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ABSTRACT

The kinetics of the pyrolysis of Douglas fir bark has been investigated by thermogravimetric analysis (TGA). The effects of various variables such as heating rate, particle size and catalysts on the decomposition of the bark have been studied. Experimental data were obtained in the temperature range 20-800°C and at atmospheric pressure.

Higher heating rates resulted in higher levels of conversion and rapid decomposition of the bark. In the range 75-710 microns, the conversion of bark to gaseous products was not influenced appreciably by varying the particle size.

The use of the alkali carbonates as catalysts had the effect of significantly increasing the rate of pyrolysis and conversion of the bark. This was most noticeable in the temperature range 270-500°C.

A kinetic model has been proposed for the pyrolysis of the non-catalyzed and catalyzed bark. It was based on the decomposition of the volatile materials in the samples. The kinetic constants were estimated. The activation energy was found to be 15.3 kcal/gmole for the non-catalyzed bark and varied from 9.0 to 15.0 kcal/gmole for the catalyzed bark. The frequency factor was 3.0×10^7 $(mgmin)^{-1}$ for the non-catalyzed bark and varied from 0.1×10^7 to 6.7×10^7 $(mg\ min)^{-1}$ for the catalyzed samples. The order of reaction was found to be two in both cases.

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NOMENCLATURE

A	Frequency Factor	$(mgmin)^{-1}$
D_p	Diameter of Particle	(microns)
$-\frac{dW}{dt}$	Rate of Weight-Loss	(mg/min)
E	Activation Energy	(kcal/gmole)
k	Reaction Rate Constant	$(mgmin)^{-1}$
LTP	Linear Temperature Programmer	
n	Order of Reaction	
R	Gas Constant	
TG	Thermogravimetry	
TGA	Thermogravimetric Analysis	
TGB	Thermogravimetric Balance	
t	Time	(min)
T	Temperature	(^{o}K)
W	Weight of Sample at Time t	(mg)
W_c	Weight of Residue	(mg)
W_0	Initial Weight of Sample	(mg)
W_{v0}	Initial Weight of Volatile Material	(mg)
X	Conversion	(%)
y	Normalized Weight, W/W_0	

CHAPTER I

INTRODUCTION

The world's supply of fluid fossil fuels is being rapidly depleted. This results from the enormous consumption of energy per capita in the developed nations. In Canada, the consumption increases by about 3.3% per capita (Science Council 1976) every year. Fossil fuels are, however, not limitless, and once they have been burned they are gone forever.

Petroleum and natural gas have been the major sources of energy since the discovery of vast oil fields in the Middle East in the early 1950's. Only within the last 10 years, and in particular since the oil embargo of 1973, has the limitation of the world supply of crude oil been recognized. In fact, the rate of consumption has exceeded the rate of discovery. This has prompted an intense effort in the development of alternate and renewable sources of energy. The three major energy alternatives being extensively investigated and developed are nuclear energy, solar energy and coal.

Nuclear energy has associated with it environmental, economic and security concerns. Solar energy is a renewable source, is essentially inexhaustible and is pollution free. However, until the overriding costs for solar equipment are reduced, the use of solar energy will not be economical.

Coal has been one of the primary resources explored by both government and industrial sectors. Extensive catalytic

science and technology are being applied to convert coal to clean-burning gaseous and liquid fuels, as well as chemical and petrochemical feedstocks. The problems involved in the conversion of coal include considerable emissions of particulates, oxides of nitrogen and oxides of sulphur. Also, people are increasingly reluctant to expose themselves to the dangers and discomforts of working in mines. Strip mining for surface coal deposits is less hazardous but involves considerable land reclamation problems.

In view of the problems mentioned in the preceding paragraphs, an economical and a clean source of fuels and chemicals becomes particularly attractive. Forest products and agricultural wastes fall into this category. These materials are collectively known as biomass. Biomass can be defined as solar energy stored in the form of plant matter or residues which have some positive value as a chemical resource. It is a renewable source of energy with minimal pollution problems, due to its low sulphur content.

