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HYDROGASIFICATION OF COAL

by

Maricy L. Torquato Bourgis

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF
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ABSTRACT

The influence of the presence of steam during the hydrogasification of "Forestburg Sub-Bituminous A" coal, was studied in pressure range of 122 to 418 KPa and in the temperature range of 811°K to 977°K in a tubular, fixed-bed reactor.

Two different sets of experiments were performed, which allowed the study of the influence of steam on the production of gases, specially that of methane, during hydrogasification.

Basically, the experiments consisted of:

i) feeding coal into the reactor through a free-falling particle mechanism once a temperature of 811°K had been reached;

ii) sequence of connecting and disconnecting steam to and from the feeding stream at different stages of hydrogasification process and during different time intervals.

The production of methane appears to have decreased with time, while steam remained part of the feeding stream and increased after steam was disconnected.

Some qualitative considerations concerning a possible mechanism for the reaction between coal and the "steam-

hydrogen" mixture were proposed involving the concept of formation of active sites.

It is suggested that:

i) the presence of steam, although increasing the number of active sites available for reaction also establishes a competition for hydrogen attack on carbon atoms;

ii) this competition decreases once steam is disconnected from the inlet stream, allowing easier access of hydrogen to the active sites.

ACKNOWLEDGEMENT

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NOMENCLATURE

H	enthalpy
R	unreactive species towards hydrogen
$\underline{R}$	retarding product
R_o	species giving rise to activated species
R^*	activated species
$\underline{RO}$	reactant
W_o	initial weight of moisture-free coal
W_f	final weight of char after run
() or []	species in adsorbed state

SUBSCRIPTS

ACT	activated or exposed
ADS	adsorbed
f	free active site
i	inactive site
INAC	inactive

CHAPTER 1

INTRODUCTION

The five major sources of energy in the world at the present time are petroleum, natural gas, coal, water power and nuclear power. Because of convenience and environmental considerations, however, petroleum and natural gas have taken over increasingly larger percentages of the growing total demand for energy, over the years - with petroleum leading the list in terms of present use.

A continued downturn in known reserves of oil and natural gas, identified by falling reserve/production ratios and the existence of natural fossil fuel resources which contain about 3% petroleum, 5% gas and 92% coal (108) has led most researchers to believe that coal will become the immediate substitute energy resource of the future - complementing or supplementing and eventually replacing oil and natural gas.

Although world natural gas reserves are still vast today, there are already some locations such as Japan and parts of the U.S.A., where the absence or depletion of indigenous natural gas has led to a call for the production of substitute natural gas (SNG) from coal - to meet the demand for a premium gaseous fuel.

The process producing gas from coal by chemical transformations is known as coal gasification (44). The gas produced can be high - BTU (900-1000 BTU/SCF), medium-BTU (300-500 BTU/SCF) or low-BTU gas (100-150 BTU/SCF), depending on the procedures used.

A high BTU or pipeline gas is composed essentially of methane and virtually free of sulfur. The medium and low BTU gas can be either catalytically upgraded to a high BTU gas or used directly for generating electricity in a combined gas-turbine, steam-turbine cycle or as synthesis gas for chemical manufacture (42, 44).

The principal methods of achieving complete gasification are by the direct attack on the coal substance by steam or by hydrogen (100).

The chemical reaction with steam may be written as

coal + steam + heat → hydrogen + carbon monoxide
+ carbon dioxide

The chemical reaction with hydrogen may be written as:

coal + hydrogen → methane + heat

In general, the initial production of low calorific value gas is achieved by the first reaction and is characteristic of current gasification technology. The production of medium calorific value gas by the second reaction is characteristic of the second generation technologies, now under development, to produce methane rich gas, because of the higher thermal efficiency that can be achieved (51, 100).

Hence, the production of a synthetic gas from coal, with a good methane content, would be highly desirable, since higher methane content would mean a higher calorific value gas.

Although significant insights into the complex chemical and physical phenomena occurring during the gasification of coal have been reached, a definitive qualitative understanding of coal and its behaviour under different gasification conditions have not been achieved yet.

Considerable amount of work has been done on the gasification of coal with either hydrogen or steam, however, relatively less information exists on the gasification of coal with the hydrogen-steam mixture. Some dispute still exists among researchers, concerning the actual effect of the presence of steam during the gasification of coal with hydrogen, as well as the qualitative mechanism of interaction of this mixture with coal.

The major purpose of this project is to observe the influence of steam on the gasification of coal with hydrogen by:

i) observing the effect of the presence of steam during hydrogasification on the rate of formation of methane;

ii) suggesting qualitatively possible interpretations concerning the reaction between coal and the hydrogen-steam mixture.

CHAPTER 2

LITERATURE SURVEY

Since the present study will involve reactions between coal and hydrogen as well as coal and steam, literature containing information concerning these reactions has been collected and reviewed, covering the period of the last three decades as well as literature disclosing the effect of pore structure on the reactions between coal and hydrogen or coal and steam over the last two decades. This survey will consist of four sections involving:

- hydrogasification reactions
- reactions between coal and steam
- reactions of carbon with "steam-hydrogen" mixtures
- effect of pyrolysis and gasification on pore structure

2.1 Hydrogasification Reactions

Hydrogasification of coal as the name implies, is the gasification of coal in the presence of hydrogen, leading mostly to the formation of methane and a solid residue,char. Since methane is the main product, hydrogasification usually gives rise to a high or medium BTU gas. This reaction, which is exothermic, can be represented as (42, 100, 123)

$$\text{coal} + 2H_2 \rightarrow CH_4 + \text{solid residue} + \text{heat} \qquad (2.1)$$

$$\Delta H = -17.87 \text{ Kcal}$$

Comparing with other gasification processes, the interest in hydrogasification started only some three to four decades ago, and from mid-seventies and on it intensified again. Therefore, a lot of evidence and propositions in the previous works remain to be proved and explained by today's new and more accurate equipment and methods.

However, some important facts have been recorded, and should be mentioned.

Hydrogen pressure has been proved to play an important role in hydrogasification - since coal conversion (19, 27, 46, 62, 67, 94) and char conversion (56, 62) to hydrocarbons increase with higher hydrogen pressures. So much so, that a high enough hydrogen pressure can cause all carbon from coal to be hydrogenated at once (94).

The influence of temperature has also been studied and the results indicate that an increase in temperature up to 1000°C increased the amount of hydrocarbons produced (29, 62, 67) as well as the amount of CO produced (19).

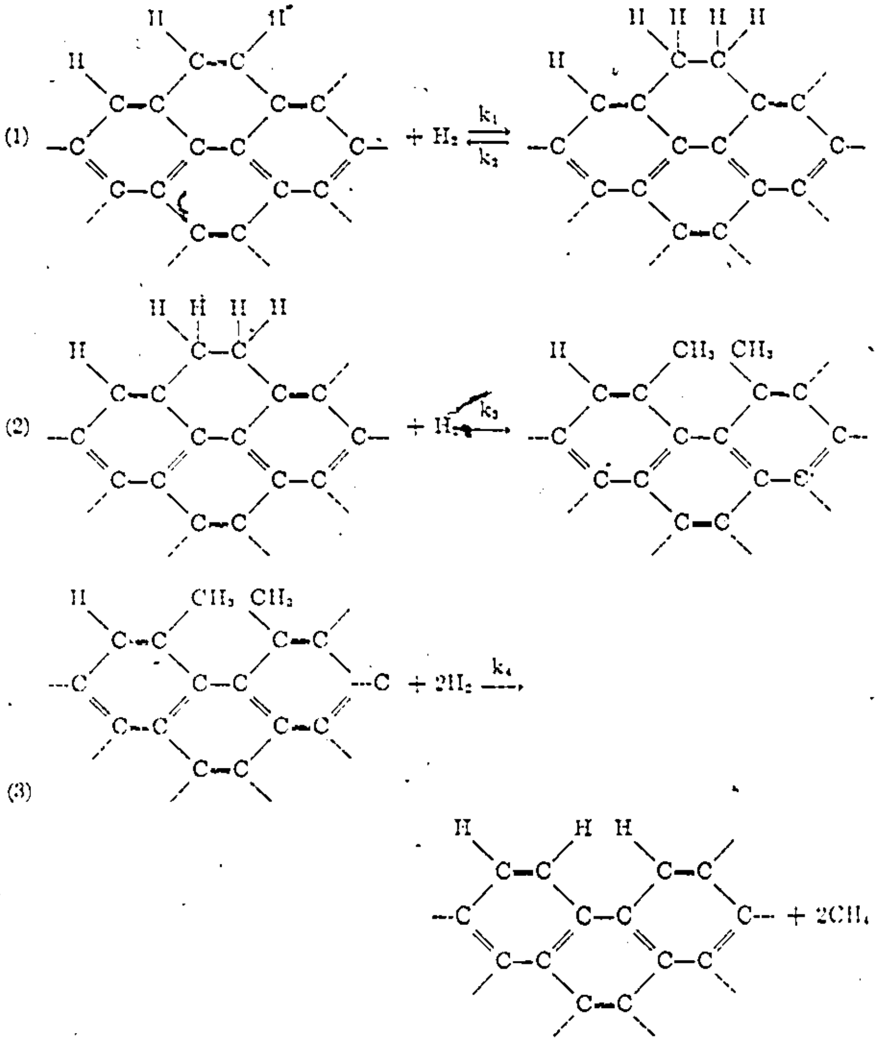
A large amount of evidence has been accumulated which shows that, in general, in any gas-carbon reaction, one of the steps involved is the chemisorption of the gas (121, 136).

For chemisorption to occur, the surface carbon atoms must have free valence electrons, in order to form strong chemical bonds - usually covalent bonds - with the gas molecules or atoms. The presence of impaired electrons has been confirmed in various types of carbons - through techniques utilizing electron paramagnetic resonance absorption (136).

The influence of several other parameters has been recorded, however, they will not be cited here, since they will not be relevant to the present study.

To explain their results, authors proposed mechanisms and two schools of thinking developed from thereon: one focussing its attention on the possible mechanisms through which hydrogen would react with carbon to give methane; the other, explaining hydrogasification as a gasification process, proposing stages which would explain the process over a period of time. Some mechanisms through which reaction (2.1) occurs, have been proposed since hydrogasification first started being studied. Some however do not prove to hold for a broader range of conditions - such as pressure and temperature.

Zielke and Gorin in 1954 (147) investigated hydrogasification of a low temperature char in a fluidized bed at temperatures between $1500^{\circ}F$ and $1700^{\circ}F$ and proposed a mechanism based on the hydrogenation of the exposed edges of the carbon lattice as represented by the $-CH=CH-$ group, as pictured below.



In the bonding arrangement pictures, an edge -CH-CH- group is generated rather than an edge -CH-CH- group. When this happens, resonance is assumed to occur and regenerate the -CH-CH- group. This results on the fact that, on the average, an equal number of new active points of attack represented by the -CH-CH- grouping are generated for each one that is consumed i.e., the number of such groupings per unit carbon is approximately constant. However, this mechanism and the equation representing it do not hold below 928°C.

However, several studies have led to a qualitative interpretation in a wide range of conditions which seems so far to explain best the reaction between carbon from coal and hydrogen. This interpretation involves the concept of formation of active sites. Active sites are regions in the coal structure which, by the action of some activating force or forces (for example, temperature) give rise to what is known as labile (= exposed, activated) carbon atoms, which will promptly react with hydrogen through some mechanism and form methane.

Blackwood, from 1958 to 1962, (8, 10, 11, 12) proposed that methane is not produced until an activated adsorption of hydrogen is virtually completed. The process steps are shown below:

$$C + H_2 = (CH)_{ADS}(H)_{ADS} \qquad (2.5)$$

$$(CH)_{ADS}(H)_{ADS} = (CH_2)_{ADS} \qquad (2.6)$$

$$(CH_2)_{ADS} + H_2 = CH_4 \qquad (2.7)$$

According to Blackwood, the process of chemisorption involves the breakdown of the hydrogen molecule into hydrogen atoms. One atom of hydrogen would be attached to a particular active carbon and the other would not necessarily attach itself to another active site (adjacent or not). The other carbon atom would attach itself anywhere on the surface, even to the original active carbon to form a $>CH_2$ group. Therefore, the function of these active sites, according to Blackwood, would be the splitting of the hydrogen molecules.

Subsequently, Blackwood also studied the path for the hydrogasification process, and proposed that the gasification of coal with hydrogen was a two-stage process in which hydrogen initially reacted very rapidly with the volatile constituents in the coal, followed by a comparatively slow reaction of hydrogen with the residual char.

Similarly, Feldkirchner and Linden (26, 62) proposed the following stages for the coal-hydrogen reactions:

> Stage 1 - A high-rate period comprising pyrolysis of the more reactive structural units such as aliphatic hydrocarbon side chains and oxygenated functional groups and hydrogenation of the intermediate pyrolysis products.
>
> Stage 2 - A low-rate period of direct attack of hydrogen on the residual aromatic carbon structure.

Several authors (8, 10, 26, 55) believe that the presence of oxygen in the active sites of coal was responsible at least for an initial activity. Groups containing oxygen such as chromene and benzrypyran attached to the coal structure would be responsible for promoting this oxygen. However, no further study was done to check these observations.

Shahin in 1962 (110), reported that hydrogen atoms produced by the action of a microwave discharge on hydrogen gas, can react with solid carbon even when the latter is in the plasma. In his study, he observed that when the location of the carbon source was systematically varied, the total amount of hydrocarbon products formed, decreased rapidly, as the carbon was moved away from the centre of the plasma. However, when oxygen replaced hydrogen in the set of experiments another fact was observed: the atoms of oxygen attacked elementary carbon even when it was far removed from the plasma region. This showed a contrast between the reactivities of oxygen and hydrogen towards carbon indicating that oxygen has a greater ability to seek for carbon atoms than hydrogen - i.e., oxygen is more reactive to elementary carbon than hydrogen.

Badzioch in 1961 (4) - on a review of the work which had been done in the U.S.S.R. on rapid decomposition of coal, suggested, on the basis of the results obtained, that the thermal decomposition of coal under rapid heating conditions could be divided into three stages:

i) Rapid carbonization proceeding at a very high rate in the beginning;

ii) Principal thermal decomposition process, proceeding at a relatively low rate;

iii) "Degassing" of coal, proceeding at very low rate for a long time.

Steck in 1968 (120), after a mass spectrometric investigation of the reaction of hydrogen with graphite, at 1900°K-2400°K proposed a mechanism involving addition and insertion reactions. According to his observations, when atomic carbon reacts with hydrogen the atomic carbon inserts itself into hydrogen to form CH_2 (methylene).

He also observed that the results obtained agreed with studies which proposed that the reaction between carbon and hydrogen was a surface reaction.

Moseley and Patterson in 1965 (92, 93, 94), studied the rapid hydrogenation of coal char and proposed a three-step mechanism which, from thereon, has been an important part of most of the pertinent literature on coal hydrogasification. Their fundamentals have been essential to subsequent studies - which sometimes, added but small modifications to their interpretation.

They assumed that the hydrogenation of "volatile" and "fixed" carbon in coal chars could not be treated separately and that, devolatilization in the presence of hydrogen would give rise to groups which would act as active sites - for further attack of hydrogen on the bulk of the "fixed" inactive carbon. This attack of hydrogen on active site groups would be similar to a free radical chain reaction, stripping-off a labile or exposed carbon atom to give a molecule of methane, and replacing it with another in the process. These active groups, although giving rise to labile carbon atoms, would not be removed themselves, except by the cross-linking polymerization reactions. The "fixed" carbon, promoted by these active sites, would be hydrogenated rapidly enough at sufficiently high hydrogen pressures, for this process to compete effectively with those leading to the stabilization of the residual carbon structure (by cross-linking polymerization reaction).

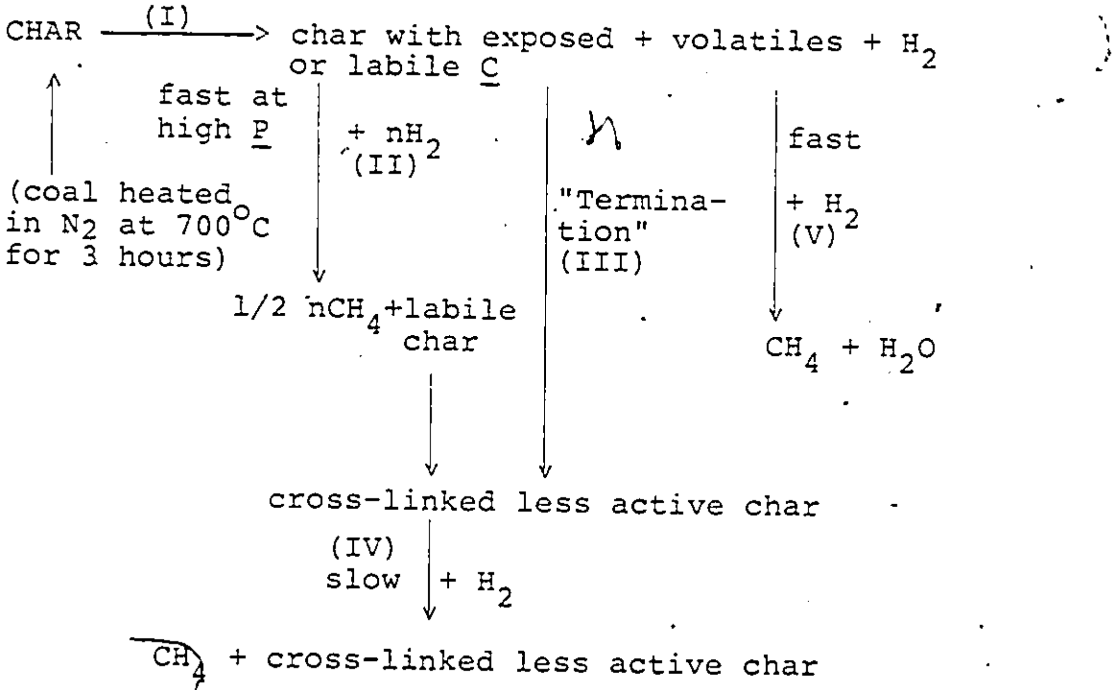
It was also observed experimentally that the total carbon that could be gasified to methane - by rapid heating - increased with increasing hydrogen partial pressure, in such a manner that, at sufficiently high pressures, virtually all the carbon in the coal char would be gasified to methane. This has also been observed by the researchers conducting experiments at the Institute of Gas Technology (62).

However, Moseley and Patterson asserted that at lower pressures, hydrogen cannot compete effectively against the other process which is happening simultaneously (cross-linking reactions). This would lead to an initial high rate of methane formation - because at the beginning, the least stable groups which have a low energy of activation are devolatilized at a rate which is independent, even of temperature. After that, a steady lower rate would follow, due to:

i) limited availability of volatile matter, which gives rise to active sites and

ii) increased degree of hindrance of devolatilization by cross-linking reactions comparing to the beginning of reaction.

Moseley and Patterson suggested, then, a possible mechanism for the hydrogasification of char:



- volatiles or volatile matter is defined (27) as the amount of material that evolves during heat-up of the coal particle. It consists mostly of tar vapors, methane, carbon monoxide, hydrogen and bound water.
- char is a totally or partially devolatized coal.

Basically, this scheme led to a three-step mechanism which follows:

1) Rapid devolatilization of char, which produces in addition to volatile products, an "active carbon" species;
2) This "active carbon" reacts either with hydrogen to form more methane or with itself in a cross-linking polymerization reaction to form inactive char;
3) Slow reaction of hydrogen with inactive char.

Most of the mechanisms which followed that of Moseley and Patterson suggested only slight changes due to the fact that different parameters were considered such as:

Feldman in 1970 (27, 28, 29) who considered, in his proposition of the mechanism, that there exists volatiles from the pyrolysis of the coal, which remain so.

He also proposed a three-step mechanism:

i) During devolatilization, bonds within the coal molecule are breaking, resulting in the formation of radicals which make coal extremely reactive;

ii) The reactive species formed, either react together to form highly condensed and therefore unreactive tars or residual carbon, or they can react with hydrogen to form hydrocarbon gases, lighter aromatics or solid reactive species that are in turn hydrogasified to hydrocarbon gases;

iii) The solid carbon structure formed by condensed radicals can be hydrogasified further, but at a much smaller rate than either the volatile matter or the reactive solid carbonaceous material.

He also suggested that the reactivity of carbon towards hydrogen is different for these three phases in the following way:

i) The most reactive carbon exists which is quickly (almost instantaneously) converted to methane. It is contained in aliphatic chains bridging the aromatic groups in coal;

ii) The carbon in this stage is associated with reactive solids - probably formed by the reaction of radicals with hydrogen. Although this carbon reacts with hydrogen at slower rate than does the carbon in aliphatic chains, its half-life is still only in the order of seconds;

iii) The residual carbon formed by condensation of radicals reacts with hydrogen. Its half-life ranges from minutes to hours.

He also concluded that it is dangerous to apply thermodynamics to a hydrogasification system to produce methane, since reversibility - which is the fundamental condition a system must satisfy to give the concept of equilibrium, meaning - of the reaction

$$\text{coal} + H_2 \rightarrow \text{char} + CH_4 \qquad (2.8)$$

has never been known to occur. Therefore, the behaviour of hydrogasification systems should be dictated, at least, to a large degree by the kinetics of reaction (2.1).

Zahradnik and Glenn in 1971 (62, 146), proposed a somewhat similar mechanism for coal hydrogasification to describe their results based on active species rather than active sites - which would disappear either by methane formation or by cross-linking reactions.

They assumed that concurrent with the complex phenomena that occurred during devolatilization of coal, even in an inert gas atmosphere, there occurred, when gaseous hydrogen was present, a hydrogen-activated decomposition of some element in the coal structure, which would rapidly give rise to an active intermediate that was responsible for the transient high reactivity of coal for methane formation. This reactivity was transient, since the active intermediate could be deactivated, possibly due to cross-linking or some polymerization process.

They stated that the following scheme would represent the reaction between coal and hydrogen:

$$\text{coal} + H_2 \rightarrow C_{ACT} + CH_4 + \text{other gases} \tag{2.9}$$

$$C_{ACT} \rightarrow C_{INAC} \tag{2.10}$$

$$C_{ACT} + H_2 \rightarrow CH_4 \tag{2.11}$$

where C_{ACT} = active intermediate.

C_{INACT} = inactive char formed by polymerization of the active intermediate.

Johnson et al. in 1975 (67, 68), suggested that the formation of active sites which promoted methane-plus-ethane formation through the interaction of gaseous hydrogen with coal, was directly related to the process in which coal hydrogen was evolved. This step would involve only thermally activated phenomena occurring independently of gaseous atmosphere. The model he proposed would occur basically in two stages:

i) It would involve thermally activated devolatilization reactions, resulting in the evolution of carbon oxides, water, oil, tar, light gaseous hydrocarbons and leading to the formation of an intermediate semi-char;

ii) Consecutive to the primary devolatilization, it would involve thermally activated decomposition reactions associated with secondary devolatilization of remaining coal hydrogen - leading to the formation of a relatively non-reactive char.

The secondary devolatilization of coal hydrogen would also promote the hydrogenation of C_3^+ light hydrocarbons.

This model was represented in the following way:

$$\underset{\text{semi-char}}{CH_x^o} \xrightarrow[\text{(thermally activated coal hydrogen evolution)}]{} \underset{\text{active intermediate}}{CH_y^*} \qquad (2.12)$$

$$\begin{tikzcd} & \underset{\text{inactive char}}{(1-m)CH_y^o} \\ CH_y^* \arrow[ur] \arrow[dr, "\text{gaseous hydrogen}"'] & \\ & m[zCH_4 + \frac{1-z}{2} C_2H_6] \end{tikzcd} \qquad (2.13)$$

He viewed the active sites, as catalyzing the reaction between fixed carbon and hydrogen, and the rate of formation of these active sites to be much slower than their subsequent decomposition.

Anthony in 1976 (2), focused his attention on the interaction of rapid hydrogasification and devolatilization.

However, according to his observations, the primary volatiles formed by devolatilization with coal particles, were of two categories: reactive and non-reactive.

The non-reactive volatiles would escape out of the particles as such, whereas a part of the reactive volatiles would deposit inside the particles by polymerization and/or cracking. Thus, only a part would escape out. This would be the main reason for higher volatiles yield in rapid heating compared to slow heating. In rapid heating the residence time of the primary decomposition products within the coal particles, would be shortened, lessening the chance of the secondary reactions within the coal.

His data, proved to be consistent with the interpretation that rapid hydrogenation proceeded in two stages:

i) Hydrogen would react with some of the volatiles to form light hydrocarbons, sufficiently stable to avoid the secondary char forming reactions;

ii) Hydrogen would react with the fresh solid residue, as proposed by Moseley and Paterson - with a rate faster than hydrogasification of older char, but slower than devolatilization.

Wen and Dutta in 1978 (140), studied solid-gas reactions in coal conversion processes for different coals in slow-heating processes using temperatures up to 1000°C with available data and proposed a two-step mechanism for hydrogasification:

i) Rapid conversion, due to the contribution of fast pyrolysis process, occurring simultaneously with hydrogasification. According to them this stage would be absent if a completely devolatilized char were used;

ii) The remaining fraction of carbon would gasify slowly.

According to their interpretation, higher hydrogen partial pressures would improve carbon conversion in the first stage for two reasons:

a) hydrogen would gasify part of the solid char;

b) it would render part of the primary volatile decomposition products unreactive, thereby helping that portion escape out of the solid particle unchanged.

Peacock et al in 1978-79 (74, 99), studying the reactivity of graphite towards hydrogen at temperatures between 1010°K and 1473°K and pressure of 1 bar, found that the reactivity of graphite at lower temperatures, increased (i.e., more methane was produced) after the samples had been exposed to hydrogen at 1473°K and they proposed 3 possible causes which would explain this increase in reactivity:

a) Deposition of carbon from methane pyrolysis;

b) The opening and creation of pores by reaction with hydrogen;

c) Increase in number of active carbon atoms.

The first one was immediately discarded, because:

i) the carbon from methane pyrolysis was always accompanied (in their experiment) by polynuclear aromatic compounds (naphthalene anthracene and fluoranthrene), and no evidence of such polynuclear material was ever found. Another experiment (99), in which a sample of graphite was forcedly covered by carbon from methane pyrolysis proved that its reactivity was only twice that of the original sample - indicating that carbon deposition was not a relevant point in the increased reactivity of graphite. Further evidence against carbon deposition came from experiments carried out on a Raman spectrometer (99).

The mechanism they proposed was that proposed by Shaw (111), which is represented below:

$$(\ldots C_f) + H_2 = (\ldots CH_2) \qquad (2.14)$$

$$(\ldots CH_2) + H_2 + n\,(\ldots C_i) = CH_4 + n\,(\ldots C_f) \qquad (2.15)$$

$$(\ldots C_f) = (\ldots C_i) \qquad (2.16)$$

where C_f = free active site

C_i = inactive site

The Institute of Gas Technology - U.S.A. - conducted studies on hydrogasification (62) from 1954-1964 and developed a correlation for pressures up to 2000 psig and temperatures up to 2000°F.

In their study, they assumed that the coal structure was comprised of base carbon (which would be the "fixed carbon" from Moseley and Paterson) to which side chains were attached. These side chains would contain essentially the components of volatile matter in the feed coal (including volatile carbon). Thus, as a coal would be heated in a hydrogen containing atmosphere, the following was assumed to happen:

i) Devolatilization: pyrolysis reactions causing gasification of side chains;

ii) Rapid methane formation: the carbon in the base structure would be gasified in the presence of an active intermediate which would be both formed and deactivated in the base structure. This would happen at the same time as devolatilization;

iii) Low rate gasification: deactivation of this intermediate and consequent slow gasification of the carbon in the base structure.

At temperatures compatible with the ones utilized in this study, three reaction steps were assumed - similar in some aspects to the model suggested by Moseley and Paterson.

$$R_0 \rightarrow R^* \qquad (2.17)$$

$$R^* \rightarrow R \qquad (2.18)$$

$$R^* + C + 2H_2 \rightarrow R^* + CH_4 \qquad (2.19)$$

where R_0: species giving rise to activated species

R^*: activated species

R : unreactive species towards H_2

They assumed that steps (2.17) and (2.18) were essentially activated by hydrogen, but became independent of hydrogen pressure at relatively low pressure.

2.2 Reactions Between Carbon and Steam

The main reactions involved in the reaction of carbon and steam have been accepted as being (58, 136):

$$C + H_2O = CO + H_2 \qquad \Delta H = +\ 31.14\ \text{Kcal} \qquad (2.20)$$

$$CO + H_2O = H_2 + CO_2 \qquad \Delta H = -\ 9.65\ \text{Kcal} \qquad (2.21)$$

$$C + CO_2 = 2CO \qquad \Delta H = +\ 40.79\ \text{Kcal} \qquad (2.22)$$

$$C + 2H_2 = CH_4 \qquad \Delta H = -\ 17.87\ \text{Kcal} \qquad (2.23)$$

Reaction (2.20) is usually referred to as the water-gas reaction and is favoured at severe conditions such as temperatures above 675°C (57, 58).

Reaction (2.21) is referred to as CO-shift or water-gas shift reaction and is favoured at less severe conditions - such as temperatures below 827°C (57, 58).

In addition to reactions (2.20) and (2.21) and depending upon conditions present, there might be further reaction between carbon monoxide and hydrogen to form hydrocarbons and other products. However, controversy still exists as to whether hydrocarbons are formed from reaction between carbon monoxide and hydrogen or from direct reaction of hydrogen with surface carbon, rather than carbon monoxide. One fact however should be borne in mind, i.e., the temperatures for steam decomposition and methane formation are not compatible (58).

Reaction (2.22) is both temperature and pressure dependent. At temperatures above 927°C and 1 atm, the conversion of carbon dioxide to carbon monoxide is unrestricted by equilibrium considerations. However, at higher pressures, the possible conversion markedly decreases (106).

The reaction (2.23), i.e., production of methane from the reaction between carbon and hydrogen originating from steam is usually considered a minor reaction occurring at very low levels and producing only traces of methane.

The overall reaction would tend to be thermally neutral below 266°C:

$$\frac{(20) + (21) + (23)}{2}: \; C + H_2O \rightarrow \frac{1}{2} CH_4 + \frac{1}{2} CO_2 \qquad (2.24)$$

Hence more attention has been paid in the literature surveyed, to the mechanisms leading to reactions (2.20) and (2.21).

The mechanism by which the reactions involved would occur, is apparently a question not readily settled, however, there seems to be a general agreement that reaction (2.20) is predominantly the primary reaction (36, 69, 122, 136, 137, 138), although not a total agreement exists on this point either, since some authors have also reported carbon dioxide as the primary product (106) at temperatures below 1000°C based on the fact that at zero time the initial products are carbon dioxide and hydrogen,formed, according to the reaction:

$$C + 2H_2O \rightarrow CO_2 + 2H_2 \qquad (2.25)$$

and some proposed that both carbon monoxide and dioxide are primary products (41) based on the assumption that two oxygen atoms would collide on the carbon surface to form CO_2.

The presence of hydrogen in the steam reacting atmosphere, tends to inhibit the carbon-steam reaction and this is explained by virtue of the fact that hydrogen is a reaction product and therefore an excess of hydrogen would shift both reactions (2.20) and (2.21) towards the left (36, 57, 62, 118, 136).

Studies on coal-steam reactions leading to the formation of methane as the main product were performed utilizing a catalyst (57, 59, 132).

Since most of the studies are geared towards an explanation of the mechanism through which reactions (2.20) and (2.21) occur - more information concerned with these reactions have been published.

Warner in 1943 (137),studied the mechanism of steam-carbon reaction and derived four important conclusions based on his data - from which further development of the study of coal-steam reactions occurred. They were:

i) The primary products of the reaction are carbon monoxide and hydrogen, and that carbon dioxide is formed from the water-gas shift reaction which reaches or tends to reach equilibrium;

ii) The rate of gasification is governed by an adsorption isotherm for steam and a steam saturation pressure exists (its value depending on the type of coal and temperature) above which, the rate of gasification at a given temperature becomes constant.

iii) With increasing steam pressure, diffusion of the reaction products from the surface is impeded.

Hence, they are adsorbed in competition with steam, which is equivalent to surface poisoning. This poisoning effect may be attributable chiefly to carbon dioxide, which is more readily formed at higher steam pressures.

iv) The proposition of a mechanism in which an intermediate adsorption complex is formed: first, adsorption - of the Langmuir type - of steam, which is largely reversible, happens. In part, this adsorption is irreversible, since the steam cannot be recovered undecomposed. This would be due either to an activated adsorption in which the steam molecules penetrate into the carbon lattice after overcoming an energy barrier, or to ordinary adsorption with localized strong fields of forces. The adsorbed steam would be alternatively re-evaporated or transformed into carbon monoxide and hydrogen.

The scheme for the proposed mechanism was:

$$C + H_2O = C(H_2O)_{ADS} = \underset{\substack{\text{adsorbed}\\ \text{formaldehyde}}}{(CH_2O)} = CO + H_2 \qquad (2.26)$$

$$CO + H_2O = (CO)_{ADS}(H_2O)_{ADS} = \underset{\substack{\text{adsorbed}\\ \text{formic acid}}}{(HCOOH)} = CO_2 + H_2 \qquad (2.27)$$

Gadsby and co-workers in 1946 (36), also investigated the steam-carbon reactions and proposed an adsorption-desorption mechanism.

The following reactions were considered to occur:

$$C + H_2O = CO + H_2 \tag{2.20}$$

$$C + 2H_2O = CO_2 + 2H_2 \tag{2.25}$$

$$CO + H_2O = CO_2 + H_2 \tag{2.21}$$

$$C + CO_2 = 2CO \tag{2.22}$$

In their proposition of a mechanism, they represented the reactant (steam) by *RO* and the retarding product (hydrogen) by *R*, and the molecules chemisorbed on the carbon surface by symbols enclosed in brackets. They proposed that both reactant (steam) and retarding product (hydrogen) were first adsorbed as such, on carbon surface, leading to the desorption of carbon monoxide and hydrogen (which would eventually be adsorbed on surface); and the rate of reaction would be proportional to the fraction of the surface covered by the reactant. The following scheme was their representation of the mechanism:

$$\underline{RO} = [RO] \tag{2.28}$$

$$\underline{R} = [R] \tag{2.29}$$

$$C + [RO] = CO + R \tag{2.30}$$

This same mechanism was quoted by Walker (136) in the following way:

$$C_f + H_2O = C(H_2O)_{ADS} \tag{2.31}$$

$$C(H_2O)_{ADS} \rightarrow H_2 + C(O)_{ADS} \tag{2.32}$$

$$C(O)_{ADS} \rightarrow CO \tag{2.33}$$

$$C_f + H_2 = C(H_2)_{ADS} \tag{2.34}$$

where he implies that the surface reaction with steam is fast, as compared with the desorption of $C(O)_{ADS}$ as carbon monoxide.

Gadsby also found that the addition of carbon monoxide to the reacting atmosphere, did not inhibit the gasification of carbon with steam other than its resulting in the production of more hydrogen which did inhibit the reaction:

$$CO + H_2O \rightarrow CO_2 + H_2 \tag{2.21}$$

Strickland-Constable in 1947 (121, 122) also studied the carbon-steam reaction and proposed a mechanism in which steam would be adsorbed in the molecular form. This was based on his observation of the fast reversible adsorption of steam on charcoal below 700°C.

By reversible adsorption of steam, he meant that in the adsorbed condition steam would react with charcoal to form carbon monoxide and hydrogen and these products would then be desorbed. However, both carbon monoxide and hydrogen were themselves "reversibly" absorbed at that temperature.

