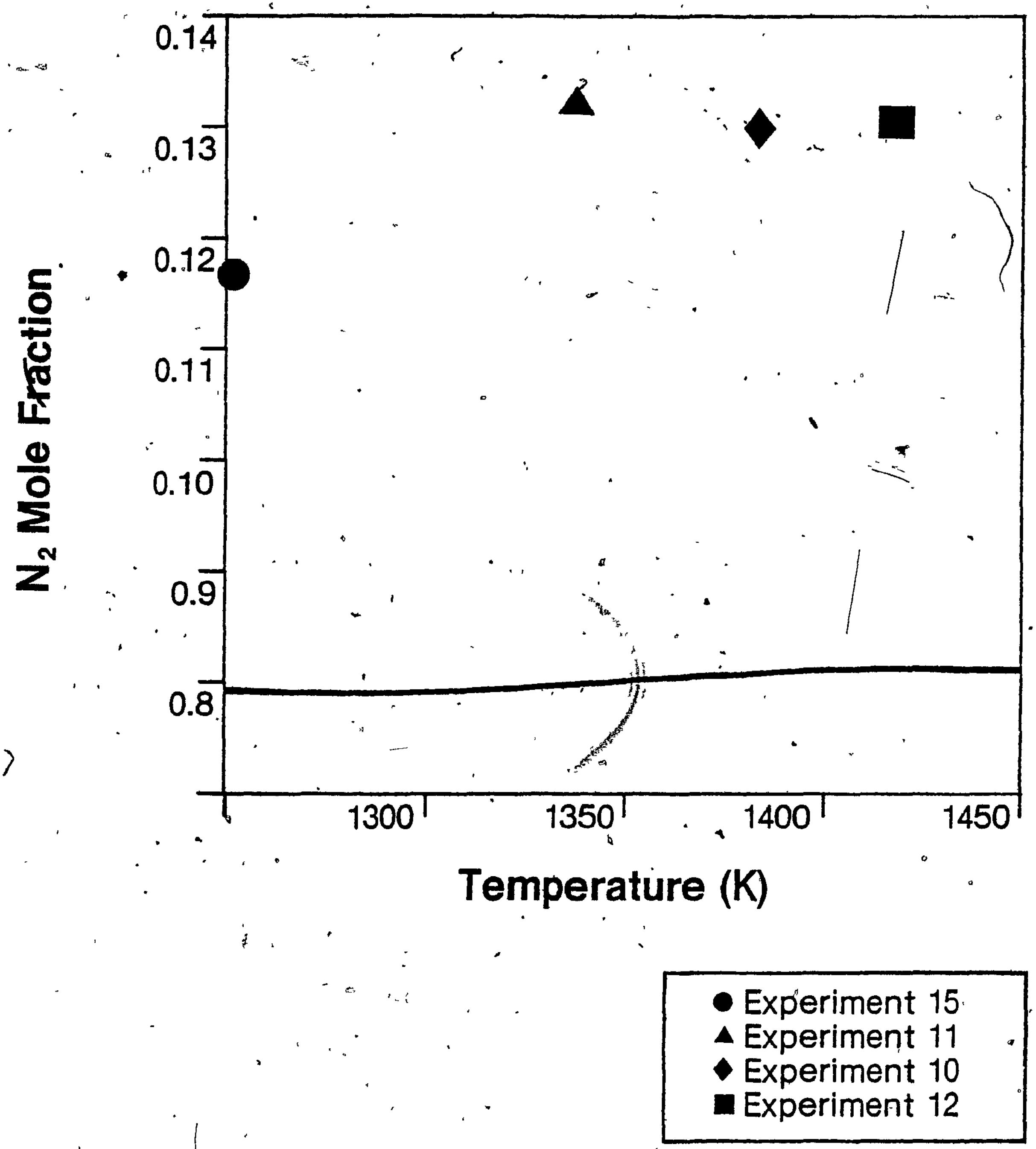

0.60
0.56
0.52
0.48
0.44
0.40
H2 Mole Fraction
1300
1350
1400
1450
Temperature (K)
● Experiment 15
▲ Experiment 11
■ Experiment 10
◆ Experiment 12

FIGURE 26:

NITROGEN MOLE FRACTION VERSUS TEMPERATURE,

INCLUDING SOME EXPERIMENTAL RESULTS



N_2 Mole Fraction
0.14
0.13
0.12
0.11
0.10
0.9
0.8
1300
1350
1400
1450
Temperature (K)
● Experiment 15
▲ Experiment 11
◆ Experiment 10
■ Experiment 12

maintained constant at 0.26 for all the equilibrium calculations. This value is the mean of experiments 10, 11, 12, and 15. Their ratios were between 0.25 and 0.27. The equilibrium values are shown by the curve, and the experimental values by the symbols.

Figure 19 gives the mole fraction of carbon dioxide versus the molar ratio. The experimental points, while they are not on the curve, follow the expected trend. The carbon dioxide mole fraction decreases with an increasing molar ratio. Figure 20 shows the increase of carbon monoxide with an increasing molar ratio. The experimental points are all above the curve, and again follow the trend. Figure 21 shows an initially constant hydrogen mole fraction, followed by a drop at higher temperatures. The experimental data show an increase in hydrogen mole fraction followed by the expected decrease. The experimental data in the increasing region show some consistency. There are two experimental points in the increasing region almost superimposed, at two molar ratios. The increasing trend could be due to reaction 5 (previously discussed) not occurring under experimental conditions to the degree predicted by equilibrium calculations.

An expected decrease in the nitrogen mole fraction with increased molar ratio is observed in Figure 22. This effect is explained by a greater peat feed rate resulting in the production of more gas product, with the nitrogen gas flow rate remaining constant. The experimental points are above the equilibrium ones due to incomplete conversion.

Figure 23 gives the mole fraction of carbon dioxide versus temperature. The expected decrease with increased temperature is observed, excluding the experiment 15 data point. Figure 24 shows data points following the trend of increasing carbon monoxide with increasing temperature except in experiment 15. In experiment 15, the bottom half of the reactor was insulated. Experimental results are produced that occur for higher reaction temperatures for this run.

Figure 25 shows that with increasing temperature, a downwards trend of hydrogen mole fraction occurs. A steady fraction is predicted using equilibrium calculations. This is explained by the gasification reaction between carbon and steam still occurring in the experimental case, resulting in increased carbon-containing products. Again, experiment 15 is anomolous. Figure 26 shows the nitrogen mole fraction fairly constant as predicted by thermodynamic equilibrium, although about 5% higher.

In conclusion, the gas compositions reflect much higher equilibrium temperatures than the measured temperatures. The trends for equilibrium calculations were followed by the experimental results. The differences may be explained in terms of incomplete carbon conversion and high equilibrium gas temperatures. Note that the "mole fraction" axes in the graphs are expanded, magnifying the differences between the equilibrium predictions and experimental points.

Analysis of Solids Compositions

Trends are expected in the rate of reaction of the different elements in the peat. Certain species should evolve preferentially under different conditions.

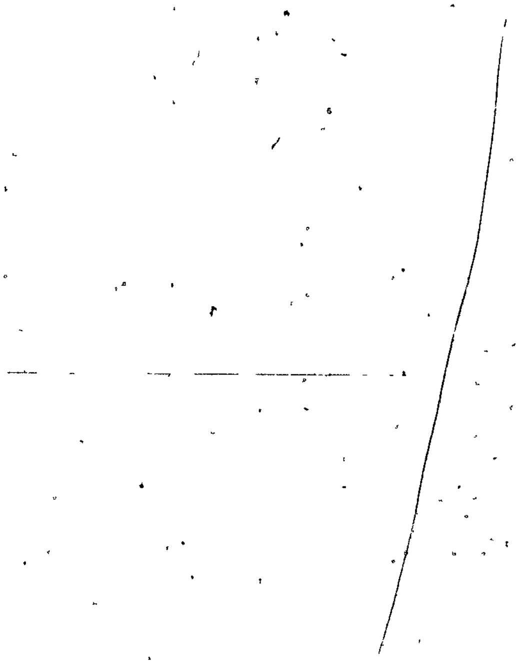
The results from the analysis are given in Figures 27 to 31. The mass percentages of the different species in the residue are plotted against average conversion. The data points from all fourteen experiments are included, and the least squares line is marked.

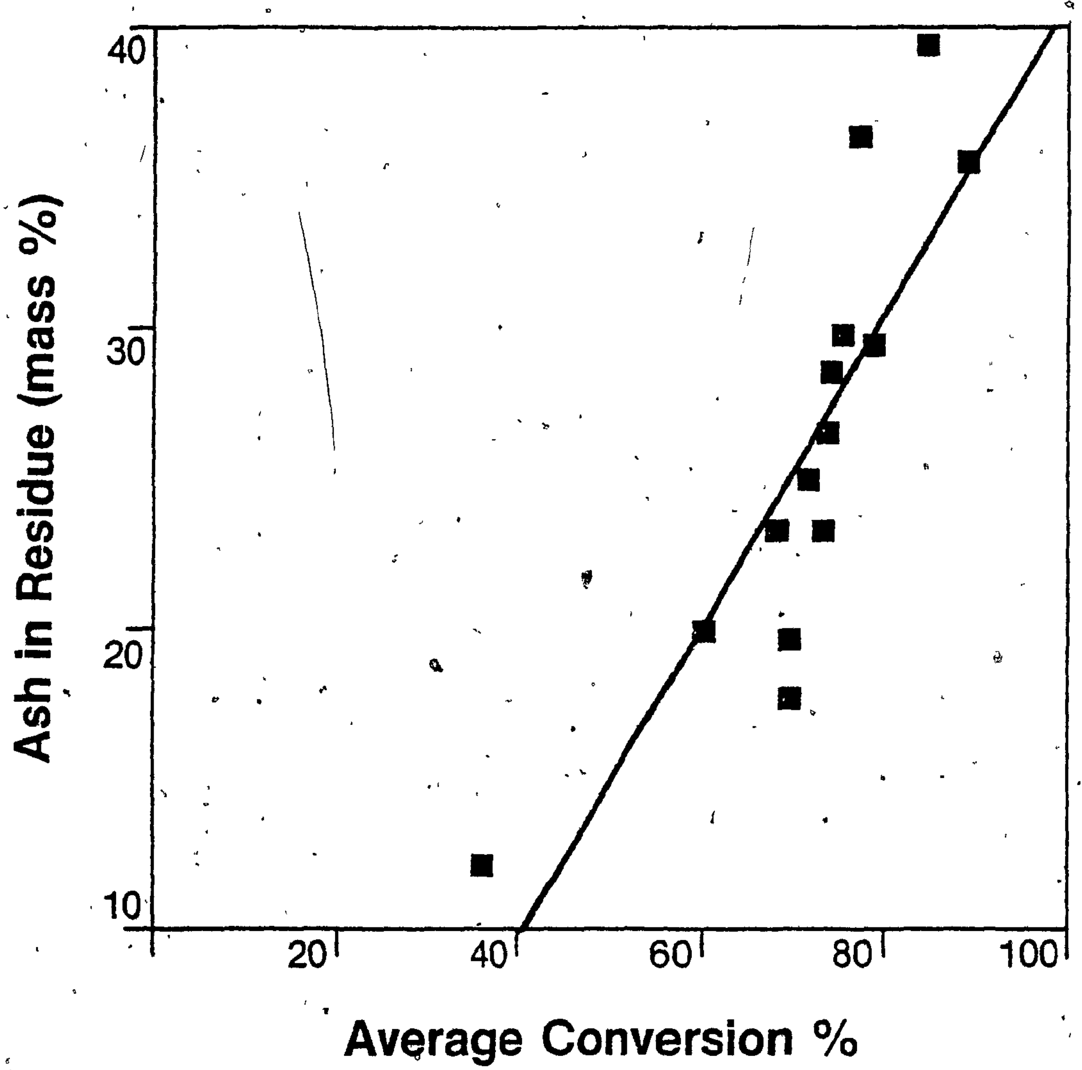
Figure 27 shows the mass percentage of ash in the product versus average conversion. An increasing conversion results in more ash in the product. For 100% conversion, the product would be 100% ash. If all the other elements in the peat reacted equally, their least squares lines would be slightly downwards sloping. This would indicate a constant proportion of the elements relative to each other and due to the increase in ash, the total mass percentage would decrease slightly.

The expected trend is observed in each case. The slopes for carbon, oxygen, hydrogen, and nitrogen mass percentages in the residue all have negative values. The magnitude of the slopes are about 1:1:20:30 respectively. These are the approximate ratios of the elements in the unreacted peat, with hydrogen and oxygen reacting somewhat preferentially.

FIGURE 27:

ASH IN RESIDUE VERSUS AVERAGE CONVERSION





Ash in Residue (mass %)
40
30
20
10
20
40
60
80
100
Average Conversion %

FIGURE 28:

CARBON IN RESIDUE VERSUS AVERAGE CONVERSION

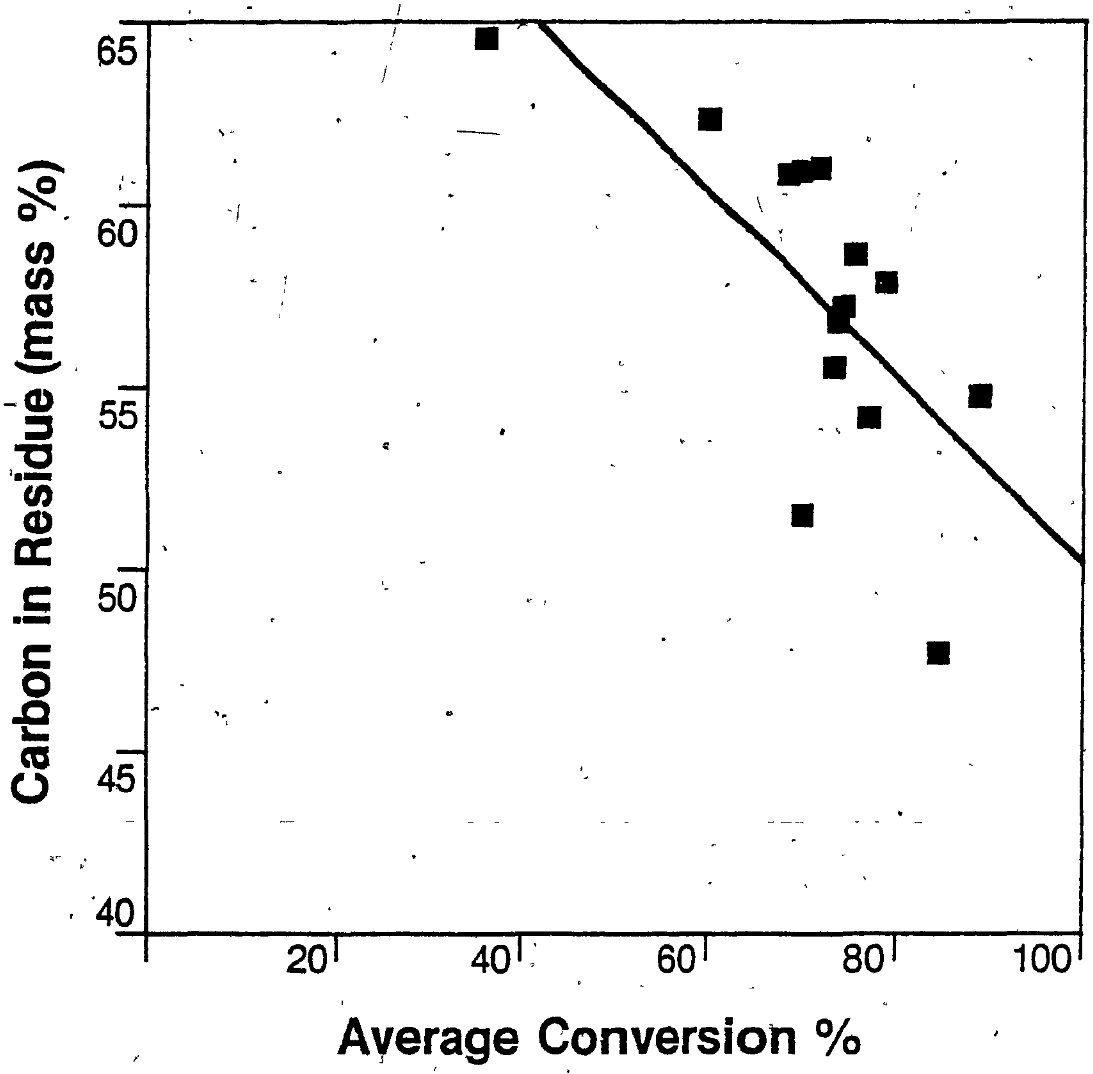

Carbon in Residue (mass %)
65
60
55
50
45
40
20
40
60
80
100
Average Conversion %