The application of biomass for energy consumption is not a new idea. Indeed, long before man knew there was oil, wood was used as fuel. In many parts of the world today, animal residue is used for fuel. These uses are very limited and provide only heat. In order to maintain our current standard of living, processes must be developed to convert plant matter and animal residues to liquid and gaseous fuels and chemical feedstocks.

Some of the principal biomass conversion technologies are:

i) direct combustion - this is the most common method of recovering energy from wood by simply burning the material in an excess of air and utilize the heat so produced;

ii) gasification - this is a complex chemical process which occurs when heat is applied to organic matter with a deficiency of oxygen. The product will be a mixture of gases containing hydrogen, carbon monoxide, carbon dioxide and hydrocarbons. The exact composition will depend on the temperature, pressure, times, and presence of catalyst. If air is used as a feed instead of oxygen, large amounts of nitrogen will also be produced - this will have to be removed to create a synthesis gas. Synthesis gas can then be used to produce methanol through catalytic combination of hydrogen and carbon monoxide, synthetic natural gas through methanation, or hydrocarbons through Fischer-Tropsch synthesis;

iii) hydrogasification - in this process, part of the biomass is first converted to hydrogen by gasification and the resultant gas is shifted to increase the hydrogen content. The hydrogen-rich gas then reacts with the remaining biomass at a high temperature and pressure to yield a product gas with a high methane content which is then upgraded to pipeline quality synthetic natural gas;

iv) hydrogenation - this is also referred to as liquefaction or carboxylolysis. It is a reduction reaction in which carbon

monoxide reacts with cellulosic material at 250-350°C and pressures of 70-350 atmospheres. The resulting liquid fuel has a heating value of about 30 MJ/kg;

v) pyrolysis - which is the physical and chemical decomposition of organic matter by the action of heat in the absence of oxygen. Varying compositions of gases, liquids and chars are produced, depending on the condition of the reaction. The gaseous mixture, liquid and char produced can be used as fuel. Synthetic natural gas, methanol, or liquid hydrocarbons can also be produced;

vi) Anaeorobic digestion - this is the conversion by bacterial action in the absence of oxygen of slurried organic material to a (70:30) gas mixture of methane and carbon dioxide. The process operates at 25°C and retention times can be as high as 15 days, thus necessitating equipment of a large volume. Lignin interferes with the process and thus may require removal beforehand.

Anaeorobid digestion is ideally suited for treatment of livestock wastes.

vii) hydrolysis - in this process cellulose can be converted into wood sugars including glucose through the action of either acids or special enzymes.

The sugars produced by acid or enzymic hydrolysis can then be fermented, using enzyme containing yeasts, to ethanol or higher alcohols. Alternatively, the sugars can be digested anaeorobically to produce a methane-rich gas. Such processes

are very time-consuming for the liquors to be fully converted.

viii) steam reforming - this is now commonly used to convert hydrocarbons, such as natural gas, to hydrogen and carbon monoxide, which can be used to produce various products such as methanol. It can also be used to convert the various hydrocarbons produced in pyrolysis/gasification process to synthesis gas. This could then be used to produce methanol.

Regardless of the type of technology, any near-term implementation of conversion processes for biomass should provide:

a) a readily marketable product,

b) operatability on a variety of feed materials,

c) economic feasibility with respect to low capital cost and utilization of conventional construction materials for components,

d) modest operating conditions, favourable kinetics, and high energy efficiency,

e) accommodation of both small, dispersed biomass sources and large, concentrated sources,

f) solution of waste disposal problems or at least, not producing additional large volumes of new wastes.

Most of the preceding requirements can be met by thermochemical gasification. This type of process involves both pyrolysis and gasification.