His explanation was that, at equilibrium, hydrogen is adsorbed much more strongly than carbon monoxide. At the same time, the adsorption and desorption of hydrogen are far more rapid than those of carbon monoxide, so that hydrogen adsorption equilibrium is established very quickly, while that of carbon monoxide much more slowly.

He observed that in the early stages of reaction, hydrogen would desorb more rapidly and hence be in excess in the gas phase. Later in the reaction, as adsorption equilibrium was approached, carbon monoxide would be in excess in the gas phase, owing to its much smaller adsorption equilibrium. However, the rate of desorption fell rapidly as pressure increased.

He also proved that when equilibrium was disrupted, hydrogen would desorb much faster than carbon monoxide in order to restore it.

According to his observations, the proposition of a mechanism involving the dissociation of steam (discussed next) would be highly unlikely to happen - in view of the known very high rates of reaction of such gases as oxygen and N_2O, H_2O and CO_2 with charcoal at the temperatures studied.

Finally, he proposed that the hydrogen retardation in the carbon-steam reaction was caused by its chemisorption on active sites, based on the observation that hydrogen was not only strongly but very rapidly adsorbed on carbon.

Long and Sykes in 1948 (80,81), proposed that the reaction between carbon and steam involved a pre-dissociation of steam into hydrogen and oxygen which would then be adsorbed separately on different reaction sites.

They ruled out the possibility that steam and hydrogen are the adsorbed species, since in their results, initially oxygen was in excess of hydrogen. They concluded therefore, that steam was dissociated into oxygen and hydrogen, separately attached to neighbouring sites. This decomposition of the steam molecule, was regarded as a natural result of the fact that adsorption at high temperatures required the formation of bonds with the surface. Therefore, they proposed that what happened was the initial formation of a chemisorbed hydrogen atom and a chemisorbed hydroxyl radical, followed by the transfer of a hydrogen atom from the hydroxyl radical to join the hydrogen atom on the adjacent carbon atom. Then, hydrogen as a molecule would rapidly evaporate, although at steady state, a considerable proportion would remain on the surface.

The following scheme represented their proposition:

$$H_2O = (OH)(H) \rightarrow (O)(H_2) \qquad (2.35)$$

$$H_2 = (H_2) \qquad (2.36)$$

$$C + (O) \rightarrow CO \qquad (2.37)$$

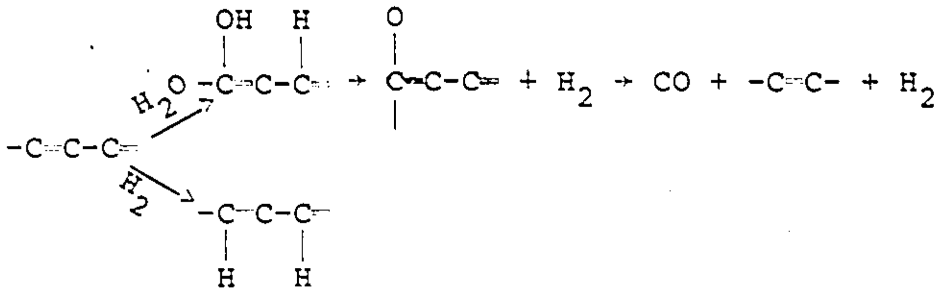
According to them, the suggestion that the adsorption of steam required its dissociation into oxygen and hydrogen and that the action of steam was retarded by hydrogen presence, would explain why steam and hydrogen were said to compete for the sites which could take up hydrogen atoms.

They asserted that oxygen would leave the surface as carbon monoxide in a very slow process. They also divided the active sites, in two separate groups:

i) the one that could accommodate two atoms of hydrogen or a molecule of carbon monoxide;

ii) the one that could accommodate only one atom of hydrogen - whose reaction with carbon would retard the reaction between carbon and steam.

Since the active sites would consist of carbon atoms which were not exerting their full valency (i.e., the ones which had the ability of adsorbing steam and hydrogen), the mechanism could be expressed in terms of carbon atoms located at the free edges which were attached to the rest of the lattice by only three bonds, and thus would have one further orbital available for interaction with other molecules:



(2.38)

Walker (136), quotes this proposed mechanism in the following way:

$$2C_f + H_2O \rightarrow C(H)_{ADS} + C(OH)_{ADS} \quad (2.39)$$

$$C(H)_{ADS} + C(OH)_{ADS} \rightarrow C(H_2)_{ADS} + C(O)_{ADS}$$

$$C(O)_{ADS} \rightarrow CO \quad (2.41)$$

$$C(H_2)_{ADS} = C_f + H_2 \quad (2.42)$$

Jolley and Poll (69), reviewed the literature in 1953 and performed experiments whose results seemed to agree mostly with the mechanism proposed by Gadsby (36).

They obtained very little methane gas as a product of the steam-coke reaction and proposed that it could have been synthesized directly from carbon and hydrogen through the reaction: $C + 2H_2 \rightarrow CH_4$ (2.23), or from carbon monoxide and hydrogen through the reaction

$$CO + 3H_2 \rightarrow CH_4 + H_2O \quad (2.43)$$

They also observed an almost linear rise in the reactivity of coke as the carbon was burnt away, and they associated thereby the known effect of activation of carbon by the action of steam with the phenomenon of "internal burning" - although they also admitted that an overall increase in surface area or a preferential gasification of the most reactive fractions of the carbon by steam could explain the observed increase in reactivity.

Pilcher in 1955 (101), found that his data agreed with the mechanism involving the adsorption concept used to explain heterogenous reactions in which the rate is determined by the concentration of gas adsorbed on the solid surface, rather than by the pressure of the gas in the homogeneous phase

He also reported the formation of an unreactive porous layer on the surface of the specimens treated with steam at 1100°C which contained a high concentration of spherical shapes that tended to floculate or collect in short chains. He assumed that these areas contained less "active carbon centres" than the other areas of the unreacted graphitized carbon - which seemed like large cotton-like areas consisting of a number of thin plate-like crystals in very disordered arrangement.

2.3 Reactions of Carbon with "Steam-Hydrogen" Mixtures

The reaction between carbon and steam-hydrogen mixtures has not been studied as extensively as the reactions between carbon and each of the components of this mixture alone. Hence, several of the results reported by different researchers are still contradictory and a definite mechanism explaining how both reactions occur is yet to be proposed and confirmed.

Steam-hydrogen mixtures were initially studied, probably with the intent of observing the "retarding" effect of hydrogen on the carbon-steam reaction, utilizing different compositions and different partial pressures.

In addition to that, researchers' interest was geared towards an alternative (42, 51, 100, 123) to the reliance on the steam-carbon reaction, (making hydrogen, carbon monoxide and dioxide and then reacting this hydrogen with carbon or carbon oxides) to produce methane. This route is usually called Methane Synthesis and can be represented by:

$$2C + 3H_2O + \text{heat}(2000^{\circ}F) \rightarrow CO + 3H_2 + CO_2 \qquad (2.44)$$

$$\underline{CO + 3H_2 \xrightarrow{\text{catalyst}} CH_4 + H_2O + \text{heat } (650^{\circ}F)} \qquad (2.43)$$

$$2C + 2H_2O \rightarrow CH_4 + CO_2 \qquad (2.45)$$

The thermodynamics and kinetics of reactions (2.44) and (2.43) are such that reaction (2.44) would have to be carried out at high temperatures while reaction (2.43) could be catalyzed and would be favoured by low temperature conditions (51). Besides, the heat released during reaction (2.43) would be at too low a temperature, to be utilized directly in reaction (2.44) - making heat exchange between them, therefore, impossible - except, maybe, in the form of high pressure process steam generation (51, 100).

The alternative would be the production of hydrogen by other means, followed by its introduction with steam; into the hot carbon bed. Three regimes of composition of the gas reacting with carbon could increase the hydrogen content of this gas.

i) gas produced by steam-oxygen mixture - requiring no heat - and producing carbon monoxide, hydrogen, steam and carbon dioxide;

ii) gas produced by steam alone, which would produce a higher H_2/CO ratio than in (i), but would require heat (either electrical or by transfer of inert solids);

iii) gas produced by addition of steam and hydrogen - with the heat required for steam decomposition being supplied by the hydrogenation reaction. The hydrogen required for this reaction could be, although not necessarily, produced by the gasification of a char residue from the hydrogenation reaction in the following way (100):

$$C + 2H_2O \rightarrow 2H_2 + CO_2 \qquad (2.25)$$

$$\underline{C + 2H_2 \rightarrow CH_4 + \text{heat } (1750^{\circ}F)} \qquad (2.23)$$

$$2C + 2H_2O \rightarrow CH_4 + CO_2 \qquad (2.45)$$

Here the heat generated by the hydrogasification reaction would be at a sufficiently high temperature to contribute directly to the thermal requirements of steam decomposition with the advantage of no need for catalysts (100, 123).

It was then for these fundamental reasons, that the hydrogenation reaction became the basis for practically all the new second generation processes for the production of SNG from coal (51).

Equilibrium relationships for the "steam-hydrogen" gasification of carbon have also been developed (25, 62) for high temperatures and pressures - and are shown in Figure 2.1 below.

The effects of temperature for three pressure levels on the equilibrium gas composition for the steam-hydrogen gasification of carbon were calculated. Ideal gas behaviour and a unit activity for carbon were assumed. The graphs indicate that as temperature increased from 1700-2300°F, the yield of methane and carbon dioxide decreased and the yield of carbon monoxide increased; and as pressure increased

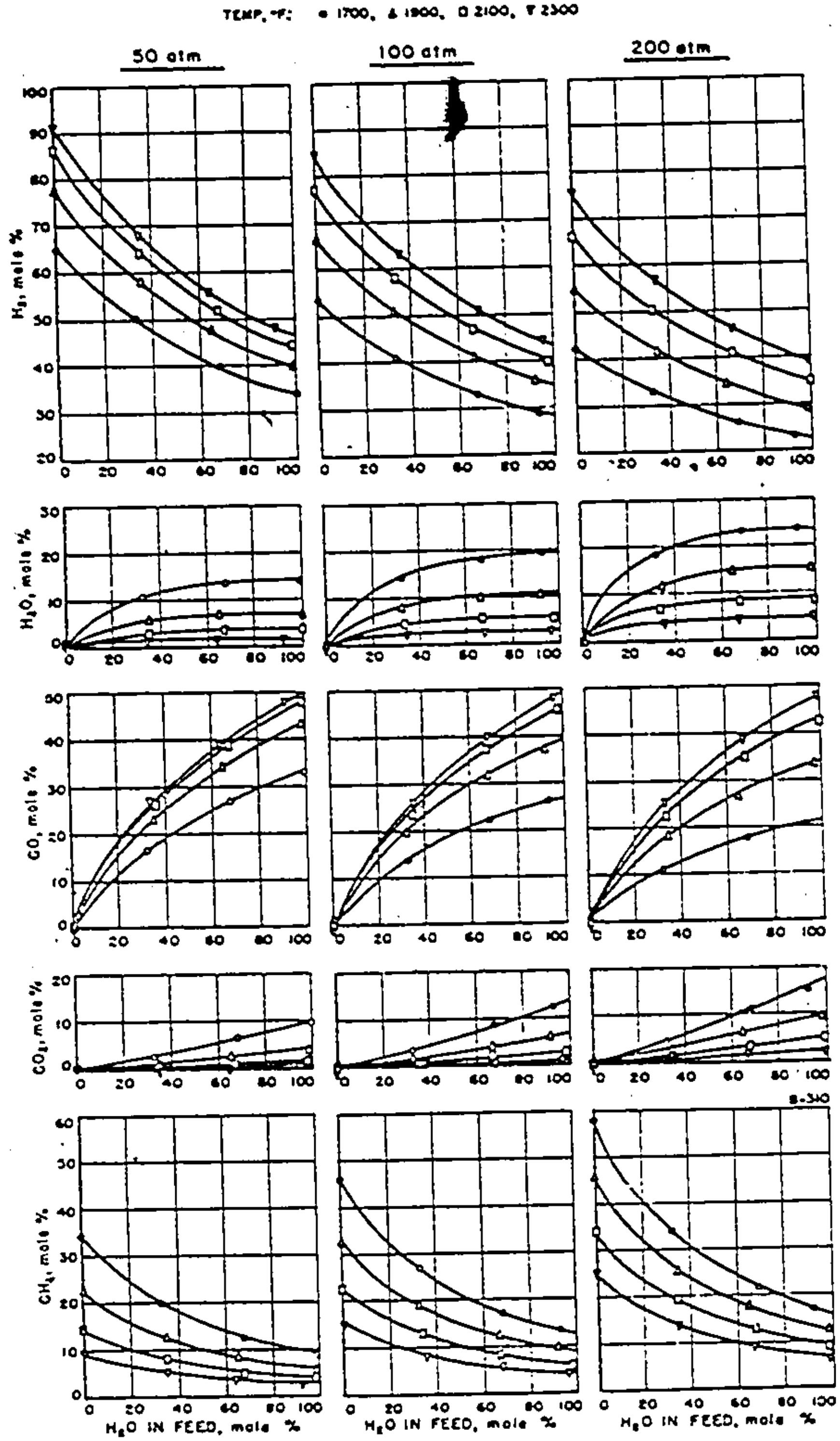


Figure 2.1 - Ideal gas equilibrium compositions for steam-hydrogen gasification at high temperatures and pressures (62).

from 50 to 200 atm the yield of methane and carbon dioxide increased while that of carbon monoxide decreased.

It seems, though, that researchers have been approaching the problem of gasification of coal in the presence of H_2-H_2O mixtures from two different standpoints:

i) one (most of the literature available) considering the addition of hydrogen to a carbon-steam reaction - in which case the main reaction considered would be that between carbon and steam;

ii) the other considering the addition of steam to a hydrogasification process - where the main reaction would be that between carbon and hydrogen.

Feldman (27), asserted that "in spite of the many efforts to develop gasification models, there is no "a priori" way of selecting a best model. Also, because of the complexity of the system, it seems that efforts to develop universally applicable kinetic models for design may be fruitless. Instead of developing additional kinetic models, efforts should concentrate on an increasing qualitative understanding of what occurs during gasification with hydrogen-steam mixtures". He reasoned that "in spite of the irreversibility of the reaction: coal + A(gas) → char + B(gas), many of the kinetic models utilize approach to equilibrium arguments to correlate their data. In spite of photomicrographs that indicate that char particles are extremely porous, shrinking core analogies have been utilized to allow correlation of data".

Goring and Curran in 1952 (39, 40, 41), investigated the effects of what they considered to be a major parameter in their study of gasification of carbon by steam at 1600°F and pressures of 1-30 atm, utilizing different steam-hydrogen composition. The parameter they investigated was carbon burnoff - and concluded that in general, the change in nature of the char surface, caused by increasing burnoff, resulted in a decrease in total gasification rate of the resulting carbon by hydrogen-steam mixtures. This depressing effect would become more pronounced with increasing hydrogen-steam ratios and/or total pressure.

They first related the mechanism of the burnoff effect (i.e., the mechanism for the decrease in total gasification rate) to a decrease in the number of active sites. Secondly, they showed that the burnoff effect was also related to the hydrogen-steam composition - implying that the decrease in the gasification rate was due not only to the number of active sites, but also to the type of active sites. They found that the decrease in methane formation rate with carbon burnoff, though, was much less pronounced than the decrease in total gasification rate.

They also observed the known "inhibiting" effect of the presence of hydrogen for the carbon-steam reactions observed by other authors (40, 41).

An increase in the total pressure was verified to cause appreciable increase in both total gasification rate and methane formation rate, and an increase in steam concentration i.e., a decrease in H_2/H_2O ratio increased both the total gasification rate and methane formation rate.

Continuing their work (41) in 1953, they concentrated on the carbon oxides formation and observed that carbon dioxide was a primary product together with carbon monoxide and postulated a mechanism for the primary formation of carbon dioxide, based on the assumption that a carbon-oxygen complex formed on the carbon surface possessed a characteristic property: "that the oxygen atoms retained on the surface, were capable of random movement thereon." This assumption permitted the proposition of the mechanism that explained the primary formation of carbon dioxide, by the collision on the carbon surface of two mobile oxygen atoms. The following three equations would describe the carbon oxides formation:

$$H_2O + C = C(O)_{ADS} + H_2 \tag{2.46}$$

$$C(O)_{ADS} \rightarrow CO \tag{2.47}$$

$$C(O)_{ADS} + C(O)_{ADS} \rightarrow CO_2 + C \tag{2.48}$$

They also made some observations about the methane formation based on their data. Their interpretation was that methane could be formed by two independent reactions:

1) by direct hydrogenation of the char;
2) by some process involving steam;

and that reaction (1) would be accelerated by hydrogen, while reaction (2) would be inhibited by hydrogen.

They concluded that at low pressures, the bulk of the methane was formed by direct interaction of carbon and steam and that the presence of hydrogen would be necessary only to obtain a high production of methane.

Feldkirchner and Huebler in 1965 (25, 62), studied the reaction of coal with steam-hydrogen mixtures at a total pressure of 1000 psig and a temperature of 1700°F and found no such "activating" effect in their experiments. On the contrary, the methane content of the product gas varied almost inversely with the feed gas steam content at higher carbon gasification levels. This effect, they explained, could be partially due to an increased steam reforming of the product methane with increases in steam partial pressure.

They also observed the "inhibiting" effect of hydrogen in the steam-char reactions previously cited (40, 41).

Wen and Talwalkar in 1966 (138), treated the coal char reaction with hydrogen-steam mixtures at high pressures

(70 atm) and temperatures (1600°F) as two simultaneous reactions taking place without interfering with each other and occurring in two phases. The first phase would be related to the amount of volatile matter and could be regarded as a volume (or mass) reaction. The first phase reaction with hydrogen was found to be proportional to its effective partial pressure and to the reactive carbon left in the char. The first phase reaction with steam would be independent of steam partial pressure and proportional to the residual reactive char.

The first phase reactions would be:

$$C^* + 2H_2 \rightarrow CH_4 \quad (2.49)$$

$$C^* + H_2O \rightarrow CO + H_2 \quad (2.50)$$

C* is the reactive carbon present in the first phase.

The second phase reactions, or reactions with the less reactive char, were characterized by the heterogeneous reaction at the carbon surface (reaction would take place at solid-gas interface) and would be strongly affected by gas velocity at elevated temperatures in the continuous moving bed hydrogasifier used. These reactions would cause the reacting surface to shrink and to leave an ash layer as the particle moved through the reactor.

The second phase reactions were considered to be:

$$C + 2H_2 = CH_4 \qquad (2.23)$$

$$C + H_2O = CO + H_2 \qquad (2.20)$$

Since the char-hydrogen reaction and the steam-char reaction were considered as taking place independently, the rates of the reactions would be additive.

As for carbon dioxide, it was assumed to be produced solely by the water-gas shift reaction, proceeding either heterogeneously on the char surface or homogeneously in the gas phase or by a combination of both.

Johnson in 1974 (62, 67), in his study of the gasification of a Bituminous coal char at (816°C to 1093°C) and pressure of 1 to 70 atm assumed that the reaction (2.51) occurred from the stoichiometric sum of reactions (2.20) and (2.23)

$$\begin{array}{ll} H_2O + C = CO + H_2 & (2.20) \\ 2H_2 + C = CH_4 & (2.23) \\ \hline H_2O + H_2 + 2C = CO + CH_4 & (2.51) \end{array}$$

in a hydrogen-steam coal char system. Although reaction (2.51) was the sum of reactions (2.20) + (2.23), he assumed that each of the three reactions would occur independently, but that the rate of each reaction would be proportional to the same surface area and surface reactivity terms.

He showed that the rate of reaction (2.51) was greater than the reverse rate of reaction (2.23) in which methane was consumed, when a potential for carbon deposition by this reaction existed.

Feistel and van Heek in 1976 (24), studied the gasification of a German Bituminous coal with steam-hydrogen mixtures at temperatures ranging from 700-1100°C and pressures of 10-40 atm.

In their interpretation of results, they took into consideration only the two reactions that would occur in either pure steam or pure hydrogen.

The Institute of Gas Technology (62) from 1954 to 1964 also performed studies on the reactions between coal char and hydrogen-steam mixtures and their results have already been discussed separately by Feldkirchner, Johnson, Huebler (25,67).

The addition of steam to hydrogen did not increase methane formation i.e., had no "activating" effect on methane production rate - probably due to the steam reforming of product chars.

No "inhibition" of steam-char reaction by hydrogen was observed.

2.4 Effect of Pyrolysis and Gasification on Pore Structure

Chemisorption experiments performed (121, 136) have shown that carbon surface is very heterogeneous, containing holes and dislocation in the lattice.

The porous structure of a carbonaceous material does not remain constant throughout gasification, either with hydrogen, steam or both. Several changes occur and these changes have been proven not only to be related to but also to exert strong influence on the reactivity of these materials (5, 97).

Bastick, Moutach and Guérin in 1957 (5), in their study of the changes in porous structure of cokes during their gasification with carbon dioxide and steam, suggested that the reactivity of a coke depended essentially on its ability to give rise to small pores as soon as it reacted with steam or carbon dioxide.

They also observed that there was a relation between the reactivity of a coke and the internal surface which developed during the reaction with steam. They noted that:

i) as soon as coke started reacting with steam, its internal surface developed very fast, due mainly to the creation of small pores which proceeded either from the opening of previously existent pores which had been constricted by small particles resulting from grinding or by the preferential combustion of active sites;

ii) an increase in pore size indicated by an enlargement of the diameter of deeper pores occurred;

iii) the disappearance of the pores with diameter less than 32Å was faster during the gasification with steam than with carbon dioxide - suggesting that carbon dioxide reacted less inside the small pores in which it penetrated less deeply. They explained this difference by proposing that carbon dioxide reacted faster than steam with carbon and did not have the time to go deeply into the smaller pores.

They also noticed that the surface of the coke treated with carbon dioxide was much smoother than that of the coke treated with steam - probably due to the smaller number of pores present on the surface treated with carbon dioxide.

Cameron and Stacy in 1958 (18), during their study of the changes in pore structure of coke during carbonization and gasification were able to make several observations based on their data, such as that coke contained two distinct types of pore systems.

a) macropores - with entrances of 400-13000Å in diameter, with the majority on the range of 7600Å;

b) micropores - with entrances smaller than 10Å in diameter.

The macropores contained many constrictions, the number of which increased with carbonization temperature up to 700°C and then remained constant.

They agreed that the volume of micropores consisted of two types of pores:

i) micropores of approximately cylindrical form and less than 10Å in diameter;
ii) micropores greater than 10Å in diameter, but with constricted entrances.

They observed that after gasification at 800°C with steam, the micro and macro volumes increased, indicating that steam molecules did penetrate and enlarge both the micro and macropore structures. Further, it would seem that the constrictions in the micropore structure also provided active sites for reaction with steam - thereby making the micropore structure more accessible to larger molecules.

The reaction was found to occur at all the internal surfaces of the coke and the constrictions in the micro and macropores were gradually removed. The micropore structure became increasingly accessible to larger molecules and pores with entrance diameter of 10-400Å were detectable after approximately 40% of the carbon had been gasified.

During carbonization at 400-500°C, the micropore volume of the coke was found to increase, probably due to the extensive evolution of volatile material from the micro structure.

Feldkirchner & Huebler in 1965 (25, 62), studied the reaction of char with steam-hydrogen mixtures at high temperatures and derived several important conclusions from the interpretation of their data. One of which was that, greater structural changes occurred on coal surface, resulting in lost reactivity, after prolonged exposures of char to steam-hydrogen mixtures at 2100°F than at lower temperatures with pure hydrogen.

Lewis in 1970 (77), in his chapter on the book "Modern Aspects of Graphite Technology" specified that cokes and synthetic graphite were porous materials with pore sizes ranging from about 10Å to several microns in diameter. This porosity would be due to the evolution of gases during carbonization. He stated that this pore structure, however, could be deliberately increased by gasification with steam, if an "activated carbon" was needed for adsorption purposes. The surface area of "activated" carbons (which was said to be similar to that of charcoals) is much greater than that of cokes. He also stated that previous studies indicated that when graphite was ground in an inert atmosphere, hydrogen, unlike oxygen, was not absorbed on the new sites produced by the grinding.

Anthony in 1976 (2), stated that the porosity of the fine structure of the char from virtually any coal increased steadily as the temperature of its formation was increased - but accessibility of these pores to penetrant molecules, only increased below 500-600°C and then decreased dramatically in the range 600-1000°C.

Nsakala in 1977 (97), trying to characterize chars produced by pyrolysis following a rapid heating of pulverized coal in a nitrogen atmosphere, found that the release of the volatile matter during pyrolysis resulted in the development of internal porosity of the material - which was considered to be a direct result of:

i) opening of previously closed pores;
ii) opening of new pores;
iii) enlargement of the existing and (or newly developed pores.

He concluded that this type of information was very important because the nature of the pore structure of a particular coal determined to a large degree the extent of its reactivity during any coal conversion process.

Koranyi and Peacock in 1978 (74),studied the reactivity of graphite towards hydrogen and asserted that no positive evidence was found that micropores played a significant part in the reactivity of the surface or that the observed increase in reactivity after a treatment with hydrogen was due to an opening up of previously restricted or closed-off micropores.

Wen and Dutta in 1978 (140),studied the solid-gas reactions involved in coal conversion processes and classified the char-gas reactions, that took place during the second stage of gasification following pyrolysis reactions, into two categories:

1) Volumetric reactions;
2) Surface reactions.

In the "volumetric reactions", the reacting gas was said to diffuse into the interior of the particles and the reaction zone to spread throughout the body of the solid. As the reaction proceeded, product solid or ash layer would build up at the outside surface of the particles as the "reacting zone" continued to shrink.

In the "surface reactions" on the other hand, the reacting gas would hardly be able to penetrate into the interior of the solid particles and the reaction would therefore be confined only to the surface of the "shrinking core of unreacted solid". In this case, the reaction interface would be sandwiched between the inner unreacted core of solid and the product solid layer (ash).

They concluded that the surface reaction occurred when the chemical reaction was very fast and then diffusion would be the controlling step. Volumetric reactions, on the other hand, would be more characteristic of slower reactions and porous solids.

These reaction steps, as well as the nature of the changes in the pore structure of a char particle, as reaction proceeds, were shown in the following way:

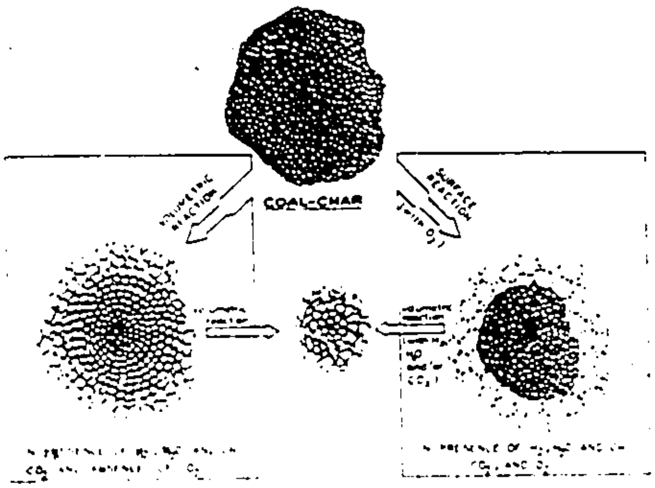


Figure 2.2 - Reaction of coal-char (140).

Mahajan, Yarzab and Walker in 1978 (83), studied coal-char gasification reactions and proposed a qualitative explanation of the mechanisms involved, on the basis of the changes in porosity and surface area they observed during the gasification of microporous char.

They utilized chars which before gasification contained closed porosity - i.e., porosity inaccessible even to helium.

During the gasification process they observed the occurrence of two phenomena:

i) enlarging of pores that were open in the unreacted char and

ii) opening up of closed pores.

Since the total number of pores increased as well as their average radius, specific pore volume and specific surface area also increased with increasing carbon burnoff. At some point, however, depending upon the pore structure of the individual char, the existing walls between pores were gasified away and the total number of open pores commenced to decrease - until complete burnoff.

Thomas in 1979 (126), using the Raman spectrometer to obtain the spectra of graphite and other carbon materials during their reaction with hydrogen, was able to prove that hydrogenation took place preferentially on the graphite surface - and that this surface became rough after reaction with hydrogen.

He also found no evidence of changes in the pore structure on the graphite samples.

Koba and Ida in 1980 (73) - studying the gasification reactivities of metallurgical cokes with carbon dioxide, steam and their mixture found that the gasification with steam developed pores within the inner region of the coke, whereas carbon dioxide reacted with coke at or near the surface, producing a relatively smooth surface, probably due to the preferential gasification of the surface region.

One of the reasons they gave for the higher reactivity of steam over carbon dioxide would be its smaller size which would be favourable for the diffusion in the micropores of the coke.

CHAPTER 3

THEORETICAL CONSIDERATIONS

This chapter involves a critical analysis of the information surveyed in the preceding chapter. It is also intended to show discrepancies among the several existing concepts concerning coal gasification, as well as to extract key information which will be valuable for the explanation of the results of this project further on.

3.1 Qualitative Review of Mechanisms

The different concepts utilized by researchers to explain their observed results will be compared for reactions between carbon and hydrogen, carbon and steam, and carbon and "hydrogen-steam" mixture.

3.1.1 Reaction Between Carbon and Hydrogen

The qualitative understanding of the reaction between carbon and hydrogen rests on propositions of mechanisms which try to account for the observed results and calculated data.

The reaction involved in hydrogasification can be represented by:

$$\text{coal} + 2H_2 \rightarrow CH_4 + \text{heat} + \text{solid residue} \qquad (2.1)$$

The concept of active sites initially approached by Blackwood (8, 10, 11, 12, 74) in 1958 and fully utilized and discussed by Moseley and Patterson (92, 93, 94) in 1965 and most subsequent workers seem to best explain the results obtained during a hydrogasification process.

The active sites would be formed during the evolution of the volatile matter (which involves the evolution of CO, CH_4, bound H_2O, H_2 and tar vapours) from the coal structure in the presence of hydrogen. They would promote or activate fixed carbon atoms for reaction with hydrogen producing methane or with another activated carbon atom leading to a polycondensation reaction. According to Moseley and Patterson (93, 94) the reaction of a carbon atom in the active sites with hydrogen would occur in the form of a free-radical chain reaction, i.e., as one carbon atom left the solid structure in the form of a molecule of methane, another atom would come and replace it in the process. In this way, the active sites would not be destroyed or deactivated. However, the polymerization reaction between two activated carbon atoms from the same or from different active sites could and would lead to the deactivation of the active sites involved. As a result of this reaction, carbon atoms would not evolve from the solid structure as gas molecules any more - leading to a decrease in the amount of gases being produced.

The formation of active sites (by the evolution of volatiles) and their deactivation (by polycondensation) -

according to Moseley and Patterson (92, 93, 94) - would be competitive reactions. The first can compete effectively with the second at high hydrogen pressures (above 500 psig) however, at lower pressures the polycondensation reactions would slowly take over the active sites leading to a decrease in the amount of gases being produced.

The number of stages involved in a hydrogasification process has also raised the interest of researchers studying this reaction.

Some workers such as Moseley and Patterson (92, 93, 94), Feldman (29), Peacock (74, 99) and the Bulletin published by the Institute of Gas Technology - IGT - (62) suggest a three-stage process, while others such as Feldkirchner and Linden (26), Johnson (67, 68) and Anthony (2, 67) propose a two-stage process.

Basically, however, the stages involved would be approximately similar. According to Moseley and Patterson (92, 93, 94) they would involve:

a) a high rate period, during which volatiles would be evolved and active sites would be formed;
b) a stage involving the reaction between the activated carbon and hydrogen or with another activated carbon;
c) a low rate period, during which hydrogen would react with the "left-over" polycondensation solid residue.

Although the concept of active sites as proposed by Moseley and Patterson, was always in the researchers' conception of a mechanism for the hydrogen-carbon reaction, subsequent workers added slight modifications this theory, according to their view of the matter.

Feldman (29) reasoned that the formation of methane during the evolution of volatile matter would be due not only to the reaction between hydrogen gas and carbon from the volatile matter (as Moseley and Patterson proposed) but also due to pyrolysis reactions, i.e., reaction which would occur even if hydrogen gas were not present in the reacting atmosphere.

Zahrádnik and Glenn (quoted in 2, 27, 62) asserted that the active sites were actually the active species themselves, and as such, would be removed by the formation of both methane and polycondensation reactions - leading in this way to a constant decrease in the number of active species available for reaction.

Anthony (2, 67) viewed the evolution of the volatile matter from a different point of view, considering that the non-reactive part of the volatile matter would escape as such into the atmosphere while the reactive part would either escape and react or stay in the solid structure and polymerize.

Therefore, compiling these concepts, one would assume, at least two facts as occurring during the "carbon-hydrogen" reaction:

i) volalite matter evolution "promotes" active sites (or species) and the number of these active sites is increased by devolatilization and decreased by cross-linking reactions and/or methane formation;

ii) the active sites, either by an extremely high rate of formation or by "not being themselves removed", would offer one "activated" carbon atom and replace it with another. These atoms could even be "fixed" carbon atoms.

3.1.2 Reactions Between Carbon and Steam

Most of the literature surveyed in this section dealt with qualitative considerations and interpretations of the reaction between carbon and steam.

The basic reactions involving steam and carbon are said to be:

$$C + H_2O = CO + H_2 \tag{2.20}$$

$$CO + H_2O = CO_2 + H_2 \tag{2.21}$$

and the reaction involving the production of methane which can be either:

$$C + 2H_2 \rightarrow CH_4 \tag{2.23}$$

or: $$CO + 3H_2 \rightarrow CH_4 + H_2O \tag{2.43}$$

usually involving the presence of a catalyst.

Most of the available information discussing the qualitative implications of the carbon-steam reaction involves an adsorption-desorption mechanism.

In this mechanism, steam would be adsorbed either in the molecular form, according to Strickland-Constable (122), Gadsby (36) and Warner (137) involving the formation of a complex or in the dissociated form according to Long and Sykes (23, 81, 136). Dissociated steam would be adsorbed as a hydroxyl radical and one hydrogen atom, on active sites (defined as carbon atoms, not exerting their full valency). The molecular adsorption could involve either a localized adsorption on activated sites or the penetration of the molecule into the carbon lattice after overcoming an energy barrier.

After the adsorption, workers such as Strickland-Constable (122), Warner (137), Gadsby (36) and Long and Sykes (23, 81, 136) all agreed that carbon monoxide and hydrogen would be desorbed as gases. Warner (129) also proposed that alternatively steam would be re-evaporated in the molecular form.

Strickland-Constable defended the theory of the reversible adsorption of steam below 700°C - which would involve, at that condition, a re-adsorption of the gases (carbon monoxide and hydrogen) produced. However, Warner (137) considered this reversible adsorption as having a poisoning effect on the char surface - retarding the reaction between carbon and steam.

Finally, most workers agree that the carbon monoxide produced, would eventually react either in the adsorbed or desorbed form with available steam to produce carbon dioxide.

Therefore, compiling all assertions and observations and reviewing them, one can derive some conclusions such as:

i) the formation of carbon dioxide, has been explained by the water-gas shift reaction by most workers;

ii) increasing the amount of hydrogen present in the reacting atmosphere would "retard" or "inhibit" reactions (2.20) and (2.21). Two explanations are available currently for this occurrence. One would involve equilibrium considerations and the fact that hydrogen - being a reaction product - would, if in excess, shift the equilibrium of both reactions towards the left, thus, "retarding" the reaction. The second explanation is the one adopted by the proponents of the sorption theory - stating that "the chemisorption of hydrogen occurring on active sites or reaction sites would "inhibit" carbon-steam reactions":

iii) there might exist active sites which would accept either steam or hydrogen for reaction and steam and hydrogen would compete for these sites.