FIGURE 29:

OXYGEN IN RESIDUE VERSUS AVERAGE CONVERSION

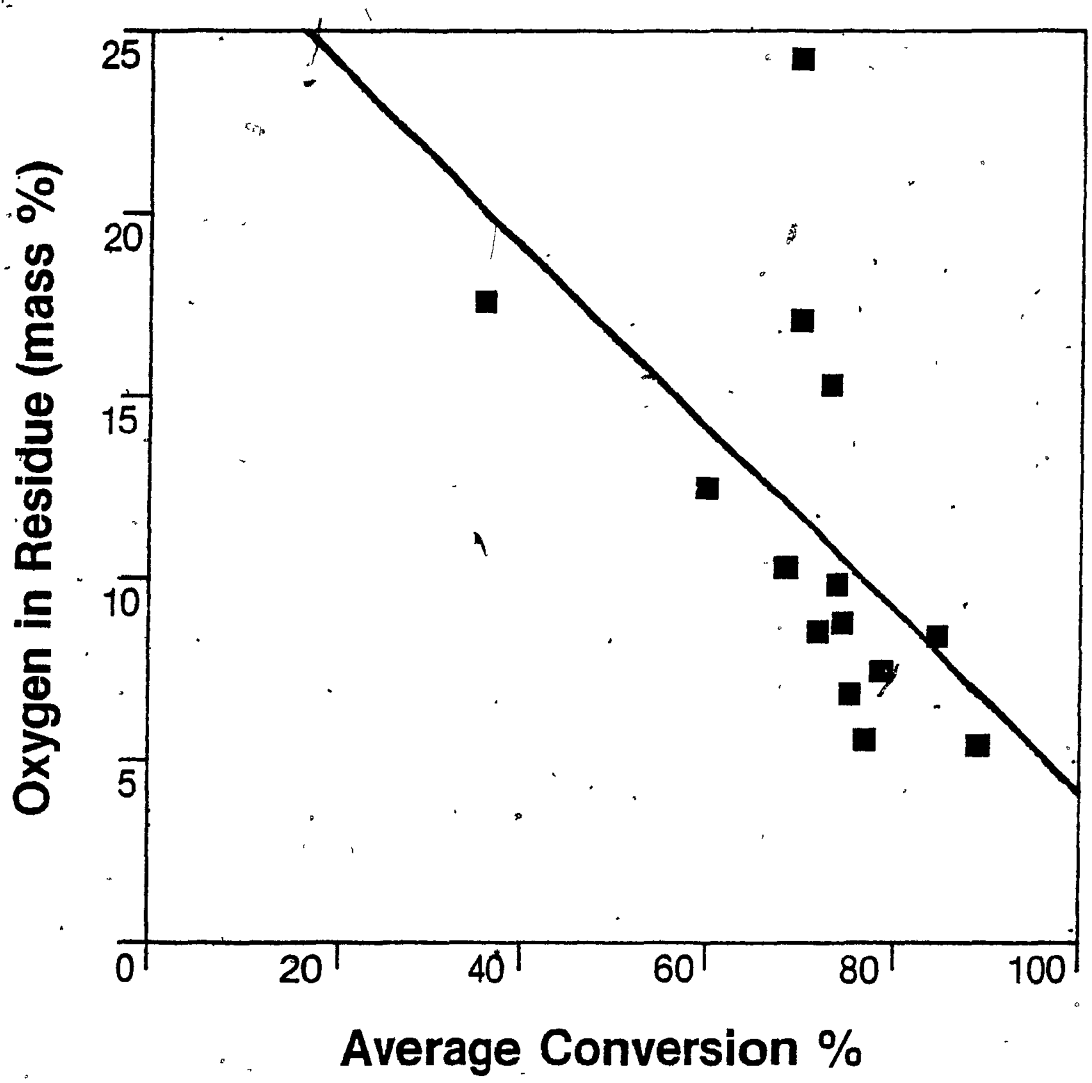

Oxygen in Residue (mass %)
25
20
15
10
5
0
20
40
60
80
100
Average Conversion %

FIGURE 30:

HYDROGEN IN RESIDUE VERSUS AVERAGE CONVERSION

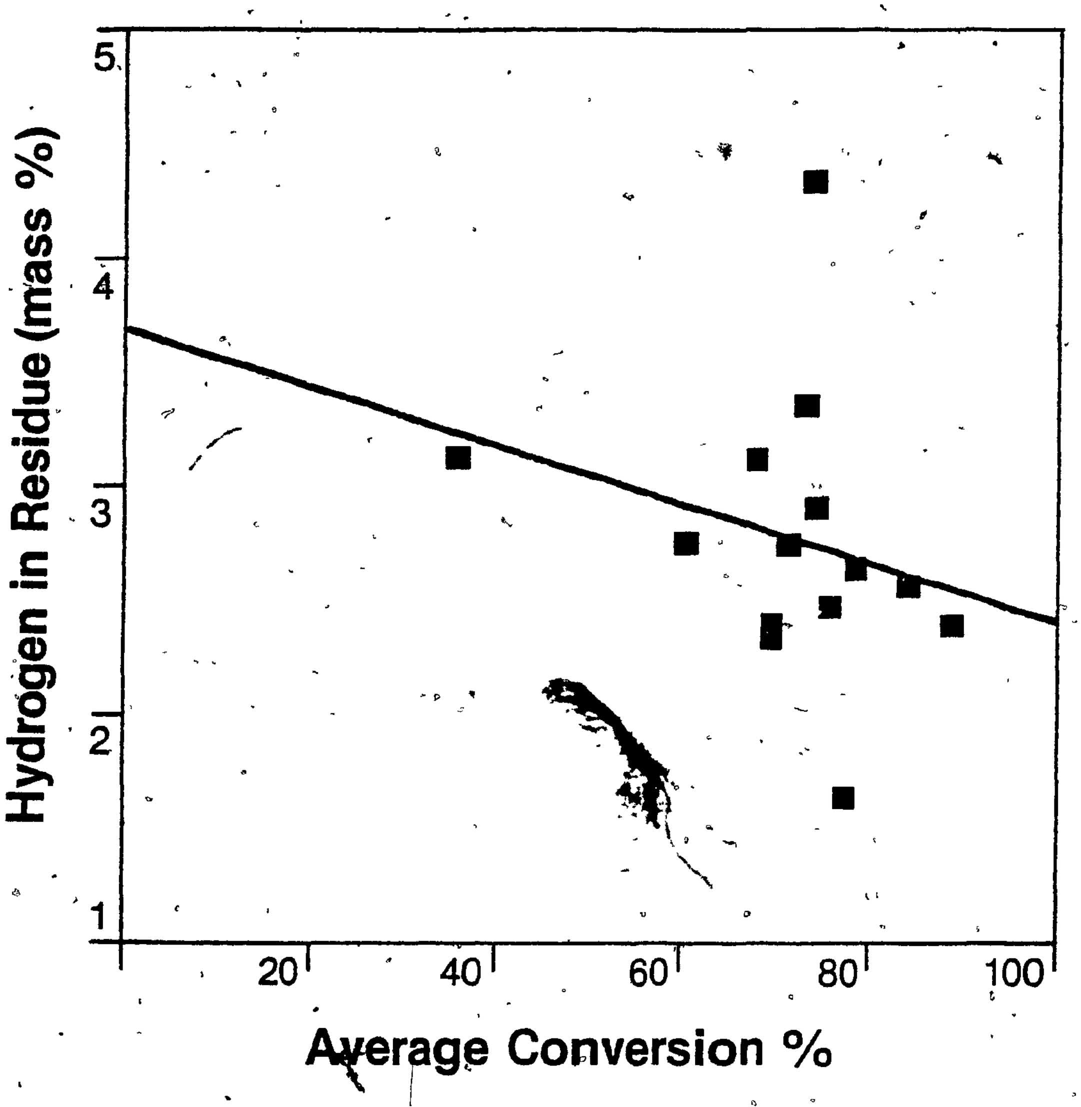
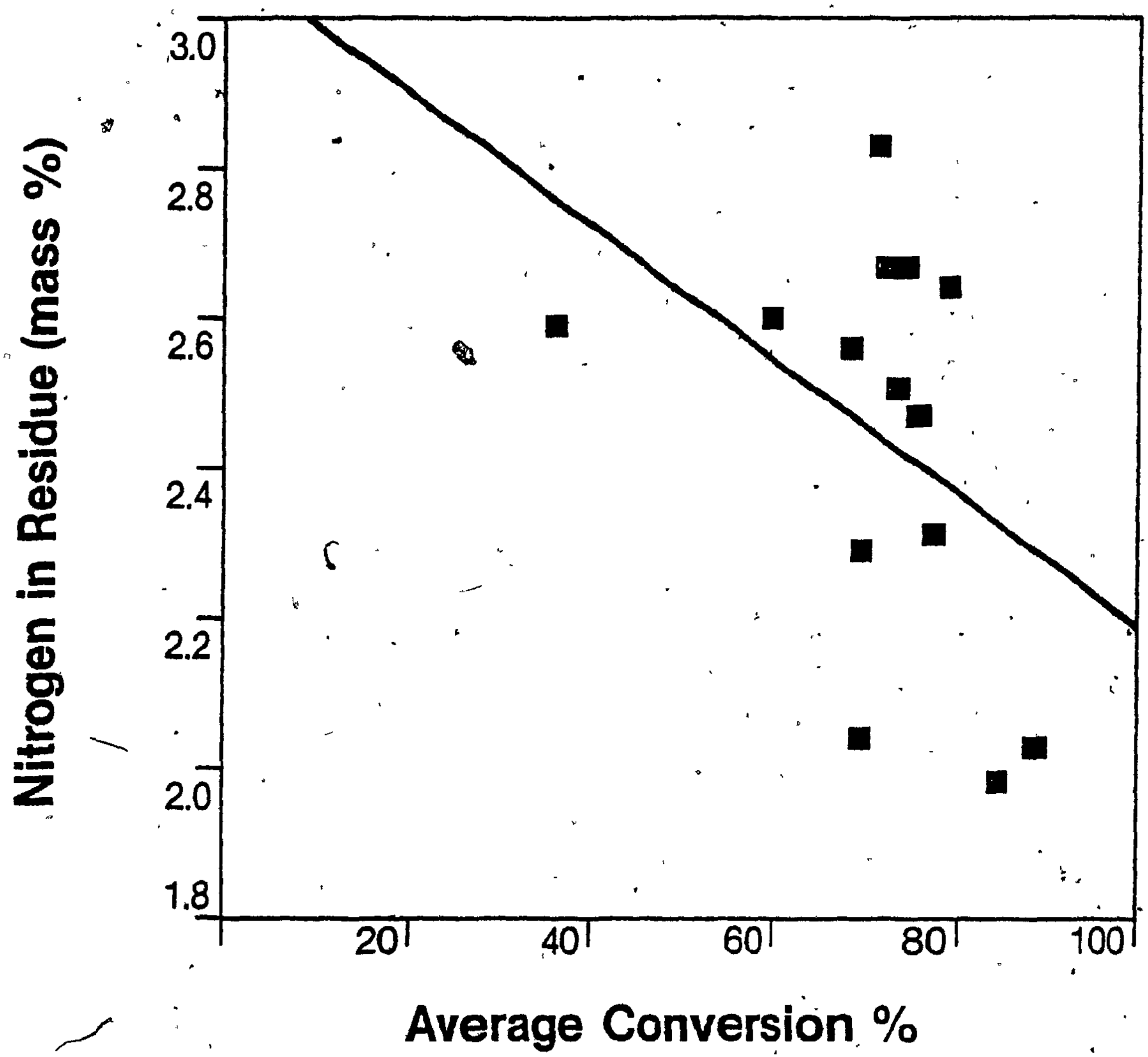

Hydrogen in Residue (mass %)
5
4
3
2
1
20
40
60
80
100
Average Conversion %

FIGURE 31

NITROGEN IN RESIDUE VERSUS AVERAGE CONVERSION


Nitrogen in Residue (mass %)
3.0
2.8
2.6
2.4
2.2
2.0
1.8
20
40
60
80
100
Average Conversion %

This is an "order of magnitude" analysis. It shows trends in the solids data are consistent with what one might expect. The graphs show that significant scatter exists in the data. The "mass percent" scale is expanded, especially in the case of the hydrogen and nitrogen graphs.

Model of Reacting System

A model of the reacting system must incorporate all of the "experimental variables" in combination. These variables, for an exact model, would have to include all the unmeasured experimental parameters previously mentioned: mixing effectiveness, plasma symmetry, pressure fluctuations etc. The model developed contains only the experimental parameters which were measured. The large scatter in the data will affect the fit of the model. Because of the problems in reproducing experimental conditions (previously discussed), only one replicate was possible in the data. This is used to estimate the scatter, but it is possible that only one replicate does not represent the scatter accurately. Two models were generated: a conversion model and a hydrogen-to-carbon monoxide molar ratio model. The models and their important statistical measures of fit are discussed. Then, the models in combination are considered.

The conversion model is based on a first-order reaction system, and developed as in the eight steps shown in Table XV. In the first-order model, the rate of reaction of species "A" (carbon) is directly proportional to the concentration of "A", portrayed in equation 1.

Table XV
Development of the Conversion Model

Equation Number	Equation
1	$-r_A = k\,C_A$
2	$-\frac{dC_A}{dt} = kC_A$
3	$-\int_{C_{AO}}^{C_A} \frac{1}{C_A}\, dC_A = k\int_{0}^{T} dt$
4	$-\ln\left(\frac{C_A}{C_{AO}}\right) = kT$
5	conversion $= Y = 1 - \left(\frac{C_A}{C_{AO}}\right)$
6	$-\frac{\ln(1-Y)}{T} = k$
7	$-\frac{\ln(1-Y)}{T} = a * \left(\frac{s}{c}\right) + b * (T - To) + c$
8	as $s/c \longrightarrow 0$, $Y \longrightarrow 0$ as $T \longrightarrow To$, $Y \longrightarrow 0$ as $\tau \longrightarrow \infty$, $Y \longrightarrow 1$

Equation 2 represents the rate as a function of time, and equation 3 integrates the differential equation between the limits of:

1. initial concentration of "A", and an unknown final concentration at the end of the reaction zone and;
2. time zero and the space time (tau) of the reaction zone.

Equation 4 shows the result of the integration. Representing conversion (Y) as in equation 5, then the model may be cast in the form of equation 6. When the constant of proportionality is a function of the measured experimental variables, equation 7 is the form of the model.

The forms of the experimental variables are discussed in terms of the limits of the equation, shown in equation 8. By considering the reciprocal of the carbon-to-steam molar ratio (S/C), and a temperature difference rather than an absolute temperature (T-To), the model fits at the indicated limits. When no steam is present, no reaction occurs. When the temperature is not above a minimum value, no transformation takes place. Fuchsman (1980) gives this minimum temperature as about 440 K. Lastly, with an infinite residence time, the conversion goes to completion.

The results of fitting the model with experimental data are given in Table XVI. The model reflects the primary variables when they are taken in combination with each other. Several comments may be made concerning the model:

1. The coefficients in both of the variables are positive, as would

Table XVI
Statistics on Conversion Model[(a)]

1. Model: $-\frac{\ln(1-Y)}{T} = 0.23124\left(\frac{S}{C}\right) + 0.00111\ (T-T_o) + 0.06073$

2. ANOVA Table:

Source of Variation	Degrees of Freedom	Sum of Squares
attributable to regression	2	4.890
deviation about regression line	11	1.656
deviation within sets	1	0.442
Total	14	6.988

3. P $(F \leq 0.75)$ = 1.4749
P $(F \leq 0.90)$ = 3.2252
F - value = 2.9347

level of significance = 0.125
for goodness of fit

4. Level of Significance of Variables

Variable	Regression Coefficient	Standard Error	T-Value	Level of Significance
S/C	0.23124	0.08796	2.629	0.022
T–To	0.00111	0.00064	1.736	0.108

(a) method of analysis is described in Himmelblau, D.M., "Process Analysis by Statistical Methods", John Wiley & Sons Incorporated (1970).

be expected. The experimental values of carbon-to-steam, temperature and residence time are also positive. The value of conversion (Y) must be positive, and lie between the values of zero and one.