The products of present thermochemical processes for pyrolysis/gasification of biomass are low (approximately 150 Btu/cu ft) to intermediate (300 to 500 Btu/cu ft) Btu

gas, and perhaps tars and char. Any utilization of these products is limited. They are most suitable for use as industrial fuels. They cannot directly replace natural gas, chemical synthesis gases, or be directly used for chemical process feeds.

In summary, the near-term application of present biomass thermochemical pyrolysis/gasification processes is limited to their inability to produce high calorific value products for which large demand exist. Methods of converting biomass to medium and/or high Btu gas are almost the same as those proposed for coal. There is increased significant research being done on pyrolysis of biomass to produce gaseous products for utilization as fuel or as raw chemical feedstocks.

An understanding of the kinetics of pyrolysis is essential to the proper choice, design and analysis of suitable reactors for this biomass conversion process. Therefore, the major objectives of this study were to

i) investigate the effects of various operating variables on the pyrolytic conversion of Douglas fir bark (a wood residual),

ii) develop a kinetic model from the weight-loss data which were to be obtained by thermogravimetric analysis (TGA),

iii) estimate kinetic parameters from the proposed model.

CHAPTER II

LITERATURE SURVEY

Introduction

The thermal or pyrolytic degradation of carbonaceous materials (e.g. wood) has a long history (1), dating back to the ancient Chinese and Egyptians, who used the tarry products for embalming. In 1792 Robert Mudoch introduced fuels produced by pyrolyzing wood (2). Coal quickly superseded wood for the production of a synthetic gas.

Within the last five years intensive research has been carried out on pyrolysis of plant material. Technical sessions and exclusive seminars are often being held on pyrolysis-gasification of biomass.

In this section, the kinetics of pyrolysis, the effects of heating rate, particle size and catalysts on the gasification of carbonaceous materials will be reviewed. In addition, some of the methods used for obtaining and analyzing pyrolytic data will be discussed.

Pyrolysis

During the past ten years many research projects (3, 4, 5, 6, 7) have been carried out on the pyrolysis of cellulosic materials. This thermal decomposition process produces a number of valuable organic compounds. However, the yield of the individual chemical species is low.

Mechanism of Pyrolysis

The product arising from the pyrolysis gasification of biomass includes a variety of combustible and non-combustible components. They are:

- carbon dioxide
- carbon monoxide
- hydrogen
- hydrocarbons (C_nH_m)
- methane
- water vapour
- tarry vapours (primarily aromatics)
- particulates (ash and carbon)
- nitrogen (inert gas medium)

The above components are known collectively as "producer gas", with a low Btu rating (150-200 Btu/sdcf).

The mechanism by which such pyrolytic components are produced involves a very complex series of poorly defined concurrent and consecutive reactions (3). Furthermore, a full understanding of the nature and extent of the individual reactions has not been properly ascertained. It has been determined that the yield of pyrolytic products are highly influenced by the physical and chemical conditions under which the pyrolysis step occurs.

A general mechanism, attributed to Shafizadeh (3) suggests that the pyrolysis process can be divided into primary and secondary reactions (see Figure 1). The primary reactions, 1, 2, and 3, are based on cellulose while the secondary ones involve the reactions of the intermediate products. Reaction 1 occurs below 250°C and involves depolymerization, hydrolysis, oxidation, decarboxylation,