3.1.3 Reactions Between Carbon and "Steam-Hydrogen" Mixtures

Considerably less information is available in the literature, involving qualitative considerations of the mechanism by which carbon would react with the mixture "steam-hydrogen".

Usually, during the initial stage of a new field in coal gasification research, the main concern among workers is the observation and report of observed facts; secondly, they try to establish a pattern for the behaviour of the carbon structure towards the gasifying gas being studied which would hold under wide ranges of pressure, temperature and composition. Finally, they propose mechanisms or modifications of existing mechanisms which would correlate their data, until one mechanism becomes available that correlates most of all the existing data. For that matter, the gasification of coal with a "steam-hydrogen" mixture is still in the early stages. This is evidenced through the disagreement in reported results concerning the so-called "activating" effect of steam on the carbon structure as described below.

Results reported by Gorin and Curran (39, 40) during the gasification of a char at 1600°F and 1 atmosphere have indicated that the presence of steam increased both the total rate of gasification (which involves the rate of production of "carbon monoxide + carbon dioxide + methane") and the rate of production of methane.

Feldkirchner and Huebler (25) also studied the gasification of a char in the presence of "steam-hydrogen" mixture at 1000 psig and 1700°F to 2000°F and concluded from their results that both the total rate of gasification and the rate of production of methane decreased in the presence of steam.

Wen and Abraham (138) studied the steam-hydrogen gasification of a char at 70 atm and 1700°F to 2000°F, and their results show that the presence of steam was beneficial both for the total rate of gasification and the rate of production of methane at 1700°F. However, the presence of steam was detrimental both for the rate of production of methane and for the total rate of gasification at 2000°F. The discrepancy in their results was attributed to the concept that at very high temperatures such as 2000°F the chemical reaction is so fast that the rate is controlled by diffusion.

Reviewing all the information gathered from the surveyed literature concerning observed results and proposed explanations, to the "steam-hydrogen" gasification of coal and chars, one is left with the clear impression that:

i) much work still remains to be done, before this process can be fully understood;

ii) some assumptions made by workers are likely to have simplified the correlation of their data - at the expense of a more detailed, more elaborated mechanism. Different compositions of hydrogen-steam mixtures have been reported by several workers (25, 39, 40, 41) as either favoring or hindering the production of different gases - suggesting that the reactions occurring strongly influence each other. However, these reactions have been, most of the times, considered as happening independently of each other and their rate proportional to the "same" carbon surface area;

iii) therefore, one is left with the idea that the reactions occurring, should not be considered independent of each other, even when this is one of the assumptions made by researchers;

iv) workers have not yet come to a definitive answer as to whether the presence of steam does indeed increase the rate of methane formation or not.

3.2 Equilibrium Considerations

Although even less information is available in the literature involving the thermodynamics of the reaction between carbon and the "steam-hydrogen" mixture, the Institute of Gas Technology (62) did produce graphs (Figure 2.1) - showing the ideal gas equilibrium oomposition for the "steam-hydrogen" gasification of carbon at high temperatures and pressures. Although the conditions at which these results were obtained are different from those utilized in this project, a trend can be observed as to the influence of pressure, temperature and steam composition during the gasification process.

The results indicate that higher pressures are advantageous for the production of a wanted product - methane and an undesirable product - carbon dioxide, and detrimental for the production of carbon monoxide.

An increase in temperature from 1700°F to 2300°F proved to be detrimental for the production of both methane and carbon dioxide; while an increase in the steam percentage in the feeding stream was beneficial for the production of carbon oxides.

3.3 Effect of Gasification on Pore Structures

Several changes have been observed to occur on the carbon structure during gasification of a coal. Several attempts have been made trying to correlate these changes with the gasification process.

Most of the literature available dealt with changes in the pore structure of coal or char during the gasification with steam or carbon dioxide. No literature was available comparing changes occurring in the pore structure during the gasification with steam or hydrogen.

Although using different data, Bastick and Guérin (5), Cameron and Stacy (18) and Lewis (77) concluded that the gasification with steam caused:

i) an enlargement in diameter of existing finer pores;
ii) creation of new pores.

However, other studies performed by Peacock (76) and Thomas (126), concerning the effect of hydrogen on the pore structures of graphite, reported that no evidence of changes in the pore structure were found.

Bastick and Guérin (5) and Wen and Dutta (140) proposed a somewhat similar concept explaining the changes in pore structure during gasification. Although their experiments differed from one another, they proposed that there is one type of reaction occurring at the external surface of the carbon structure, which is a fast reaction giving the gas no time to penetrate into the interior of solid particles. The other type of reaction is the one occurring in the interior of the solid particles, which is a slower reaction, giving the reacting gas, time to penetrate into the interior of the particles. Steam would be included in the second category and oxygen in the first. However, no single study was performed to compare steam and hydrogen.

Reviewing all the observed facts reported by different researchers, one is left with the idea that:

i) steam is able to react in the inner finer pores of the carbon structure or to diffuse into the interior of the solid particles for reaction;

ii) most of the comparisons were performed between steam and carbon dioxide or steam and oxygen - showing that, still, much work remains to be done, comparing the pore structure of coal after gasification with steam, hydrogen and both;

iii) no concluding observations exist as to hydrogen showing preference for an external surface reaction. However, one is led to believe that, hydrogen would not react as deeply in the interior of solid particles as steam would - showing, in this way, some preference for the surface reaction - even though its molecule is smaller in diameter than that of steam. This could, then, lead to the suggestion that hydrogen would react faster than steam with the carbon structure, and therefore, hydrogen would not have the time to go deeply into the carbon structure in the interior of the solid particles.

CHAPTER 4

EQUIPMENT AND EXPERIMENTAL PROCEDURE

In this chapter, characteristics of the equipment used as well as details of the two types of experiments performed, will be discussed and explained.

4.1. Equipment

The equipment utilized to gasify coal consisted of reactor and auxiliary system. The auxiliary system comprised both the "clean-up" equipment and analysis equipment.

4.1.1 The Reactor

The reactor consisted of a stainless steel type 316 tube, 0.60 m long, 0.0263 m inside diameter and 0.0331 m outside diameter. A stainless steel bolting cloth, supplied by B.&S.H. Thompson & Co. Ltd., 230 meshes/in, was located in a cross-sectional position, at 0.127 m from the bottom of the reactor. The reactor is schematically represented in Figure 4.1.

Two chromel-alumel, type K thermocouples supplied by Thermo-Electric extended from the top into the reactor, 0.135 m and 0.450 m from the bottom respectively, in order to measure the temperatures of the coal on top of the bolting cloth and that at the top of the reactor where coal is fed into the reactor. Both thermocouples were connected to a

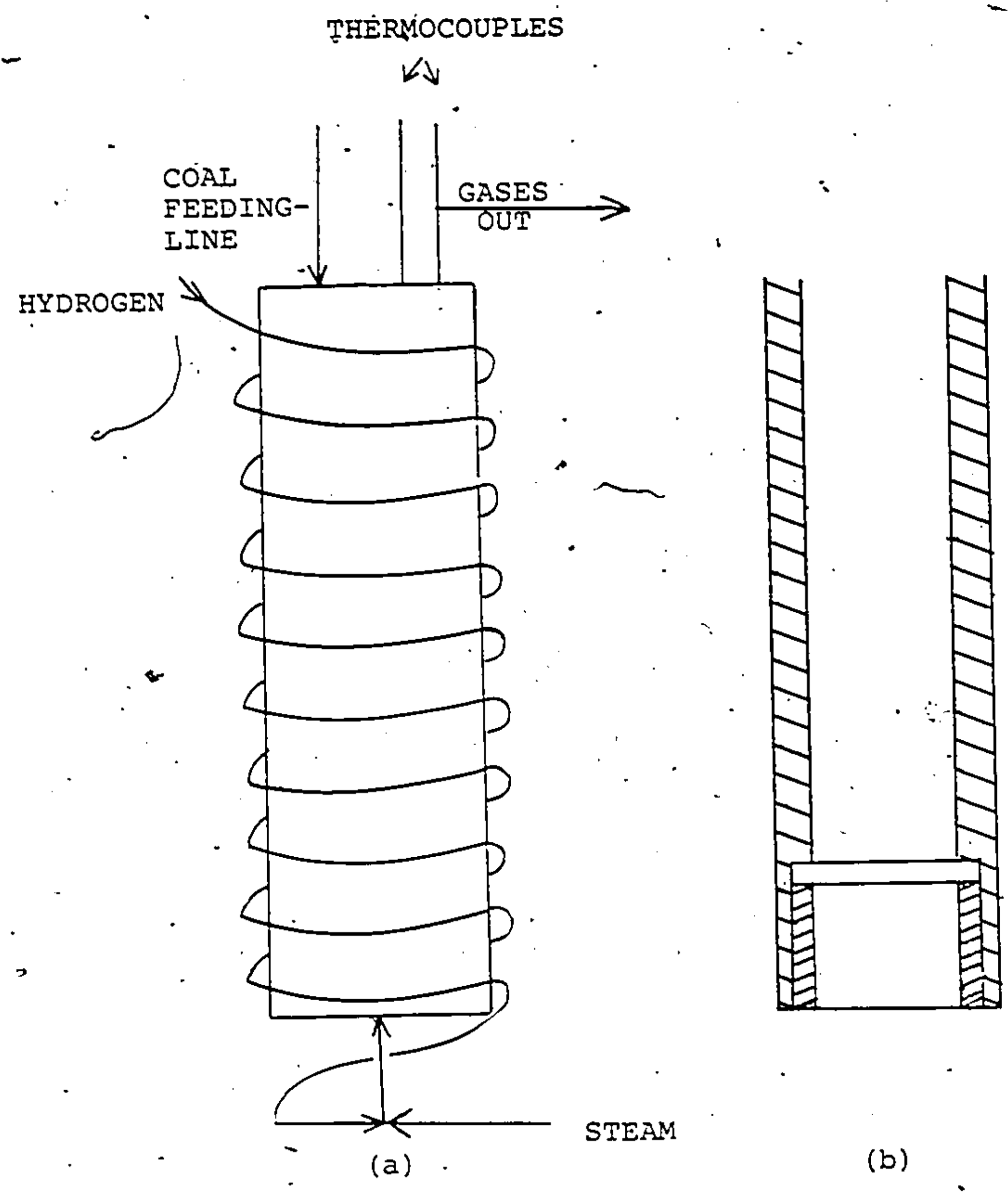


Figure 4.1 - Schematic Diagram of Reactor:

a) hydrogen tubing coiled around reactor
b) Cross-sectional view

temperature controller, supplied by Honeywell through a switch which allowed one temperature to be read and controlled at a time. The top of the reactor also consisted of an inlet for coal feeding and an outlet for the product gases.

The reactor was electrically heated by two heating resistance wires. One worked as a "booster-heater" and it was controlled manually by a powerstat. The other, which was the main heater, was controlled by the temperature controller. The heating resistance wires were coiled around a ceramic fiber tube 0.70 m long and 0.08 m inside diameter. The reactor stayed inside this ceramic tube during the runs.

The reactor was insulated with a 0.150 m thick layer of mica and two layers of pink fiber glass.

Hydrogen flowing into the reactor from the bottom was heated to a temperature close to that inside the reactor when passing through a stainless steel 0.003175 m (1/8") O.D. diameter tube coiled in a close wound around the reactor.

4.1.2 Auxiliary Equipment

A process flow-sheet diagram of the equipment is represented in Figure 4.2.

An air-tight coal container, made of plexiglas was connected to the top of the reactor by a stainless steel tube 0.006350 m in diameter. An on-off-service ball-valve type

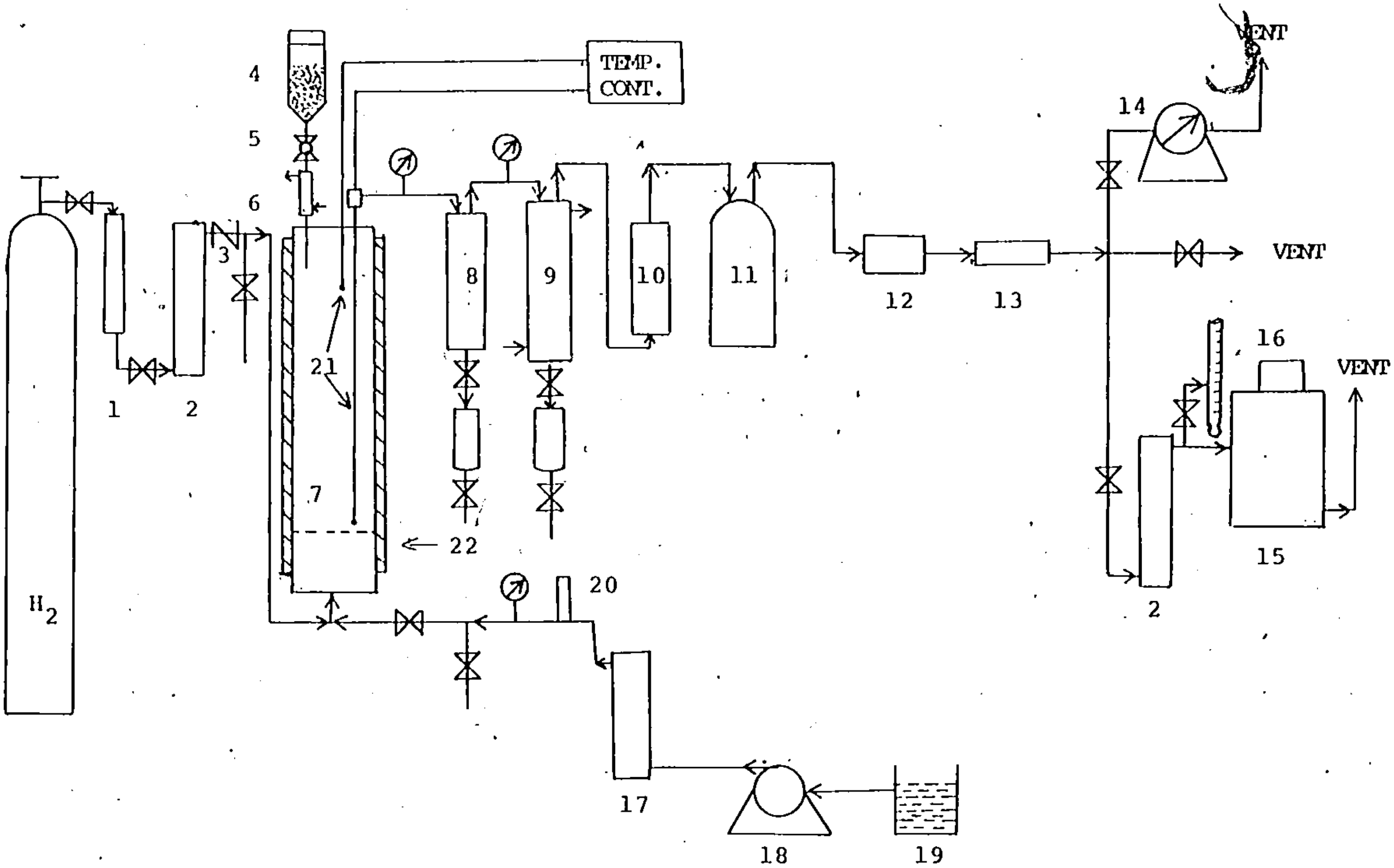


Figure 4.2 - Flow Diagram of Apparatus

1. Deoxo Unit
2. Rotameter
3. Check-valve
4. Coal Reservoir
5. On-Off-Ball Valve
6. Cool-Water-Jacket
7. Reactor
8. Air-Cooled Condenser
9. Water-Cooled Condenser
10. Glass-Wool Filter
11. Particle Trap
12. Microfilter
13. Drying Tube
14. Wet-Test-Meter
15. Gas Chromatograph
16. Valve-Timer
17. Vaporizer
18. Water-Pump
19. Water-Reservoir
20. Thermometer
21. Thermocouples
22. Reactor Heating System

SS-2MG supplied by Nupro, allowed coal to fall from container into the reactor when open, and kept coal inside container without any contact with the gases in the reactor, when closed. The ball valve was kept cold by cool-water-jacket.

The coal was fed into the reactor with the help of a vibrator (Type BVI, supplied by Fisher).

A pressure gauge from Matheson of Canada, type SS-63-3212, located outside the reactor measured the pressure inside it, at all times.

The gases coming out of the reactor passed through a condensing system, a glass wool filter, a particle trap, a microfilter and a drying tube filled with Drierite before going into the chromatograph, and the Wet-Test-Meter.

The condensing system consisted of an air-cooled condenser followed by a cold water-cooled condenser. Both condensers were adapted with a condensate collector.

The glass wool filter consisted of a stainless steel vessel filled with glass wool.

The particle trap consisted of an empty stainless steel vessel with both inlet and outlet connected at the top of the vessel.

The microfilter supplied by Nupro, type SS-2F, was used to retain smaller particles. The gases coming out of the microfilter would go through the drying tube and then divided into two streams. One stream would go into a Wet-

Test-Meter from Precision Scientific Company (measuring 0.1 SCF per complete rotation) and from there to vent. The other stream would go into the chromatograph to be analyzed, after being measured. The gases leaving the chromatograph were then vented.

The gas chromatograph was a Hewlett-Packard model 5700A, adapted with a recorder model MT-21 from Westronics and an integrator model HP-3373B from Hewlett-Packard.

The chromatograph was equipped with a Thermal Conductivity Detector with a platinum filament and two stainless steel (0.003175 m "OD" x 2.1 m length) identical columns, packed with Carbosieve S,100/120 mesh,for the analysis of the gases. The columns were supplied by Supelco-USA. One of these columns served as an analytical column and the other one was used as a reference column. Helium was used as carrier gas, flowing into the chromatograph at a rate of 60 ml/min after passing through a drying tube consisting of a stainless steel tube, filled with silica-gel.

Information concerning the calibration of the Thermal Conductivity Detector (TCD) is given in Appendix A.

The thermal Conductivity Detector was frequently calibrated every two runs by passing standard samples of all the gases involved in the experiment, through the chromatograph. These mixtures were supplied by Matheson, Can.

Gas samples from the exit gas, coming from the reactor, were injected every twelve minutes by an air-operated-dual-loop-sampling-valve. The volume of each loop was 0.022 l, including the internal volume of the valve. The sampling valve was automatically operated by a valve-timer supplied by Hewlett-Packard which was used to "time" the injections every twelve minutes.

The hydrogen flowing into the reactor was provided by a hydrogen cylinder supplied by Liquid Carbonic Can. Ltd. and purified by a Deoxo unit, manufactured by Baker Inc. The hydrogen flow was measured by a flowmeter from Matheson of Canada, tube number 601. Information concerning the calibration of the flowmeter is given in Appendix A. The flowmeter was connected to a stainless steel check-valve supplied by Matheson of Canada, type 401-X.

Water for the production of steam was supplied by a pump (Type D-61-175R from M. Royal). The pump was used to feed water at a constant rate. The calibration of the pump is presented in Appendix A.

Steam was produced by passing the pumped water through a pre-heater, which consisted of a heating element inside a copper tube. The heating element consisted of a heating resistance wire inside a copper tube which was filled with ceramic cement. A pressure gauge from Matheson of Canada, type SS-63-3212 and a thermometer from Canlab were used to measure the pressure and temperature at which steam was being produced.

Both the steam line and hydrogen stream were connected in line before entering the reactor.

This would allow the pre-heated steam to reach reactor temperature before actually entering the reactor. The steam-hydrogen mixture entered the reactor from the bottom in a continuous flow process.

4.1.3 Coal Sample

A "Forestburg Sub-Bituminous-A" coal was obtained from the Energy Mines and Resources Research Lab, Ottawa, which had the following composition:

Table 4.1

COAL ANALYSIS

Proximate Analysis

	As Received	Dry
Moisture	11.76	0.00
Ash	7.08	8.02

Ultimate Analysis

	As Received	Dry
C	58.34	66.12
H_2	3.35	3.80
S	0.47	0.53
N_2	1.50	1.70
Ash	7.08	8.02
O_2 (By Diff.)	17.50	19.83

Coal was ground and screened with U.S. Standard Sieve Screens. Different size fractions were obtained, but mostly, coal particles in the size range of -40 to + 60 mesh were used in the experiments.

Before coal was used, it was kept in the presence of silica-gel in an air-tight vacuumed reservoir until its weight remained constant for approximately two days.

4.2 Experimental Procedure

Two sets of runs were performed which allowed the observation of the effects of the presence of steam during hydrogasification. They will be referred to as Type A and Type B. In Type A experiments, steam was allowed to flow into the reactor from the beginning of the experiment. In Type B - only some time after the beginning of the experiments. Both Type A and Type B experiments will be described later on in this chapter.

4.2.1 General Characteristics of Experiments

All equipment was purged with helium for one hour before the beginning of each run.

Before coal was used, it was kept in the presence of silica-gel in a vacuumed reservoir until its weight remained constant for at least two days.

A rapid heating of particles was desired in order to avoid, as much as possible, polycondensation reactions leading to the formation of solid polymers.

Literature researched (2, 27, 28, 29) indicated that the best way to achieve, at least a partially fast heat-up of particles, would be by feeding the coal to the reactor only when the desired temperature inside the reactor had been reached. It was, then, decided that by feeding coal in a countercurrent flow to the reactant gas flow, would result in a better heat transfer between the two media.

Apparently, the heating of particles was not as fast as expected - since some time elapsed before reaction between coal and reactants could be observed in the chromatograph. It is possible that by introducing coal particles into the reactor, only after the three-hour-heating period, the formation of premature "inactive carbons" - by polycondensation reaction - was minimized.

Six grams of coal were usually fed from the coal reservoir into the reactor at a rate of approximately 1.0 g/min, with the use of a vibrator, once the temperatures at the top and bottom of the reactor were 755°K and 811°K respectively. This first stage would, thus, consist mostly of creating an adequate atmosphere for coal to undergo a relatively rapid heating.

After the first hour of experiment, the temperature at the bottom of the reactor would be raised to 977°K. After that, the reaction was allowed to proceed isothermally, until the end of the experiment.

The last stage in both Type A and Type B experiments would be the observation of how the production of gases would be affected if the presence of steam in the feeding stream were "discontinued". This would be accomplished by closing the valve which allowed steam to join the hydrogen stream before entering the reactor. Hydrogen would then be the sole reactant flowing into the reactor until the end of the experiment.

The gases produced during the experiment were cooled and analyzed automatically every twelve minutes by the gas chromatograph. Their flow was also measured by the Wet-Test-Meter every twelve minutes.

Each run lasted for 4.6 hours or 5.8 hours.

Approximately 2.0 ml of water - as steam - were consumed in the reaction during the experiments.

4.2.2 Procedure for Blank Experiments

Blank runs consisted of runs utilizing helium, hydrogen and steam separately.

Blank runs were performed at different pressures for each one of the gases.

The blank runs with helium were performed at 336 KPa and 398 KPa (34 psig and 43 psig respectively); with hydrogen at 273, 336 and 398 KPa (equivalent to 25, 34 and 43 psig respectively); and with steam at 350 and 418 KPa (equivalent to 36 and 46 psig respectively).

The general procedure for the blank runs was the same for the three different gases.

Helium, hydrogen or steam alone would constitute the atmosphere for the falling particles of coal, when the bottom temperature of the reactor was approximately 811°K.

Both helium and hydrogen flows were kept at approximately 0.0215 ℓ/min, while water for steam would be supplied at a constant rate of 0.105 g/min.

Hydrogen or helium or steam would be flowing into the reactor from the beginning of each experiment, and allowed to flow until the end of each run.

The reactor pressure during each blank run was not changed.

The temperature inside the reactor would usually be increased after the first hour of experiment (except for the run performed with hydrogen at 273 KPa, when the temperature was increased during the first hour).

The blank runs were allowed to continue for 4.6 hours.

4.2.3 Procedure for Type A Experiment

Type A experiments were performed at four different total pressures, namely, 142, 280, 350 and 418 KPa (equivalent to 6, 26, 36 and 46 psig).

During these experiments, steam would be allowed to flow into the reactor from the start of each run, i.e., before the devolatilization stage. A mixture of hydrogen and steam flowing continuously at known pressure and flow would constitute the reacting atmosphere for the falling particles of coal at a temperature of 811°K at the bottom of the reactor.

Water for steam production was pumped at a rate of 0.105 g H_2O/min or 0.175 g H_2O/min and hydrogen flow was 0.0215 ℓ/min.

Both the hydrogen flow rate and the water pumping rate were kept constant through each run. Steam temperature was brought close to that of the reactor - by mixing it with hot hydrogen before entering the reactor.

The temperature inside the reactor would, then, be increased from 811°K to 977°K - after the first hour of experiment.

Approximately 2.8 hours after the beginning of the run, the steam line would be disconnected from the feeding stream. As a consequence, the total reactor pressure would usually drop about 20 KPa (equivalent to 3 psi). Hydrogen was then left as the sole constituent of the feeding stream for the remainder of the run.

Type A runs lasted for 4.6 hours.

4.2.4 Procedure for Type B Experiments

Type B experiments were performed at four different total pressures, namely, 122, 274, 336 and 398 KPa (equivalent to 3, 25, 34 and 43 psig respectively).

Hydrogen gas alone would constitute the reacting atmosphere for the falling particles of coal, at a temperature of 811°K at the bottom of the reactor.

During the first 1.5 hours of the experiment, hydrogen flowing at 0.0215 ℓ/min was the sole constituent of the feeding stream.

Steam was connected to the feeding stream after the first 1.5 hours or 1.8 hours of reaction, i.e., well after the devolatilization stage and after the increase in temperature to 977°K took place. A hydrogen-steam mixture would constitute the feeding stream until 3.2 hours after the start of the run. After that, steam would be disconnected from the feeding stream, and hydrogen would be the sole reactant flowing into the reactor for the remainder of the run.

The increase in temperature took place before steam was connected to the feeding line (in most cases), in an attempt to identify the changes in the quality (composition) of the product gas due to the increase in temperature, and due to steam addition, separately.

The total pressure inside the reactor increased about 20 KPa after the introduction of steam and decreased approximately 20 KPa after steam was disconnected from the feeding stream.

Water for steam production was pumped either at the rate of 0.105 g/min or 0.175 g/min.

Each run lasted for 4.6 hours.

CHAPTER 5

PRESENTATION OF RESULTS

In this chapter, the results obtained during blank runs, Type A and Type B experiments at different pressures will be reported.

5.1 Calculation of Results

As it was stated in Chapter 4, both the exit gas flow rate (in ml/min) and the exit gas composition (in mole %) were recorded every twelve minutes. From these two values the number of moles of each gas being produced per minute were calculated. From the number of moles, the mass of carbon gasified as methane, carbon monoxide and carbon dioxide could be calculated in terms of (g C as CH_4, CO, CO_2/min). This value was further divided by the total amount of C fed to the reactor in each run (as g C fed) - in order to normalize the results obtained.

In order to make the graphs less "crowded", the hourly rates for Type "A" and Type "B" experiments were further plotted in terms of: (g C as CH_4 or CO or CO_2/g C fed-hr). The values to plot these graphs were obtained by integrating the points of each curve plotted as g C as CH_4, CO, CO_2/g C fed-min) versus time (min) every hour on the hour.

A more detailed sample calculation of the results is presented in Appendix B.

5.2 Blank Experiments

The results for the blank runs were plotted in the same figures as Type "A" and Type "B" runs, with the exception of helium blank runs. This was to facilitate their comparison.

The rates of production of carbon dioxide were not included in the figures to avoid excessively "crowded" graphs and an excessive number of graphs. Their respective values, however, are indicated in Appendix C.

5.2.1 Helium Blank Experiments

The results for helium blank runs are plotted in Figure 5.0, showing the rates of production of methane and carbon monoxide in terms of (g C as CO or CH_4/g C fed-min) x 10^5 versus time in minutes, at 336 and 398 KPa (equivalent to 34 and 43 psig respectively) total pressures.

5.2.2 Steam Blank Experiments

The results for steam blank runs are plotted in Figures 5.3 and 5.4, indicating the rates of production of methane and carbon monoxide in terms of (g C as CO or CH_4/g C feed-min) x 10^5 versus time in minutes for

350 and 418 KPa (equivalent to 36 and 46 psig respectively).

5.2.3 Hydrogen Blank Experiments

The results for hydrogen blank runs are plotted in Figures 5.8, 5.9 and 5.10, indicating the rates of production of methane and carbon monoxide in terms of (g C as CO or CH_4/g C feed-min) x 10^5 versus time in minutes, at 273, 336 and 398 KPa (equivalent to 25, 34 and 43 psig respectively).

5.3 Type A Experiments

The results for Type A experiments are plotted in Figures 5.1 to 5.6. The rates of production of methane and carbon monoxide in terms of (g C as CO or CH_4/g C fed-min) x 10^5 versus time in min for 142, 280, 350 and 418 KPa (equivalent to 6, 26, 36, 46 psig respectively) total pressures, are plotted in Figures 5.1, 5.2, 5.3 and 5.4 respectively. The rate of production of carbon dioxide in terms of (g C as CO_2/g C fed-min) x 10^5 versus time in minutes are plotted in Figure 5.5 for 142 and 280 KPa total pressures and in Figure 5.6 for 350 and 418 KPa, total pressure.

The hourly rates of methane and carbon monoxide production at different pressures are plotted in Figures 5.13 and 5.14 respectively in terms of (g C as CH_4 or CO/g C feeed-hr) x 10^3 versus time in hours.

5.4 . Type B Experiments

The results of Type B experiments are plotted in Figures 5.7 to 5.12. The rates of production of methane and carbon monoxide in terms of (g C as CO or CH_4/g C fed-min) x 10^5 versus time in minutes are plotted for 122, 274, 336 and 398 KPa (equivalent to 3, 25, 34, psig respectively) total pressures in Figures 5.7, 5.8, 5.9 and 5.10 respectively. The rate of production of carbon dioxide is plotted in terms of (g C as CO_2/g C fed-min) x 10^5 versus time in minutes for 122, 274 and 336 KPa total pressure in Figure 5.11 and for 398 KPa total pressure in Figure 5.12.

The hourly rates of production of methane for 122, 274 and 336 KPa total pressures are plotted in Figure 5.15 and the hourly rate of production of carbon monoxide for the same total pressures mentioned above is plotted in Figure 5.16. The hourly rates of production of both methane and carbon monoxide at 398 KPa total pressure are plotted in Figure 5.17 separately - because in this run, steam remained in contact with coal for only one hour.

5.5 Specific Runs

The results obtained for two slightly different runs are plotted in Figures 5.18 to 5.21.

The rates of production of both methane and carbon monoxide in terms of (g C as CO or CH_4/g C fed-min) x 10^5 versus time in minutes are plotted in Figure 5.18 for a Type A run at 329 KPa (36 psig) total pressure in which the amount of steam being fed is increased from 0.105 g/min to 0.175 g/min, before being disconnected from the feeding line. The rate of production of carbon monoxide in terms of (g C as CO_2/g C fed-min) x 10^5 versus time in minutes for the same run is plotted in Figure 5.19.

Finally, the rates of production of methane and carbon monoxide in terms of (g C as CO or CH_4/g C feeeed-min) x 10^5 versus time in minutes are plotted for a Type B run at approximately 398 KPa (43 psig) total pressure, in which the steam flow into the reactor is 0.175 g/min, and not 0.105 g/min as in all other Type B runs.

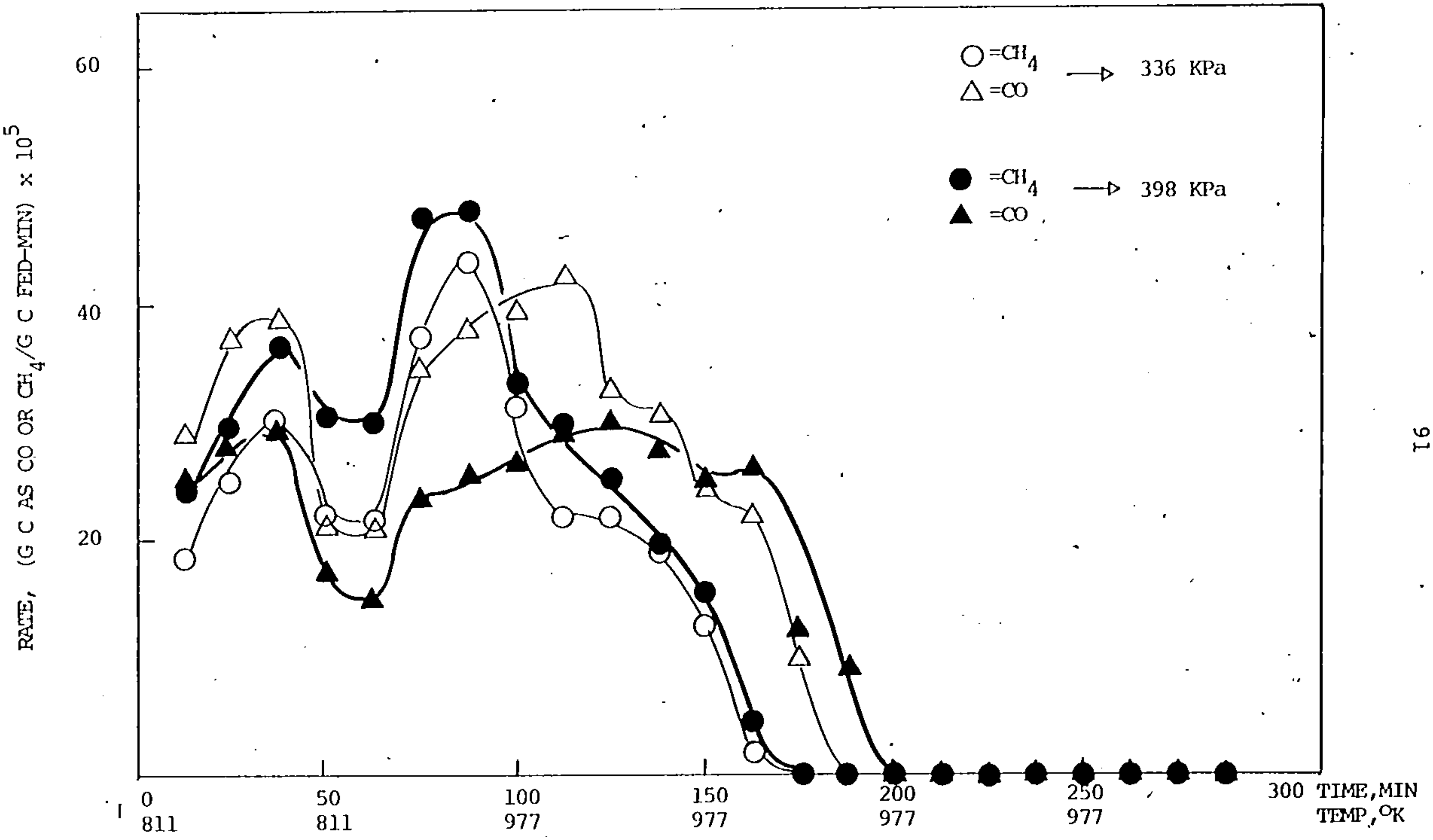


Figure 5.0 - Rate of Production of Methane and Carbon Monoxide at 336 KPa (35 psig) and 398 KPa (43 psig) for Blank Run with Helium.