2. By multiplying the coefficients of the variables by their ranges in the experiments, the effect of the steam-to-carbon molar ratio is over 5.5 times the effect of temperature on the "outcome". The "outcome" is a function of a logarithmic dependence on conversion and an inverse dependence on residence time.

3. If a residence time of 0.7 seconds is assumed, the least squares line gives a conversion of about 4%, assuming no steam plasma and a temperature of To. The intercept from the least squares line is near to the origin, as expected from the theoretical deductions.

The statistics dealing with the goodness of fit for the model are also presented in Table XVI. The ANOVA (ANalysis Of VAriance) table is presented, which breaks-up the total sum of squares of the error. Interpolating between the two F-values (point 3, Table XVI), a level of significance of 0.125 is obtained for the fit of the model to the data. While a value of 0.1 or less would be preferable, this model fits the data much better than other models that were tried. The level of significance is based upon how well the single replicate reflects the scatter in the data. A larger difference in the conversions of experiments 3 and 4 would have resulted in a better (lower) level of significance. The level of significance for the effect of each of the two variables are given. While the steam-to-carbon molar ratio is certainly most significant, both values are acceptable. The temperature is less significant due to the small range over which it varied.

The limits of the model within the experimental region are shown in Table XVII. Using the best case (with all variables maximized), an 85.1% conversion is predicted. A 47.3% conversion is predicted in the worst case. If the model is extended outside the experimental region for one variable at a time, conditions for 90% carbon conversion can be estimated. A temperature of 1635 Celcius (or 1908 K) is predicted. While this temperature can easily be generated by the plasma, stainless steel reactors cannot contain the temperature. Refractory lining would have to be used. A steam-to-carbon molar ratio of 8.605 or a carbon-to-steam molar ratio of 0.116 is predicted. This condition is attainable using the present system. In a commercial system, the quantities of steam being boiled and condensed should be minimized. A residence time of 0.89 seconds is predicted by extending the model for 90% coversion. This is certainly feasible by maintaining the "hot zone" temperatures over a longer reactor length. A multiple torch system and proper insulation would achieve this result. Residence times near to one second are the expected requirement in most gasification systems.

The <u>hydrogen-to-carbon monoxide molar ratio model</u> was obtained by equating the ratio to the experimental variables directly (cast in the same way as in the previous model). The level of significance for the model was good, but the effect of temperature on the model was not

Table XVII
Extension of Conversion Model

Type of Extension		Value of Parameters			
		Y (%)	τ (secs)	$\frac{S}{C}$	T-To (K)
1	best case in experimental region	85.1	0.735	6.250	975
2	worst case in experimental region	47.3	0.547	1.053	780
3	extension for 90% conversion with τ	90.0	0.890	6.250	975
4	extension for 90% conversion with S/C	90.0	0.735	8.605	975
5	extension with 90% conversion with T-To	90.0	0.735	6.250	1465

significant. The model was run again using just the steam-to-carbon molar ratio as an independent variable. The results are given in Table XVIII. Comments on this model are:

1. The hydrogen-to-carbon monoxide molar ratio in the product gas increases with an increased steam-to-carbon molar ratio in the feed.
2. The value of the intercept has no physical significance in this model.

While temperature did not affect the value of the molar ratio, the steam-to-carbon had a strong effect. The statistics of the model in Table XVIII show the level of significance to be 0.064 for the model. This high level of significance reflects the high scatter in the data: the hydrogen-to-carbon monoxide molar ratios resulting in experiments 3 and 4 are very different. The level of significance of the variable coefficient is 0.003, showing that the effect of the independent variable is important.

The model predicts values between 1.19 and 2.16 for the hydrogen-to-carbon monoxide molar ratio, within the experimental region covered. A value of 2.0 is obtained using a steam-to-carbon molar ratio of 5.37 or a carbon-to-steam ratio of 0.186. Experimental values as low as 0.16 were used. These data are summarized in Table XIX.

Table XVIII
Statistics on Hydrogen-to-Carbon Monoxide Molar Ratio Model[(a)]

1. Model: $\left(\frac{H_2}{CO}\right) = 0.18791 \left(\frac{S}{C}\right) + 0.99056$

2. ANOVA Table:

Source of Variation	Degrees of Freedom	Sum of Squares
attributable to regression	1	0.882
deviation about regression line	11	0.224
deviation within sets	1	0.564
Total	13	1.670

3. $P(F \leq 0.90) = 3.2252$
$P(F \leq 0.95) = 4.8443$
F - value = 4.3811

level of significance = 0.064
for goodness of fit

4. Level of Significance of Variable

Variable	Regression Coefficient	Standard Error	T-Value	Level of Significance
S/C	0.18791	0.05127	3.665	0.003

(a) method of analysis is described in Himmelblau, D.M., "Process Analysis by Statistical Methods", John Wiley & Sons Incorporated (1970).

Table XIX
Extension of Hydrogen-to-Carbon Monoxide Molar Ratio Model

Type of Extension	Value of Parameters[a]	
	$\frac{H_2}{CO}$	$\frac{S}{C}$
1 highest value in experimental region	2.16	6.250
2 lowest value in experimental region	1.19	1.053
3 best value in experimental region	2.00	5.370

(a) the model predicts no temperature dependance, over the range of temperatures investigated.

The models in combination may now be considered. The results are summarized in Table XX. The steam-to-carbon ratio is fixed by the hydrogen-to-carbon monoxide molar ratio model and the values of temperature and residence time are calculated from the conversion model. While the models are being used outside the experimental region, this analysis gives an indication of likely conditions for 90% conversion and a synthesis gas of the desired composition. The results show that a temperature of 1819 Celsius (or 2092 K), or a residence time of 0.966 seconds is required. Both of these values are feasible with modifications to the reactor.

Special Experiments

Five experiments were run to obtain insight into other physical parameters than peat feed rate. These are summarized:

1. Experiments 10, 11, and 12 were ones with increasing currents. They used currents of 150, 200, and 250 amperes respectively. The current used in all other experiments was 130 amperes.

2. Experiment 14 used a higher steam plasma flow rate. A flow of 223 litres per minute (measured at room temperature and atmospheric pressure) was used, whereas 210 litres per minute was used in all other experiments.

3. Experiment 15 used the usual peat flow rate, plasma flow rate, and current, but the reactor was insulated over the area below the "hot zone".

Table XX
Conditions Using Both Models in Combination

Type of Extension	Value of Parameters				
	Y (%)	$\frac{H_2}{CO}$	T (secs)	$\frac{S}{C}$(a)	T-To (K)
conditions for best case, extended in T	90	2.0	0.966	5.37	975
conditions for best case, extended in T-To	90	2.0	0.735	5.37	1649

(a) value of S/C is fixed by H_2/CO model

The experiments with increased current did not produce improved results. The wall and gas temperatures were higher than in other experiments, but the carbon conversions and hydrogen-to-carbon monoxide ratios did not improve significantly. This does not imply that higher temperatures do not produce better results, but rather the "unmeasured parameters" altered enough to dampen the effect of increased power. The effect of higher energy on temperature is also reduced by the increased heat losses with higher temperatures.

The small increase in steam plasma flow rate (6%) resulted in higher wall and gas temperatures, but again no real improvement in conversion or molar ratio. The added chemical energy from the exothermic reaction is large with increased hydrogen and oxygen gas flows, and the extra mass of gas present did not absorb adequate energy to keep temperatures down.

Insulating the reactor did not improve the carbon conversion or the molar ratio on first consideration of the data. The Gas Analysis section showed how the gas composition resulting from the warmer lower section, was similar to compositions of gases obtained at higher reaction temperatures. The reactor wall was bright red over its entire length for this experiment, instead of the top 50 cm normally obtained.

Economics

The economics of a process based on the production of synthesis gas using steam plasma is discussed in light of the experimental results. The study by Gauvin and Duncan (1982) is considered.

A reaction temperature of 1500 Celsius (1773 K), a pressure of 10,000 kPa (100 atmospheres), and a carbon-to-steam molar ratio of 0.307 are assumed in the study, with a residence time of 3 seconds. These conditions, in light of the present experimental results are conservative: less aggressive conditions would be necessary for the desired conversion and gas composition.

While some technological points have not yet been established concerning the preliminary economic study, the present work points towards an encouraging future.

G. CONCLUSIONS

An ASTR-based system was designed and built in which peat was reacted with steam plasma. Gases with compositions near to a synthesis gas for methanol production were obtained, with the production of unwanted by-products less than 20% in most cases. A carbon conversion of 89% and a hydrogen/carbon monoxide molar ratio of 1.8 in the product gas were achieved. Experimental conditions were explored to examine the effect of temperature and carbon-to-steam molar ratio in the feed on the carbon conversion and the hydrogen-to-carbon monoxide ratio in the product gas.

Gas compositions reflected equilibrium mixtures at higher temperatures than those measured by the thermocouples. The trends for varying temperature and carbon-to-steam molar ratio predicted by equilibrium calculations were followed by the experimental results. The elements in the solids react in nearly constant proportions, with hydrogen and oxygen reacting somewhat preferentially.

Mass balances were made to establish consistency in the data, and calculate carbon conversions. The data consistency was most sensitive to the mass of peat fed to the reactor, the ash content of the solids, and the nitrogen percent in the product gas. The balances were consistent to within 15%.

Models were developed to represent the data, and the fit obtained was reasonable in each case. Extending beyond the experimental region, the models predicted that a residence time of near to one second or a temperature of about 1800 Celsius would be required for 90% carbon conversion and the desired synthesis gas. These conditions would be difficult to obtain without significant changes to the existing apparatus.

It is proposed that a new reactor be made for future work on this system. The following are some constraints which should be taken into consideration:

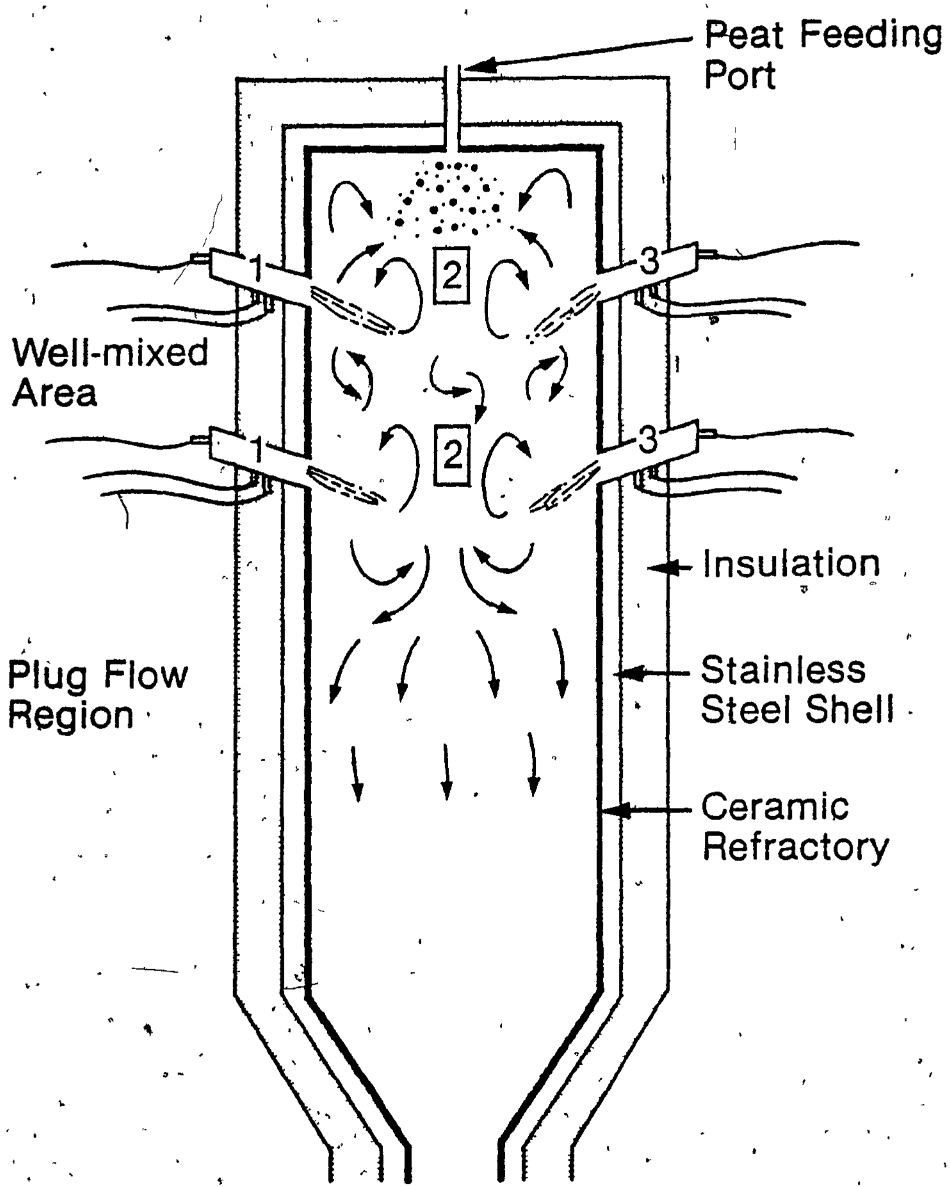
1. Most importantly, the "unmeasured parameters" variation must be eliminated. The mixing characteristics should be constant, if not completely characterized. An authentic steam plasma torch should be characterized and used. It would have a more symmetrical flame. The pressure fluctuations in the system should be eliminated.

2. While carbon-to-steam molar ratios similar to the present work can be used, longer residence times and higher temperatures should be provided for. This could involve a reactor of similar geometry, with adequate refractory and insulation.

A system of the design shown in Figure 32 is proposed. A reactor shell of an increased diameter is used (40 cm) to accomodate the two sets of three torches. The reactor would have ceramic refractory, a thick shell of stainless steel type 307 or 308 for higher temperatures, and insulation on the exterior. No reactor cooling would be used. The steam

FIGURE 32

PROPOSED REACTOR DESIGN


Peat Feeding Port
1
2
3
Well-mixed Area
1
2
3
Insulation
Plug Flow Region
Stainless Steel Shell
Ceramic Refractory

plasma torches would produce a highly turbulent gas mixture of higher temperatures. The angle to which the torches are inclined would have to be determined by experiment, in view of the refractory cracking with extended use. The peat would be blown into the center of the reactor top. It would heat-up prior to the hottest region (at the torches), undergoing pyrolysis. At the torch region, gasification would take place in an extended zone of high temperatures. The intense mixing would ensure that the peat would all react in the high temperature environment.

A much higher peat feed could be used in this system due to the six torches being available as steam sources. A single feed could be used, or multiple feeds if the peat is not dispersing efficiently. This effect is vital for high conversion. The vertical ASTR-type reactor would still result in insignificant accumulation of residue in the reactor.

The present project shows promise. A conversion of 90% and a synthesis gas having a hydrogen-to-carbon dioxide ratio of 2 is certainly possible. Experiment 2 of this work resulted in an 89% conversion and a molar ratio of 1.8. With a new design, the system will be better able to generate conditions for results with less scatter than the present work. It would also be an energy efficient system, with which data may be produced to confirm economic studies on the process.

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I. NOMENCLATURE

a,b,c	model constants
C_A	carbon concentration
H	length along reactor
k	reaction rate coefficient
r_A	rate of disappearance of carbon
S/C	steam to carbon ratio in the feed
t	time
T	reaction temperature
T_o	minimum temperature at which reaction occurs
Y	carbon conversion
τ	residence time in reaction zone

APPENDICES

APPENDIX I: DETAILS ON APPARATUS

A. INTRODUCTION

The construction of this apparatus was done over a period of sixteen months. The final system was able to produce the required data, even given time and cost constraints. A description of the different sections of the apparatus is given:

1. the plasma feeding system;
2. the peat feeding system;
3. the reactor;
4. the effluent system and;
5. the sample train.