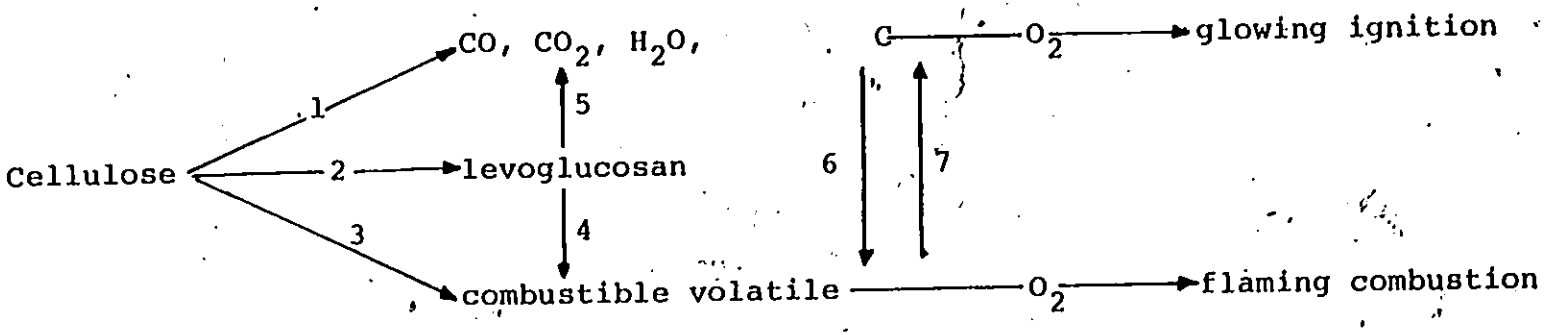

Figure 1. Pyrolysis Reactions

dehydration, and the formation of carbonaceous char. Reaction 2 is the formation of levoglucosan and takes place above 250°C. Reaction 3 involves fragmentation and formation of combustible products. These reactions are competing for the same initial reactant, so depending upon the reaction conditions, one could have dominance over the others. Shafizadeh (3) further pointed out that it is difficult to extend the data obtained from the pyrolysis of cellulosic material to wood and plant cell walls, because the latter contain not only a substantial amount of cellulose but also some hemicellulose and lignins.

The Reaction Kinetics of Pyrolysis

There is a general concensus among investigators studying the kinetics of pyrolysis of carbonaceous materials, that it is almost impossible to study each pyrolysis reaction individually (3). The application of thermal analysis techniques does not provide accurate identification and definition of each separate reaction.

Tran and Rai (8) have summarized the results reported by various workers using different types of feed stocks and experimental conditions (see Tables 1 and 2). It is seen that the values for the activation energy vary from 3.5 to 54.3 kcal/gmole whereas the frequency factor varies from 3.2 to 1.6×10^{20} min^{-1}. Some researchers have concluded that the pyrolysis process follows the kinetics

Table 1

FEEDSTOCKS AND EXPERIMENTAL CONDITIONS OF PYROLYSIS

Author	Feedstocks	Sample Size	Temperature ($^{\circ}$C)
Stamm	Douglas fir stick		93.5– 250
	Douglas fir sawdust		110 – 220
	Cellulose from Douglas fir		110 – 220
	Hemicellulose from D. fir		110 – 220
	Lignin from Douglas fir		110 – 220
Browne & Tang	Ponderosa wood	250–500 mg	200 – 400
Chatterjee	Cotton	100 mg	270 – 310
Lipska & Parke	α–cellulose	173–191 mg	250 – 300
Akita & Kase	α–cellulose Modified cellulose	100–200 mg	250 – 300
Mack & Donaldson	Cotton	10– 17 mg	300 – 450
Maa	Birch wood Douglas fir	Birch cylinder 6/33 in. dia. 1½ in. long	400 –1200
Leu	Spruce, redwood	-40 mesh	250 – 450
Barooah & Long	Wood Cellulose	40 g	180 – 400
Tran & Rai	Bark from Douglas fir	20 mg	25 – 850