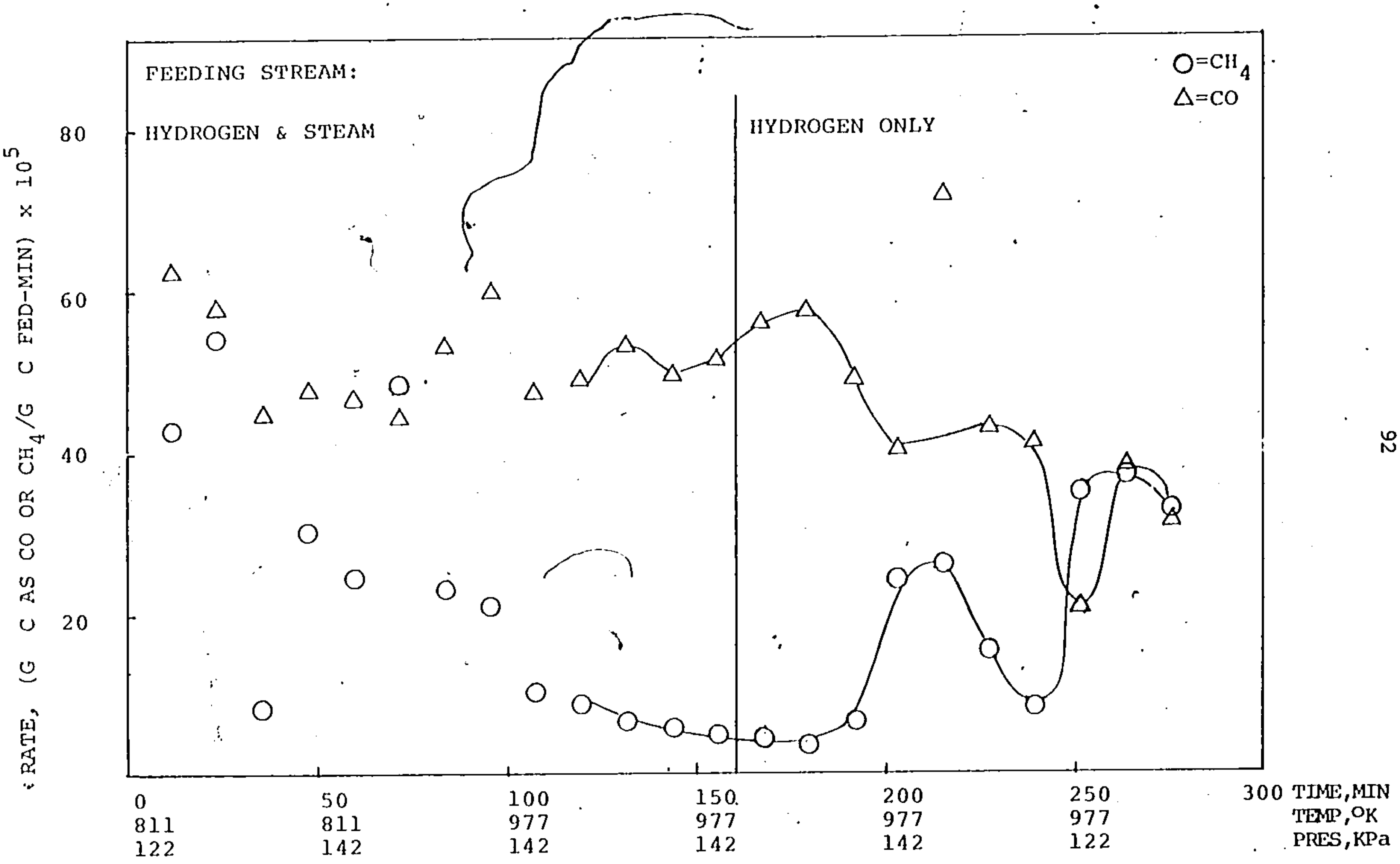


Figure 5.1 - Rate of Production of Carbon Monoxide and Methane at 142 KPa(6 psig) for Type A Experiment.

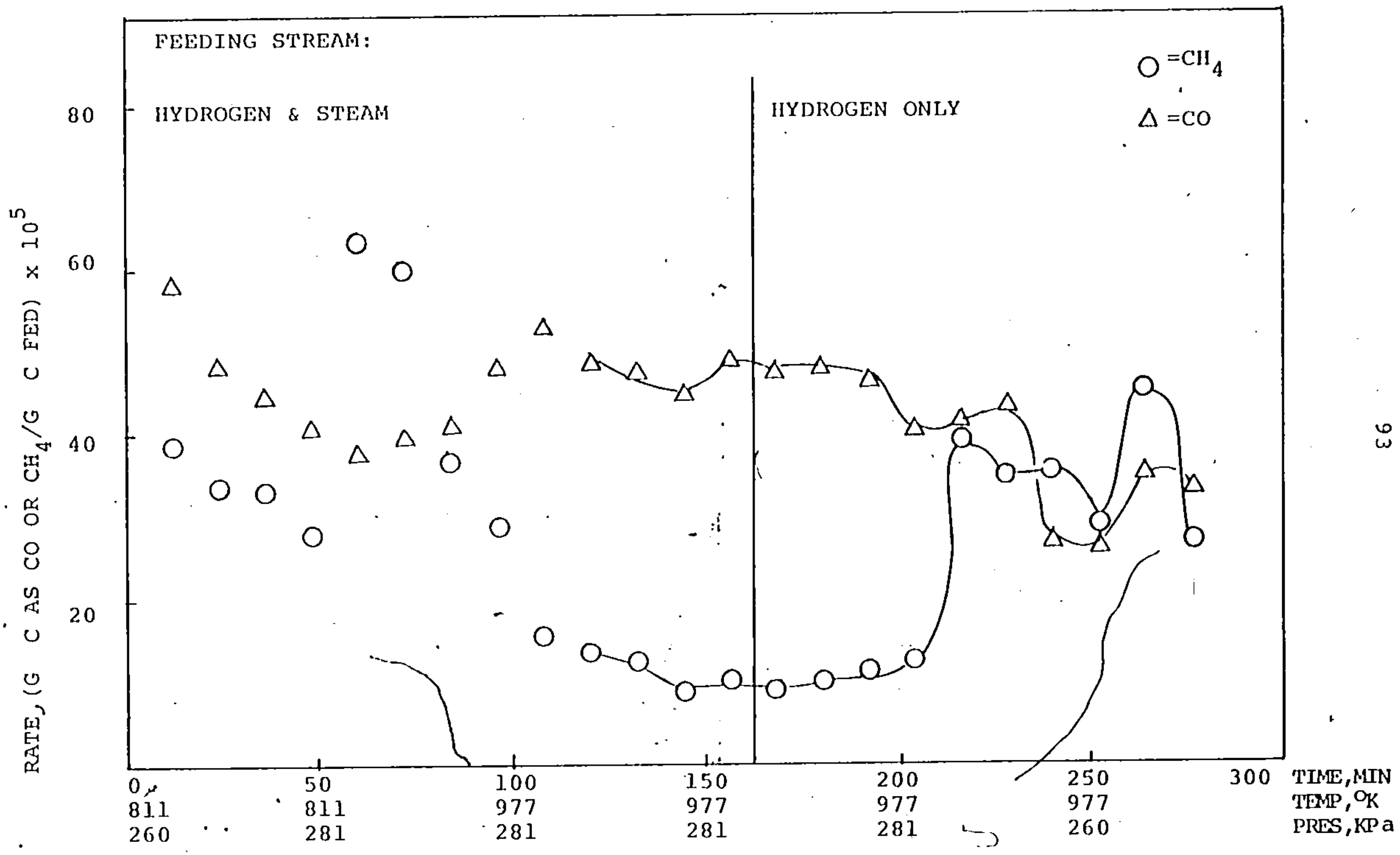


Figure 5.2 - Rate of Production of Carbon Monoxide and Methane at 281 KPa (26 psig) for Type A Experiment.

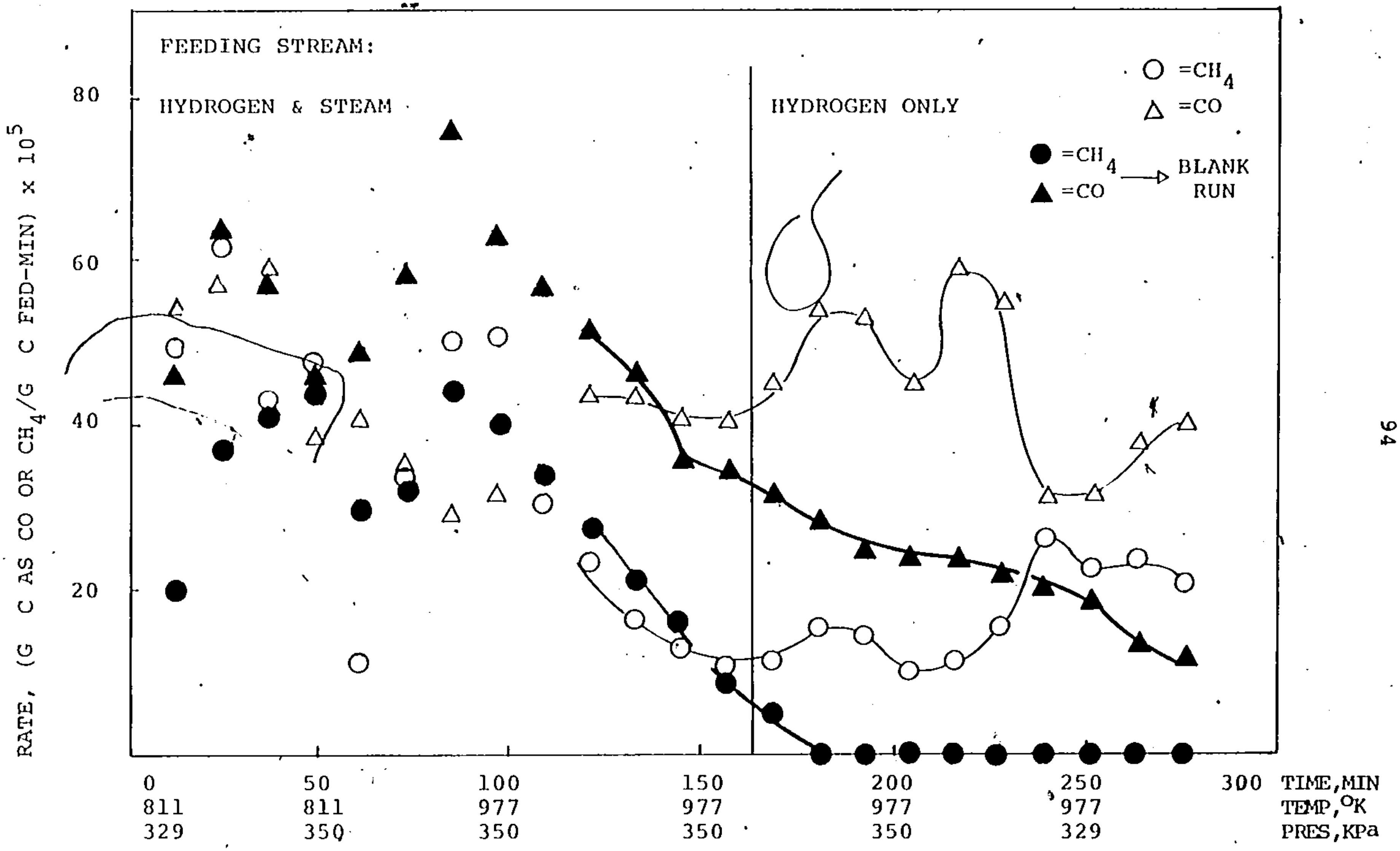


Figure 5.3 - Rate of Production of Methane and Carbon Monoxide at 350 KPa (36 psig) for Type A Experiment and for Blank Run with Steam.

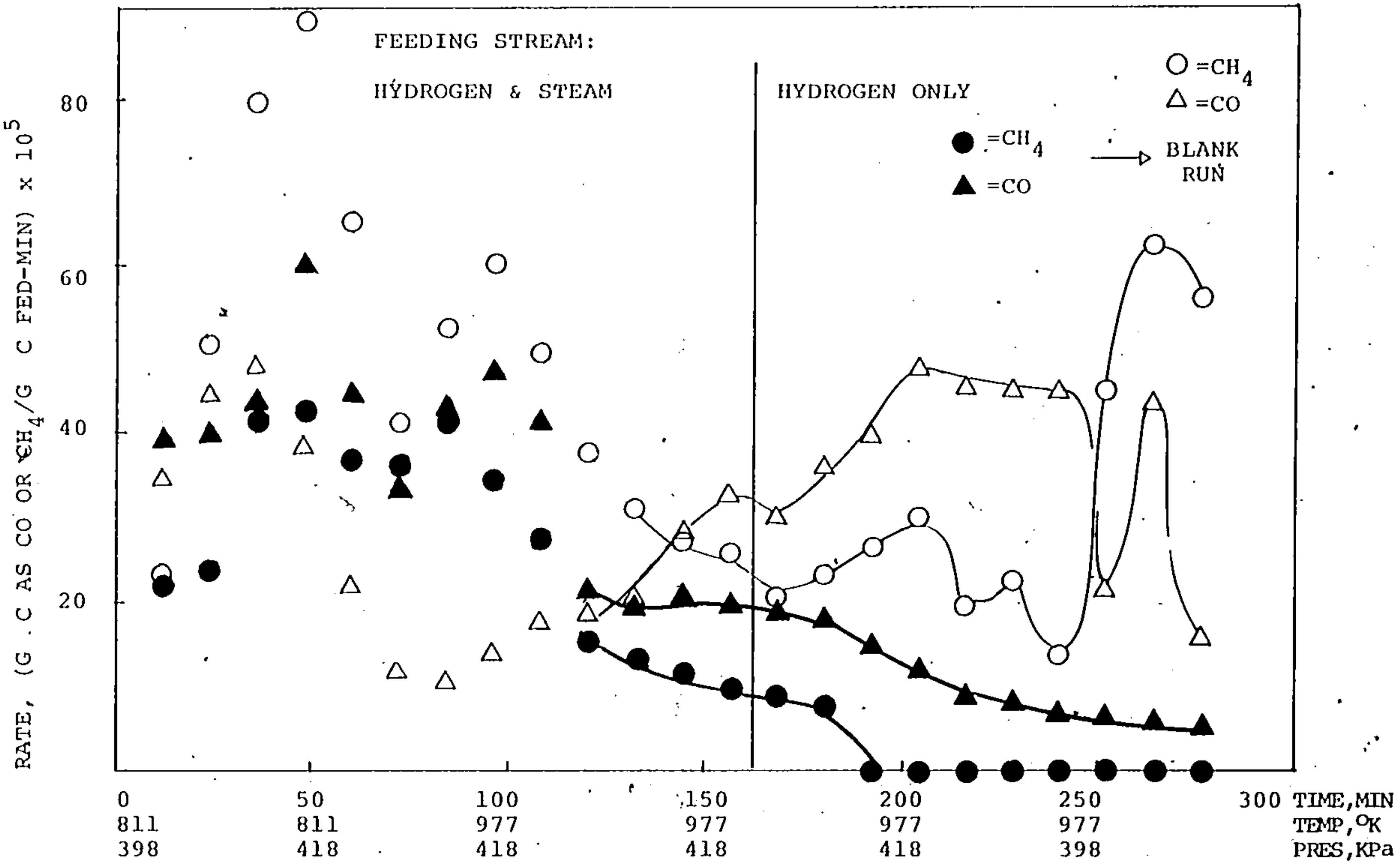


Figure 5.4 - Rate of Production of Methane and Carbon Monoxide at 418 KPa (46 psig) for Type A Experiment and for Blank Run with Steam.

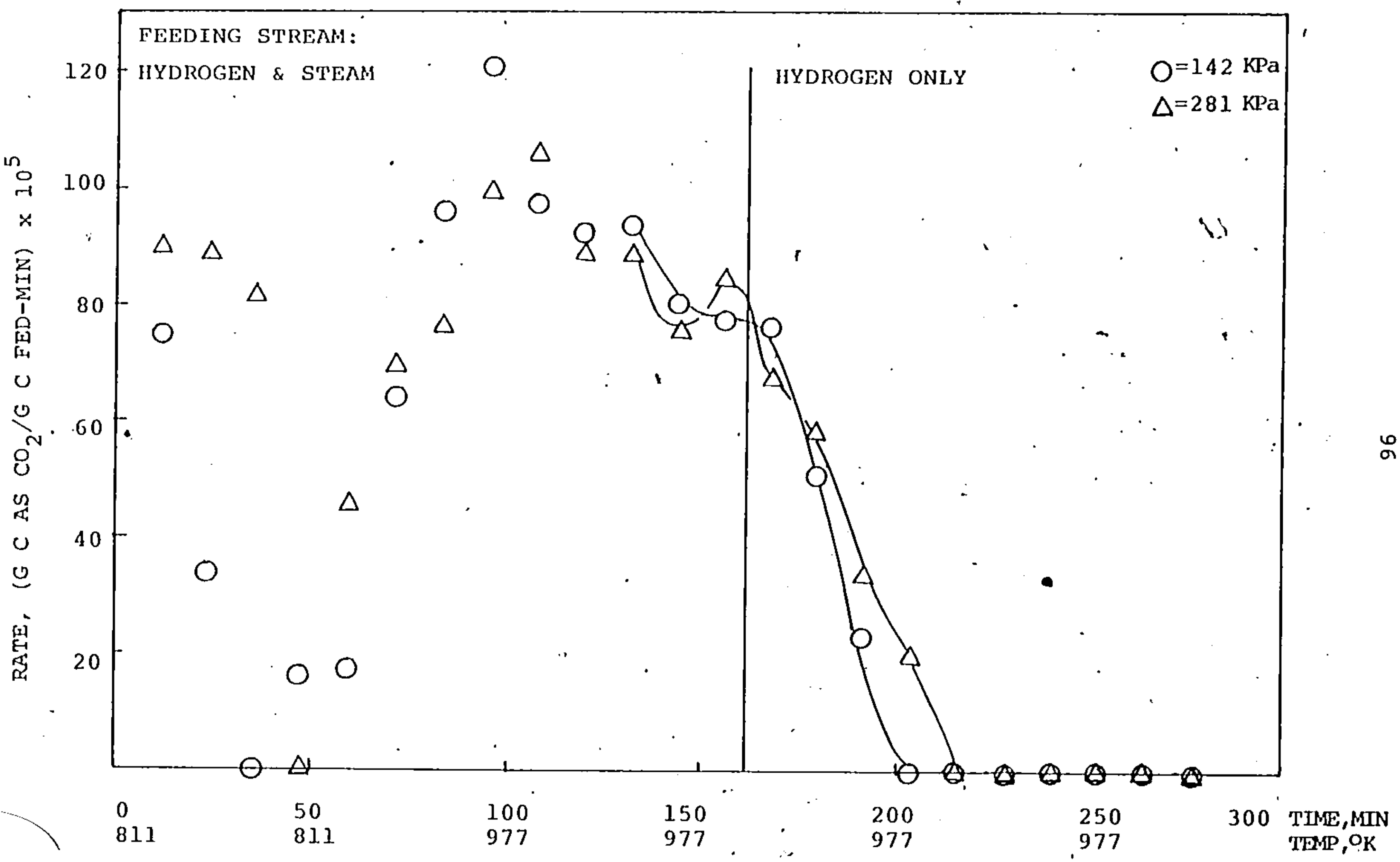


Figure 5.5 - Rate of Production of Carbon Dioxide at 142 KPa & 281 KPa for Type A Experiment.

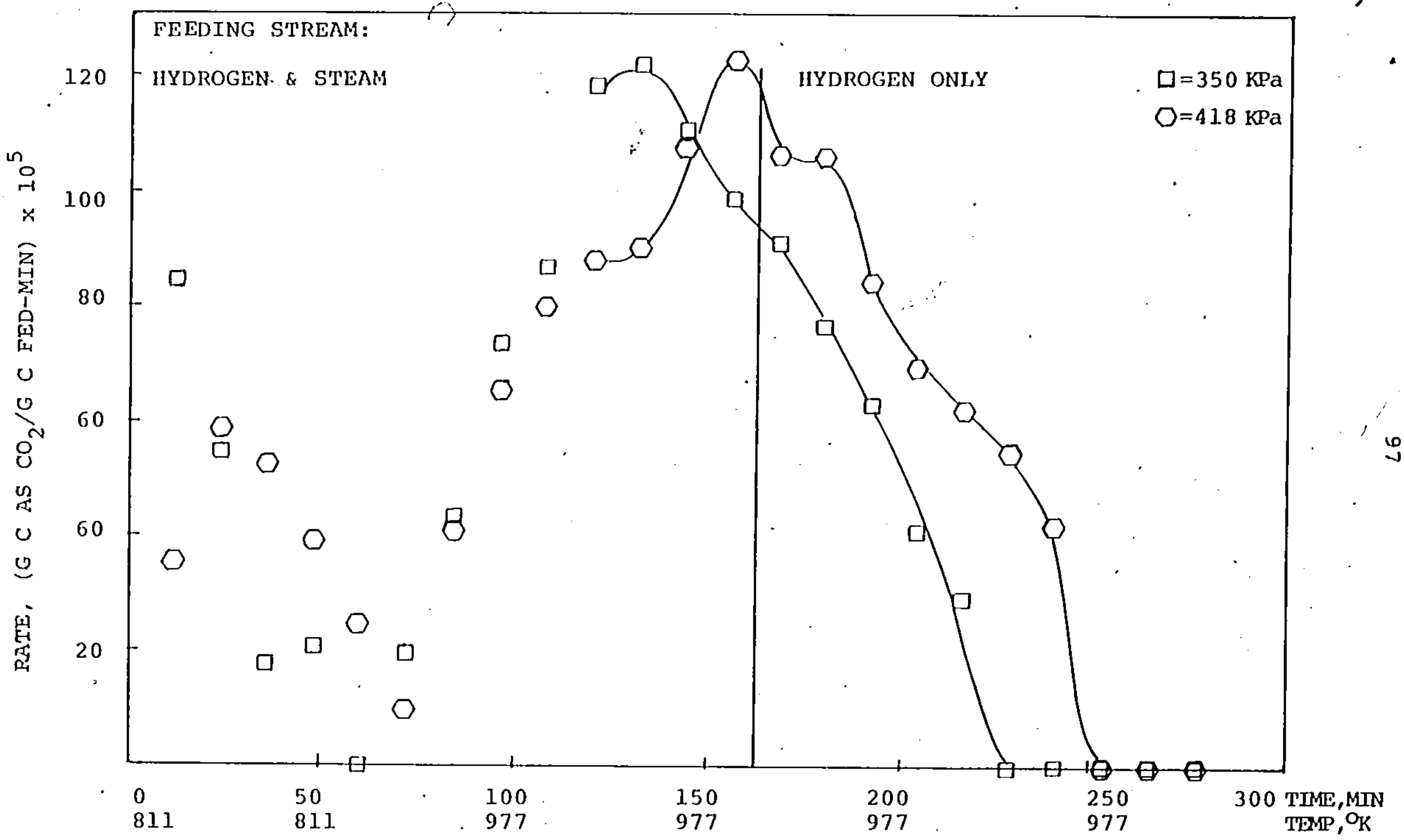


Figure 5.6 - Rate of Production of Carbon Dioxide at 350 KPa & 418 KPa for Type A Experiment.

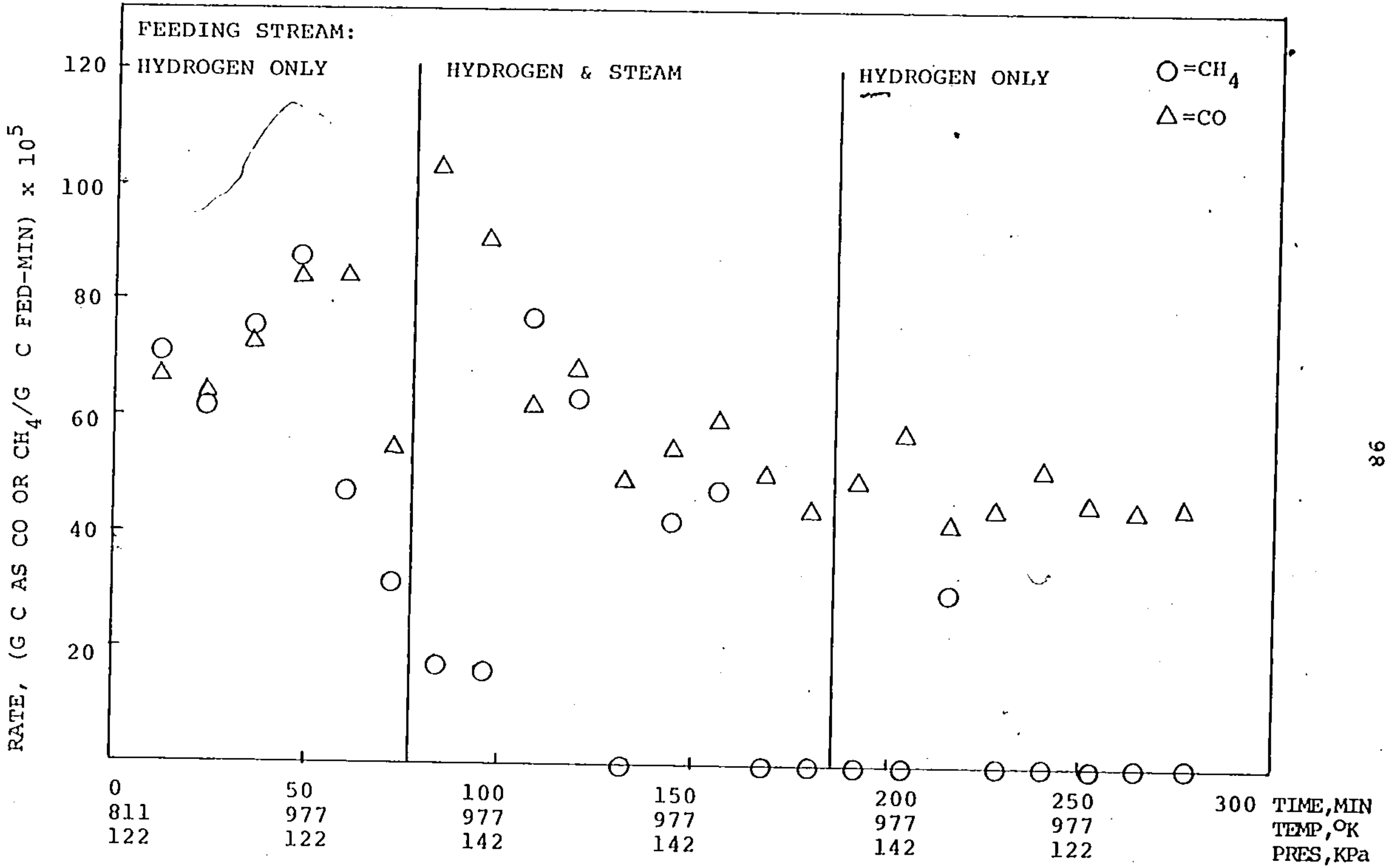


Figure 5.7 - Rate of Production of Methane and Carbon Monoxide at 122 KPa(3 psig) for Type B Experiment.

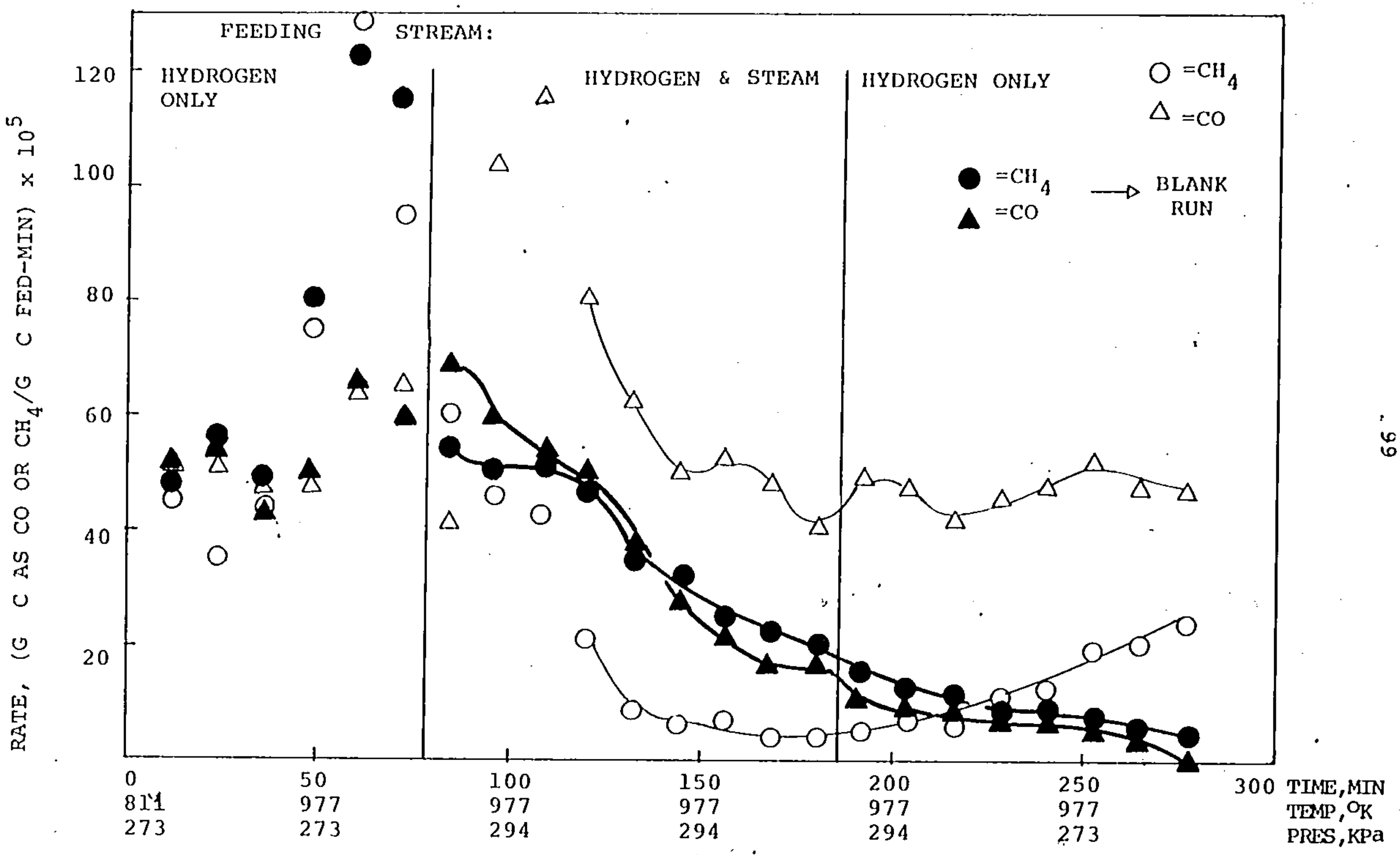


Figure 5.8 - Rate of Production of Methane and Carbon Monoxide at 273 KPa (25 psig) for Type B Experiment and for Blank Run with Hydrogen.

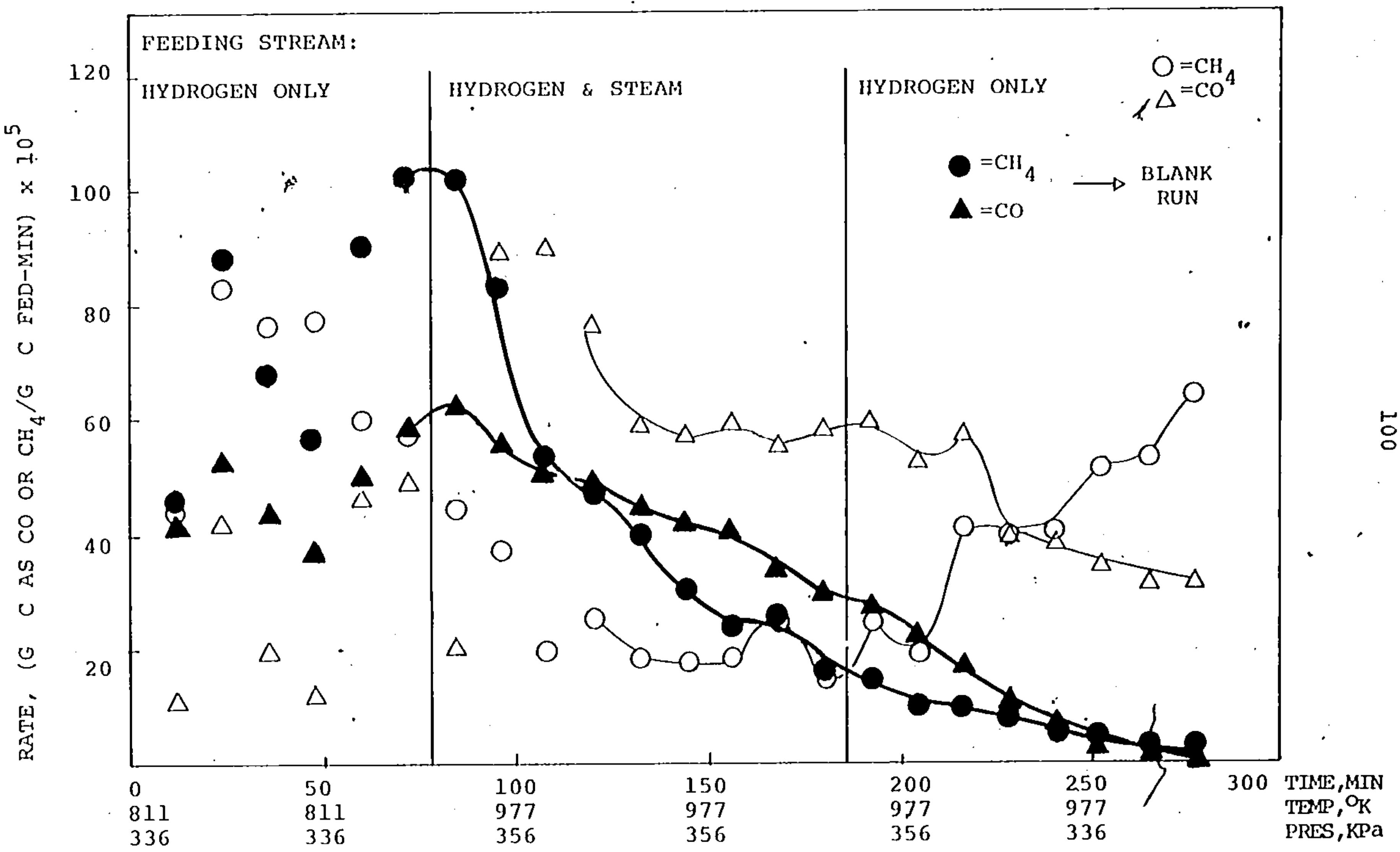


Figure 5.9 - Rate of Production of Methane and Carbon Monoxide at 336 KPa (34 psig) for Type B Experiment and for Blank Run with Hydrogen.