The sixteen month period of design and construction may be divided into four periods of four months. During the first four months, the laboratory was prepared, and the rectifier was installed. The equipment design and laboratory lay-out was established over the next four months. Materials of construction were ordered, and requisitions placed in the workshop for reactor construction. The following four months were used to build the reactor, calibrate all the instruments, and perform the steam plasma exploratory experiments. The last four months were used to assemble the apparatus and go through a series of commissioning experiments to have an operating system.

This appendix describes the results of this work.

B. THE PLASMA FEEDING SYSTEM

Introduction

The utilities required to produce a DC plasma are cooling water, DC current, and compressed gases. They are regulated by the control console, and then go to the plasma torch.

Utilities for Plasma Generation

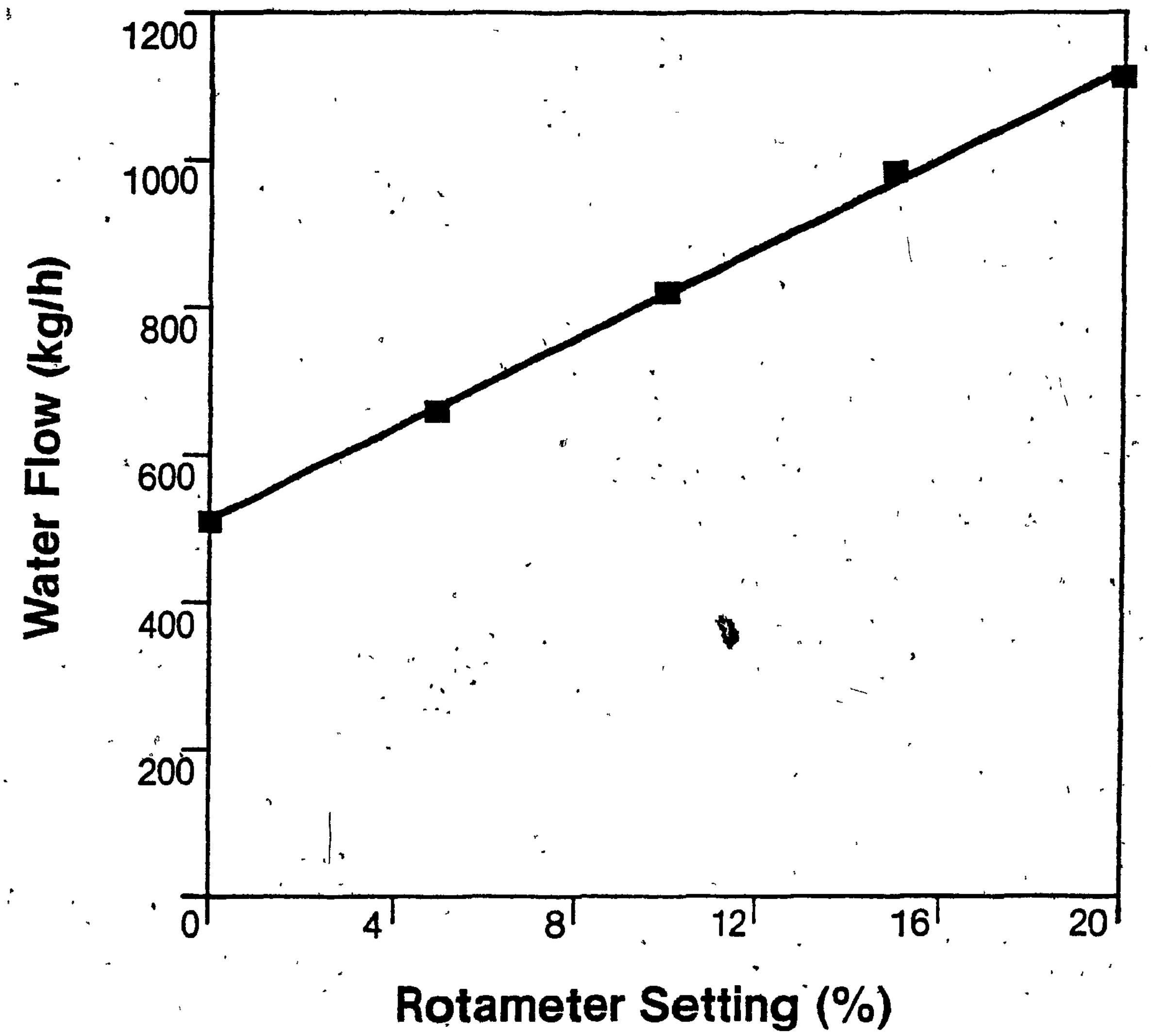
The cooling water passed through a Schutte & Koerting rotameter, the control console, the torch, and then to the drain. The calibration curve for the rotameter is given in Figure 1. The maximum flow rate of water through the torch was obtained at a reading of 22%. The pressure drop in the lines and the torch did not permit higher flow rates. A flow rate close to this maximum was used in all experiments, and provided adequate cooling. A temperature rise of about 4 Celsius was found, when the flow rate of cooling water was 18%. The backpressure of the water was 540 kPa (80 psig).

Several o-rings in the torch prevented water leakage. When a leak developed, and water passed between the anode and the cathode of the torch, the electrical resistance was reduced between them. This caused a short-circuit, and the system was shut-down.

FIGURE 1:

COOLING WATER ROTAMETER CALIBRATION

Cooling Water
Rotameter Calibration



A thermocouple was placed in the outlet water line from the torch. The water temperature, prior to the production of plasma, was taken. Then temperatures throughout the course of the experiment were recorded. Making simple energy calculations allowed the heat dissipated to the cooling water to be known. The rest of the energy was carried away by the plasma gas. Torch efficiencies, defined in the thesis body, were calculated. The results are given in Table I. With the normal hydrogen flow rate of 210 liters per minute, measured at room temperature and atmospheric pressure, the efficiencies for different conditions are shown. The efficiency with pure argon, pure hydrogen (oxygen addition did not affect this value), and peat addition into the reactor are 86.5%, 77.5%, and 72.8% respectively. The lower efficiency with peat addition is due to the pressure in the reactor. Table I shows that with increased plasma gas flow, the efficiency increased. All of these efficiencies are surprisingly high; probably a result of the large gas flow rates.

Three gas sources were required to produce the steam plasma used in this work. The argon, oxygen and hydrogen were all purchased from the Standard Welding Company in Montreal. All three gases passed through Fischer & Porter rotameters; the calibration curves are given in Figures 2, 3, and 4. All volumes were measured at room temperature and atmospheric pressure. Nitrogen gas was required to provide a pressure to the control console to bypass a safety mechanism.

Table I
Results of Efficiency Calculations

Trial	Conditions		Results		
Number	Argon Flow (l/min)	Hydrogen Flow (l/min)	Efficiency With Argon (%)	Efficiency With Steam (%)	Efficiency With Peat (%)
1	94	210	86.5	77.5	72.8
2	94	236	86.6	82.8	75.1

FIGURE 2:

ARGON ROTAMETER CALIBRATION

Argon
Rotameter Calibration

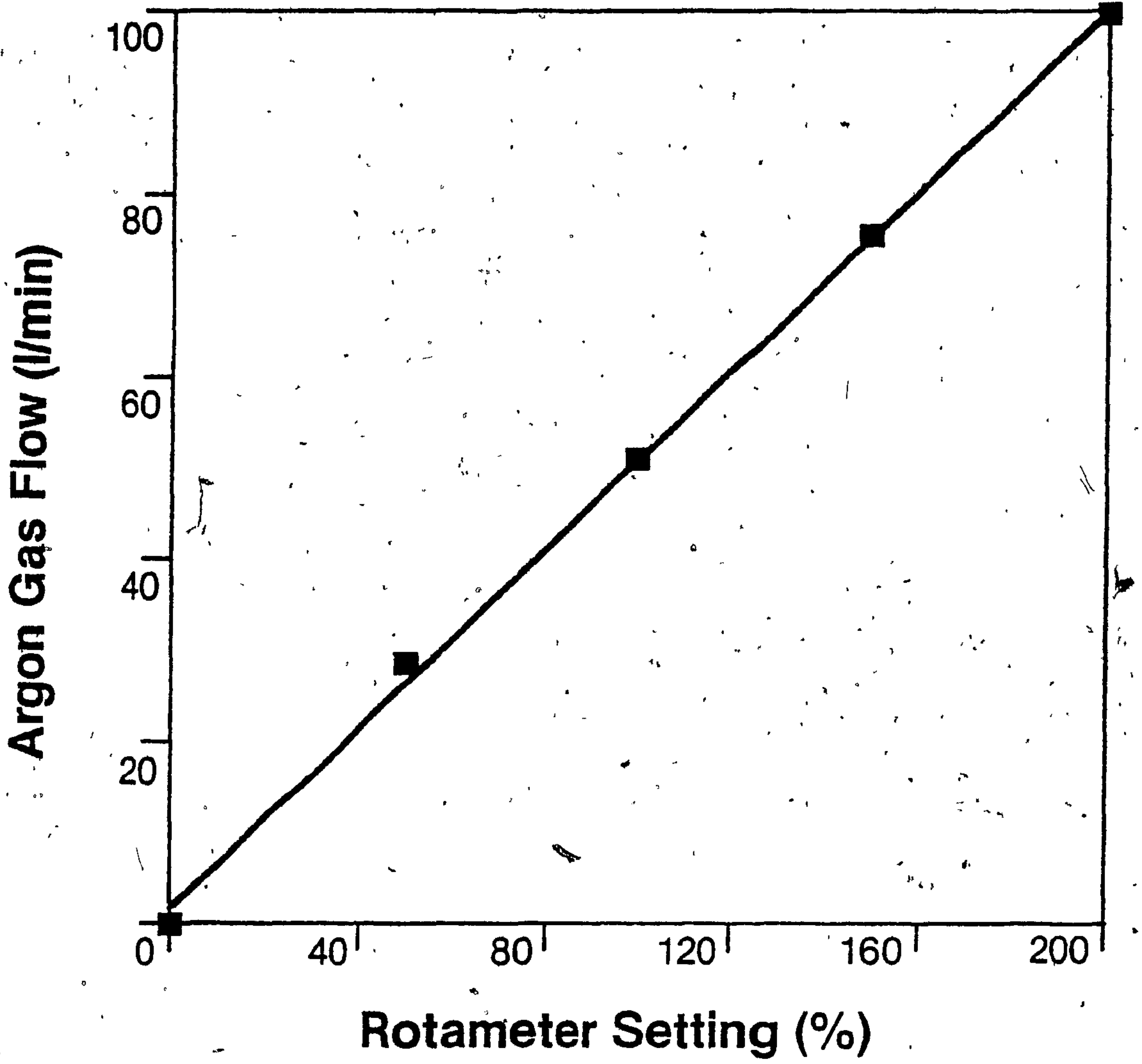


FIGURE 3:

OXYGEN ROTAMETER CALIBRATION

Oxygen
Rotameter Calibration

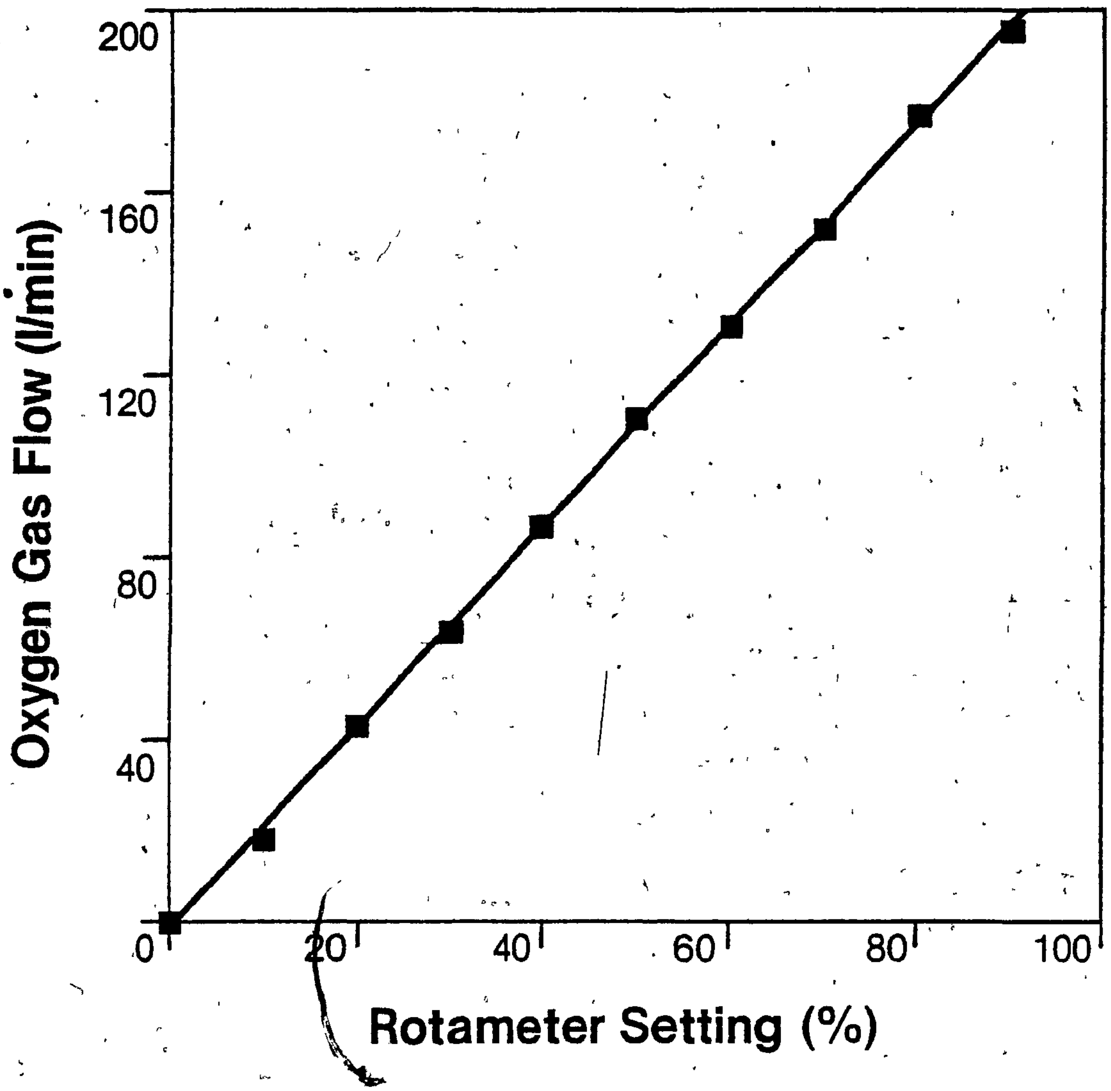
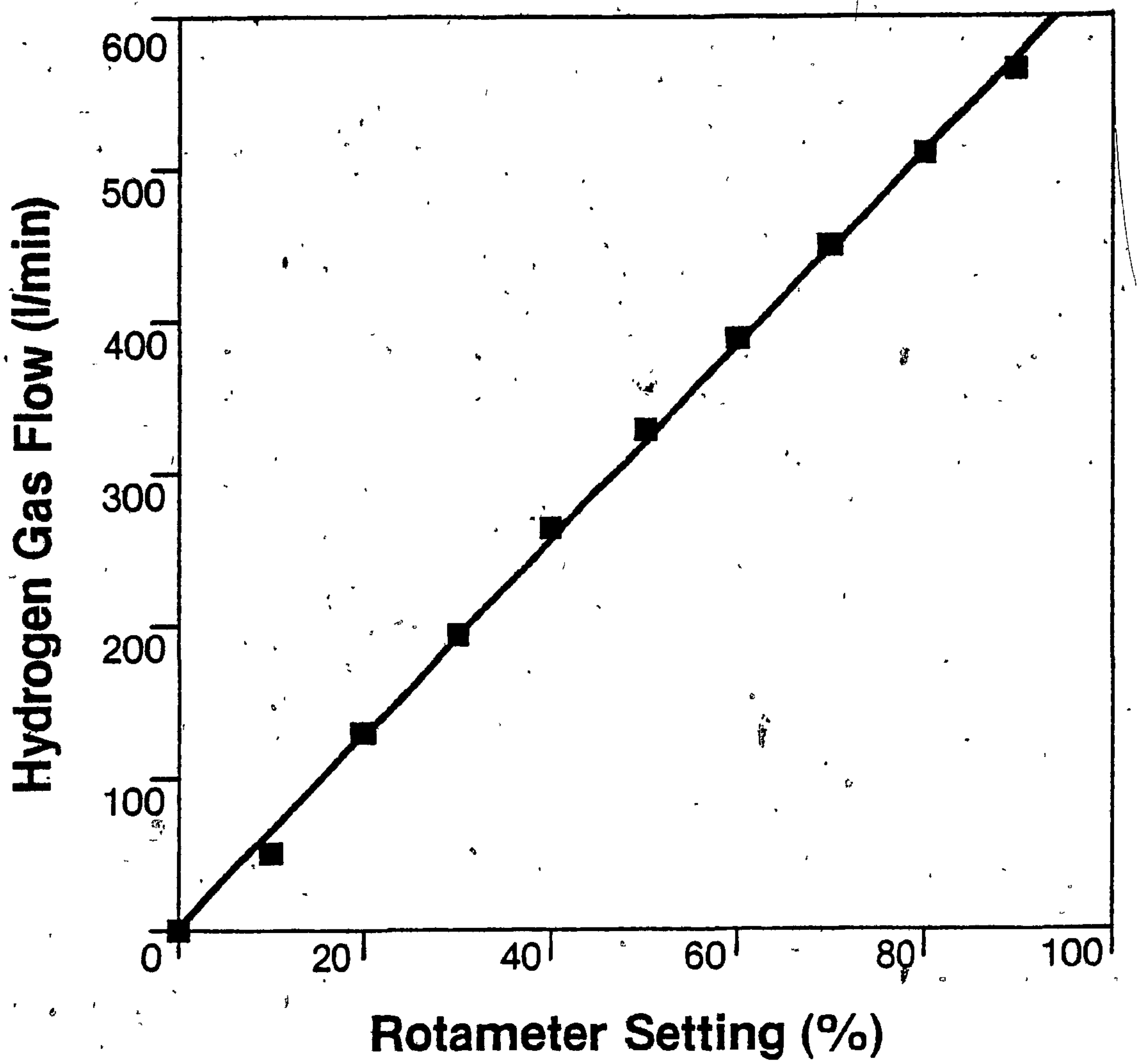