Table 2

KINETIC PARAMETERS OF PYROLYSIS AS OBTAINED BY VARIOUS WORKERS

Author	Feedstocks	Activation Energy (kcal/gmole)	Frequency Factor (min^{-1})
Stamm	Douglas fir stick	29.5	3.1×10^{13}
	Douglas fir sawdust	25.0	1.1×10^{11}
	Cellulose from Douglas fir	26.0	2.0×10^{11}
	Hemicellulose from D. fir	25.7	2.2×10^{12}
	Lignin from Douglas fir	23.0	8.4×10^{11}
Browne & Tang	Ponderosa wood	35.8	
Chatterjee	Cotton	54.3	
		33.0	
Lipska & Parke	α-cellulose	50.0	
Akita & Kase	α-cellulose	53.5	$1.0 \times 10^{18.8}$
	Modified cellulose	32.0	
Mack & Donaldson	Cotton	41.2	
Maa	Birch wood	7.5	0.1 cm/sec
	Douglas fir	3.5	0.03 cm/sec
Leu	Spruce < 54% conv/	51.9	1.6×10^{20}
	> 54% conv.		7.3×10^{17}
	Redwood < 54% conv.	44.2	3.3×10^{19}
	> 54% conv.		1.0×10^{16}
Barooah & Long	Wood	4.3 (<330°C)	3.2
		20.0 (>330°C)	1.4×10^{6}
	Cellulose	17.0	2.4×10^{6}
Tran & Rai	Bark from Douglas fir	24.5–45.0	1.28×10^{10}

of a first-order (or pseudo first-order) reaction. However, the difficulties in understanding the mechanism of the pyrolysis of carbonaceous materials have produced conflicting kinetic data, resulting in a wide range of kinetic parameters.

Most investigators have proposed kinetic models based on the weight of residue and tried to obtain lumped kinetic parameters of primary and secondary reactions of pyrolysis. The equations of Stamm and van Krevelen are often used to describe the pyrolytic data of many investigators.

The equation proposed by Stamm (5) is as follows:

$$\frac{dW_L}{dt} = k(1-W_L) \qquad (1)$$

It is based on the premise of a simple first-order reaction with respect to the fraction of the weight loss, W_L. It also implies an equilibrium state of complete weight loss and therefore is not likely to be valid at high value of conversion (8). For this reason, van Krevelen (9) suggested a different model incorporating both the weight of the residue, W, and the weight loss after an infinite time, W_∞:

$$\frac{dW}{dt} = k(1-W/W_\infty)^n \qquad (2)$$

where n is the order of reaction.

The estimation of W_∞ is a difficult task and its definition varies from one investigator to another. Barooah and Long (10) have proposed that Stamm's model be used to describe the

primary stage of decomposition and van Krevelen's equation with n=2 to describe the secondary stage. They found that the primary stage covers about 85% of the total weight loss while the secondary stage covers the last 15% of the weight loss (8).

Effects of Heating Rate

The yield of pyrolytic products from cellulosic materials depends on the heating rate (11). With slow heating rate processes more char, little tar, and some flammable gas are produced. For slow heating rate, the decomposition occurs in an orderly manner, hence, stable molecules are formed. Such molecules are richer in carbon and converge toward the more stable hexagonal structure of graphite carbon (12, 13). Hence, the reactivity of carbon is decreased and less flammable gas is produced during slow heating rate processes.

Rapid heating of cellulosic materials tends to yield more tar, less char, and more flammable gas of higher heat content, that is, rich in hydrogen, hydrocarbons, and carbon monoxide (8).

The literature has not revealed sufficient data on the effect of heating rate on the pyrolysis of wood and wood residuals (e.g. bark). Furthermore, Shafizadeh (3) has pointed out the difficulty in trying to extend the data obtained from cellulosic materials to wood wastes,

because the latter contain some lignins and hemicellulose plus cellulose.

Heinrich (14) and Goldfarb (15) found that at very high heating rates, higher temperatures are needed to achieve a specified weight loss for wood. This fact was later confirmed by Sliepcevich and Leu (16).