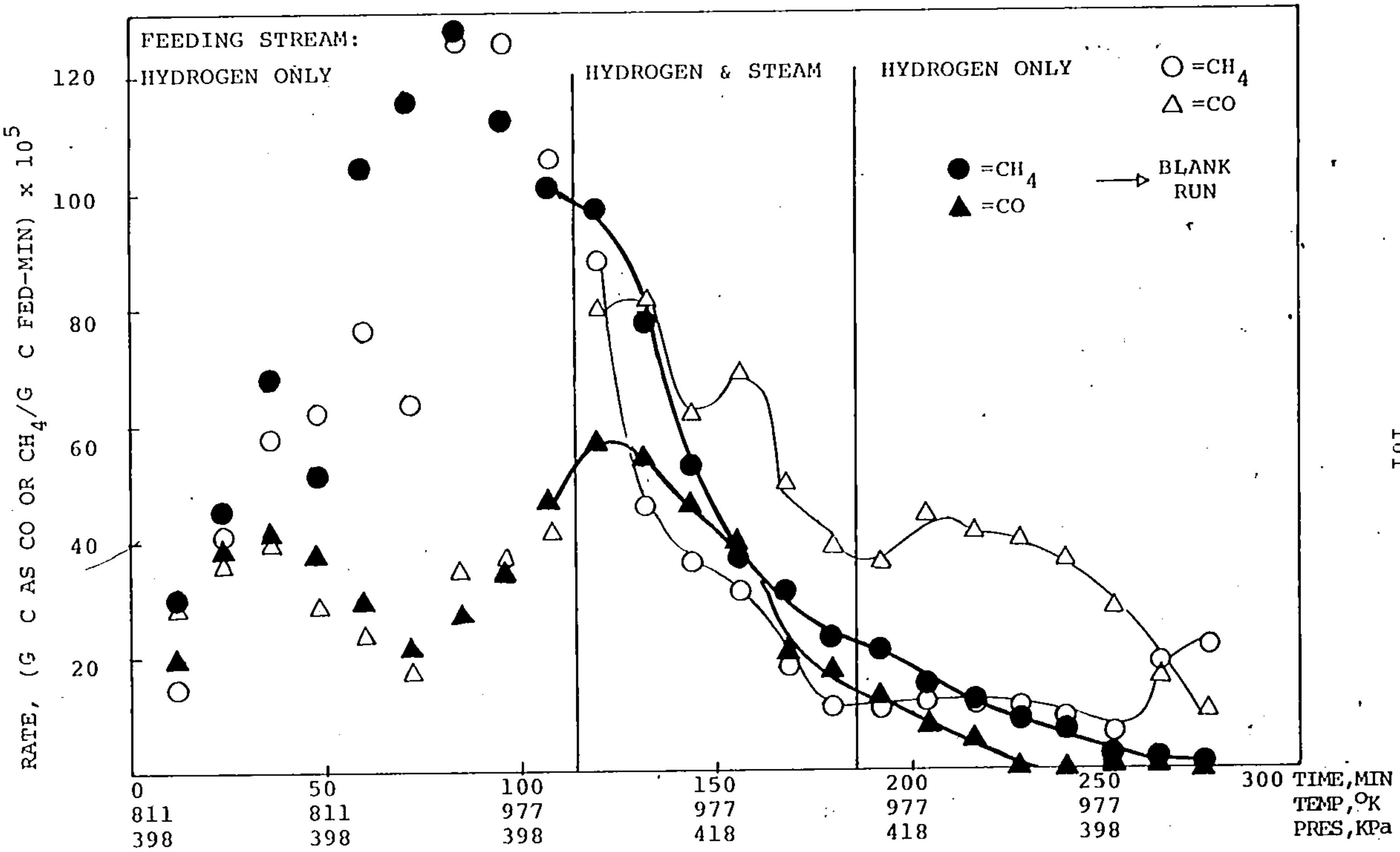


Figure 5.10 - Rate of Production of Methane and Carbon Monoxide at 398 KPa (43 psig) for Type B Experiment and for Blank Run with Hydrogen.

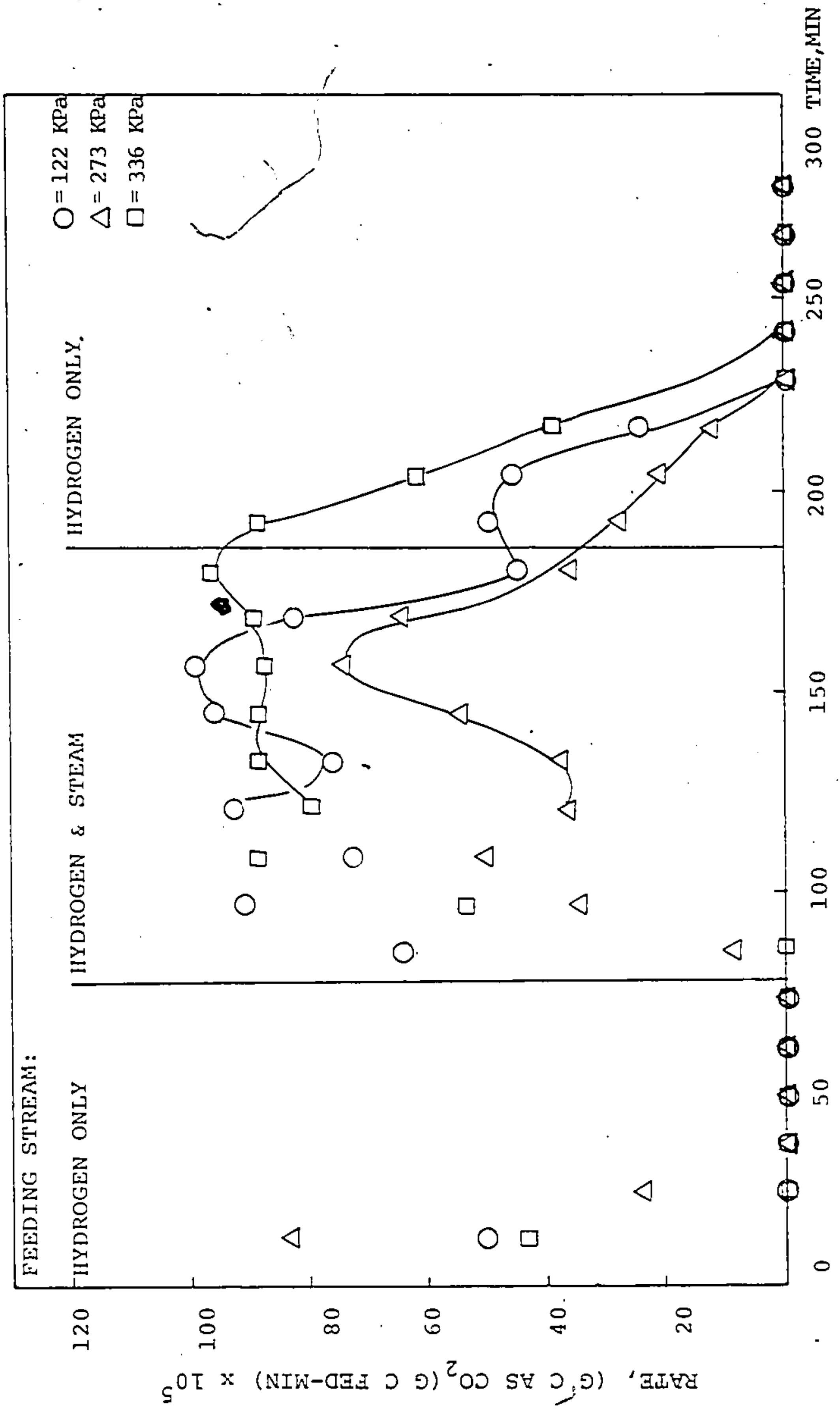


Figure 5.11 - Rate of Production of Carbon Dioxide at 122 KPa, 273 KPa and 336 KPa for Type B Experiment.

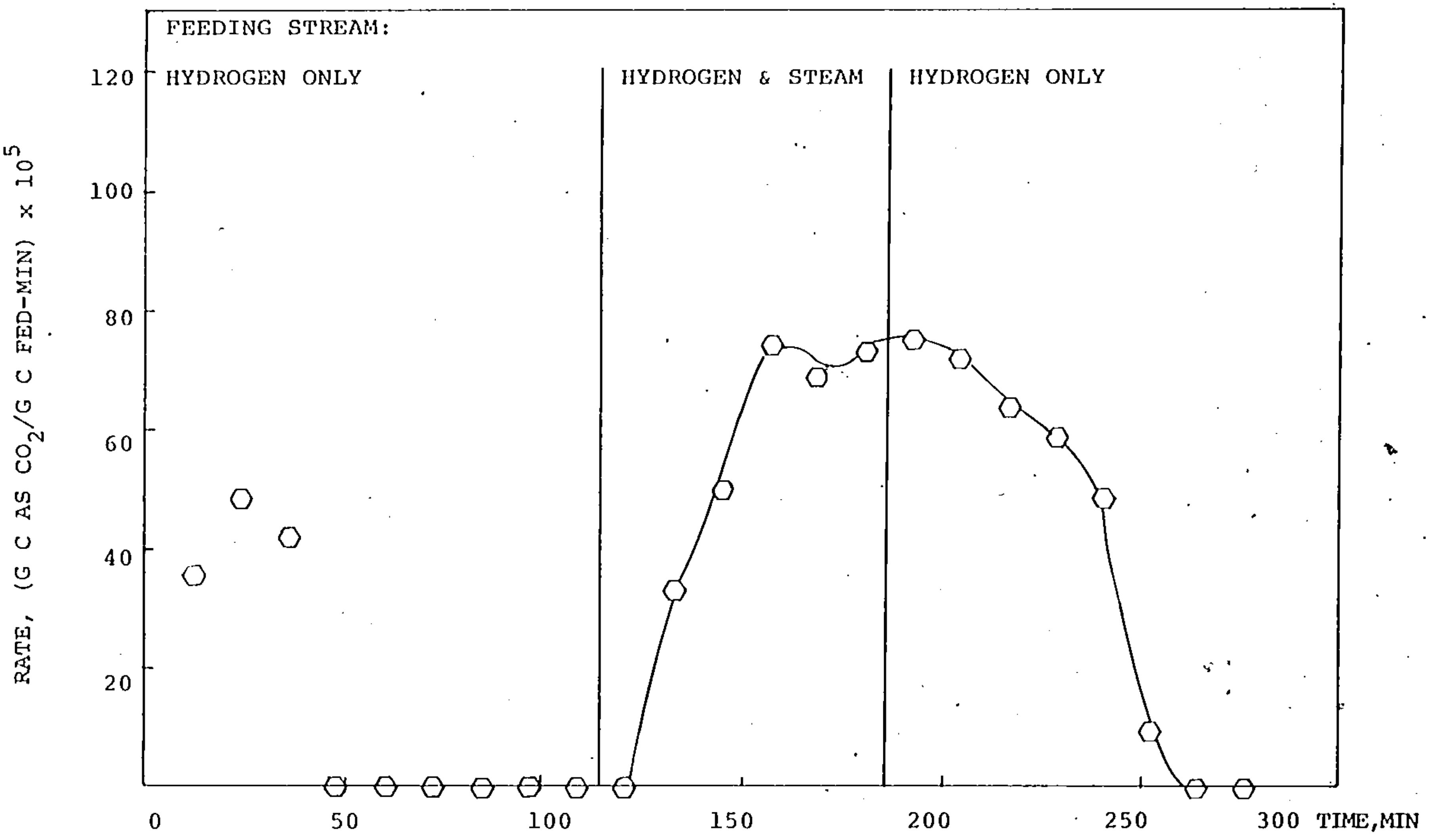


Figure 5.12 - Rate of Production of Carbon Dioxide at 398 KPa for Type B Experiment.

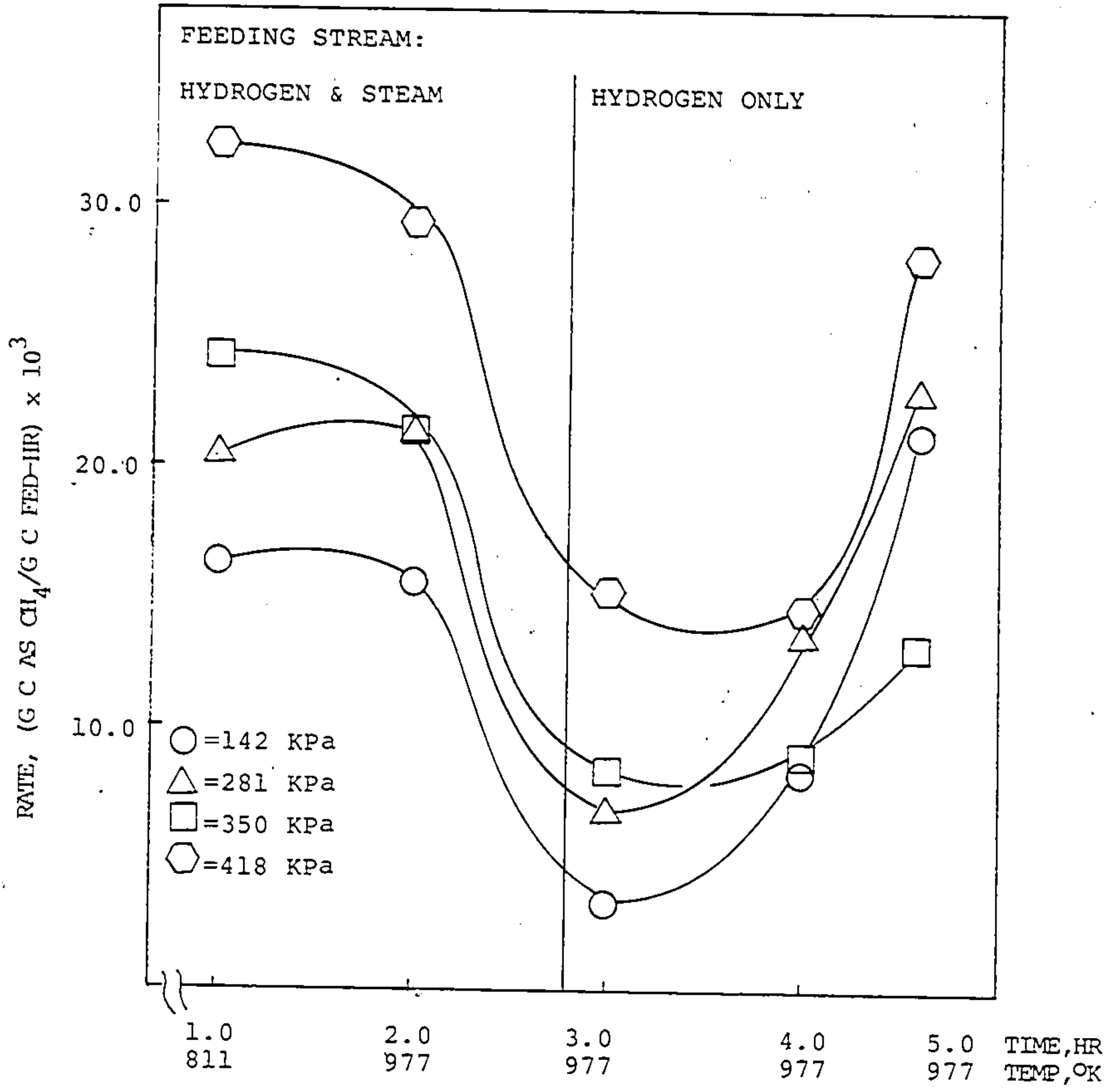


Figure 5.13 - Rate of Production of Methane for Type A Experiments.

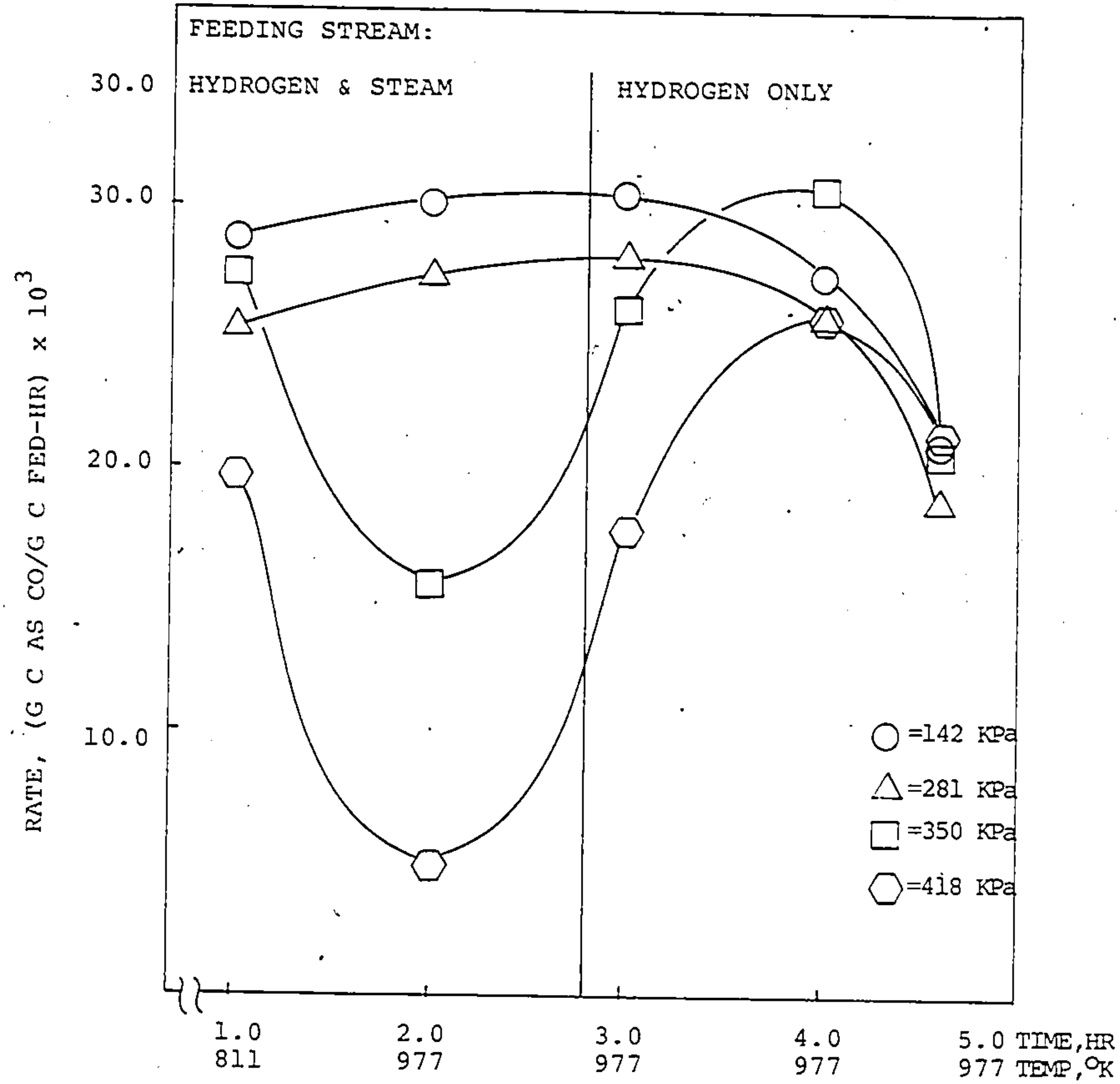


Figure 5.14 - Rate of Production of Carbon Monoxide for Type A Experiments.

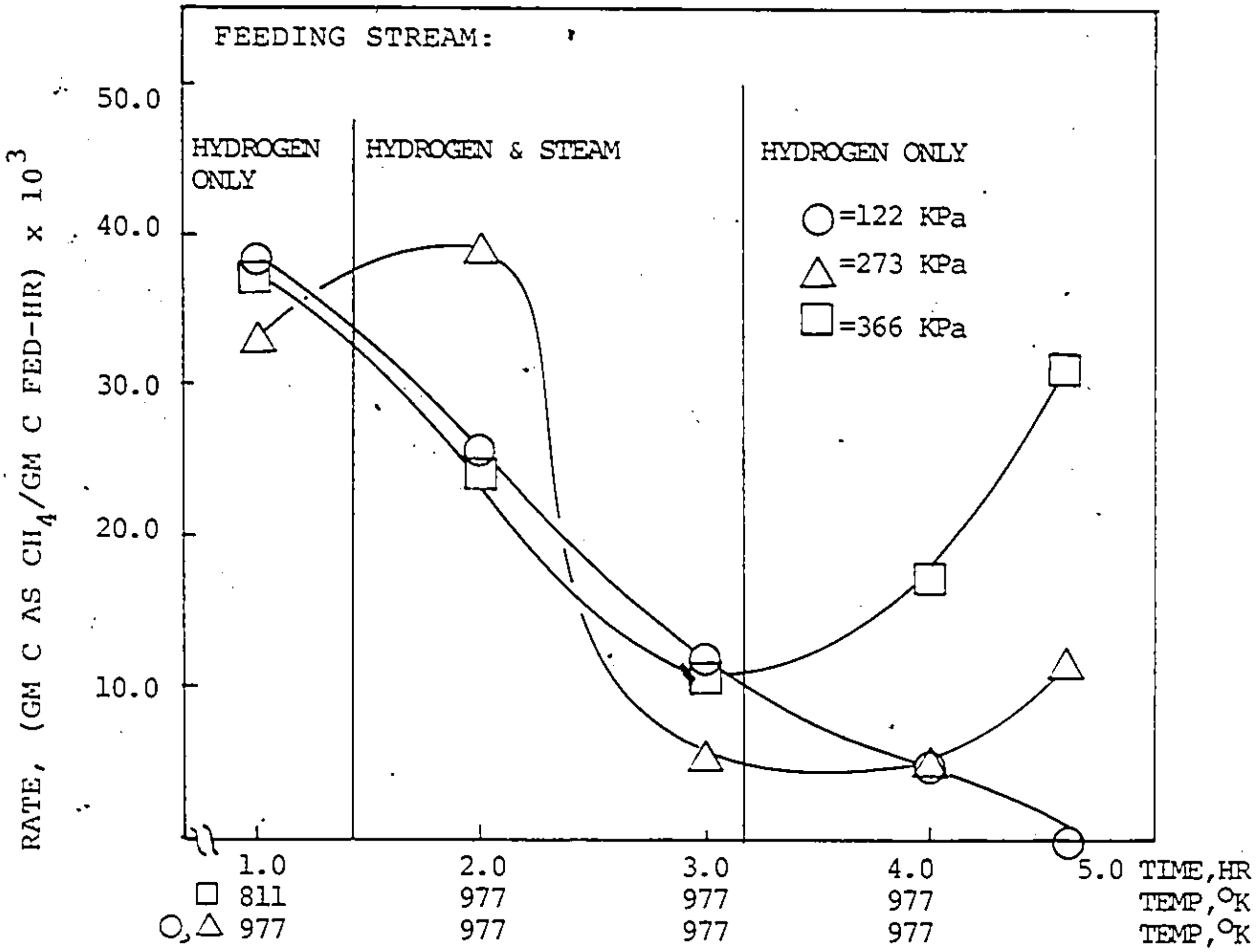


Figure 5.15 - Rate of Production of Methane for Type B Experiment.

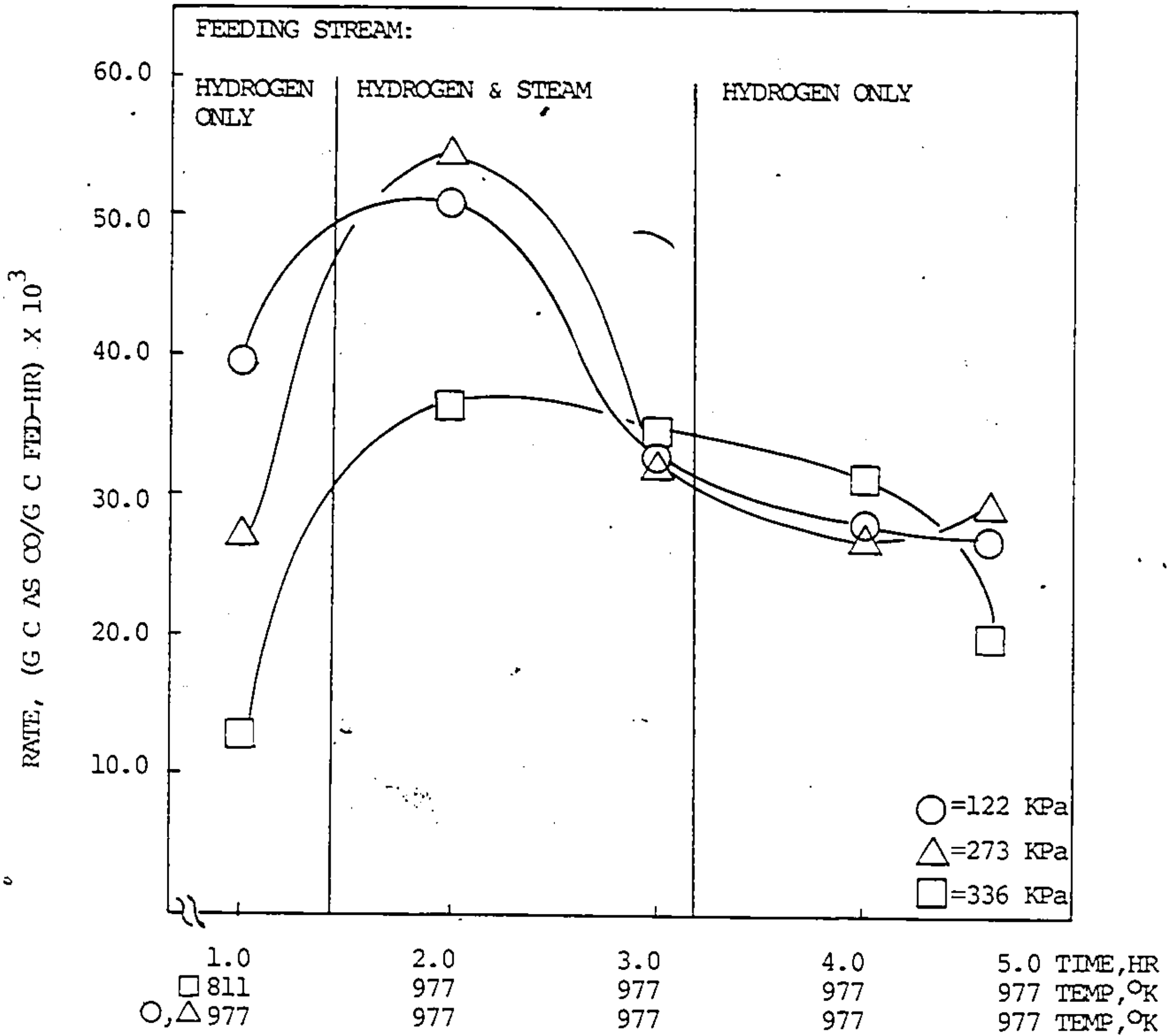


Figure 5.16 - Rate of Production of Carbon Monoxide for Type B Experiments.

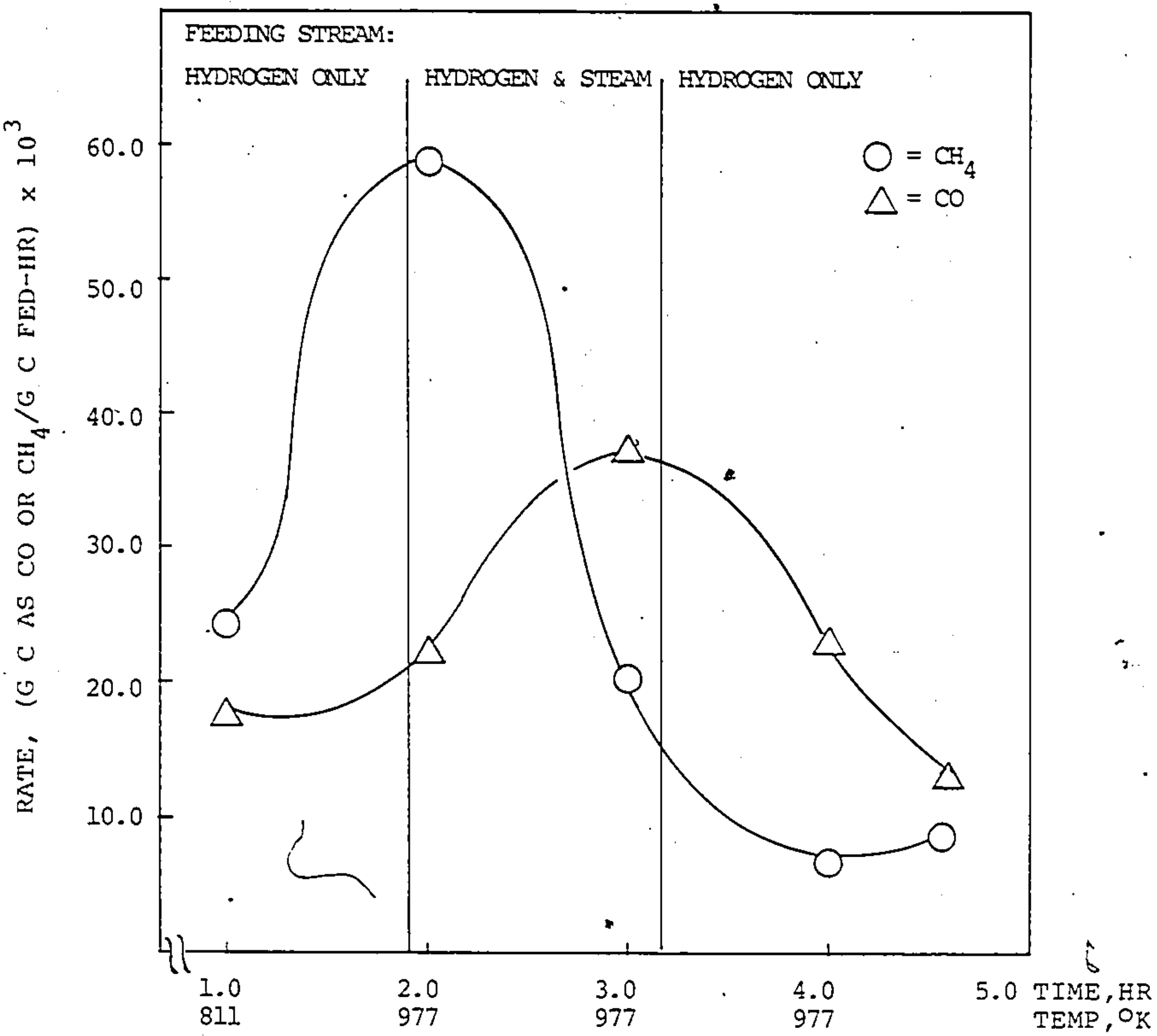


Figure 5.17 - Rate of Production of Methane and Carbon Monoxide for Type B Experiment.