FIGURE 4:

HYDROGEN ROTAMETER CALIBRATION

Hydrogen Rotameter Calibration



The electrical energy was obtained from a 3-phase, 60 hertz, 575 volt power supply. The 3-phase power was converted to DC power using a transformer manufactured by the Miller Electric Manufacturing Company (model SR-1500F7). This transformer produced DC current using completely sealed selenium rectifiers, as described in the manufacturer's manual (1969). Three open-circuit voltages were possible with the transformer: 100, 200, and 400 volts. A 400 volt open-circuit was used in this work. The operating characteristics with this setting were adequate for the experimental requirements.

The rectified DC power was monitored at the control console, and thick cables extended to the torch where the electric potential was applied.

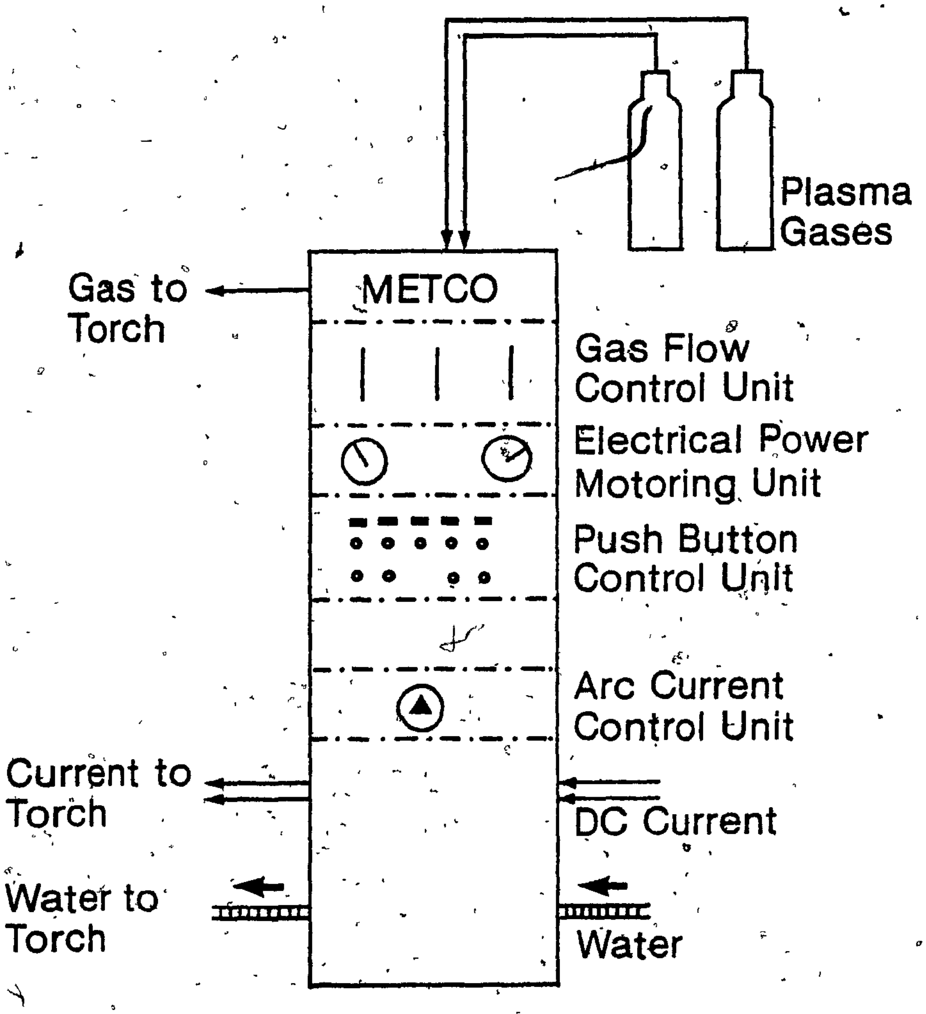
The Control Console

The control console was manufactured by Metco Incorporated. The Metco Type 2M Plasma Flame Control Unit is described in the instruction manual (1964). It was designed for the spraying of high melting point materials. The console was 60 cm (24 in.) wide, 57.5 cm (23 in.) deep, and 222.5 cm (69 in.) high. The front panel, shown in Figure 5, was divided into four units:

1. the gas flow control unit;
2. the electrical power monitoring unit;
3. the push button control unit and;

FIGURE 5:

CONTROL CONSOLE


Plasma
Gases
Gas to
Torch
METCO
Gas Flow
Control Unit
Electrical Power
Motoring Unit
Push Button
Control Unit
Arc Current
Control Unit
Current to
Torch
DC Current
Water to
Torch
Water

4. the arc current control unit.

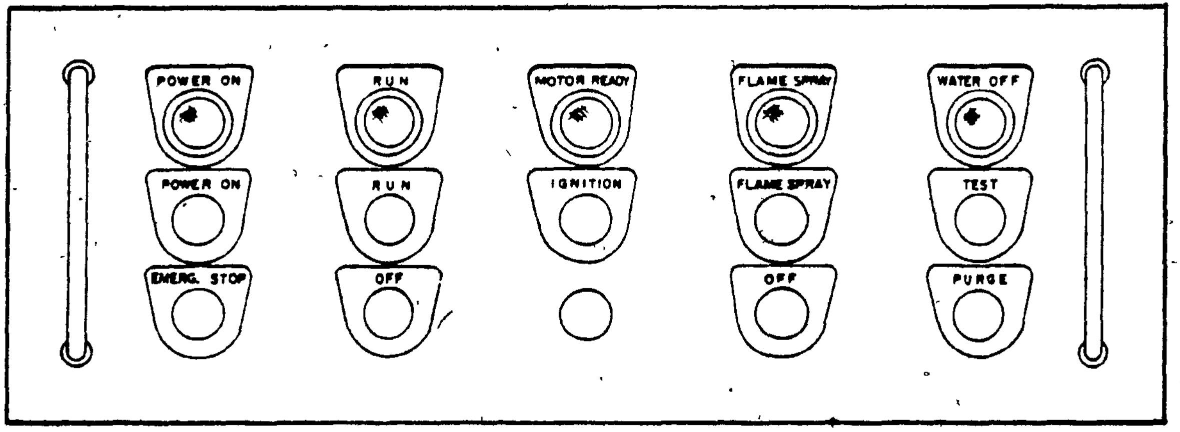
The gas flow control unit consisted of rotameters to measure and control the gas flows. A board was attached to the console to support the larger rotameters for the hydrogen and oxygen gases. Inside the unit were solenoid valves, and a safety mechanism for inadequate gas pressures.

The electrical power monitoring unit contained an ammeter and voltmeter. The measured voltage was across the torch as well as the cables leading to the torch. This latter voltage is approximately 3 volts (depending on operating conditions). This was corrected for in efficiency calculations.

A close-up of the push button control unit is given in Figure 6. The top line of circles represents indicator lights, and the bottom two lines represent push buttons. The "power on" button engaged the transformer. The "purge" button activated the solenoid valves, and allowed verification of gas flows. The "test" button initiated a high-frequency arc between the anode and cathode. If the arc was not concentric or was weak, the anode was centered and spacing was adjusted. The "run" button applied the open-circuit voltage to the torch, and activated the solenoids so gas flow began. The "ignition" button produced a high-frequency arc between the anode and cathode, which in combination with the open-circuit voltage and gas flow, caused the plasma arc to start and be sustained.

FIGURE 6:

PUSH BUTTON CONTROL UNIT


POWER ON
RUN
MOTOR READY
FLAME SPRAY
WATER OFF
POWER ON
RUN
IGNITION
FLAME SPRAY
TEST
EMERG. STOP
OFF
OFF
PURGE

The arc current control unit consisted of a rheostat. This was used continually during operation to adjust and stabilize current.

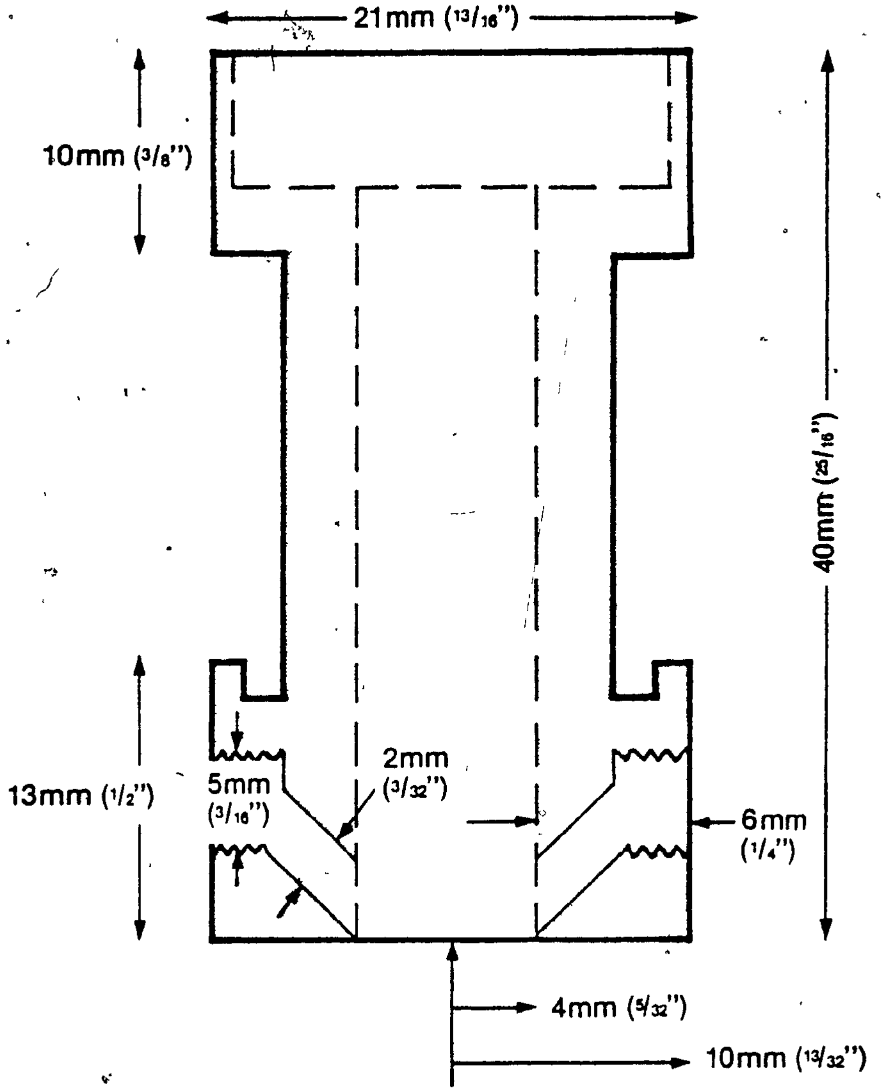
The Plasma Torch

The plasma torch was manufactured by Thermal Dynamics Corporation. The torch model (U-51) is described in the manual (1962). The torch schematic is provided in the body of this thesis. Several problems were encountered with the hydrogen/oxygen feeding configuration, and these are discussed in this section.

It was found that injecting oxygen into the anode in a direction perpendicular to the hydrogen plasma caused significant errosion, resulting in rapid anode degradation. The configuration used to ammend this problem is shown in the scale drawing of the anode in Figure 7. Oxygen entry ports were drilled in two diametrically opposed sides of the anode. An initial length was "tapped" with 32 millimeter (1/8 in.) pipe thread. The remainder of the entry channel was drilled at 45 degrees, in the direction of the hydrogen plasma flow. Most of the hydrogen/oxygen combustion occurred just outside the mouth of the plasma torch, and the large heat of reaction did not melt the anode. Also, a reducing atmosphere of hydrogen resulted in longer anode life.

FIGURE 7:

TORCH ANODE

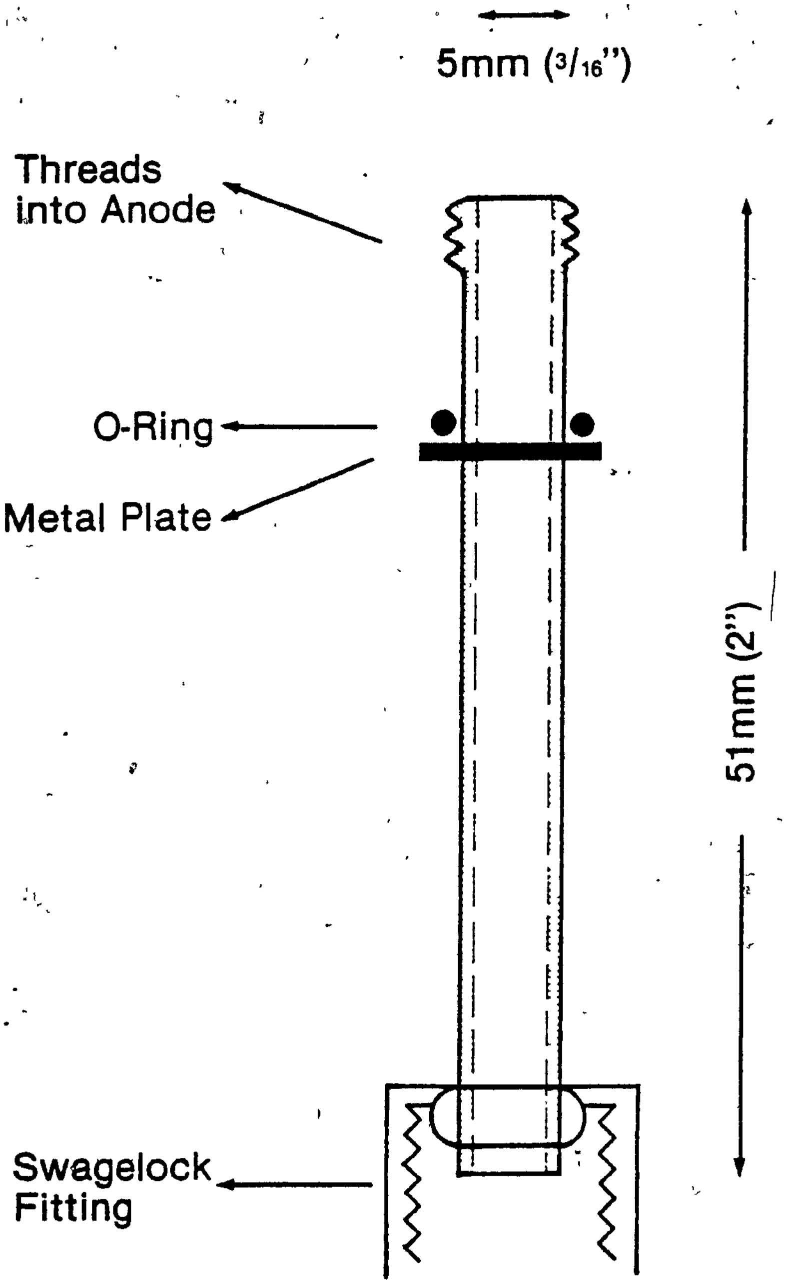

21mm (13/16")
10mm (3/8")
40mm (25/16")
13mm (1/2")
5mm (3/16")
2mm (3/32")
6mm (1/4")
4mm (5/32")
10mm (13/32")

The split of the steam plasma was described in the thesis. A configuration to minimize this split was investigated, by adjusting the diameter of the oxygen entry port (and hence the oxygen gas velocity relative to the hydrogen plasma velocity). As the oxygen entry diameter reduced, the split was less evident. Reducing the port to a diameter of 16 millimeters (1/16 in.), limited oxygen flow to below levels required for stoichiometry. The ports had a diameter of 24 millimeters (3/32 in.) for experimentation.