Effect of Particle Size

According to the work of Maa (17), the pyrolysis of wood at high temperature, in the range of 400 to 1200°C, is influenced by the particle size. He concluded that for particles with a radius less than 0.1 cm, the rate of pyrolysis is controlled by chemical reactions. This conclusion was based on the assumption of first-order kinetics and using the unreacted shrinking core model. On the other hand, for those particles having a radius of greater than 2 cm the rate is controlled by heat transfer processes. Finally, for particles with radius between 0.1 and 2 cm both chemical reactions and heat transfer are important.

Tran (18), using a fixed bed flow reactor with Boise Cascade bark, studied the effect of particle size on pyrolysis. The diameter of the reactor was 2.54 cm, and particles between 0.64 and 1.3 cm were tested. He concluded that for particle sizes smaller than 0.64 cm, the particle size has no influence on either the amount of product gas or its heating value.

Pyrolysis - The Role of Catalysis

The present pyrolysis-gasification systems are generally uneconomical because of their poor thermal efficiency and the heterogeneous nature of the product which must be further refined to produce an acceptably pure "syngas" (primarily CO and H_2). The production of methanol requires a 2:1 stoichiometric ratio of hydrogen to carbon monoxide. Hence N_2, CO_2, CH_4, and other hydrocarbons must be removed or "shifted" for efficient methanol synthesis. Conventional gasifiers (pyrolyzers) require high temperatures (>800^{0}C) for good gas yields, channelling often occurs in the fuel beds, and fusion or clinkering of products and ash may also occur within the fuel bed. Catalysts may help to alleviate some of these drawbacks by lowering the operating temperatures and by producing a high yield of the syngas product. This would result in greater thermal efficiency, greater methanol yield, and a reduction of technical problems such as channelling and fusion (19).

The advantages of catalytic pyrolysis -- gasification are:

i) increased reaction rates

ii) lowered operating temperatures (greater efficiency)

iii) cracking of heavier hydrocarbons to form desirable syngas products such as CO and H_2.

Furthermore, the syngas product desirable for methanol production results from the low temperature catalytic cracking of pyrolytic liquids or from direct gasification at high temperatures (20).

In gasification technology, two classes of catalysts are of particular interest: those which crack the tars and pyroligneous acids to yield lighter molecular weight gases and, secondly, those which alter the product distribution of gases by cracking methane and other light hydrocarbons to yield CO, CO_2 and H_2.

Some of the catalysts employed in pyrolysis-gasification research include inorganic salts, metals, and metallic oxides.

Inorganic Salts

The influence of inorganic impurities on the kinetics of the pyrolysis of carbon is widely known. Even very small concentrations of salts of the alkali and transition metals exert great catalytic effects on the various reactions which occur during pyrolysis (21, 22).

Early gasification research revealed that alkali carbonates such as K_2CO_3 and Na_2CO_3 were excellent catalysts for carbonaceous materials. Studies by White (23, 24) found K_2CO_3 to be a good catalyst and that the optimum carbonate catalyst proportion is 20 percent (by weight) of the carbonaceous fuel feed. He further noted that alkali carbonates also catalyzed the water-gas shift reaction during steam gasification:

$$CO + H_2O \xrightarrow{\text{Alkali Carbonate}} CO_2 + H_2$$

The investigation of Lewis et al (25) was on the rate of gasification of wood charcoal catalyzed with K_2CO_3 (10 percent by weight) at 650°C. This catalyst greatly increased reaction rates. The catalyzed rates at 650°C were approximately equal to the non-catalyzed rates at 870°C.

Appell et al (26) recommended the use of Na_2CO_3 for the pyrolysis of solid municipal waste, using temperatures from 250-380°C and pressures between 500 and 5000 psig. Fung (27) noted that cellulose treated with Na_2CO_3 yielded less tar and more CO_2, CO, and H_2O than untreated cellulose at the expense of levoglucosan (a tar component).

Tran (18) found that K_2CO_3 and black liquor concentrates were very effective in increasing the amount of gas produced and the rate of pyrolysis of Douglas fir bark. About 15 weight percent of potassium carbonate or 20 weight percent black liquor concentrate was found to be the optimum for maximizing the rate of gasification.