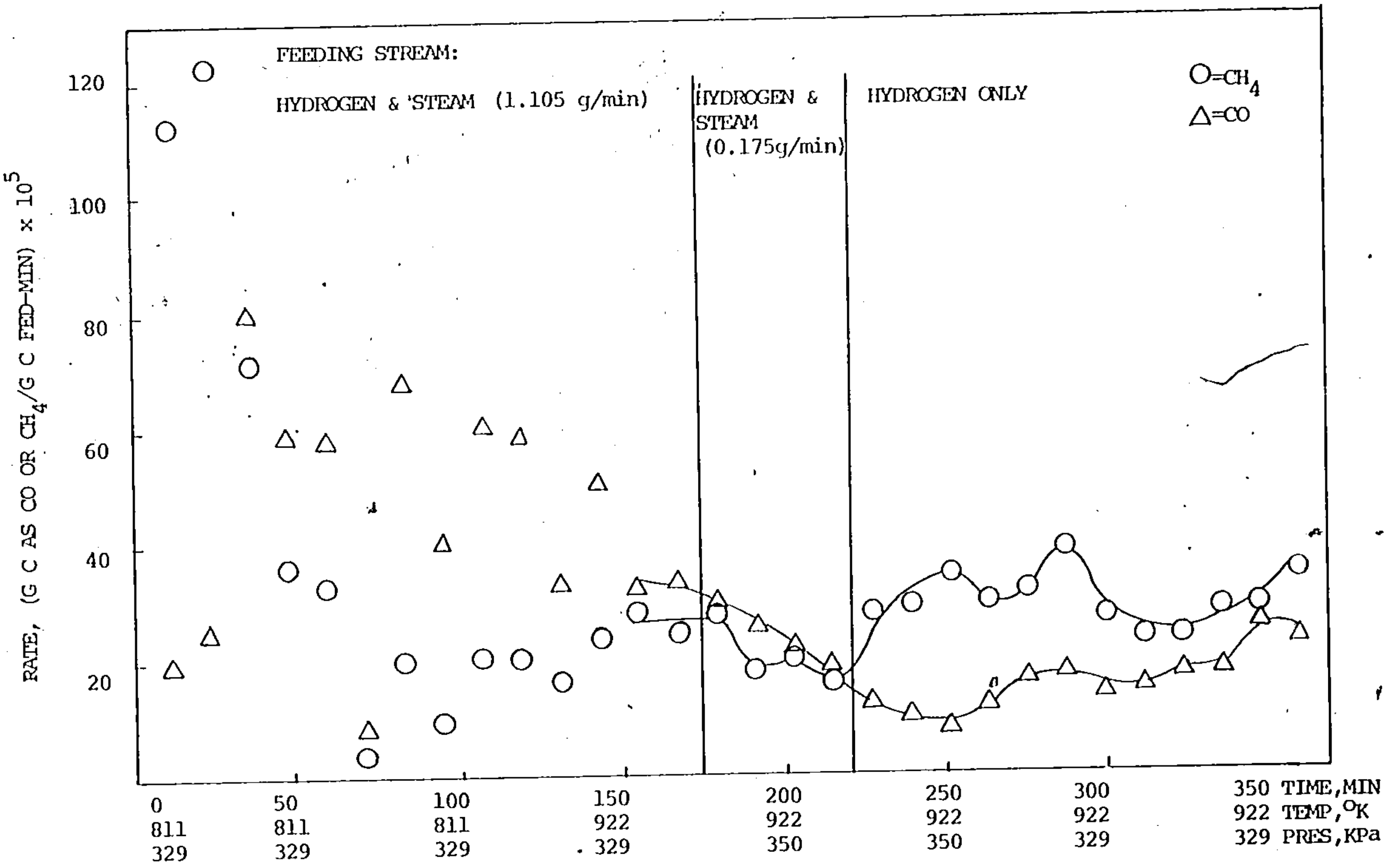


Figure 5.18 - Rate of Production of Methane and Carbon Monoxide at 329 KPa

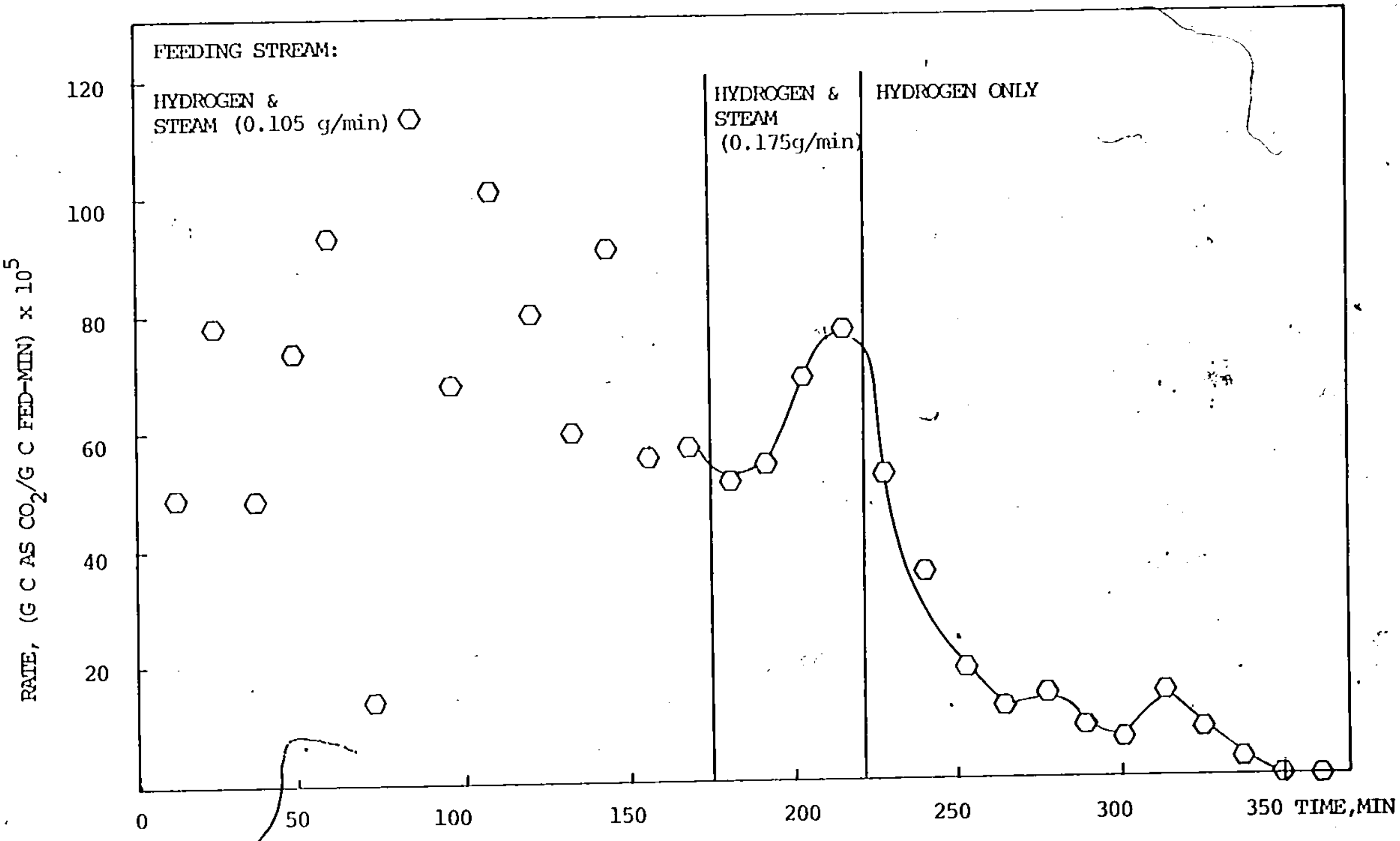


Figure 5.19 - Rate of Production of Carbon Dioxide at 329 KPa

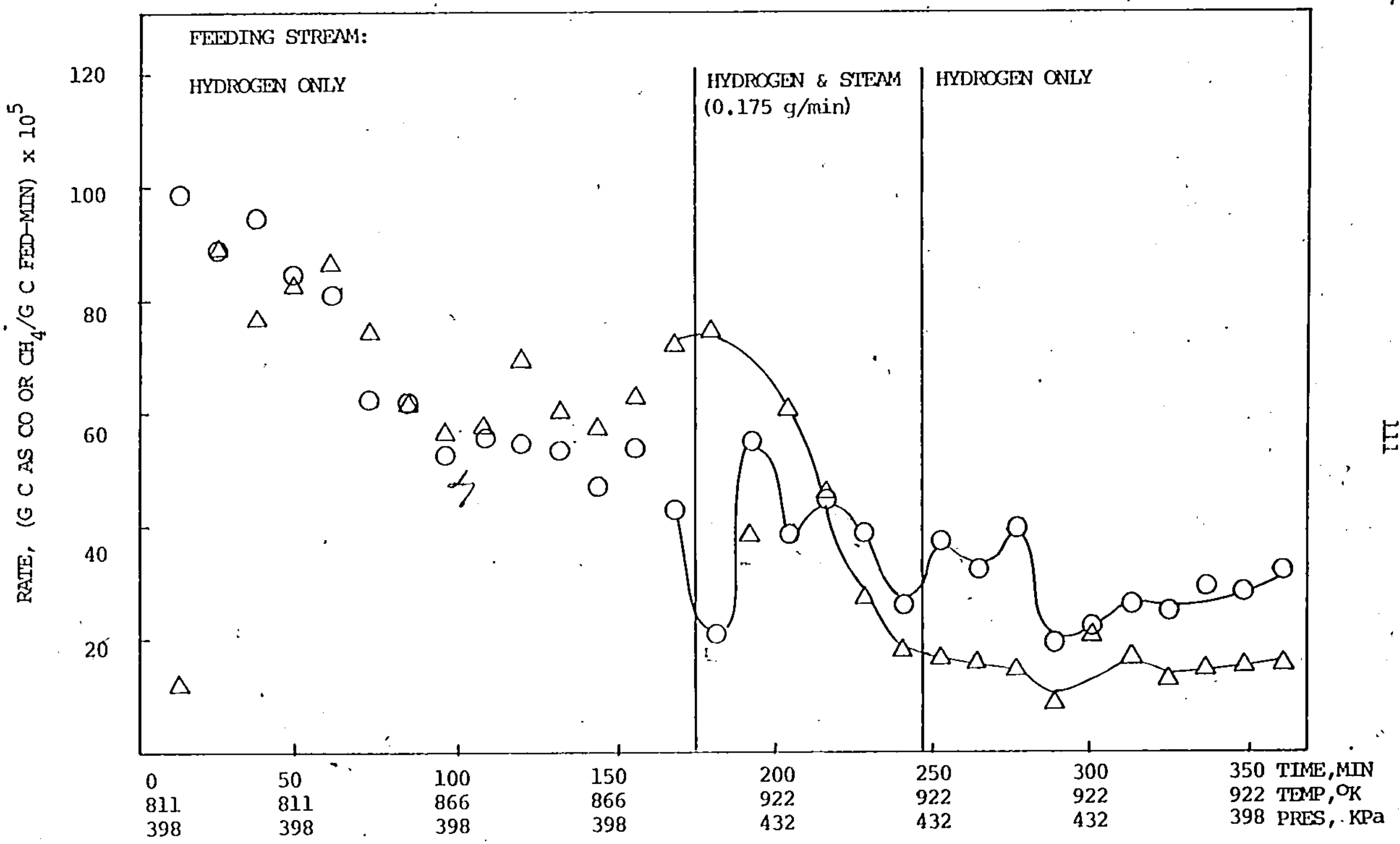


Figure 5.20 - Rate of Production of Methane and Carbon Monoxide at 398 KPa

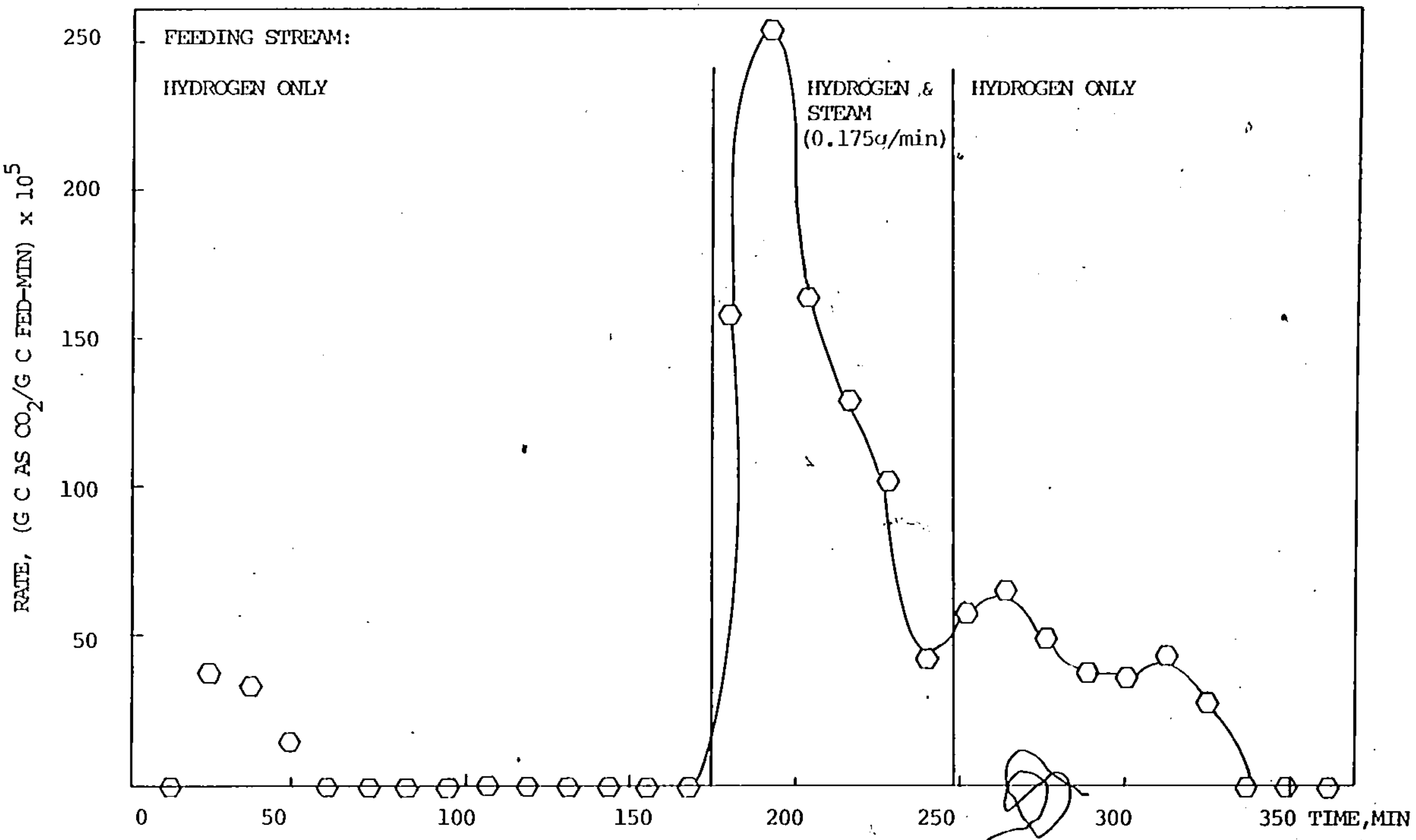


Figure 5.21 - Rate of Production of Carbon Dioxide at 398 KPa

CHAPTER 6

DISCUSSION OF RESULTS

In this chapter, the results reported in Chapter 5 will be compared and interpreted. The apparent influence of the presence and subsequent interruption of steam feeding in the inlet stream will be discussed and compared with blank experiments. This chapter is also aimed to provide background for qualitative interpretations concerning a possible explanation for the reactions occurring.

6.1 The Blank Experiments

The results obtained during the blank runs performed with hydrogen, helium and steam seemed to exhibit the same general behaviour, although varying in degree.

In the beginning of the experiments the rates of production of methane and carbon dioxide were high. It seems that a small surge in those rates could be identified during the beginning of each experiment. This surge is believed to be due to the devolatization stage of coal.

A second surge in the rates of production of both methane and carbon monoxide also seemed to exist during the time the temperature inside the reactor was increased.

After the increase in temperature, when reaction conditions were allowed to stabilize, the rate of production of both methane and carbon monoxide seemed to decrease slowly but continuously.

During the blank runs performed with helium, the amount of gases being produced after 2.3 hours was too low to be identified, perhaps due to the completion of the devolatization process. The reaction was therefore considered to last only 2.3-2.5 hours during blank runs with helium. It seems that during the runs performed with helium at the higher pressure, higher rates of production were obtained for methane and lower for carbon monoxide. However, the difference in pressure between the two experiments was small and the equipment utilized may not have been sensitive enough to <u>conclusively</u> differentiate between the two pressures. The behaviour of the rates of production of both methane and carbon monoxide can only be identified by a <u>trend</u>, i.e., by what is believed to be a possible tendency for the reaction. This reasoning also applies to hydrogen and steam blank experiments.

The rate of production of carbon dioxide during helium and hydrogen blank runs was visible during what seemed to be the devolatization stage. After this initial period of reaction, the rate dropped to zero and did not change for the remainder of the experiment.

The rate of production of carbon dioxide during the blank runs performed with steam, was high even after the devolatization stage. It showed a big increase when the temperature inside the reactor was increased. However, it also started to decrease slowly towards the end of the experiment.

The rate of production of methane during the blank runs with hydrogen seemed to be higher than that during blank experiments with helium or steam.

It became clear, during the blank runs that the rates of production of all product gases tended to decrease after approximately 2.3-2.5 hours of experiment.

6.2 General Discussion Common to all Type A and Type B Experiments

It is essential, at this point, to acknowledge certain characteristics inherent to the results of both Type A and Type B experiments as shown graphically in Figures 5.1 to 5.12.

In the majority of graphs plotted (except for Figure 5.7) two types of data seem to exist for each experiment, specially where Type B results are concerned.

One is related to the data plotted during approximately the first two hours of experiment, and the other, to the time thereafter.

6.2.1 First Part of Experiments

The data plotted during approximately the first two hours was very scattered and this fact made it difficult to identify any reaction trends during that time of experiments. Several possible factors occurring simultaneously may have contributed to this scattering. They are:

(i) feeding of coal occurring in the beginning of the run;

(ii) devolatization stage occurring during and after the time coal was fed;

(iii) temperature rising after the first hour (most of the time), just when a trend could start to develop;

(iv) steam introduction not too long after (or before) the increase in temperature. This factor also minimized the possibility of any trend development.

Therefore, it is safe to say that during those first two hours, the reaction and the environment for it to occur were not considered stable enough to establish a reaction trend.

That was the reason why the data points during the first couple of hours of experiment are not connected in any way.

However, one is forced to identify the existence of at least one surge in the rates of production of both methane and carbon monoxide, during the first two hours of the experiment. This surge indicated what is believed to be the devolatization stage of coal. The presence of a second surge in the rate of production of methane which could sometimes be easily identified in Type A (and blank) runs is believed to be due to the increase in reactor temperature to 977°K.

6.2.2 Second Part of Experiments

During the second half of the experiments (after initial two-hour-period), the scatter in the data seemed to decrease (except for Figure 5.7) - as conditions tended to stabilize. It became easier to visualize how the data points could be joined.

The presence of factors which would usually develop unstable conditions in the system is not felt so strongly any more. Reaction is, therefore, allowed to proceed without much disruption. When steam is finally disconnected from the feeding stream, some unstable conditions are identified again (as it would be expected), but they slowly seemed to stabilize.

That was the reason why the data points are connected in the second half of experiments, i.e., to call one's attention to the fact that the possibility of a trend exists.

6.2.3 Carbon Dioxide Production

The above discussion is relevant first to the rate of production of methane and secondly to that of carbon monoxide.

The rate of production of carbon dioxide was not included in the previous section because the reasoning presented previously does not seem to apply to carbon dioxide production.

The production of carbon dioxide seemed to be connected mostly to the presence of steam inside the reactor. If steam was not present or if it was discontinued from the feeding stream, the rate of production of carbon dioxide would decrease and drop to zero. This was observed in all experiments, independent of the presence of factors which contributed to the appearance of unstable conditions.

Also, once carbon dioxide was being produced, it was difficult to establish anything but "a possible trend" of how its rate of production seemed to change.

This leads one to believe that the presence of steam brought about high rates of production of carbon dioxide.

6.2.4 Hydrogen Content in Product Gas

Hydrogen production was not plotted because, since the hydrogen content of the exit gas represented both the unreacted hydrogen gas feed and the hydrogen producted from steam reaction with carbon - there was no way of separating these two sources of hydrogen. In this way, smaller changes occurring in the hydrogen content of the exit gas were not taken into consideration because they could not be taken as a significative indication of a specific change in the reactions occurring. It would be very difficult to determine whether any change was due to the hydrogen gas-carbon reaction or to the steam-carbon reaction. That is why, only greater changes in the hydrogen content of the exit gas are reported.

6.3 Effect of Steam

The effect of steam was studied in both types of experiments by connecting and disconnecting steam flow from the feeding stream.

6.3.1 Type A Experiments

When steam was discontinued from the feeding line, an increase in the rate of production of methane was noticed.

In most cases, this increase seemed to be greater at higher pressures.

The rate of methane production, as shown in Figures 5.1 to 5.4 and 5.13 seemed to improve when steam was discontinued from the feeding stream. This apparent improvement did not seem to follow any specific patterns.

However, the appearance of two small peaks in methane production rate after steam was discontinued seemed to occur in all runs.

The first one seemed to occur when the rate of production of carbon dioxide started to decrease. The second one, apparently coincided with a decrease in the rate of production of carbon monoxide. One possible explanation for these observations could be that the activated carbon atoms which were being used for reaction with steam, started being used by hydrogen once steam was disconnected.

The rate of production of carbon monoxide seemed either to increase or to remain constant, as soon as steam was discontinued. It decreased only later on in the process, as shown in Figures 5.1 to 5.4 and 5.14.

Carbon dioxide exhibited a different pattern. Its rate of production during this time was approximately equal to the rate of production of methane and carbon monoxide together.

Hydrogen content in the outcoming product gas seemed to increase when steam was discontinued from the feeding line.

The total rate of gasification which includes the rate of production of "carbon monoxide + methane + carbon dioxide" decreased when steam was disconnected from the feeding line.

6.3.2 Type B Experiments

The results of Type "B" experiments can be better understood if compared with hydrogen blank runs. That is why both the hydrogen blank runs and Type "B" runs were plotted in the same figures (Figures 5.8, 5.9 and 5.10).

The following discussion does not, however, apply to Run #39 (Figure 5.7). It is believed that the pressure at which that experiment was performed was too low to produce any significant results for comparison with the other experiments. In addition, the data obtained during that experiment was too scattered to lead to any conclusions. Therefore, only experiments performed at higher pressures will be taken into consideration in this discussion.

By comparing Type "B" blank runs experiments with hydrogen blank runs, one observes that the natural course of the run would lead to a reduction in the rate of production of methane (at approximately the same time steam would usually be introduced) - regardless of steam being present in the reactor or not. This can also be observed in Type "B" experiments, where the rate of production of methane would start decreasing even <u>before</u> steam was introduced. However, one should also observe that the rate of production of methane seems to be much lower for Type "B" experiments than that for the hydrogen blank runs.

After comparing the results of the two types of experiments it seems that the introduction of steam in the reactor might have contributed to a faster decrease in the rate of production of methane. One might say then, based on those results, that the presence of steam was detrimental to the rate of production of methane.

The rate of production of carbon monoxide apparently underwent a surge in the presence of steam - as compared to the hydrogen blank runs (where steam was never introduced).

The rate of carbon dioxide production, shown in Figures 5.11 and 5.12, and as expected, exhibited a decrease in rate of production which went down to zero before steam was connected. While steam was a part of the feeding mixture, an increase in production rate was observed. Its rate of production was approximately equal to the rate of production of methane and carbon monoxide together.

It was very difficult to establish a pattern of the hydrogen content in the product gases when steam was connected to the feeding stream - since it varied considerably.

Once steam was disconnected from the feeding stream, the rate of production of methane seemed to undergo a small increase.

Although only one experiment was performed during which steam was kept flowing into the reactor for one hour and ten minutes (Run #33, Figure 5.10), instead of the usual one hour and forty minutes. The results for that run indicated that a much smaller increase in the rate of production of methane occurred when steam was disconnected. This observation, suggested that the advocated increase in the rate of production of methane, might be greater when steam stays in contact with coal for a longer time.

However, it is believed that this matter should be further investigated before any decisive conclusions are drawn.

The rate of production of carbon monoxide tended to either remain constant (Run #37, Figure 5.8) or to decrease (Figures 5.9 and 5.10) when steam was disconnected from the feeding stream.

As far as the rate of carbon dioxide is concerned, it decreased and dropped to zero, as expected, once steam was discontinued.

Hydrogen content in the exit product gas seemed to be higher when steam was disconnected. This pattern was also observed for Type A experiments.

The total rate of gasification practically doubled its previous value when steam was introduced. It decreased when steam was disconnected from the feeding stream.

6.4 Results of 'Specific Runs'

After these two sets of experiments were performed, a few more specific runs were performed using a higher amount of steam in the feeding stream.

Runs were performed to observe the effects of an increase in the amount of steam in the feeding line from 0.105 g H_2O/min or 0.175 g H_2O/min, and subsequent disconnection of steam.

The same reasoning given in Section 6.2 for data scattering should also be applied for these runs.

Although data scattering in these experiments was very much visible, a possible decrease in the rate of production of methane seemed to occur when flow of steam into the reactor was increased (refer to Figure 5.18).

The rate of production of methane seemed to increase when steam was disconnected from the feeding stream.

It was also observed that it took a longer time for the rates of production of carbon monoxide as well as of carbon dioxide to decrease after steam (at a higher concentration) was disconnected from the feeding line than when steam was disconnected at a lower concentration - in Type A experiments.

The rate of production of carbon monoxide seemed to decrease when steam concentration in the feeding line was increased. However, the rate of production of carbon dioxide underwent an increase at the same time.

A Type B run was performed at 398 KPa total pressure, but with steam flowing at 0.175 g H_2O/min rather than the usual 0.105 g H_2/min used in previous Type B experiments (refer to Figures 5.20 and 5.21).

Data scattering was, once again, very much visible in this experiment - making it difficult to identify any path, but the possibility of a trend in the reactions taking place. From the results plotted in Figures 5.20 and 5.21, it could be explained that the unfavorable effect of steam, outlined in other Type B runs, seemed to have been partially counterbalanced by a simultaneous increase in temperature from 866 to 922°K. However, as it was mentioned, the effect was probably only "partially" counterbalanced, since the rate of production of methane tended to decrease after the temperature stabilized at 922°K to approximately 32 x 10^{-5} g C as CH_4/g C fed-min, which is much lower than 50 x 10^{-5} g C as CH_4/g C fed-min which was the value it had stabilized at, before the temperature was raised and steam introduced into the feeding stream.

In this case, as in the preceding one, where a higher steam concentration in the feeding line was used - the time it took for the rates of production of carbon monoxide and dioxide to decrease was much longer than the time it took for those rates to decrease in the other Type B runs.

6.5 Further Comparison Between Results Obtained for Type A and Type B Experiments

If coal conversion is defined by the expression $[(W_o-W_f)/W_o]$, where "W_o" represents the initial weight of moisture-free coal before each run and "W_f" represents the final weight of the char at the end of each run - it seems that Type A experiments gave a relatively higher coal conversion than Type B experiments. This is shown in Figure 6.1 where it can be seen that the coal conversion for Type A experiments is at least five percent higher than that for Type B experiments.

However, it must be noted that, although a higher coal conversion was attained for every run in Type A experiments, a higher conversion to methane seemed to occur for Type B experiments. This is shown in Figure 6.2 which plots the total production of methane as (g C as CH_4/g C fed) x 10^2 versus total pressure for Type A and Type B experiments at different pressures. This was likely due to the fact that during the initial stage of each run (devolatilization stage) the amount of methane produced was much greater for Type B runs (when only hydrogen is present as the reacting gas) than Type A runs.

The increase in the rate of methane formation, observed in most cases when steam was disconnected from the feeding stream, seemed greater in Type A experiments than

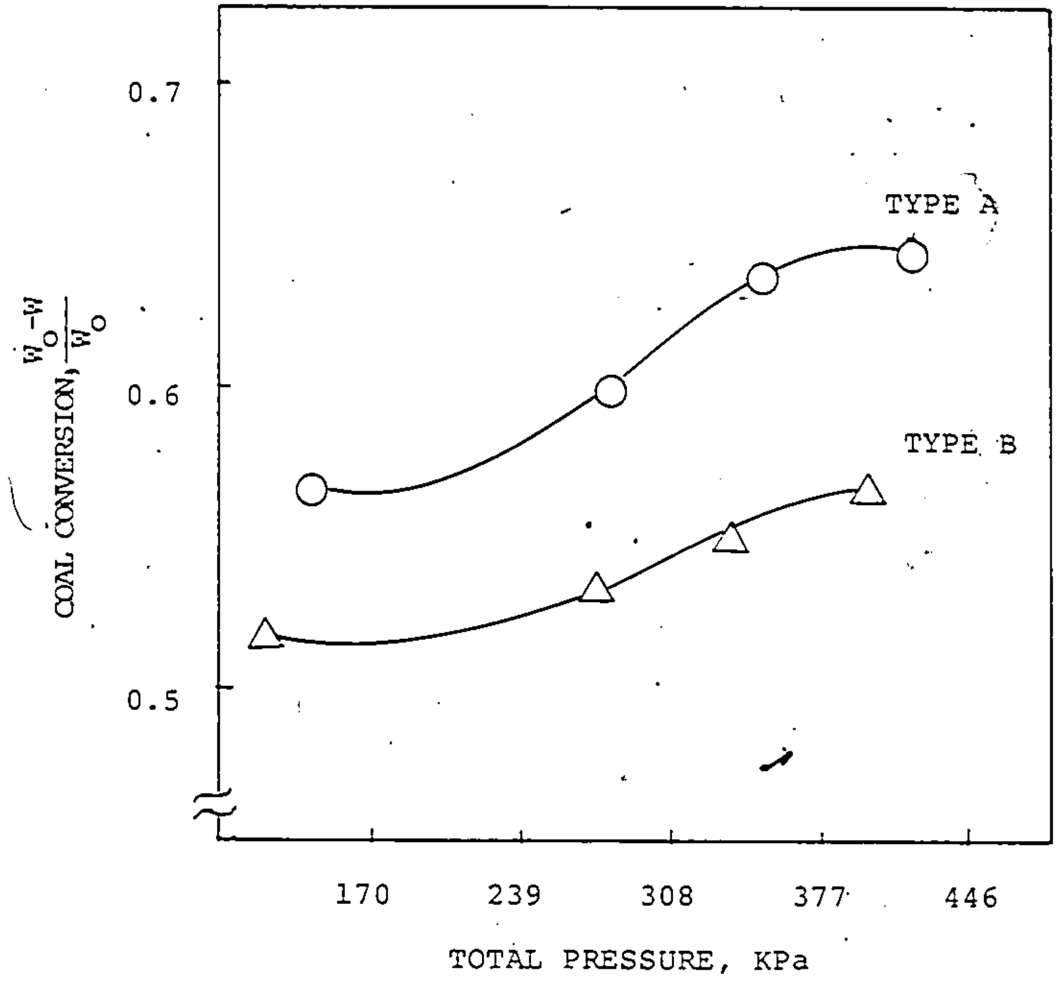


Figure 6.1.- Coal Conversion for Type A and Type B Experiments.

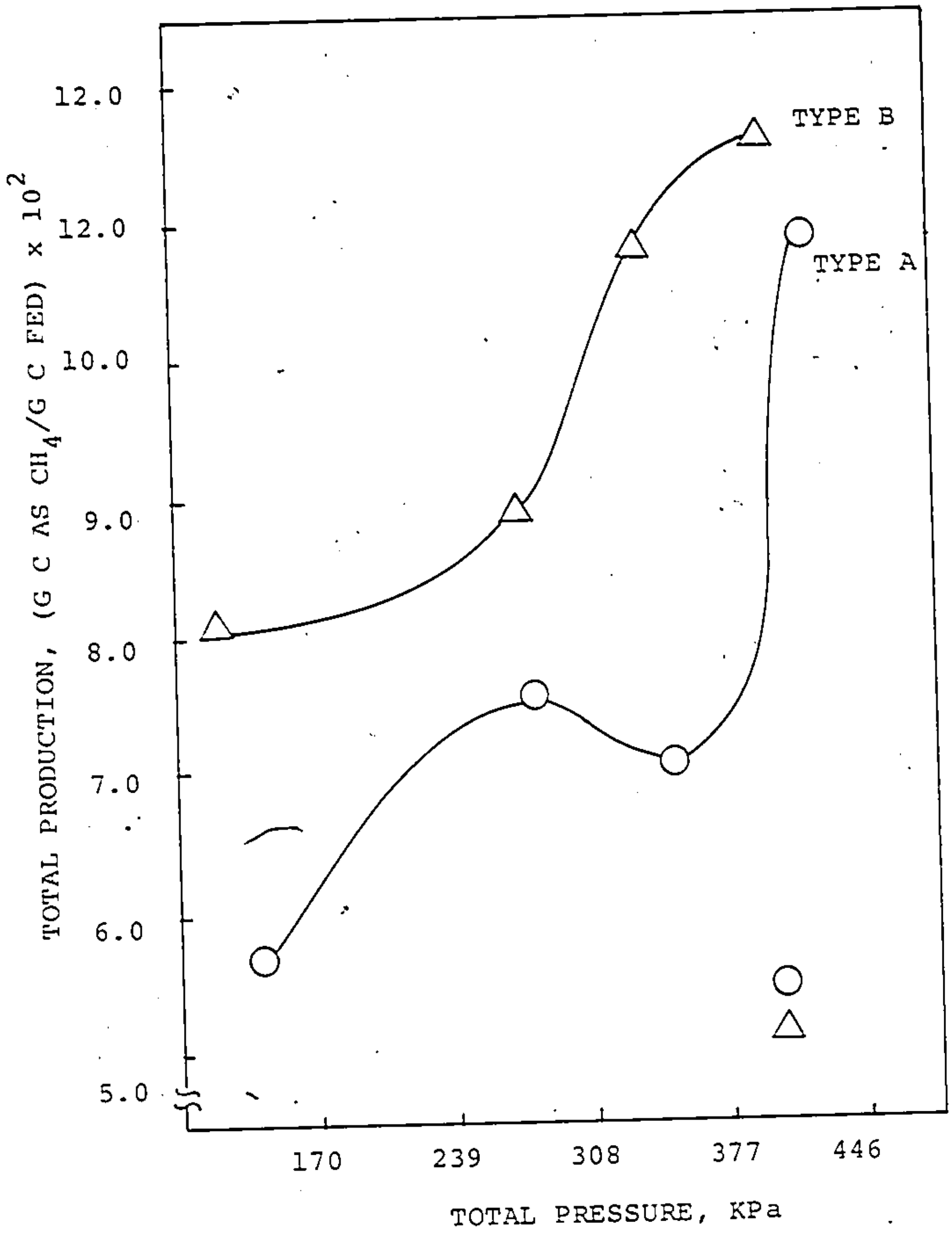


Figure 6.2 - Total Production of Methane for Type A and Type B Experiments.

in Type B experiments for most pressures studied, i.e., it was greater for the runs during which steam was allowed to flow into the reactor from the beginning of the experiment.

Although the rate of methane production appeared to have decreased while steam was part of the feeding stream, the total gasification rate, greatly increased to almost twice its previous value - for both Type A and Type B experiments.

Another trend was observed for carbon monoxide which seemed to indicate a higher total production during Type B experiments than Type A experiments as it is shown in Figure 6.3, where the total production of carbon monoxide is plotted (g C as CO/g C fed) x 10^2 versus total pressure, for Type A and Type B experiments.

Also, an apparent pattern for the production of carbon dioxide indicated a higher rate of production for Type A experiments.

6.6 Interpretation of Results

In this section, an attempt is made to account for the meaning of similarities and dissimilarities in the obtained results.

The reported observation that the increase in methane rate of production after disconnecting steam from the feeding stream appeared to be greater for Type A than Type B

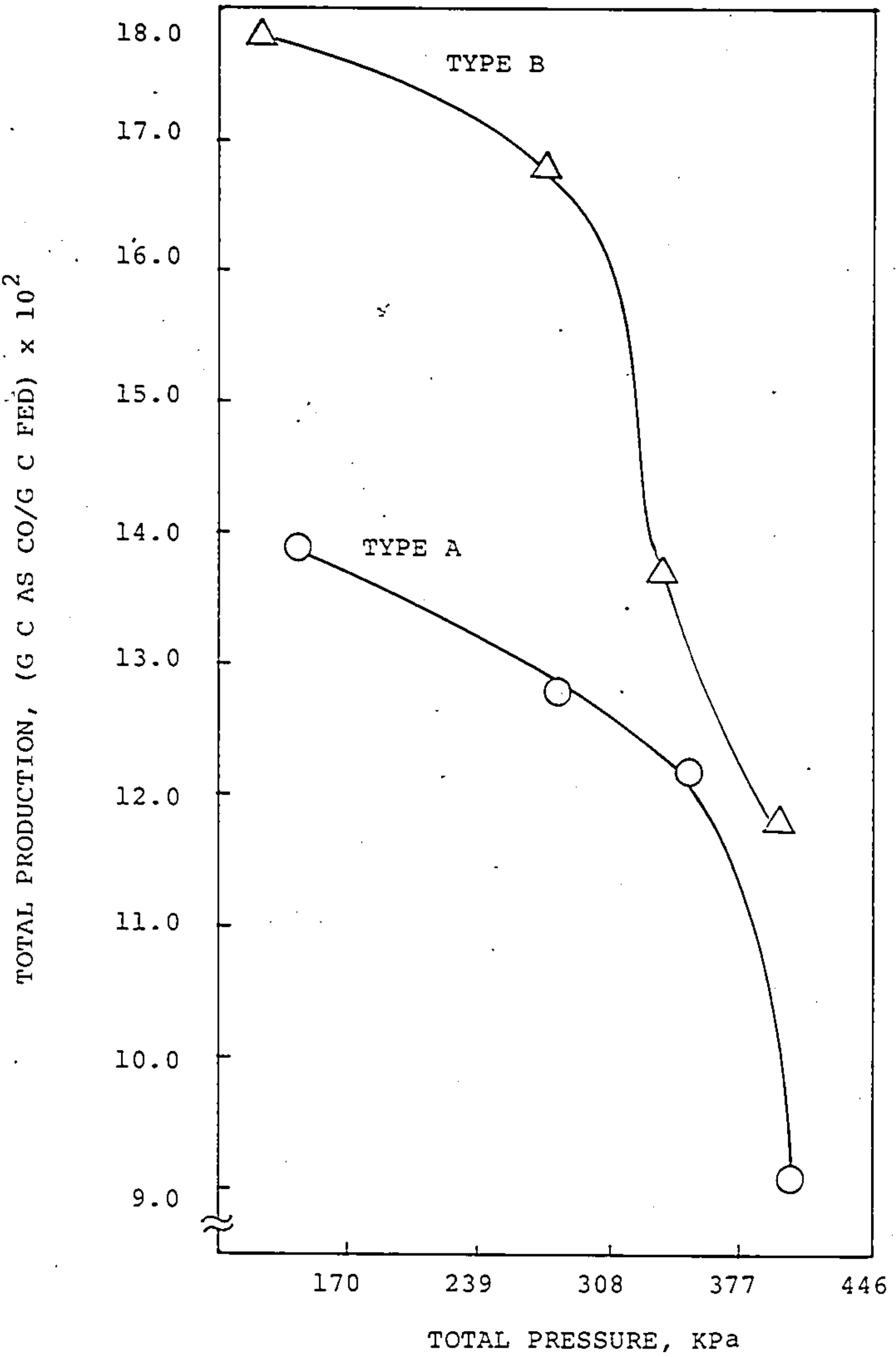


Figure 6.3 - Total Production of Carbon Monoxide for Type A and Type B Experiments

experiments. This suggests that ceasing the steam flow into the reactor after exposure of coal to it, from the beginning of the experiment, would tend to increase the "sensitivity of carbon towards hydrogen".

It is important though, to clarify here that this higher increase in methane production when coal is exposed to steam from the beginning of the run could not be the result of a reduced rate of production in the early stage of devolatilization. The reason why less methane was produced at that stage is believed to be that most of the carbon atoms which were "ready" to react, did so in the presence of steam to produce carbon dioxide (which in the case of the present study is the undesirable product), or maybe carbon monoxide. Therefore, an explanation based on the assumption that since less methane was produced in the initial stage of gasification (devolatilization) more methane should be produced at the end of the process is irrelevant and should not be considered as an alternative explanation.

A general trend for a decrease in total production of carbon monoxide seemed to occur for both Type A and Type B experiments, at higher pressures. This observation is probably related to:

i) equilibrium considerations discussed in Chapter 2 - in which high pressures are shown to be detrimental for its production in the "hydrogen-steam" gasification of a char. Even though the conditions utilized in this project were different from those used in the equilibrium composition study, and even though the experiments in this project may not have reached equilibrium at all, a trend could be considered. This trend was also observed at the conditions studied in this project, and/or;

ii) the known effect that high pressures exert on gas desorption - in this case, the desorption of carbon monoxide gas from the carbon surface, and/or;

iii) to the "retarding" effect of the presence of excess hydrogen on the production of carbon oxides which should be stronger at higher hydrogen partial pressures.