To eliminate gas leakage, oxygen entry taps were designed as shown in Figure 8. The taps screwed directly into the anode. An o-ring supported by a welded plate was placed on the tap length to allow a gas-tight fit on the anode holder, but not permit the angled length of the port (in the anode) to be covered by the tap.

FIGURE 8:

OXYGEN ENTRY TAPS


5mm (3/16")
Threads into Anode
O-Ring
Metal Plate
51mm (2")
Swagelock Fitting

C. THE PEAT FEEDING SYSTEM

The peat feeding system used was problematic with respect to the experimental results. Pressure fluctuations in the reactor developed with peat feed.

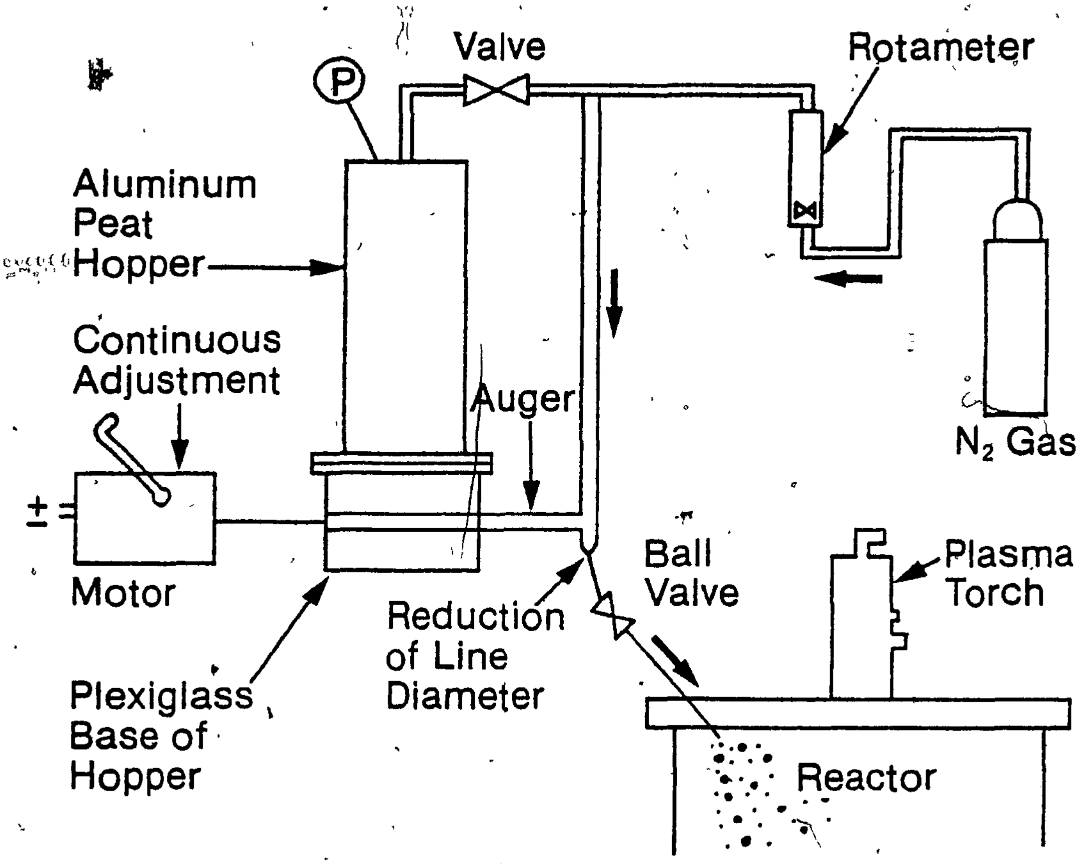
The peat feeding equipment is shown in Figure 9. The peat hopper was made of a 12.5 cm (5 in.) inside diameter aluminum pipe, seated on a square base of 1.25 cm (1/2 in.) thick plexiglass. The auger extended through the plexiglass base, to a 1/3 horsepower Zero-Max motor on one side, and in the feeding barrel on the other side. The speed of auger revolution was varied by a continuous adjustment on the motor.

The auger conveyed the peat into the nitrogen line, where it was blown into the reactor at a 45 degree angle to the steam plasma feed. A ball valve was on the line to the reactor, for isolating the peat feeder from any pressure fluctuations or moisture seepage. A pressure equalizing line entered the top of the peat hopper.

During experimental runs, pressure fluctuations were produced in the reactor with peat addition. This pressure effect was produced back to the feed system, resulting in nitrogen gas entering into and purging from the peat hopper. The low density of the peat resulted in it blowing out with the nitrogen purge. This produced an increased peat flow rate to that

FIGURE 9:

PEAT FEEDING EQUIPMENT


Valve
Rotameter
P
Aluminum Peat Hopper
Continuous Adjustment
Auger
N₂ Gas
±
Motor
Ball Valve
Plasma Torch
Reduction of Line Diameter
Plexiglass Base of Hopper
Reactor

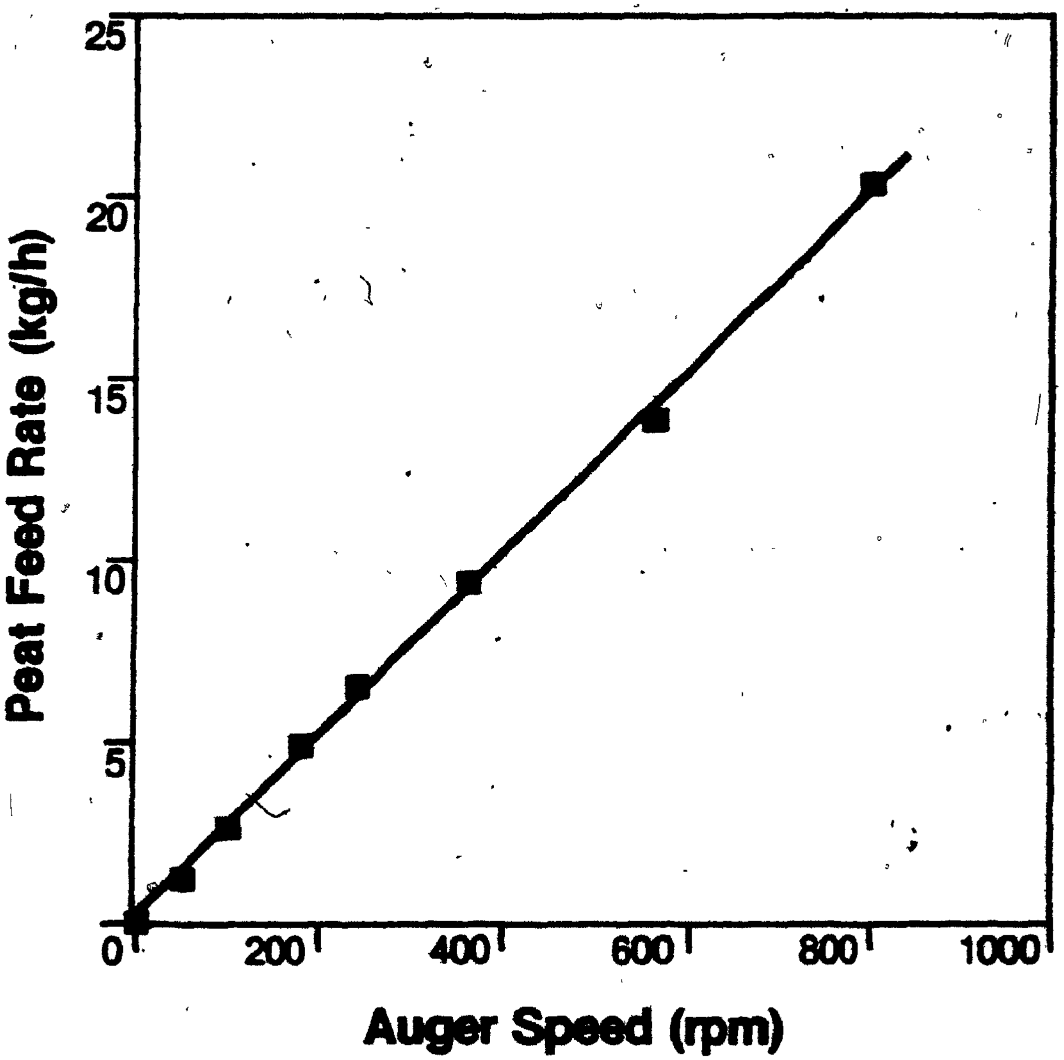
predicted. The magnitude of the increase depended on the magnitude of the pressure fluctuations, and varied between experiments. The peat feeder calibration curve is given in Figure 10. This calibration was done by collecting the peat fed for various motor speeds, in a vessel at the end of the auger. The steady atmospheric pressure did not reflect experimental conditions, and a lower calibration feed rate resulted with a given motor speed.

It is believed that much of the pressure fluctuation problem can be alleviated by using a "closed screw": a screw which does not allow direct access of gas through the barrel, but rather has wide turns covering the barrel width.

FIGURE 10:

PEAT FEEDER CALIBRATION

Peat Feeder Calibration



D. THE REACTOR

The reactor was designed using an ASTR system, in view of the constraints listed in the thesis body:

1. high temperature;
2. small pressure generation;
3. adequate residence time and;
4. minimum cost.

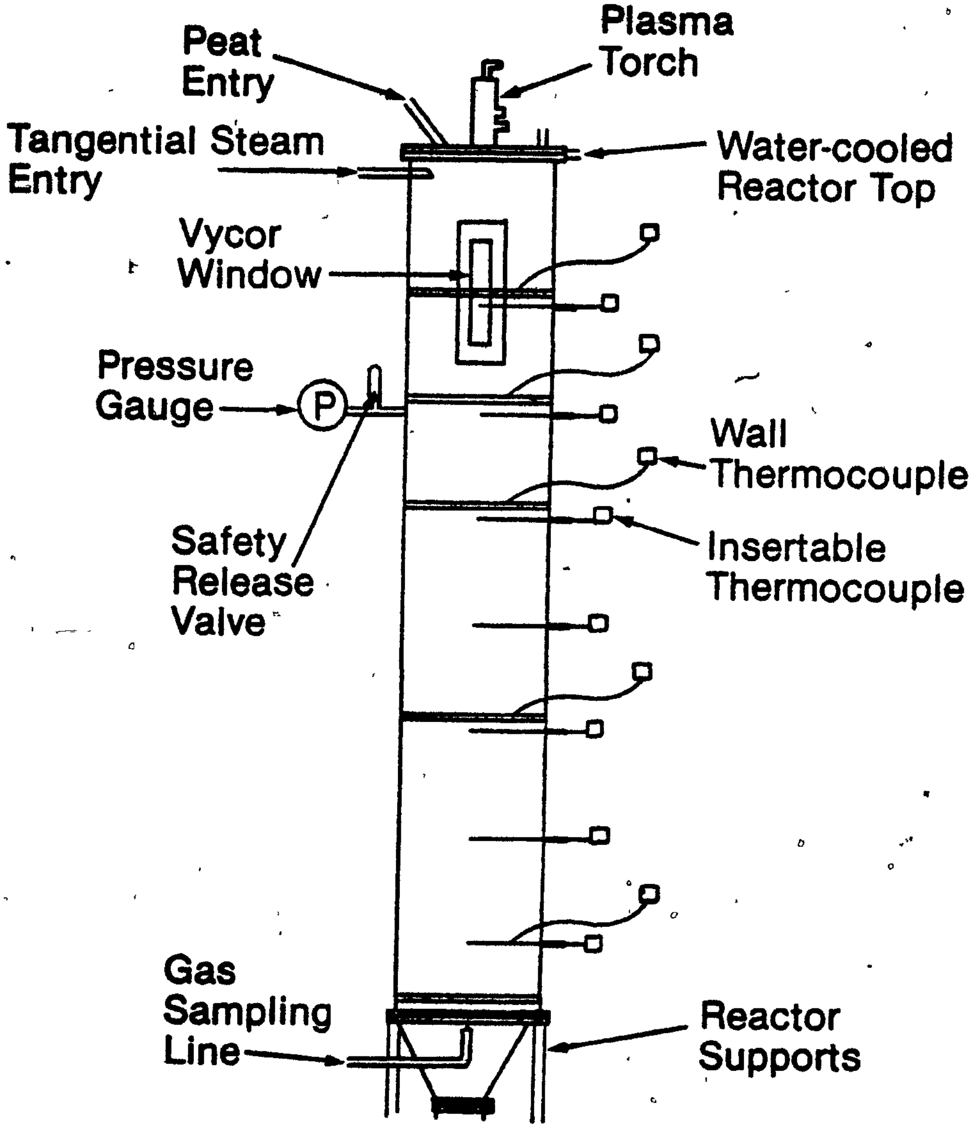
In addition, it was decided not to use insulation on the reactor. This was to allow maximum heat loss in view of the high energy of the gas, and also permit a thermal steady state in relatively short periods of time.

Figure 11 shows the reactor. It was constructed using type 304 stainless steel schedule 10 pipe. The reactor body had a diameter of 20 cm (8 in.), and a length of 120 cm (48 in.). This provided a length-to-diameter ratio of 6. There are several features of the equipment:

1. The reactor had a tangential steam entry port. A Reimer steam boiler produced the steam, which flowed in heated lines through a valve and to the reactor. A thermocouple in the line near the reactor measured the steam temperature to be 107 Celsius for most experiments. The flow

FIGURE 11:

REACTOR


Peat Entry
Plasma Torch
Tangential Steam Entry
Water-cooled Reactor Top
Vycor Window
Pressure Gauge
P
Wall Thermocouple
Insertable Thermocouple
Safety Release Valve
Gas Sampling Line
Reactor Supports

rate of the auxiliary steam was calibrated to be 4.64 kilograms per hour. This compares with a usual flow rate of steam plasma of 9.26 kilograms per hour.

2. Five wall thermocouples down the length of the reactor existed, and their readings were continually recorded on the Thermoelectric strip chart recorder. The readings were from one point on the reactor wall. An asymmetrical plasma flame resulted in uneven temperatures around the reactor radius at a given height. While the warmest wall position was difficult to predict, it was attempted to place the uppermost wall thermocouple near where it might appear.

3. Seven insertable thermocouples were placed down the length of the reactor. These were left at the reactor centerline for most experiments, though this resulted in the melting of the uppermost thermocouple.

4. A vycor viewing window existed so that the peat entry port and the steam entry location could be seen. The window was recessed and water-cooled to prevent melting. The shape was long and narrow to give maximum viewing capability, but collect the minimum peat in its cavity.

5. A pressure gauge was required to establish when pressure fluctuations developed in the reactor. The combination of pressures with the high temperatures in the system were a potential danger, so this gauge was constantly monitored. It was recessed to prevent damage from the high temperatures.