6.7 Possible Explanation for the Reactions Occurring

Based on the literature surveyed, on the results reported in Chapter 5, and on their interpretation discussed earlier in the chapter, an attempt will be made to qualitatively outline the possible effects that steam might have on the carbon-hydrogen reaction, based on the proposition of an analogy.

6.7.1 Outline of an Analogy

Bearing in mind the results reported earlier, and the theories surveyed in Chapter 2 and 3 - an analogy between the increase in temperature and the introduction of steam in the feeding stream is proposed:

"An increase in the number of active sites available for reaction, similar to the one induced by an increase in temperature during a hydrogasification process, would also be occurring whenever feeding of steam is initiated for the first time".

When hydrogen is present alone in the reacting atmosphere, the main reaction leading to the formation of methane is assumed to be the chemisorption of hydrogen by an active site. Any "activation" - such as an increase in temperature - leading to an increase in the number of active sites, should result in the increase of the rate of methane production, because of a more effective competition for the formation of active sites against cross-linking reactions.

When steam is introduced in the feeding line, and once in contact with the carbon structure, steam would penetrate in-between chains of carbon-atoms (acting more or less like a plasticizer), separating them first and "breaking" them after. By separating chains, steam would destroy any regular crystalline structure which might exist at that level and would lessen the energy necessary to break these chains.

This would make it much more difficult for activated carbon atoms, either from the same active site or from different active sites, to react - since the carbon chains to which these carbon atoms are attached would be further apart. In other words, by penetrating in-between chains, steam would decrease the possibility of polycondensation reactions between activated carbons and this decrease in the number of possible polycondensation reactions should result in an increase in the amount of gas being produced.

By "breaking" chains, (which had already been "separated"), steam would be creating new active sites, i.e., would be starting new free radical chain reactions.

Both the decrease in the possible number of polycondensation reactions and the increase in the number of active sites available for reaction in "separated chains should lead to an increase in the total rate of gasification - once steam was introduced in the feeding line. However, steam, although creating new active "separated" sites would also be competing for and reacting with these sites against hydrogen and against polycondensation reactions.

Once the strongly competitive presence of steam was not felt any more, hydrogen would have an easier access both to the newly created and the previously existing active sites. Therefore, methane production would be enhanced, since a larger number of active sites would become available for reaction with hydrogen, as compared to when steam was present.

In the end, the competition for activated carbon atoms would again be between hydrogen (leading to the production of methane) and activated carbon atoms themselves (leading to polycondensation reactions) - since steam is not present any longer to separate the chains. This last effect was also observed experimentally when the total rate of gasification slowly decreased once steam feeding was discontinued.

CHAPTER 7

SUMMARY AND CONCLUSIONS

Problems such as data scattering and a frequent changing of variables during the experiments made it difficult to interpret the results reported in this study. However, ideas for a new path to follow as well as the possible development of a theory have been initiated and some useful results have been obtained.

It was indicated that the possibility of a trend exists when steam is disconnected from an inlet reactant stream constituted of a hydrogen-steam mixture. This possible trend would indicate that the amount of methane being produced would increase after steam would be disconnected from the feeding line.

Another possible trend was that the extent of this advocated increase in the rate of production of methane would be somehow, connected to the duration and timing of steam introduction. However, further confirmation is required.

One possible reason why the mixture steam-hydrogen has been said by some researchers to be advantageous for the production of methane, could be that under the conditions studied by those workers, the reaction

$$CO + 3H_2 \rightarrow CH_4 + H_2O \qquad (2.46)$$

might have taken place.

A possible explanation based on theories surveyed and on the possible trends previously outlined was proposed. It suggested that steam would penetrate in-between chains of carbon atoms separating them, and in this way, decreasing the number of polycondensation reactions occurring. Steam would then break these chains, giving rise to new active sites, "ready" to react. Competition for these sites would then start among steam, hydrogen and active sites themselves (causing polycondensation reactions). Finally, when steam would be removed from the reaction environment, hydrogen would have an easier access to active sites and the rate of producton of methane would increase.

To conclude what has been proposed and discussed so far, it is believed that the possibility exists that steam might "activate" the carbon structure of a coal or char.

CHAPTER 8

RECOMMENDATIONS FOR FURTHER WORK

This chapter will deal with means to improve both the procedure utilized in this study, as well as its results and reliability. Suggestions will be made for further work in this area, which might bring more significant, conclusive and better organized results than the ones obtained in this study.

The following suggestions will be classified by areas and might improve the meaningfulness and reliability of results of further work in this area.

8.1 Procedure

(i) Variables, such as temperature, amount of steam in, amount of hydrogen in, pressure and $H_2O/H2$ ratio should be investigated on a broader range. They should also be investigated individually or with longer time lags between them. This would ensure that the effect of changing one variable would not be confused with that of changing another variable.

(ii) Less amounts of steam should be utilized relatively to the amount of coal present. In this way, the risk of having an excessive amount of steam, inside the reactor, hindering any possible ongoing reactions between carbon and hydrogen, would be avoided.

(iii) Type B experiments should be performed, keeping steam flowing into the reactor for different time lengths. This procedure would allow the researcher to check if the increase in the rate of production of methane advocated in this study is indeed related to the time of contact between steam and coal.

(iv) Experiments should be performed utilizing the same procedure "several times", i.e., feeding steam and discontinuing it, then, feeding it again and discontinuing again. This type of experiment, if performed with the correct type of equipment, should provide the researcher with a lot more information on the new procedure proposed in this study.

(v) Higher temperatures and pressures should be utilized in future experiments, to obtain more conclusive results.

8.2 Equipment

(i) The reactor should be longer, to allow for the falling particles of coal to actually heat-up, during the feeding operation.

(ii) The reactor material as well as auxiliary heating equipment should be chosen as to be able to withstand longer experiment duration (twenty-four-hour-runs , if necessary), and higher temperatures.

8.3 Auxiliary Activities

(i) An improved way to feed the coal into the reactor should be investigated. Maybe forcing the coal inside the reactor by equalizing the pressure inside the reactor and that inside the coal reservoir.

(ii) Coal should not be left inside the reactor either during heat-up periods or cool-down periods. The first would allow for premature polycondensation reactions to take place. The latter would allow for further reaction to occur when experiment was considered to be finished.

(iii) Other reactant gases should be used. Instead of using hydrogen and steam, maybe hydrogen and/or carbon monoxide and/or steam should be tried.

(iv) Coal samples should always be analyzed for carbon, oxygen, nitrogen, hydrogen and sulphur before and after every experiment - to allow for a proper mass balance.

(v) The possibility of observing the porous structure changes in coal particles, should be investigated. It could disclose evidence to identify how reactions proceed, i.e., if they are mainly surface reactions or bulk reactions. Maybe a comparison between the char porous structure after reaction with hydrogen, steam and both, could identify how a hydrogen-steam mixture compete for carbon from coal. This would enable the researcher to decide how and when to best utilize reactants.

(vi) Experiments should be carried out utilizing greater amounts of coal, namely, 10-100 g. The reason for this being that, greater amounts of coal would increase the possibility of getting a more homogeneous sample. With the small amounts of coal utilized in this study, any variation in coal properties within the sample (and coal properties are known to vary within the same sample) is bound to have a considerable influence in the results observed. A larger sample would, therefore, render the results more significant.

It is, therefore, recommended for those who wish to follow this study, to retain its initial concept of introduction/disconnecting of steam. The results obtained in this initial study may not have been very conclusive, since this project was dealing with a new idea. However, it is a fresh path worth following, which might bring positive results in future research - leading to the reactivation of the carbon structure of a carbon char.

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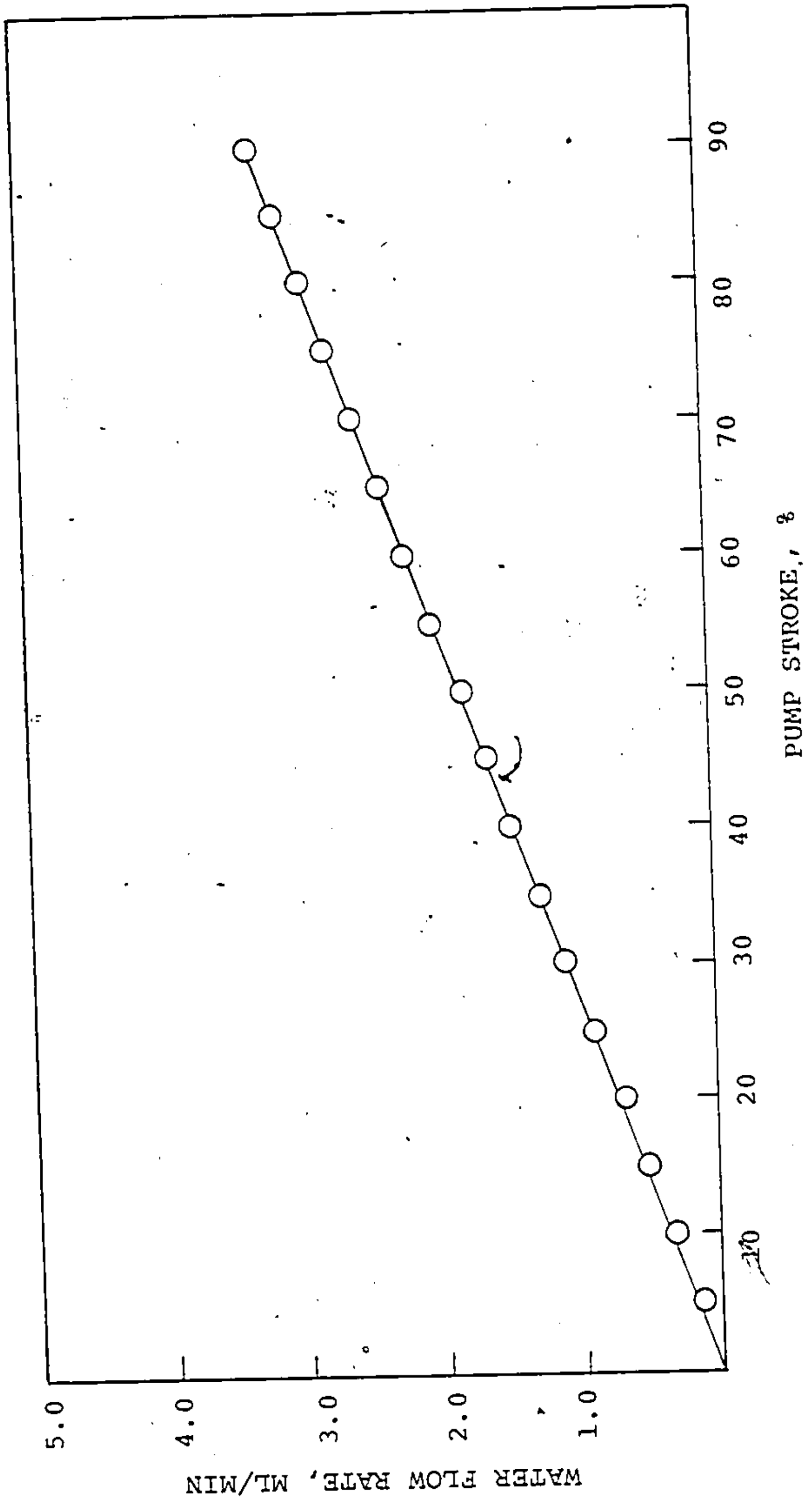
APPENDIX A

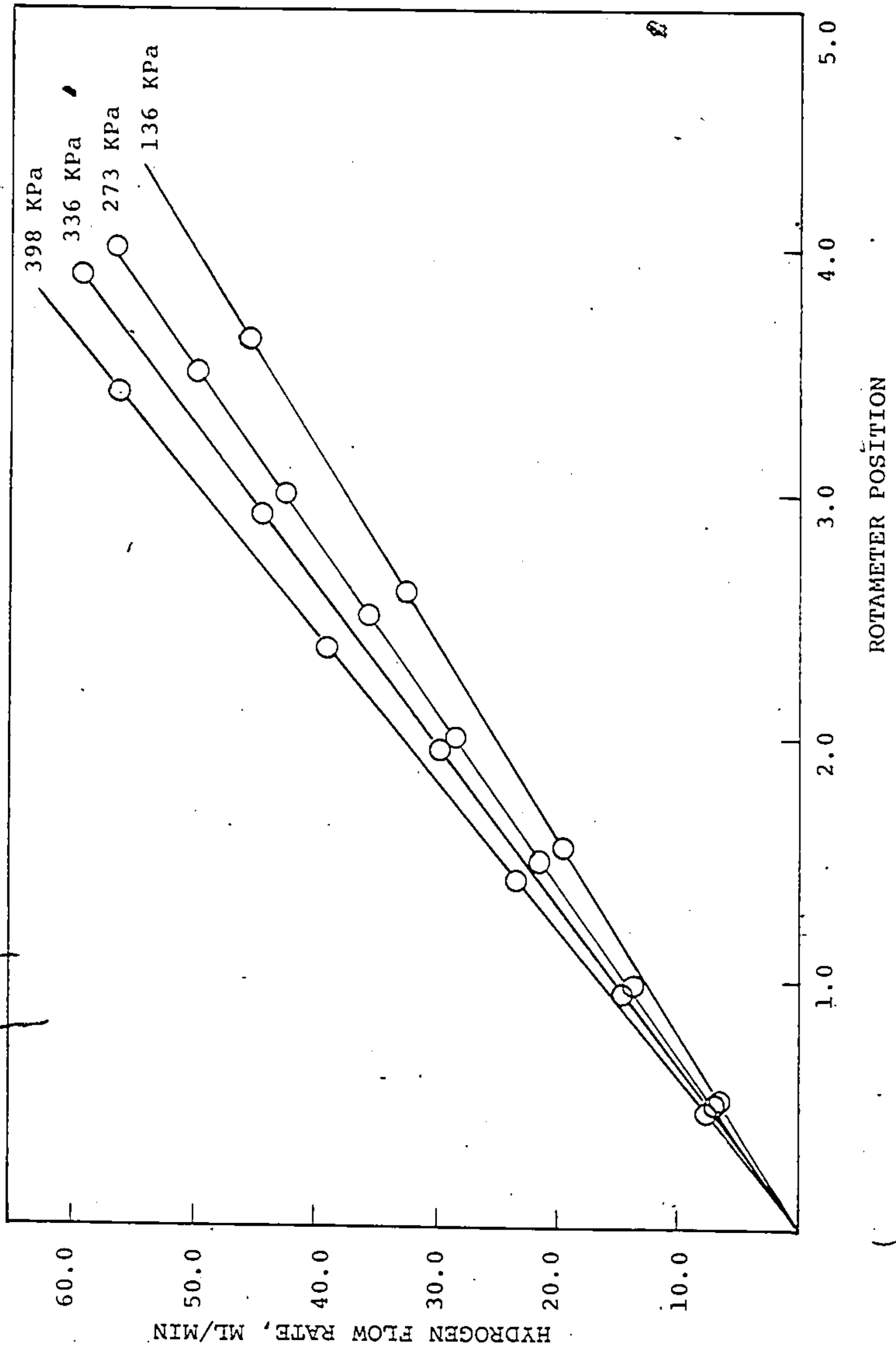
Calibration Curves

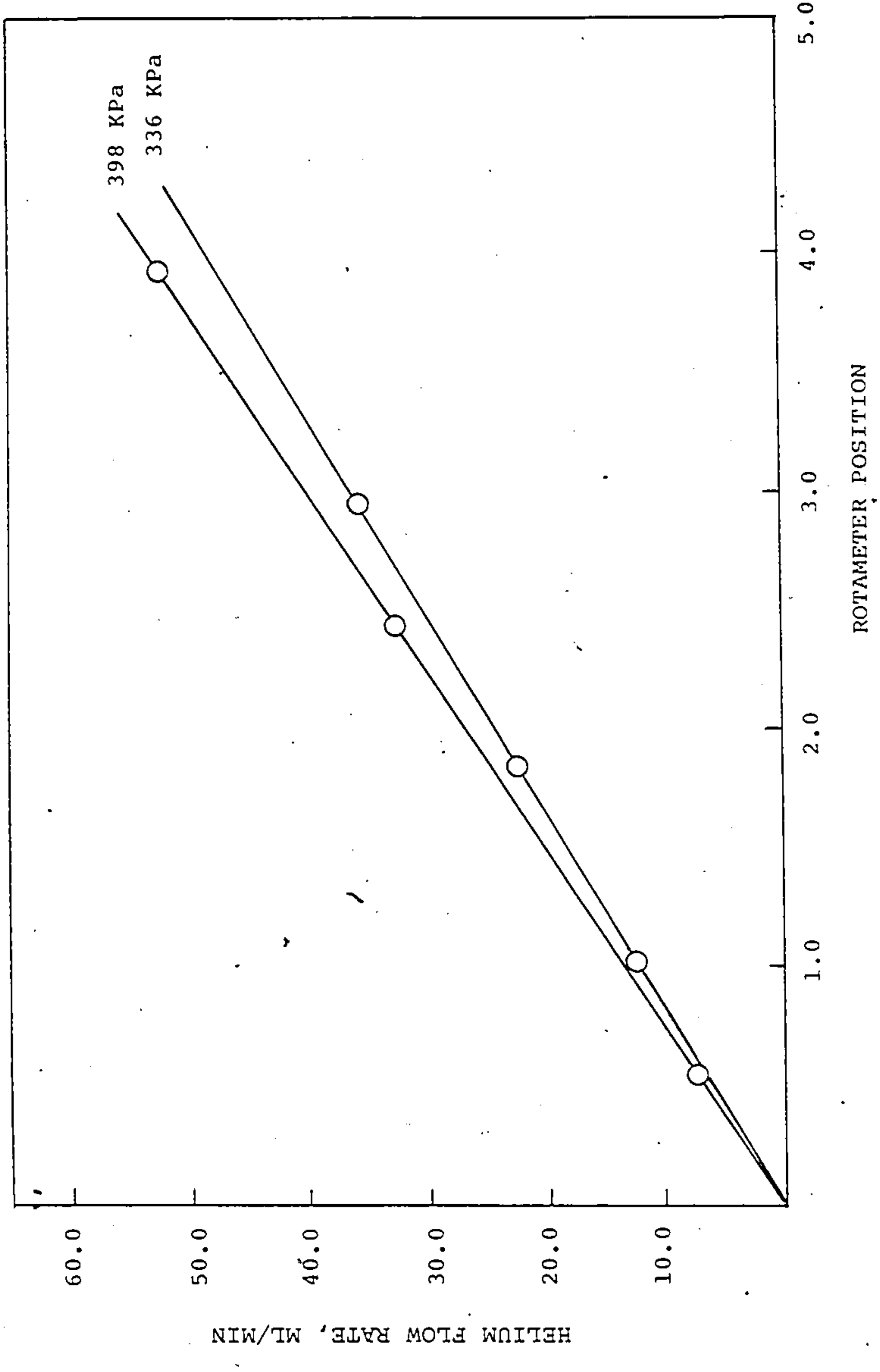
- Calibration curve for water pump
- Calibration curve for hydrogen flow through rotameter
- Calibration curve for helium flow through rotameter
- Calibration curves for quantitative analysis of gases from chromatograph:
  - nitrogen
  - carbon monoxide
  - carbon dioxide

CALIBRATION CURVE FOR WATER PUMP

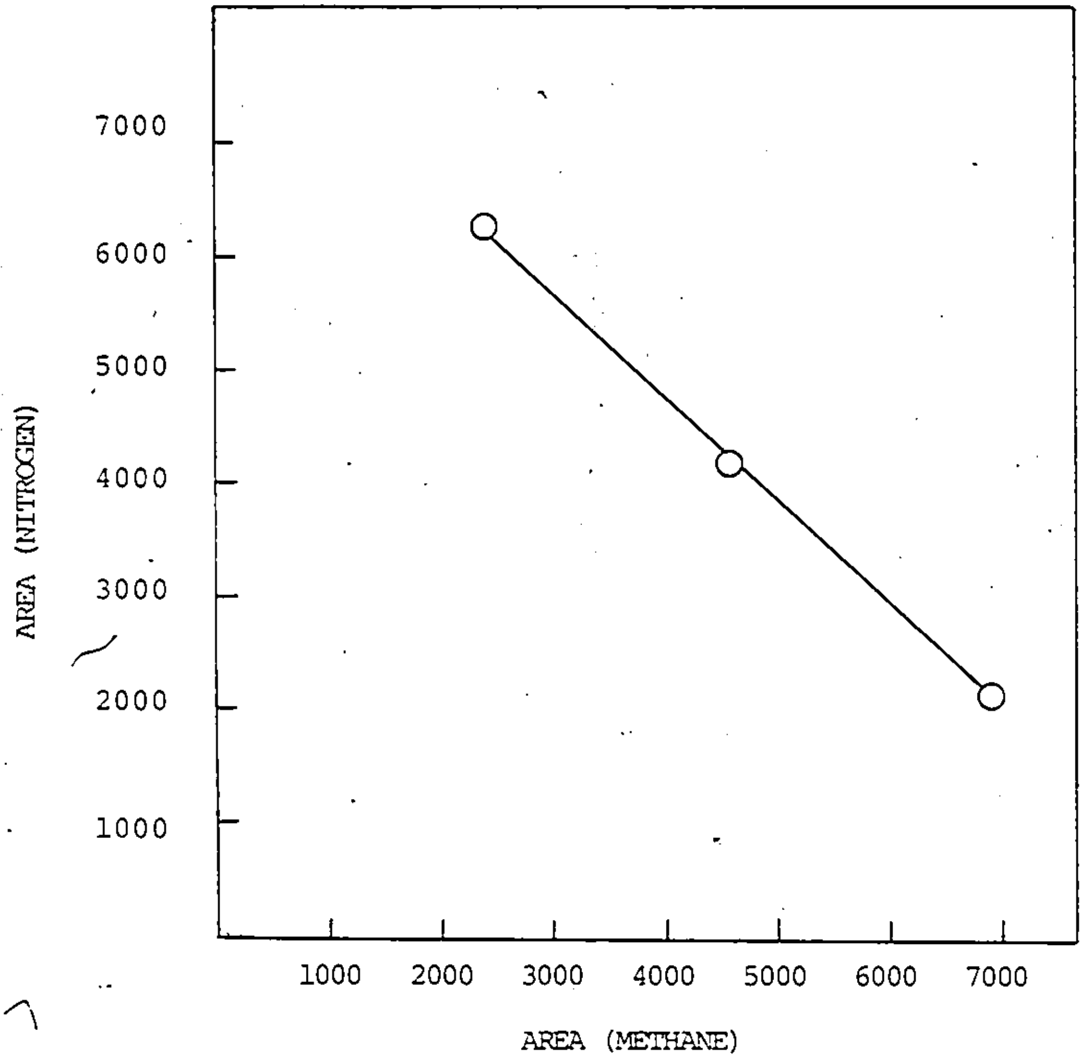


CALIBRATION CURVE FOR HYDROGEN FLOW

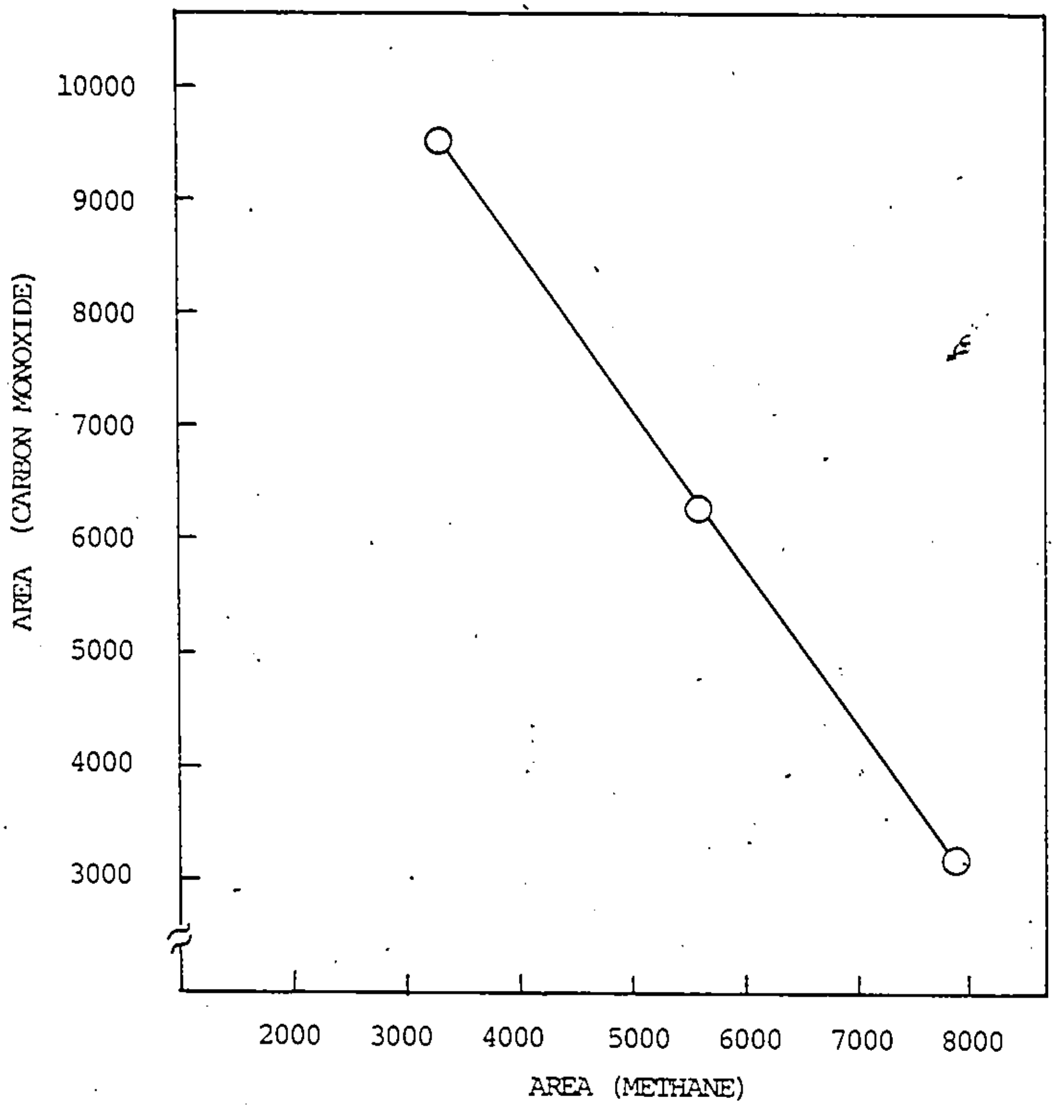



398 KPa
336 KPa
60.0
50.0
40.0
30.0
20.0
10.0
HELIUM FLOW RATE, ML/MIN
1.0
2.0
3.0
4.0
5.0
ROTAMETER POSITION

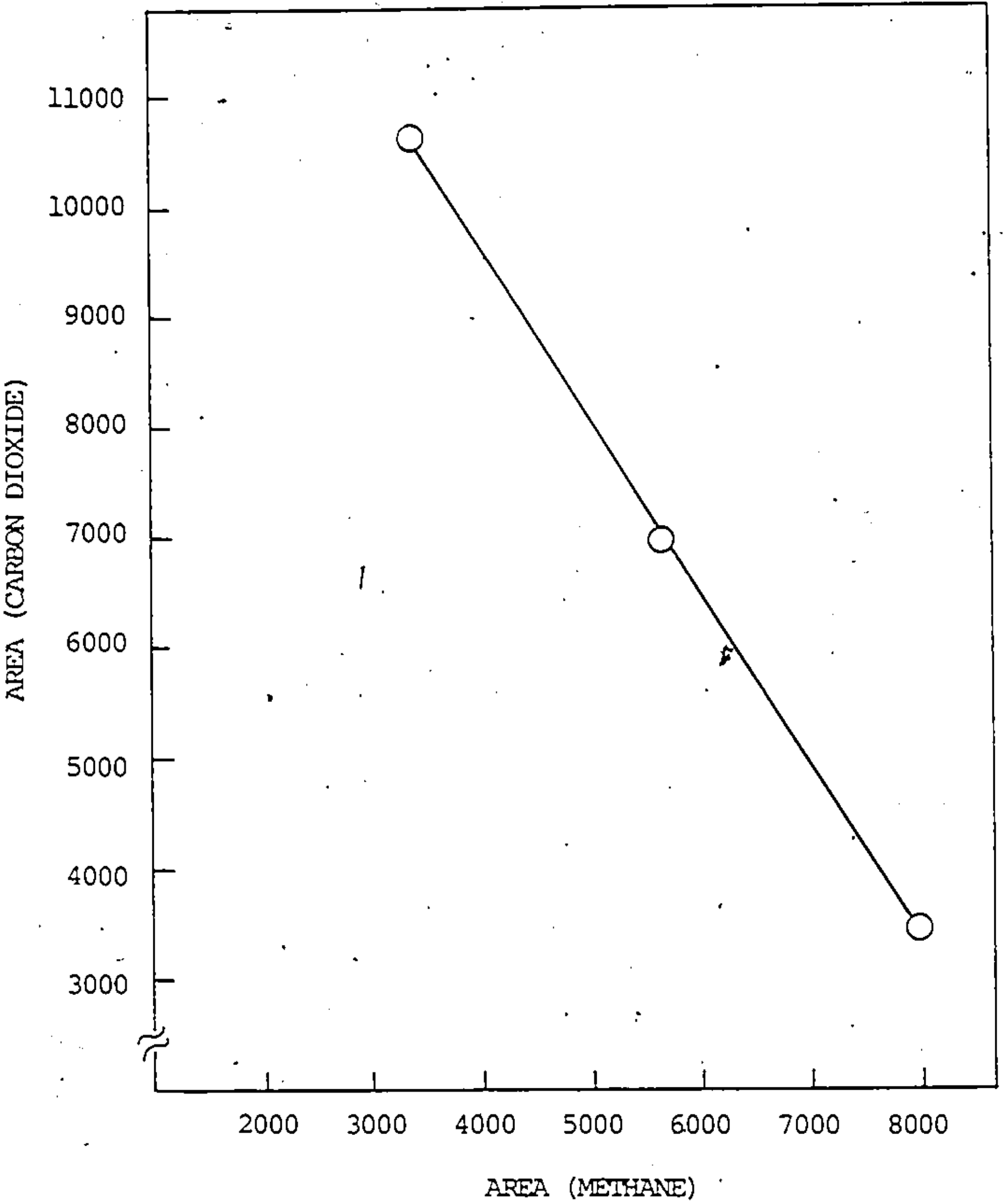
CALIBRATION CURVE FOR QUANTITATIVE
ANALYSIS OF NITROGEN



CALIBRATION CURVE FOR QUANTITATIVE ANALYSIS OF CARBON MONOXIDE



CALIBRATION FOR QUANTITATIVE ANALYSIS
OF CARBON DIOXIDE



APPENDIX B

SAMPLE CALCULATION

SAMPLE CALCULATION

- Rate, G C as CH_4/G C fed-min):

$$\text{exit gas flow rate, } \left(\frac{\text{CC}}{\text{min}}\right) \times \frac{\text{1 g mole}}{\text{24,303.21 CC}} \times$$

$$\frac{\text{total moles of } CH_4}{\text{1 mole of exit gas}} \times \frac{\text{12.011 g C/g mole C}}{\text{total C fed, (g)}}$$

- Rate, G C as CO/G C fed-min:

$$\text{exit gas flow rate, } \left(\frac{\text{CC}}{\text{min}}\right) \times \frac{\text{1 g mole}}{\text{24,303.21 CC}} \times$$

$$\frac{\text{total moles of CO}}{\text{1 mole of exit gas}} \times \frac{\text{12.011 g C/g mole C}}{\text{total C fed, (g)}}$$

- Rate, G C as CO_2/G C fed-min:

$$\text{exit gas flow, } \left(\frac{\text{CC}}{\text{min}}\right) \times \frac{\text{1 g mole}}{\text{24,303.21 CC}} \times$$

$$\frac{\text{total moles of } CO_2}{\text{1 mole of exit gas}} \times \frac{\text{12.011 g C/g mole C}}{\text{total C fed, (g)}}$$

APPENDIX C

Runs number one to thirteen are not included because several problems during the feeding of the coal into the reactor did not allow the experiments to be consistent.