6. A safety release valve was on the reactor. The release pressure was adjustable, and set at about seven pounds.

7. The reactor top was water-cooled to prevent it melting. A single baffle was placed in a space between two stainless steel flanges to provide this cooling.

8. A hole in the conical reactor bottom allowed the insertion of the gas sampling line. This was placed at the centerline, and could be revolved. It was facing downwards for most experiments to minimize solids gathering.

9. The reactor was supported at the bottom. Any increase in length with increased temperature could be absorbed by a rise in the reactor top. Only the peat feeder would have to adjust its height correspondingly. The flexible gas, water, and electrical lines to the plasma torch were supported on scaffolding to minimize torque on the reactor.

E. THE EFFLUENT SYSTEM

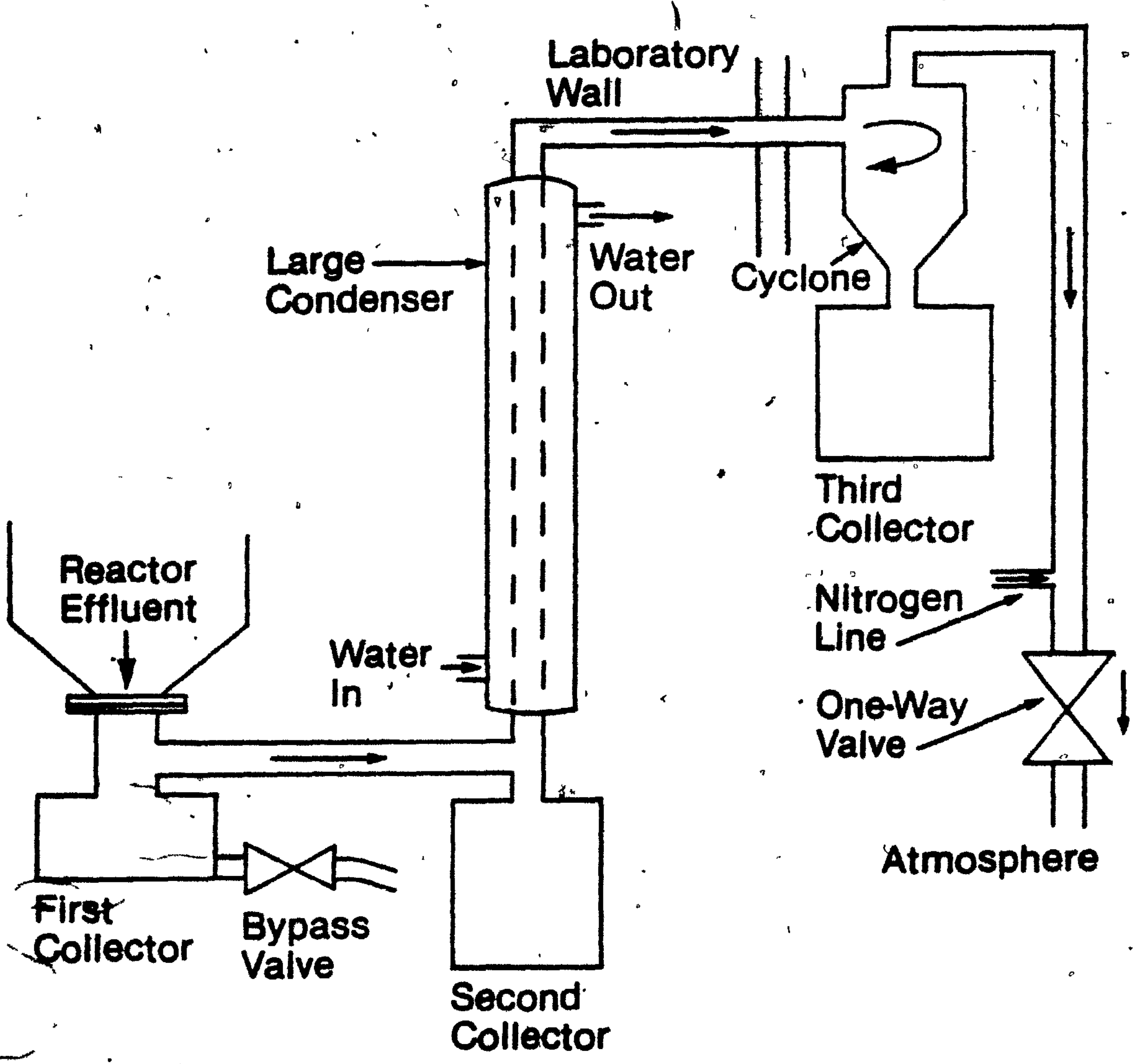
The effluent system was designed to result in a minimum pressure drop. An increased pressure drop resulted in an increase in the pressure of the reactor, which was undesirable. The effluent system had to also be fairly effective in collecting the majority of the solids produced.

The system used is shown in Figure 12. The line is 2.5 cm (1 in.) diameter, and made of carbon steel. The components of the effluent line may be summarized:

1. A collector, made of stainless steel, was directly below the reactor. Very few solids collected here. The solids which did collect were larger peat particles, and some copper from the degradation of the anode. A valve at the bottom of this collector allowed start-up of the reactor without argon having to flow through the complete effluent line. The valve was closed while closely monitoring the pressure in the reactor. Any clogging of the lines between experiments would have been detected at this point, and the valve immediately reopened before dangerous pressure levels were reached.

FIGURE 12:

EFFLUENT SYSTEM


Laboratory Wall
Large Condenser
Water Out
Cyclone
Third Collector
Nitrogen Line
One-Way Valve
Atmosphere
Reactor Effluent
Water In
First Collector
Bypass Valve
Second Collector

2. A 180 cm (72 in.) condenser with a large aluminium collector below it was in the line. About one third of the solids were collected here, in a large quantity of water.

3. A cyclone was installed with a collector below it. About two thirds of the peat collected was retrieved at this location, with small amounts of water.

4. A line from a nitrogen cylinder intersected the effluent line. On shut-down of the system, nitrogen would flood the effluent line at this point for safety reasons, as described in the body of the thesis.

5. A one-way valve was on the line just prior to the gas purge to the atmosphere. This allowed the gas to flow out of the system with minimum pressure drop, and minimize the inflow of air into the system in the event of shut-down.

F. THE SAMPLE TRAIN

The sample train was designed in view of obtaining gas samples in bottles, without causing a high pressure drop in the system. To do this, a 1 cm (3/8 in.) line was inserted into the bottom of the reactor to withdraw a small stream. The passage of large volumes of gas through this line would result in high pressure drops. With the present system, small gas volumes flowed through the sample line due to the pressure within the reactor. No pumping was required.

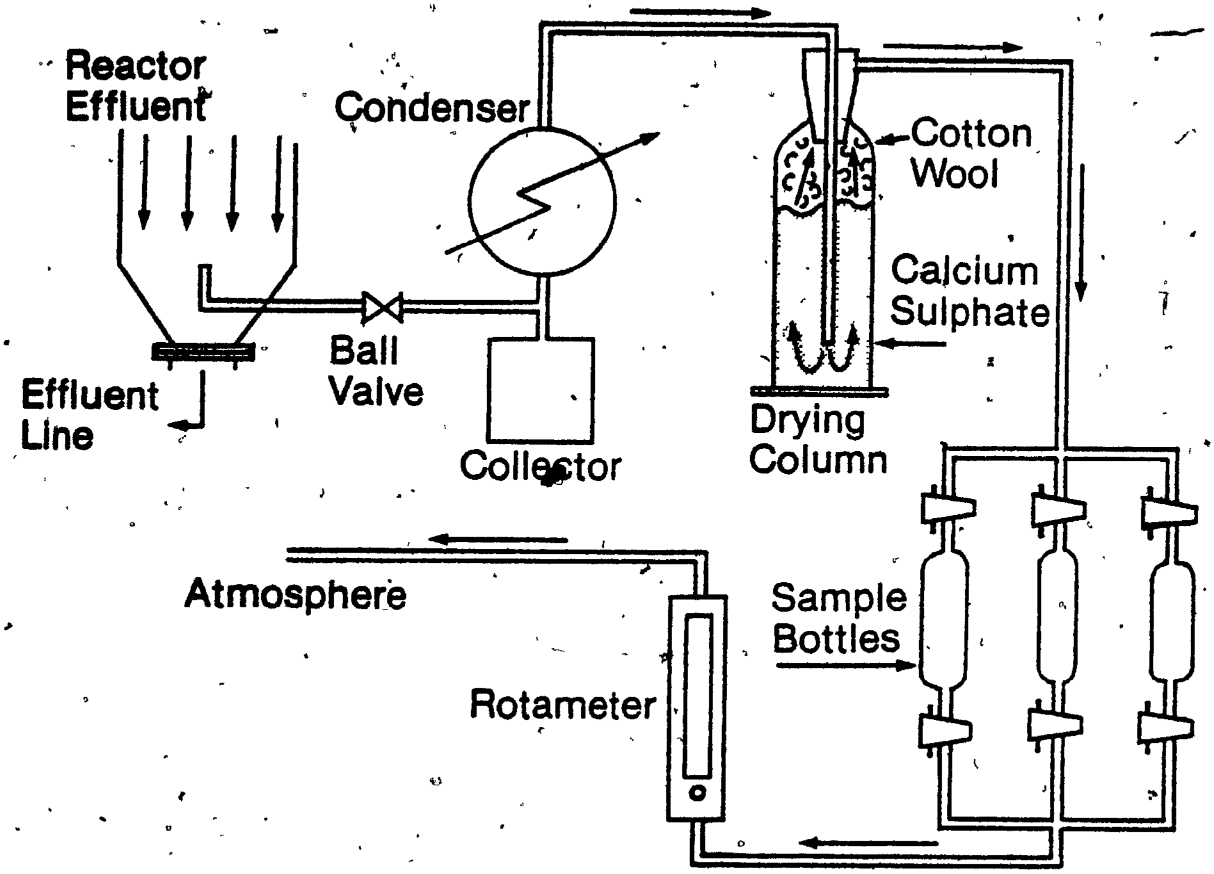
The sample train is shown in Figure 13, and the main components are summarized:

1. A valve was in the line to isolate the sample line from the reactor until purge conditions or reaction conditions were evident. This minimized moisture and solids accumulation in the line.

2. A condenser, with a collection vessel below it, was on the sample line. Only small amounts of solids and liquids collected. This condenser had a high collection efficiency.

FIGURE 13:

SAMPLE TRAIN


Reactor Effluent
Condenser
Cotton Wool
Calcium Sulphate
Ball Valve
Effluent Line
Collector
Drying Column
Atmosphere
Sample Bottles
Rotameter

3. A drying column/filter was in the line. This was a bottle packed with moisture absorbing calcium sulfate, covered by cotton wool. The gas was introduced at the bottom of the column, and had to filter through the bottle.

4. The clean dry gas then passed through one of three sample bottles. Stopcocks at the beginning and end of the bottles allowed the routing of the gas stream. The sample-taking procedure is described in the body of the thesis.

5. A rotameter was in the line in order to have a good indication of the gas flow. It was adjusted to the same level for each experiment by the rotameter valve.

G. REFERENCES

1. Anon., "Installation, Operation and Maintenance Manual", Miller Electric Manufacturing Company, form 10M-262-10/69 (1969)

2. Anon., "Type 2M Plasma Flame Spray System Instructions", Metco Incorporated, form G-6027 (1964)

3. Anon., "Instruction Manual, 50 Series", Thermal Dynamics Corporation, form U-51-2 (1962)

APPENDIX II: RAW DATA

A. INTRODUCTION

In this section, the important data from the experiments are given. The data are presented in the following order:

1. product gas compositions and;
2. solid residue compositions.

B. PRODUCT GAS COMPOSITIONS

Table II
Product Gas Compositions[a][b]

Experiment Number	Carbon Dioxide (vol.%)	Carbon Monoxide (vol.%)	Methane (vol.%)	Hydrogen (vol.%)	Nitrogen (vol.%)
1	19.2	19.0	0.0	45.5	17.0
2	15.7	24.9	0.0	44.7	13.9
3	15.5	23.7	0.0	49.3	12.9
4	17.7	28.3	0.4	39.8	13.7
5	16.8	22.6	0.0	47.4	13.0
6	14.4	31.4	0.3	42.0	11.9
7	18.1	29.1	0.5	50.1	12.2
8	13.2	31.4	0.9	44.6	9.3
9	12.9	35.8	0.9	41.0	8.6
10	15.4	27.2	0.0	44.2	13.1
11	15.9	23.1	0.0	47.6	13.3
12	14.2	29.8	0.0	42.1	13.0
14	16.2	22.8	0.0	43.9	16.6
15	15.6	25.1	0.1	47.2	11.7

(a) all values are on a steam-free basis

(b) while traces of oxygen were found in almost every case, these are not noted.

C. SOLID RESIDUE COMPOSITIONS

Table III
Reacted Solids Compositions(d)(e)

Experiment Number	Carbon (mass%)	Hydrogen (mass%)	Nitrogen (mass%)	Ash (mass%)	Oxygen (mass%)	Oxygen by Difference (mass%)
peat	44.54	6.09	2.09	5.11	39.54	42.17
peat(a)	45.39	5.74	2.26	6.09	39.92	40.52
peat(b)	45.40	5.88	2.37	5.83	39.68	40.52
1	50.06	3.77	2.29	25.47	-	18.41
2	47.36	3.55	1.76	30.74	-	16.59
3	53.61	3.85	2.32	19.60	19.68	20.62
3(a)	52.75	4.11	2.31	17.09	21.90	23.74
3(a)	55.42	3.68	2.13	14.97	23.17	23.80
4	43.36	3.33	1.80	35.82	-	15.69
5	51.62	4.96	2.28	24.10	-	17.04
6(c)	58.22	4.01	2.85	23.73	-	11.19
6	50.66	3.63	2.14	25.74	18.27	17.83
7	47.57	3.26	1.86	30.33	-	16.98
7(a)	46.28	2.64	2.34	28.44	19.88	20.30
7(b)	46.70	2.79	1.81	33.75	-	14.95
7(b)	47.03	2.89	1.97	33.28	-	14.83
8	52.70	3.55	1.77	15.28	-	26.70

(a) repeat analysis of the same sample
(b) analysis of a different sample from the same experiment
(c) analysis considered invalid
(d) values corrected for moisture content in mass balances
(e) analysis done by Dr. C. Daessle, Organic Microanalyses, Montreal

Table III (continued)
Reacted Solids Compositions[d][e]

Experiment Number	Carbon (mass%)	Hydrogen (mass%)	Nitrogen (mass%)	Ash (mass%)	Oxygen (mass%)	Oxygen by Difference (mass%)
9	55.88	4.14	2.20	10.60	-	27.18
9[a]	55.84	4.27	2.31	10.36	-	27.22
10	49.30	4.13	2.30	24.61	18.61	19.66
10[a]	49.76	4.03	2.23	24.70	18.89	19.28
10[a]	49.38	4.11	2.45	24.89	18.32	19.17
10[b]	49.49	3.71	2.26	24.60	-	19.94
11	52.64	4.19	2.22	20.15	-	20.80
12[c]	48.22	4.41	2.42	14.54	-	30.41
12	52.80	3.86	2.45	21.60	17.74	19.29
14	46.81	3.14	2.08	17.85	-	30.12
15	50.45	4.06	2.43	21.09	21.10	21.97

(a) repeat analysis of the same experiment
(b) analysis of a different sample from the same experiment
(c) analysis considered invalid
(d) values corrected for moisture content in mass balances
(e) analysis done by Dr. C. Daessle, Organic Microanalyses, Montreal

APPENDIX III: COMPUTER PROGRAMS

A. INTRODUCTION

The computer programs that were used to calculate the data are provided or discussed in this section. The programs considered are:

1. mass balance program;
2. F*A*C*T and;
3. Statpak.

B. MASS BALANCE PROGRAM

```
                              *BATCH PRINTA CFM0000 CXV5 (999,9999)
                              ***********************************************************************************

/ID MUSJOB          CXV5 000 010 050 000  R=BH106 C=1 F=                                 SUN NOV 20, 1983
**EXCESSIVE TIME ESTIMATED  ASSUMING   180 SERVICE UNITS
/LOAD WATFIV
            REAL PEATIN, CIN, HIN, OIN, NIN, ASHIN, H2OIN, N2IN, AUXIN, PLASMA
            REAL N2ROT, H2ROT
            REAL PTMASS, PTTIME, VOLT, AMPS, EFF
            REAL CO2OUT, COOUT, CH4OUT, H2OUT, O2OUT, N2OUT
            REAL COUT, HOUT, OOUT, NOUT, ASHOUT
            REAL WCOUT, WHOUT, WOOUT, WNOUT, WASHOU, DRYPR, W
            REAL DRYPT, CPT, HPT, OPT, NPT, ASHPT
            REAL DRYPCT, CPRINT, HPRINT, OPRINT, NPRINT, ASHPRI
            REAL CARMOL, NCAR, H2PSMA, HPSMA, O2PSMA, OPSMA
            REAL AUXMOL, HAUX, OAUX
            REAL CTOT1, HTOT1, OTOT1, NTOT1, ASHTOT
            REAL CRAT, H2ORAT, INRAT
            REAL ASHSOL, DRYSOL, CSOL, HSOL, OSOL, NSOL
            REAL NGAS, N2MOL, TOTMOL, CO2MOL, COMOL, CH4MOL, H2MOL, O2MOL
            REAL OUTRAT, NTOT2, NDIFF
            REAL CMOL, CGAS, CCONV1, CCONV2, CCONV, CTOT2, CDIFF
            REAL HMOL, HGAS, HTOT, OMOL, OGAS, OTOT
            REAL HEXC, OEXC, O2EXC, H2EXC, H2OEXC, HEXC1, OEXC1
            REAL HTOT2, OTOT2, HDIFF, ODIFF
            REAL CPCT, HPCT, OPCT, NPCT, ASHPCT
            REAL EPOWER, CPOWER, POWER, PCTE, PCTC, POWPT
      C
      C ***************************************************************************
      C                                   1  INPUT DATA
      C ***************************************************************************
      C
            VOLT=157.0
            AMPS=130.0
            EFF=0.728
            PTMASS=236.768
            PTTIME=209.0
            PEATIN=(PTMASS/1000.0)*3600.0/PTTIME
            CIN=45.11
            HIN=5.90
            OIN=41.59
            NIN=2.24
            ASHIN=5.16
            H2OIN=15.5
            N2ROT=150.0
            N2IN=0.2587*N2ROT-2.15
            AUXIN=4.64
            H2ROT=33.0
            PLASMA=900.0/65.0*H2ROT-31500.0/65.0+500.0
      C
      C ***************************************************************************
      C                                   2  OUTPUT DATA
      C ***************************************************************************
      C
            CO2OUT=14.9
            COOUT=31.2
            CH4OUT=0.0
            H2OUT=40.5
            O2OUT=0.0
            N2OUT=13.4
            WCOUT=46.81
            WHOUT=3.14
            WOOUT=30.12
```

```
      WNOUT=2.08
      WASHOU=17.85
      W=4.00
C
C **********************************************************
C                       2A  DRY SOLIDS COMPOSITIONS
C **********************************************************
C
      DRYPR=(100.0+W)/100.0
      COUT=WCOUT*DRYPR
      NOUT=WNOUT*DRYPR
      ASHOUT=WASHOU*DRYPR
      HOUT=WHOUT*DRYPR-(W*2.0/18.0)
      OOUT=WOOUT*DRYPR-(W*16.0/18.0)
      DRYPCT=(100.0+H2OIN)/100.0
      CPRINT=CIN*DRYPCT
      NPRINT=NIN*DRYPCT
      ASHPRI=ASHIN*DRYPCT
      HPRINT=HIN*DRYPCT-(H2OIN*2.0/18.0)
      OPRINT=OIN*DRYPCT-(H2OIN*16.0/18.0)
C
C **********************************************************
C                      3.  MASS-IN CALCULATIONS
C **********************************************************
C
      DRYPT=PEATIN*100.0/(H2OIN+100.0)
      CPT=DRYPT*CIN/100.0
      HPT=DRYPT*HIN/100.0
      OPT=DRYPT*OIN/100.0
      NPT=DRYPT*NIN/100.0
      ASHPT=DRYPT*ASHIN/100.0
      CARMOL=N2IN*(1000.0/35.3147)*(273.0/298.0)/22.414
      NCAR=CARMOL*28.0/1000.0
      H2PSMA=PLASMA*(1000.0/35.3147)*(273.0/298.0)/22.414
      HPSMA=H2PSMA*2.0/1000.0
      O2PSMA=H2PSMA/2.0
      OPSMA=O2PSMA*32.0/1000.0
      AUXMOL=AUXIN*1000.0/18.0
      HAUX=AUXMOL*2.0/1000.0
      OAUX=AUXMOL*16.0/1000.0
      CTOT1=CPT
      HTOT1=HPT+HPSMA+HAUX
      OTOT1=OPT+OPSMA+OAUX
      NTOT1=NPT+NCAR
      ASHTOT=ASHPT
      CRAT=CTOT1*1000.0/12.0
      H2ORAT=((PEATIN-DRYPT)*1000.0/18.0)+AUXMOL+H2PSMA
      INRAT=CRAT/H2ORAT
C
C **********************************************************
C                 4.  MASS-OUT CALCULATIONS
C **********************************************************
C                        A) SOLIDS
C **********************************************************
C
      ASHSOL=ASHTOT
      DRYSOL=ASHSOL/ASHOUT*100.0
      CSOL=DRYSOL*COUT/100.0
      HSOL=DRYSOL*HOUT/100.0
      OSOL=DRYSOL*OOUT/100.0
```

```
      NSOL=DRYSOL*NOUT/100.0
C **********************************************************************
C                      B) GASES
C **********************************************************************
C
      NGAS=NTOT1-NSOL
      N2MOL=NGAS*1000.0/28.0
      TOTMOL=N2MOL/N2OUT
      CO2MOL=TOTMOL*CO2OUT
      COMOL=TOTMOL*COOUT
      CH4MOL=TOTMOL*CH4OUT
      H2MOL=TOTMOL*H2OUT
      O2MOL=TOTMOL*O2OUT
      OUTRAT=H2MOL/COMOL
      NTOT2=NSOL+NGAS
C
C **********************************************************************
C                       5. CARBON CHECK
C **********************************************************************
C
      CMOL=CO2MOL+COMOL+CH4MOL
      CGAS=CMOL*12.0/1000.0
      CTOT2=CGAS+CSOL
      CCONV1=CGAS/CTOT1*100.0
      CCONV2=(CTOT1-CSOL)/CTOT1*100.0
      CCONV=(CCONV1+CCONV2)/2.0
      CDIFF=CTOT2-CTOT1
C
C **********************************************************************
C                  6. HYDROGEN/OXYGEN CHECK
C **********************************************************************
C
      HMOL=2.0*CH4MOL+H2MOL
      HGAS=HMOL*2.0/1000.0
      HTOT=HGAS+HSOL
      OMOL=CO2MOL+0.5*COMOL+O2MOL
      OGAS=OMOL*32.0/1000.0
      OTOT=OGAS+OSOL
      HEXC=HTOT1-HTOT
      OEXC=OTOT1-OTOT
      H2EXC=HEXC*1000.0/2.0
      O2EXC=OEXC*1000.0/32.0
      H2OEXC=(H2EXC+2.0*O2EXC)/2.0
      HEXC1=H2OEXC*2.0/1000.0
      OEXC1=0.5*H2OEXC*32.0/1000.0
      HTOT2=HEXC1+HTOT
      OTOT2=OEXC1+OTOT
      HDIFF=HTOT2-HTOT1
      ODIFF=OTOT2-OTOT1
C
C **********************************************************************
C                      7. ERROR CALCULATIONS
C **********************************************************************
C
      CPCT=CDIFF/CTOT1*100.0
      HPCT=HDIFF/HTOT1*100.0
      OPCT=ODIFF/OTOT1*100.0
      NPCT=0.0
      ASHPCT=0.0
```

```
C
C *********************************************************************
C                         8. ENERGY CALCULATIONS
C *********************************************************************
C
      EPOWER=VOLT*AMPS*EFF/1000.0
      CPOWER=H2PSMA*68317.0*1.162222E-06
      POWER=EPOWER+CPOWER
      PCTE=EPOWER*100.0/POWER
      PCTC=CPOWER*100 0/POWER
      POWPT=POWER/PEATIN
      BTU=((COOUT*67636 0+CH4OUT*212800.0+H2OUT*68317.0)/100.0)
     $*0 0039683207*(100.0/(100.0-N2OUT))*1.3790459
C
C *********************************************************************
C                         9. OUTPUT
C *********************************************************************
C
      WRITE (6,10)
10    FORMAT('1')
      WRITE (6,20)
20    FORMAT(//,72('*'))
      WRITE (6,30)
30    FORMAT(//,15X,' EXPERIMENT NUMBER 15 ')
      WRITE (6,40)
40    FORMAT(//,15X,'      NOVEMBER 3        ')
      WRITE (6,20)
      WRITE (6,48) PTMASS
48    FORMAT(//,5X,' TOTAL MASS OF PEAT FED IN KG/H IS ',F6.2)
      WRITE (6,49) PTTIME
49    FORMAT(//,5X,' OVER A PERIOD OF TIME IN SECONDS OF ',F4.0)
      WRITE (6,50) PEATIN
50    FORMAT(//,5X,' MASS FLOW OF WET PEAT IN KG/H IS ',F6.2)
      WRITE (6,60) N2IN
60    FORMAT(//,5X,' FLOW OF NITROGEN CONVEYOR GAS IN CFH IS ',F6 2)
      WRITE (6,70) AUXIN
70    FORMAT(//,5X,' MASS FLOW OF AUXILIARY STEAM IN KG/H IS ',F6.2)
      WRITE (6,80) PLASMA
80    FORMAT(//,5X,' FLOW OF PLASMA STEAM IN CFH AT ROOM T IS ',F6.2)
      WRITE (6,100) INRAT
      WRITE (6,110) OUTRAT
      WRITE (6,120) CCONV1
      WRITE (6,121) CCONV2
      WRITE (6,122) CCONV
      WRITE (6,123) EPOWER
      WRITE (6,124) PCTE
      WRITE (6,125) CPOWER
      WRITE (6,126) PCTC
      WRITE (6,127) POWER
      WRITE (6,128) POWPT
      WRITE (6,138) BTU
      WRITE (6,20)
      WRITE (6,90)
      WRITE (6,20)
      WRITE (6,81)
81    FORMAT(//,'*   ELEMENT    *   WEIGHT   *   WEIGHT    ** **   COMPOUN
     $D  *   MOLAR     *')
      WRITE (6,82)
82    FORMAT   ( '*  IN SOLIDS  * PERCENTAGE * PERCENTAGE ** **   IN GAS
     $ES  * PERCENTAGE *')
```

```
      WRITE (6,300)
  300 FORMAT   ( '*                       *  IN PEAT   * IN PRODUCT ** **
     $    *            *')
      WRITE (6,20)
      WRITE (6,83) CPRINT, COUT, CO2OUT
   83 FORMAT(//,'*    CARBON      *',4X,F5.2,3X,'*',4X,F5.2,3X,'** **     CO
     $2          *',4X,F5.2,3X,'*')
      WRITE (6,84) HPRINT, HOUT, COOUT
   84 FORMAT(//,'*    HYDROGEN   *',4X,F5.2,3X,'*',4X,F5.2,3X,'** **     CO
     $           *',4X,F5.2,3X,'*')
      WRITE (6,85) OPRINT, OOUT, CH4OUT
   85 FORMAT(//,'*    OXYGEN      *',4X,F5.2,3X,'*',4X,F5.2,3X,'** **     CH
     $4          *',4X,F5.2,3X,'*')
      WRITE (6,86) NPRINT, NOUT, H2OUT
   86 FORMAT(//,'*    NITROGEN   *',4X,F5.2,3X,'*',4X,F5.2,3X,'** **     H2
     $           *',4X,F5.2,3X,'*')
      WRITE (6,87) ASHPRI, ASHOUT, O2OUT
   87 FORMAT(//,'*    ASH         *',4X,F5.2,3X,'*',4X,F5.2,3X,'** **     O2
     $           *',4X,F5.2,3X,'*')
      WRITE (6,88) N2OUT
   88 FORMAT(//,41X,'** **     N2          *',4X,F5.2,3X,'*')
      WRITE (6,20)
      WRITE (6,10)
   90 FORMAT(//,15X,'          RESULTS         ')
  100 FORMAT(//,5X,' INLET CARBON TO STEAM RATIO IS ',F6.2)
  110 FORMAT(//,5X,' OUTLET HYDROGEN TO CARBON MONOXIDE RATIO IS ',F6.2)
  120 FORMAT(//,5X,' CARBON CONVERSION BASED ON GAS FLOWS IS ',F6.2)
  121 FORMAT(//,5X,' CARBON CONVERSION BASED ON SOLID FLOWS IS ',F6.2)
  122 FORMAT(//,5X,' AVERAGE VALUE OF CARBON CONVERSION (%) IS ',F6.2)
  123 FORMAT(//,5X,' THE ELECTRICAL POWER IN KW IS ',F8.2)
  124 FORMAT(5X,' PROVIDING A PERCENTAGE OF THE TOTAL POWER OF ',F5.1)
  125 FORMAT(//,5X,' THE CHEMICAL POWER IN KW IS ',F8.2)
  126 FORMAT(5X,' PROVIDING A PERCENTAGE OF THE TOTAL POWER OF ',F5.1)
  127 FORMAT(//,5X,' THE TOTAL POWER IN KW IS ',F8.2)
  128 FORMAT(//,5X,' GIVING A POWER TO PEAT FLOW RATIO IN KW-H/KG OF ',F
     $7.2)
  138 FORMAT(//,5X,' THE ENERGY CONTENT OF THE GAS IN BTU/FT3 IS ',F7.2)
      WRITE (6,139)
  139 FORMAT(/////)
      WRITE (6,20)
      WRITE (6,140)
  140 FORMAT(//,9X,' * ELEMENT  * MASS-IN  * MASS-OUT * DIFFERENCE *')
      WRITE (6,150)
  150 FORMAT(9X ,' *          *  (KG/H)  *  (KG/H)  *    (%)     *')
      WRITE (6,20)
      WRITE (6,160)CTOT1, CTOT2, CPCT
  160 FORMAT(//,9X,' *  CARBON  *',F7.3,2X,' *',F7.3,2X,' *',F7.2,4X,' *
     $')
      WRITE (6,170) HTOT1, HTOT2, HPCT
  170 FORMAT(//,9X,' * HYDROGEN *',F7.3,2X,' *',F7.3,2X,' *',F7.2,4X,' *
     $')
      WRITE (6,180) OTOT1, OTOT2, OPCT
  180 FORMAT(//,9X,' * OXYGEN   *',F7.3,2X,' *',F7.3,2X,' *',F7.2,4X,' *
     $')
      WRITE (6,190) NTOT1, NTOT2, NPCT
  190 FORMAT(//,9X,' * NITROGEN *',F7.3,2X,' *',F7.3,2X,' *',F7.2,4X,' *
     $')
      WRITE (6,200) ASHTOT, ASHTOT, ASHPCT
  200 FORMAT(//,9X,' * ASH      *',F7.3,2X,' *',F7.3,2X,' *',F7.2,4X,' *
     $')
```

C. F*A*C*T

F*A*C*T is an abbreviation for The Facility for the Analysis of Chemical Thermodynamics. It is a package computer program available to McGill University Students on the MUSIC (McGill University System for Interactive Computing) system by Professors Thompson, Bale, and Pelton. The system has a data base of over 1600 compounds and binary solutions. The EQUILIB program available on the F*A*C*T system was used in this work.

Reference:

Bale, C.W., Pelton, A.D., and Thompson, W.T.
F*A*C*T User's Guide
McGill University/ Ecole Polytechnique
1st Edition, June 1979

D. STATPAK

Statpak is a conversational supplied program available on MUSIC (McGill University System for Interactive Computing) for the calculation of statistics. A variety of statistical information is available with the program, including multiple and polynomial regressions.

Reference:

Gordon, M.
MUSIC/STATPAK Reference Manual
McGill University
2nd Edition, October 1977