RUN #14

Coal Sample Wt: 6.00 g
Run Type A
Reactor Pressure: 329-350 KPa

	Experimental Conditions				Product Gas Composition				
Injection #	Product Gas Rate (CC/min)	Total Press. (KPa)	Temp. (°K)	Steam Flow (g/min)	H_2	N_2	CO	CH_4	CO_2
1	21.10	329	811	0.105	0.2737	0.0341	0.0738	0.4301	0.1883
2	29.30	329	811	0.105	0.3495	0.0285	0.0686	0.3388	0.2145
3	26.06	329	811	0.105	0.3638	0.0181	0.2464	0.2212	0.1505
4	20.94	329	811	0.105	0.3435	0.0082	0.2247	0.1400	0.2836
5	22.31	329	811	0.105	0.3305	0.0021	0.2101	0.1192	0.3381
6	31.41	329	811	0.105	0.3286	0.0015	0.2131	0.0971	0.3597
7	24.69	329	811	0.105	0.3376	0.0016	0.2215	0.0659	0.3734
8	14.13	329	811	0.105	0.3316	0.0019	0.2247	0.0560	0.3858
9	23.36	329	850	0.105	0.3679	0.0019	0.2095	0.0728	0.3479
10	23.36	329	880	0.105	0.3778	0.0016	0.2008	0.0717	0.3481
11	15.01	329	900	0.105	0.4160	-	0.1773	0.0980	0.3159
12	24.03	329	922	0.105	0.4462	-	0.1685	0.0806	0.3047
13	17.08	329	922	0.105	0.4548	-	0.1511	0.1334	0.2607
14	17.58	329	922	0.105	0.4741	-	0.1538	0.1123	0.2598
15	16.37	340	922	0.175	0.4645	-	0.1456	0.1370	0.2529
16	14.60	350	922	0.175	0.4587	-	0.1396	0.1002	0.3015
17	16.25	350	922	0.175	0.4627	-	0.0948	0.1010	0.3415
18	15.14	350	922	0.175	0.5047	-	0.0807	0.0712	0.3434
19	18.09	350	922	0.00	0.5874	-	0.0550	0.1243	0.2333
20	17.11	350	922	0.00	0.6494	-	0.0450	0.1381	0.1675
21	16.22	350	922	0.00	0.3052	-	0.0382	0.1771	0.0959
22	15.75	350	922	0.00	0.7253	-	0.0599	0.1495	0.0653
23	16.64	350	922	0.00	0.6957	-	0.0790	0.1553	0.0700
24	15.59	350	922	0.00	0.6606	-	0.0905	0.2023	0.0466
25	8.81	350	922	0.00	0.5602	-	0.1255	0.2481	0.0662
26	8.71	340	922	0.00	0.5025	-	0.1379	0.2192	0.1404
27	8.79	329	922	0.00	0.5424	-	0.1609	0.2195	0.0772
28	9.33	329	922	0.00	0.5692	-	0.1530	0.2460	0.0318
29	16.03	329	922	0.00	0.7210	-	0.1307	0.1483	-
30	15.54	329	922	0.00	0.7002	-	0.1189	0.1809	-

RUN #15

Coal Sample Wt: 6.00 g
Run Type B
Total Reactor Pressure: 398-432 KPa

	Experimental Conditions				Product Gas Compositions				
Injection #	Product Gas Rate (CC/min)	Total Press. (KPa)	Temp. (°K)	Steam Flow (g/min)	H_2	N_2	CO	CH_4	CO_2
1	19.42	398	811	0.00	0.4172	0.1199	0.0516	0.4113	–
2	20.69	398	811	0.00	0.1544	0.0047	0.3468	0.3473	0.1468
3	20.53	398	811	0.00	0.1554	0.0387	0.3009	0.3718	0.1332
4	20.22	398	811	0.00	0.2396	0.0398	0.3296	0.3372	0.0538
5	20.97	398	811	0.00	0.3286	0.0287	0.3311	0.3116	–
6	18.57	398	840	0.00	0.3835	0.0226	0.3220	0.2719	–
7	17.05	398	860	0.00	0.3934	0.0217	0.2930	0.2919	–
8	16.23	398	866	0.00	0.4395	0.0175	0.2824	0.2606	–
9	16.85	398	866	0.00	0.4377	0.0148	0.2765	0.2710	–
10	18.56	398	866	0.00	0.4442	0.0128	0.3059	0.2371	–
11	17.63	398	866	0.00	0.4612	0.0110	0.2837	0.2551	–
12	16.24	398	866	0.00	0.4706	0.0109	0.2849	0.2336	–
13	16.67	398	880	0.00	0.4374	–	0.3029	0.2597	–
14	16.38	398	900	0.00	0.4330	–	0.3559	0.2111	–
15	29.95	410	900	0.175	0.3182	–	0.2001	0.0563	0.4254
16	44.64	432	920	0.175	0.3719	–	0.0691	0.1005	0.4585
17	32.53	432	922	0.175	0.3491	–	0.1500	0.0944	0.4065
18	30.24	432	922	0.175	0.4149	–	0.1195	0.1189	0.3467
19	25.05	432	922	0.175	0.4557	–	0.0882	0.1252	0.3309
20	14.22	432	922	0.175	0.5059	–	0.1027	0.1503	0.2411
21	17.40	432	922	0.00	0.4788	–	0.0779	0.1734	0.2699
22	17.95	432	922	0.00	0.4902	–	0.0704	0.1434	0.2960
23	17.14	432	922	0.00	0.5137	–	0.0667	0.1857	0.2339
24	8.48	432	922	0.00	0.5497	–	0.0833	0.1851	0.1819
25	8.26	432	922	0.00	0.5348	–	0.0931	0.2112	0.1600
26	11.23	410	922	0.00	0.5687	–	0.1403	0.1911	0.0999
27	10.25	398	922	0.00	0.6228	–	0.1274	0.2498	–
28	11.92	398	922	0.00	0.6132	–	0.1301	0.2567	–
29	11.98	398	922	0.00	0.6327	–	0.1271	0.2402	–
30	12.26	398	922	0.00	0.6117	–	0.1251	0.2632	–

RUN #16

Coal Sample Wt: 6.00 g
Blank Run with Helium
Reactor Pressure: 336 KPa

	Experimental Conditions			Product Gas Composition				
Injection #	Product Gas Rate (CC/min)	Total Press. (KPa)	Temp. (°K)	H_2	N_2	CO	CH_4	CO_2
1	9.21	336	811	0.2416	0.0036	0.2538	0.1629	0.3381
2	9.45	336	811	0.1211	0.0049	0.3161	0.2154	0.3425
3	10.23	336	811	0.1452	0.0166	0.3050	0.2828	0.2504
4	8.38	336	811	0.3260	0.0016	0.2038	0.2142	0.2544
5	8.53	336	811	0.3362	0.0128	0.1936	0.2091	0.2483
6	9.36	336	850	0.1721	–	0.2990	0.3217	0.2072
7	9.98	336	900	0.1646	–	0.3062	0.3517	0.1775
8	10.25	336	950	0.2873	–	0.3098	0.2469	0.1560
9	9.83	336	977	0.3111	0.0263	0.3433	0.1867	0.1326
10	8.58	336	977	0.2778	0.0808	0.3085	0.2066	0.1263
11	8.04	336	977	0.2837	0.0991	0.3048	0.1935	0.1189
12	6.37	336	977	0.2980	0.1054	0.3048	0.1613	0.1305
13	4.61	336	977	0.4200	0.1563	0.3873	0.0364	
14	2.14	336	977	0.1194	0.1472	0.3726	–	–
15	–	–	–	–	–	–	–	–
16	–	–	–	–	–	–	–	–
17	–	–	–	–	–	–	–	–
18	–	–	–	–	–	–	–	–
19	–	–	–	–	–	–	–	–
20	–	–	–	–	–	–	–	–
21	–	–	–	–	–	–	–	–
22	–	–	–	–	–	–	–	–
23	–	–	–	–	–	–	–	–

RUN #20

Coal Sample Wt: 6.00 g
Blank Run with Helium
Reactor Pressure: 398 KPa

	Experimental Conditions			Product Gas Composition				
Injection #	Product Gas Rate (CC/min)	Total Press. (KPa)	Temp. (°K)	H_2	N_2	CO	CH_4	CO_2
1	11.98	398	811	0.2312	0.0754	0.1719	0.1633	0.3582
2	11.14	398	811	0.1550	0.0020	0.2037	0.2158	0.4235
3	10.07	398	811	0.0979	0.0019	0.2370	0.2940	0.3692
4	9.52	398	811	0.2539	0.0024	0.1453	0.2563	0.3421
5	10.02	398	811	0.3149	0.0046	0.1213	0.2475	0.3117
6	10.56	398	850	0.1709	0.0065	0.1804	0.3619	0.2803
7	10.53	398	900	0.1596	0.0124	0.1973	0.3658	0.2649
8	9.44	398	950	0.1746	0.0390	0.2263	0.2844	0.2757
9	10.03	398	977	0.2012	0.0599	0.2396	0.2409	0.2584
10	9.71	398	977	0.2174	0.0771	0.2494	0.2084	0.2477
11	8.45	398	977	0.2217	0.0855	0.2610	0.1878	0.2440
12	7.85	398	977	0.2620	0.1000	0.2556	0.1594	0.2230
13	5.21	398	977	0.3234	0.2005	0.4038	0.0723	–
14	1.32	398	977	0.1463	0.0936	0.7601	–	–
15	0.90	398	977	0.1990	0.8010	–	–	–
16	–	–	–	–	–	–	–	–
17	–	–	–	–	–	–	–	–
18	–	–	–	–	–	–	–	–
19	–	–	–	–	–	–	–	–
20	–	–	–	–	–	–	–	–
21	–	–	–	–	–	–	–	–
22	–	–	–	–	–	–	–	–
23	–	–	–	–	–	–	–	–

RUN #21

Coal Sample Wt: 6.00 g
Blank Run with Hydrogen
Reactor Pressure: 273 KPa

	Experimental Conditions			Product Gas Composition				
Injection #	Product Gas Rate (CC/min)	Total Press. (KPa)	Temp. (^oK)	H_2	N_2	CO	CH_4	CO_2
1	19.50	273	811	0.2514	0.0210	0.2097	0.2005	0.3174
2	23.10	273	839	0.5062	0.0141	0.1943	0.1974	0.1021
3	18.05	273	911	0.5240	0.0300	0.2022	0.2145	0.0293
4	17.91	273	944	0.6128	0.0120	0.2338	0.3670	–
5	21.90	273	977	0.2846	0.0180	0.2417	0.4557	–
6	21.57	273	977	0.3245	0.0194	0.2174	0.4387	–
7	21.04	273	977	0.5161	0.0100	0.2591	0.2148	–
8	22.03	273	977	0.5815	–	0.2259	0.1926	–
9	21.50	273	977	0.5905	–	0.2079	0.2016	–
10	20.95	273	977	0.6109	–	0.1994	0.1897	–
11	21.73	273	977	0.7085	–	0.1513	0.1402	–
12	21.47	273	977	0.7683	–	0.1029	0.1288	–
13	20.42	273	977	0.8016	–	0.0911	0.1073	–
14	19.91	273	977	0.8268	–	0.0734	0.0998	–
15	19.33	273	977	0.8245	–	0.0871	0.0884	–
16	19.48	273	977	0.8491	–	0.0700	0.0809	–
17	20.09	273	977	0.8826	–	0.0588	0.0686	–
18	19.92	273	977	0.8776	–	0.0654	0.0570	–
19	19.56	273	977	0.9092	–	0.0458	0.0450	–
20	19.73	273	977	0.9200	–	0.0391	0.0409	–
21	19.45	273	977	0.9454	–	0.0217	0.0329	–
22	20.38	273	977	0.9639	–	0.0112	0.0249	–
23	19.41	273	977	0.9887	–	–	0.0113	–

RUN #22

Coal Sample Wt: 6.00 g
Blank Run with Hydrogen
Reactor Pressure; 398 KPa

	Experimental Conditions			Product Gas Composition				
Injection #	Product Gas Rate (CC/min)	Total Press. (KPa)	Temp. (°K)	H_2	N_2	CO	CH_4	CO_2
1	15.54	398	811	0.3311	–	0.1075	0.1470	0.4144
2	16.73	398	811	0.2790	0.0324	0.1780	0.2190	0.2916
3	16.88	398	811	0.3436	0.0453	0.1918	0.3256	0.0937
4	15.97	398	811	0.4690	0.0621	0.1865	0.2589	0.0235
5	17.04	398	811	0.3363	0.0347	0.1394	0.4896	–
6	17.36	398	850	0.4596	0.0225	0.1007	0.4172	–
7	17.81	398	900	0.2095	0.0140	0.2033	0.5732	–
8	16.52	398	950	0.2704	0.0125	0.1742	0.5429	–
9	16.07	398	977	0.2554	0.0105	0.2336	0.5005	–
10	17.42	398	977	0.2940	–	0.2587	0.4473	–
11	17.94	398	977	0.4132	–	0.2417	0.3451	–
12	16.71	398	977	0.5187	–	0.2279	0.2534	–
13	15.80	398	977	0.6181	–	0.1932	0.1887	–
14	16.04	398	977	0.7468	–	0.0988	0.1544	–
15	16.88	398	977	0.8058	–	0.0814	0.1128	–
16	18.35	398	977	0.8479	–	0.0575	0.0946	–
17	17.30	398	977	0.8962	–	0.0311	0.0727	–
18	16.33	398	977	0.9200	–	0.0250	0.0550	–
19	17.49	398	977	0.9569	–	–	0.0431	–
20	16.77	398	977	0.9581	–	–	0.0419	–
21	15.31	398	977	0.9790	–	–	0.0210	–
22	16.01	398	977	0.9707	–	–	0.0193	–
23	16.72	398	977	0.9875	–	–	0.0125	–

Coal Sample Wt: 6.00 g
Blank Run with Hydrogen
Reactor Pressure: 336 KPa

	Experimental Conditions			Product Gas Composition				
Injection #	Product Gas Rate (CC/min)	Total Press. (KPa)	Temp. (°K)	H_2	N_2	CO	CH_4	CO_2
1	15.32	338	811	0.1686	0.0029	0.2184	0.2368	0.3733
2	18.81	338	811	0.1667	0.0034	0.2236	0.3772	0.2291
3	17.32	338	811	0.5928	0.0041	0.2017	0.3154	0.0716
4	16.92	338	811	0.5431	0.0134	0.1733	0.2702	–
5	17.10	338	811	0.3346	0.0079	0.2349	0.4226	–
6	18.21	338	850	0.2787	0.0083	0.2591	0.4539	–
7	21.74	338	900	0.3849	0.0032	0.2332	0.3787	–
8	20.36	338	950	0.4448	0.0057	0.2214	0.3281	–
9	20.02	338	977	0.5737	0.0033	0.2097	0.2133	–
10	19.57	338	977	0.6105	0.0019	0.1955	0.1921	–
11	19.36	338	977	0.6480	–	0.1861	0.1659	–
12	18.94	338	977	0.6919	–	0.1787	0.1294	–
13	18.51	338	977	0.7179	–	0.1777	0.1044	–
14	18.17	338	977	0.7338	–	0.1531	0.1131	–
15	17.90	338	977	0.7976	–	0.1302	0.0722	–
16	18.71	338	977	0.8051	–	0.1255	0.0694	–
17	17.02	338	977	0.8404	–	0.1095	0.0501	–
18	16.33	338	977	0.8640	–	0.0887	0.0473	–
19	16.82	338	977	0.9105	–	0.0538	0.0357	–
20	16.21	338	977	0.9488	–	0.0279	0.0233	–
21	15.38	338	977	0.9551	–	0.0217	0.0232	–
22	15.33	338	977	0.9689	–	0.0124	0.0187	–
23	15.21	338	977	0.9847	–	–	0.0153	–

RUN #24-A

Coal Sample Wt: 4.00 g
Run Type B
Reactor Pressure: 336-356 KPa

	Experimental Conditions				Product Gas Composition				
Injection #	Product Gas Rate (CC/min)	Total Press. (KPa)	Temp. (^oK)	Steam Flow (g/min)	H_2	N_2	CO	CH_4	CO_2
1	7.47	336	811	0.00	0.2451	-	0.1167	0.3169	0.3213
2	13.43	336	811	0.00	0.4873	0.0127	0.1674	0.3326	-
3	9.62	336	811	0.00	0.4570	0.0081	0.1061	0.4288	-
4	8.42	336	811	0.00	0.4178	0.0089	0.0786	0.4947	-
5	14.00	336	811	0.00	0.5849	0.0071	0.1773	0.2307	-
6	15.16	336	850	0.00	0.6236	-	0.1723	0.2041	-
7	10.87	346	900	0.105	0.6789	-	0.1030	0.2181	-
8	30.45	356	950	0.105	0.6810	-	0.1573	0.0658	0.0959
9	15.48	356	977	0.105	0.3139	-	0.3092	0.0683	0.3086
10	12.61	356	977	0.105	0.2276	-	0.3233	0.1082	0.3409
11	12.66	356	977	0.105	0.2976	-	0.2491	0.0786	0.3747
12	13.84	356	977	0.105	0.3667	-	0.2194	0.0698	0.3441
13	14.79	356	977	0.105	0.4001	-	0.2130	0.0685	0.3184
14	21.02	356	977	0.105	0.5683	-	0.1409	0.0628	0.2280
15	20.37	356	977	0.105	0.5536	-	0.1533	0.0383	0.2548
16	23.33	356	977	0.00	0.6031	-	0.1362	0.0562	0.2045
17	22.43	356	977	0.00	0.6569	-	0.1243	0.0463	0.1725
18	14.76	356	977	0.00	0.5002	-	0.2070	0.1499	0.1429
19	8.36	356	977	0.00	0.4962	-	0.2523	0.2515	-
20	7.95	346	977	0.00	0.4751	-	0.2562	0.2687	-
21	7.91	336	977	0.00	0.4243	-	0.2298	0.3459	-
22	9.59	336	977	0.00	0.5302	-	0.1726	0.2972	-
23	9.69	336	977	0.00	0.4745	-	0.1703	0.3552	-

RUN #25

Coal Sample Wt: 6.00 g
Blank Run with Steam
Reactor Pressure: 418 KPa

	Experimental Conditions							
Injection #	Product Gas Rate (CC/min)	Total Press. (KPa)	Temp. (°K)	H_2	N_2	CO	CH_4	CO_2
1	13.21	418	811	0.2566	–	0.2291	0.1354	0.3789
2	10.94	418	811	0.0446	0.0013	0.2846	0.1742	0.4953
3	12.53	418	811	0.0481	0.0016	0.2689	0.2581	0.4233
4	13.02	418	811	0.0043	–	0.3578	0.2532	0.3847
5	12.58	418	811	0.1455	–	0.2752	0.2289	0.3504
6	12.95	418	850	0.3320	0.0024	0.2005	0.2078	0.2573
7	12.39	418	900	0.1445	0.0038	0.2657	0.2592	0.3268
8	12.87	418	950	0.1235	0.0039	0.2816	0.2115	0.3795
9	12.32	418	977	0.0037	0.0053	0.2582	0.1771	0.5567
10	12.77	418	977	0.0030	–	0.1350	0.0918	0.7702
11	12.59	418	977	0.0279	–	0.1279	0.0844	0.7598
12	12.31	418	977	0.1026	0.0042	0.1295	0.0772	0.6865
13	11.94	418	977	0.0450	0.0136	0.1280	0.0705	0.7429
14	10.53	418	977	0.0121	–	0.1401	0.0720	0.7758
15	10.28	418	977	0.0059	–	0.1373	0.0550	0.7842
16	10.05	418	977	0.1090	–	0.1225	–	0.7536
17	9.98	418	977	0.1637	–	0.0942	–	0.7421
18	9.74	418	977	0.1939	0.0032	0.0735	–	0.7294
19	9.52	418	977	0.2042	0.0057	0.0722	–	0.7179
20	8.83	418	977	0.2320	0.0073	0.0638	–	0.6969
21	8.42	418	977	0.2221	0.0054	0.0651	–	0.7074
22	8.25	418	977	0.2872	0.0049	0.0543	–	0.6536
23	8.13	418	977	0.3937	0.0045	0.0520	–	0.5498

RUN #26

Coal Sample Wt: 6.00 g
Blank Run with Steam
Reactor Pressure: 350 KPa

	Experimental Conditions							
Injection #	Product Gas Rate (CC/min)	Total Press. (KPa)	Temp. (°K)	H_2	N_2	CO	CH_4	CO_2
1	15.49	350	811	0.4118	–	0.2317	0.1061	0.2504
2	16.37	350	811	0.2232	0.0017	0.3049	0.1731	0.2971
3	15.05	350	811	0.2649	0.0025	0.2953	0.2098	0.2275
4	14.17	350	811	0.2875	0.0033	0.2589	0.2241	0.2262
5	13.21	350	811	0.3722	–	0.2914	0.1728	0.1636
6	14.26	350	850	0.3674	–	0.3176	0.1733	0.1417
7	15.97	350	900	0.1640	0.0022	0.3671	0.2124	0.2543
8	15.54	350	950	0.1898	0.0041	0.3141	0.1979	0.2941
9	15.03	350	977	0.1684	0.0049	0.2916	0.1778	0.3573
10	14.54	350	977	0.0628	0.0073	0.2737	0.1523	0.5039
11	13.94	350	977	0.0561	0.0033	0.2594	0.1124	0.5688
12	13.33	350	977	0.0838	0.0029	0.2071	0.0916	0.6146
13	13.21	350	977	0.1384	0.0017	0.2039	0.0532	0.6028
14	12.97	350	977	0.1671	0.0012	0.1913	0.0279	0.6125
15	11.58	350	977	0.1515	–	0.1891	–	0.6594
16	11.07	350	977	0.1785	–	0.1733	–	0.6482
17	10.85	350	977	0.2166	–	0.1697	–	0.6137
18	10.36	350	977	0.2138	–	0.1775	–	0.6087
19	9.74	350	977	0.2432	–	0.1739	–	0.5829
20	9.17	350	977	0.2380	–	0.1687	–	0.5933
21	9.01	350	977	0.2735	–	0.1551	–	0.5714
22	8.87	350	977	0.3182	–	0.1136	–	0.5682
23	8.71	350	977	0.3533	–	0.0940	–	0.5527

RUN #32

Coal Sample Wt: 5.00 g
Run Type A
Reactor Pressure: 398-418 KPa

	Experimental Conditions				Product Gas Composition				
Injection #	Product Gas Rate (CC/min)	Total Press. (KPa)	Temp. (°K)	Steam Flow (g/min)	H_2	N_2	CO	CH_4	CO_2
1	15.45	418	811	0.105	0.5750	0.0196	0.1507	0.1028	0.1519
2	13.58	418	811	0.105	0.2365	0.0034	0.2206	0.2511	0.2884
3	16.30	418	811	0.105	0.2556	0.0041	0.1984	0.3283	0.2136
4	17.67	418	811	0.105	0.3605	0.0053	0.1462	0.3413	0.1467
5	16.12	418	811	0.105	0.5297	0.0061	0.0901	0.2723	0.1018
6	16.16	418	850	0.105	0.7310	0.0088	0.0481	0.1725	0.0396
7	16.96	418	900	0.105	0.5909	–	0.0409	0.2089	0.1593
8	15.50	418	950	0.105	0.4005	–	0.0604	0.2603	0.2788
9	15.95	418	977	0.105	0.3834	–	0.0721	0.2096	0.3349
10	15.98	418	977	0.105	0.3965	–	0.0775	0.1594	0.3666
11	16.28	418	977	0.105	0.4159	–	0.0847	0.1291	0.3703
12	16.21	418	977	0.105	0.3282	–	0.1146	0.1126	0.4446
13	18.41	418	977	0.105	0.3414	–	0.1187	0.0941	0.4458
14	15.85	418	977	0.00	0.3372	–	0.1269	0.0872	0.4486
15	17.17	418	977	0.00	0.3562	–	0.1412	0.0905	0.4121
16	16.28	418	977	0.00	0.3832	–	0.1636	0.1094	0.3438
17	18.61	418	977	0.00	0.4364	–	0.1722	0.1082	0.2832
18	17.24	418	977	0.00	0.4826	–	0.1771	0.1020	0.2383
19	15.62	418	977	0.00	0.4755	0.0031	0.1937	0.0952	0.2325
20	16.14	408	977	0.00	0.5731	0.0102	0.1872	0.0576	0.1719
21	18.63	398	977	0.00	0.7492	0.0110	0.0766	0.1632	–
22	18.08	398	977	0.00	0.7425	0.0096	0.0162	0.2317	–
23	17.54	398	977	0.00	0.7784	–	0.0059	0.2157	–

RUN #33

Coal Sample Wt: 6.00 g
Run Type B
Reactor Pressure 398-418 KPa

	Experimental Conditions				Product Gas Composition				
Injection #	Product Gas Rate (CC/min)	Total Press. (KPa)	Temp. (°K)	Steam Flow (g/min)	H_2	N_2	CO	CH_4	CO_2
1	16.68	398	811	0.00	0.6159	–	0.1370	0.0728	0.1743
2	13.27	398	811	0.00	0.2356	0.0013	0.2172	0.2510	0.2949
3	15.91	398	811	0.00	0.2902	–	0.2011	0.2943	0.2144
4	15.92	398	811	0.00	0.4714	–	0.1452	0.3169	0.0665
5	16.35	398	811	0.00	0.5060	–	0.1166	0.3774	–
6	16.37	398	850	0.00	0.6033	–	0.0841	0.3126	–
7	15.80	398	900	0.00	0.1790	0.0042	0.1756	0.6412	–
8	16.79	398	950	0.00	0.1825	0.0343	0.1776	0.6056	–
9	16.38	398	977	0.00	0.2257	0.0482	0.2036	0.5225	–
10	20.44	408	977	0.105	0.3101	0.0288	0.3133	0.3478	–
11	21.13	418	977	0.105	0.3829	0.0066	0.3086	0.1762	0.1257
12	20.90	418	977	0.105	0.4280	0.0037	0.2360	0.1393	0.1930
13	24.07	418	977	0.105	0.4136	0.0050	0.2283	0.1049	0.2482
14	20.37	418	977	0.105	0.4598	–	0.1952	0.0725	0.2725
15	15.80	418	977	0.105	0.3703	–	0.1965	0.0568	0.3764
16	18.28	418	977	0.00	0.4629	–	0.1566	0.0487	0.3318
17	15.82	418	977	0.00	0.3389	0.0052	0.2247	0.0625	0.3687
18	17.28	418	977	0.00	0.4538	0.0035	0.1905	0.0532	0.2990
19	15.81	418	977	0.00	0.4383	0.0046	0.2012	0.0547	0.3012
20	18.13	408	977	0.00	0.5750	0.0061	0.1618	0.0397	0.2174
21	17.21	398	977	0.00	0.7920	0.0063	0.1275	0.0283	0.0459
22	16.16	398	977	0.00	0.8394	–	0.0737	0.0869	–
23	16.80	398	977	0.00	0.8500	–	0.0495	0.1005	–

RUN #34

Coal Sample Wt: 6.10 g
Run Type A
Reactor Pressure: 329-350 KPa

	Experimental Conditions				Product Gas Composition				
Injection #	Product Gas Rate (CC/min)	Total Press. (KPa)	Temp. (°K)	Steam Flow (g/min)	H_2	N_2	CO	CH_4	CO_2
1	20.27	350	811	0.105	0.2405	-	0.2190	0.2016	0.3389
2	22.36	350	811	0.105	0.3638	0.0017	0.2088	0.2273	0.1984
3	21.53	350	811	0.105	0.5943	0.0024	0.1727	0.1647	0.0659
4	21.22	350	811	0.105	0.5843	0.0025	0.1486	0.1860	0.0786
5	21.49	350	811	0.105	0.7974	0.0039	0.1553	0.0434	-
6	20.93	350	850	0.105	0.6543	0.0027	0.1357	0.1322	0.0751
7	20.18	350	900	0.105	0.5010	0.0019	0.1178	0.2044	0.1749
8	21.07	350	950	0.105	0.3935	0.0012	0.1226	0.1982	0.2845
9	18.82	350	977	0.105	0.3405	0.0007	0.1508	0.1329	0.3751
10	22.03	350	977	0.105	0.3124	-	0.1632	0.0875	0.4369
11	22.27	350	977	0.105	0.3331	0.0007	0.1598	0.0606	0.4458
12	22.50	350	977	0.105	0.4011	0.0010	0.1486	0.0481	0.4012
13	20.97	350	977	0.105	0.4133	0.0010	0.1584	0.0438	0.3835
14	21.45	350	977	0.00	0.4358	0.0013	0.1731	0.0442	0.3456
15	20.04	350	977	0.00	0.4001	0.0015	0.2225	0.0637	0.3122
16	20.08	350	977	0.00	0.4648	0.0017	0.2190	0.0591	0.2554
17	15.81	350	977	0.00	0.5021	0.0020	0.2326	0.0521	0.2102
18	19.98	350	977	0.00	0.5531	-	0.2428	0.0469	0.1572
19	20.37	350	977	0.00	0.7155	-	0.2215	0.0630	-
20	18.49	339	977	0.00	0.7397	0.0054	0.1392	0.1157	-
21	17.97	329	977	0.00	0.7482	0.0052	0.1438	0.1028	-
22	19.87	329	977	0.00	0.7406	0.0053	0.1563	0.0978	-
23	20.78	329	977	0.00	0.7537	0.0051	0.1586	0.0826	-

RUN #36

Coal Sample Wt: 6.00 g
Run Type A
Reactor Pressure: 260–281 KPa

	Experimental Conditions				Product Gas Composition				
Injection #	Product Gas Rate (CC/min)	Total Press. (KPa)	Temp. (°K)	Steam Flow (g/min)	H_2	N_2	CO	CH_4	CO_2
1	21.55	281	811	0.105	0.3004	–	0.2163	0.1457	0.3376
2	21.04	281	811	0.105	0.5403	0.0015	0.1841	0.1305	0.1436
3	21.43	281	811	0.105	0.6799	0.0026	0.1664	0.1204	0.0307
4	21.14	281	811	0.105	0.7356	0.0029	0.1543	0.1072	–
5	21.62	281	811	0.105	0.4484	0.0015	0.1401	0.2386	0.1714
6	21.54	281	850	0.105	0.3682	0.0012	0.1464	0.2261	0.2581
7	21.52	281	900	0.105	0.4025	0.0011	0.1526	0.1383	0.3055
8	22.13	281	950	0.105	0.3578	0.0009	0.1754	0.1058	0.3601
9	22.85	281	977	0.105	0.3682	0.0009	0.1864	0.0715	0.3730
10	21.96	281	977	0.105	0.4474	0.0012	0.1764	0.0501	0.3261
11	21.36	281	977	0.105	0.4387	0.0012	0.1775	0.0477	0.3349
12	20.91	281	977	0.105	0.5017	0.0017	0.1708	0.0349	0.2909
13	21.32	281	977	0.105	0.4562	0.0013	0.1844	0.0389	0.3192
14	20.74	281	977	0.00	0.4802	0.0015	0.1829	0.0357	0.2997
15	18.76	281	977	0.00	0.5419	0.0020	0.2046	0.0440	0.2075
16	17.26	281	977	0.00	0.5745	0.0022	0.2134	0.0527	0.1572
17	15.16	281	977	0.00	0.6136	0.0030	0.2154	0.0645	0.1035
18	16.99	281	977	0.00	0.5797	–	0.1955	0.1856	0.0392
19	20.09	281	977	0.00	0.6878	–	0.1727	0.1395	–
20	19.68	270	977	0.00	0.7409	0.0055	0.1087	0.1449	–
21	19.64	260	977	0.00	0.7676	0.0056	0.1080	0.1188	–
22	20.56	260	977	0.00	0.6795	0.0071	0.1367	0.1767	–
23	20.06	260	977	0.00	0.7583	0.0058	0.1308	0.1051	–

RUN #37

Coal Sample Wt: 6.00 g
Run Type B
Reactor Pressure: 273-294 KPa

	Experimental Conditions				Product Gas Composition				
Injection #	Product Gas Rate (CC/min)	Total Press. (KPa)	Temp. (°K)	Steam Flow (g/min)	H_2	N_2	CO	CH_4	CO_2
1	19.28	273	811	0.00	0.2449	–	0.2161	0.1901	0.3489
2	22.15	273	839	0.00	0.5924	0.0020	0.1876	0.1302	0.0878
3	17.97	273	911	0.00	0.5823	0.0025	0.2114	0.2038	–
4	17.27	273	944	0.00	0.4314	0.0016	0.2201	0.3469	–
5	22.15	273	977	0.00	0.2750	0.0220	0.2322	0.4708	–
6	21.46	273	977	0.00	0.3490	0.0495	0.2456	0.3559	–
7	20.67	294	977	0.105	0.5663	–	0.1629	0.2355	0.0353
8	29.20	294	977	0.105	0.4894	–	0.2855	0.1289	0.0962
9	32.42	294	977	0.105	0.4792	–	0.2876	0.1072	0.1260
10	26.66	294	977	0.105	0.5781	0.0026	0.2430	0.0653	0.1110
11	22.43	294	977	0.105	0.6046	0.0025	0.2250	0.0329	0.1350
12	21.74	294	977	0.105	0.5860	0.0019	0.1856	0.0243	0.2022
13	21.88	294	977	0.105	0.5042	0.0017	0.1935	0.0260	0.2746
14	21.78	294	977	0.105	0.5694	0.0019	0.1795	0.0184	0.2384
15	17.72	294	977	0.105	0.6247	0.0027	0.1868	0.0205	0.1653
16	21.48	294	977	0.00	0.6894	0.0027	0.1846	0.0204	0.1029
17	20.94	294	977	0.00	0.7049	0.0028	0.1832	0.0281	0.0810
18	16.03	294	977	0.00	0.6830	0.0051	0.2171	0.0317	0.0631
19	19.05	294	977	0.00	0.7524	0.0052	0.1936	0.0488	–
20	21.04	284	977	0.00	0.7608	0.0045	0.1846	0.0501	–
21	21.56	273	977	0.00	0.7272	0.0044	0.1948	0.0736	–
22	23.07	273	977	0.00	0.7552	0.0040	0.1683	0.0725	–
23	21.12	273	977	0.00	0.7234	0.0042	0.1797	0.0927	–

RUN #38

Coal Sample Wt: 6.00 g
Run Type A
Reactor Pressure: 122-142 KPa

Injection #	Experimental Conditions Product Gas Rate (CC/min)	Total Press. (KPa)	Temp. (°K)	Steam Flow (g/min)	Product Gas Composition H_2	N_2	CO	CH_4	CO_2
1	24.04	142	811	0.105	0.3551	0.0016	0.2074	0.1424	0.2935
2	21.43	142	811	0.105	0.4536	0.0019	0.2153	0.2012	0.1280
3	21.44	142	811	0.105	0.7897	0.0039	0.1738	0.0326	-
4	21.44	142	811	0.105	0.6473	0.0036	0.1770	0.1117	0.0604
5	21.51	142	811	0.105	0.6720	0.0029	0.1706	0.0902	0.0643
6	21.88	142	850	0.105	0.4241	0.0016	0.1612	0.1770	0.2361
7	21.32	142	900	0.105	0.3517	-	0.1981	0.0850	0.3652
8	29.05	142	950	0.105	0.4179	0.0244	0.1645	0.0568	0.3364
9	20.43	142	977	0.105	0.3912	0.0016	0.1846	0.0387	0.3839
10	21.79	142	977	0.105	0.4455	0.0016	0.1801	0.0307	0.3421
11	23.76	142	977	0.105	0.4820	0.0021	0.1784	0.0195	0.3180
12	21.53	142	977	0.105	0.4947	0.0018	0.1825	0.0206	0.3004
13	21.54	142	977	0.105	0.5013	0.0018	0.1893	0.0166	0.2910
14	21.89	142	977	0.00	0.4979	0.0021	0.2033	0.0159	0.2803
15	20.47	142	977	0.00	0.5589	0.0022	0.2241	0.0134	0.2014
16	15.62	142	977	0.00	0.5905	0.0065	0.2507	0.0298	0.1225
17	16.15	142	977	0.00	0.6713	0.0076	0.2022	0.1189	-
18	26.86	142	977	0.00	0.7006	0.0094	0.2136	0.0764	-
19	20.75	142	977	0.00	0.7748	0.0042	0.1636	0.0574	-
20	20.79	132	977	0.00	0.8073	0.0045	0.1578	0.0304	-
21	20.22	122	977	0.00	0.7775	0.0042	0.0804	0.1379	-
22	21.28	122	977	0.00	0.7150	0.0045	0.1414	0.1391	-
23	21.15	122	977	0.00	0.7561	0.0037	0.1169	0.1233	-

RUN #39

Coal Sample Wt: 5.98 g
Run Type B
Reactor Pressure: 122-142 KPa

	Experimental Conditions				Product Gas Composition				
Injection #	Product Gas Rate (CC/min)	Total Press. (KPa)	Temp. (°K)	Steam Flow (g/min)	H_2	N_2	CO	CH_4	CO_2
1	20.81	122	811	0.00	0.2751	0.0010	0.2572	0.2726	0.1941
2	20.82	122	839	0.00	0.5163	0.0025	0.2458	0.2354	–
3	20.98	122	911	0.00	0.4379	–	0.2759	0.2862	–
4	20.97	122	944	0.00	0.3001	0.0506	0.3169	0.3324	–
5	20.88	122	977	0.00	0.4450	0.0548	0.3205	0.1797	–
6	20.88	122	977	0.00	0.6103	0.0434	0.2269	0.1194	–
7	27.15	132	977	0.105	0.4599	–	0.3023	0.0502	0.1876
8	27.10	142	977	0.105	0.4806	0.0019	0.2650	0.0464	0.2665
9	21.93	142	977	0.105	0.4826	0.0016	0.2234	0.0279	0.2645
10	26.98	142	977	0.105	0.5049	0.0022	0.2012	0.0185	0.2732
11	25.23	142	977	0.105	0.6071	0.0022	0.1540	–	0.2389
12	23.42	142	977	0.105	0.4713	0.0021	0.1861	0.0143	0.3262
13	25.82	142	977	0.105	0.4981	0.0018	0.1824	0.0146	0.3031
14	23.34	142	977	0.105	0.5447	0.0024	0.1721	–	0.2802
15	20.85	142	977	0.105	0.6593	0.0027	0.1669	–	0.1711
16	20.91	142	977	0.00	0.6193	0.0031	0.1869	–	0.1907
17	20.89	142	977	0.00	0.6064	0.0028	0.2171	–	0.1737
18	13.10	142	977	0.00	0.5724	0.0065	0.2545	0.0180	0.1486
19	18.21	142	977	0.00	0.8015	0.0072	0.1913	–	–
20	20.83	132	977	0.00	0.7995	0.0048	0.1957	–	–
21	20.79	122	977	0.00	0.8228	0.0043	0.1729	–	–
22	20.34	122	977	0.00	0.8218	0.0044	0.1738	–	–
23	21.73	122	977	0.00	0.8232	0.0043	0.1725	–	–