Further literature review of the work of Madorsky et al (28), Appell (29), Hooverman (30), Love (31), and Tang (32) has given reinforcement to the evidence that alkali carbonates increase reaction rates and overall gas yields in pyrolytic-gasification of biomass, cellulose and refuse. The overall concensus is that these carbonates catalyze the water-gas shift and carbon-steam reactions.

Metals

Many investigators have found that certain metals, acting as catalysts, can greatly enhance gas yields and gasification rates. The alkali and group VIII transition metals are of particular value with nickel being recognized as one of the most effective catalysts. The results of using nickel indicate a greater net yield of combustible gaseous products than would otherwise be realized.

During the gasification of bark and spent pulping liquors at atmospheric pressure and 1000°C, with a nickel catalyst (33) higher conversion of residual hydrocarbons occurred. In addition, only 0.01 to 0.09 per cent by volume of methane in the product gas remained, compared to 2.3 to 3.0 percent in the non-catalyzed product gas. Therefore, syngas yields could be catalytically increased by 10 percent using nickel and this catalyst increased the CO and H_2 proportion in the product gas at the expense of CH_4 and CO_2.

In the gasification of bark and pulping liquors, Tran and Rai (22) referred to nickel as the methanation catalyst. They found that nickel did not increase the amount of gas produced or the overall gasification rate. However, at 600°C and atmospheric pressure, nickel promoted the methanation reaction, resulting in a higher BTU gas than would normally be produced under non-catalytic conditions.

Nickel appears to be an excellent catalyst for gasification reactions, however, some confusion exists as to the

exact product distribution of the gases under varying conditions of pressure and temperature (19). An examination of the thermodynamics of the reactions catalyzed by nickel should provide a solution. Nickel is costly and must be maintained in a highly reduced state, therefore, these factors are against its commercial use in large-scale gasification.

Cobalt, a group VIII transition metal has proved to be an excellent catalyst. Weiss (34) has reported that cobalt sulphide and cobalt hydroxide gave good liquid yields in the pyrolysis of wood at 400°C. Appell and Pantages (26) showed that cobalt, added as cobalt carbonyl in the gasification of sawdust at 625°C, increased the gas yield by 50 percent and favoured the production of hydrogen and carbon monoxide. Nickel is reported to be superior to cobalt in catalytic gasification. Both nickel and cobalt exhibited high activity and selectivity in promoting the direct decomposition of carbonaceous material to hydrogen and carbon monoxide.

Stern (35) used steel wool as a catalyst in the direct gasification of sawdust and sugar at 1000°C and atmospheric pressure. Hydrocarbons formed as initial pyrolysis products of wood were cracked by the steel wool and he suggested the following reaction shifted to the right in the presence of this catalyst:

$$CH_4 + H_2O \xrightarrow[\text{Steel Wool}]{} CO + 3H_2$$

This is only one of the many gasification reactions that result in the production of hydrogen and carbon monoxide or both. Stern's experimental results indicate a reduction in methane but a significant increase in the CO, H_2, and net gas yield. Gasification on steel wool resulted in an overall equimolar mixture of hydrogen and carbon monoxide whereas non-catalytic gasification gave considerable quantities of methane and higher molecular weight hydrocarbons (19). Therefore, steel wool appears to be of particular interest for the production of a relatively pure syngas mixture suitable for methanol synthesis.

Metallic Oxides

Several metallic oxides have been used in the catalytic gasification of carbon, biomass and coal. Willson (35) reviewed some of the relevant literature and concluded that metallic oxides act similarly to alkali carbonates by favouring the production of lighter hydrocarbons and by catalyzing the carbon-steam reactions. Oxides of copper, iron, lithium, magnesium, molybdenum, potassium, strontium, and zinc have been utilized as effective catalysts in the gasification of coal, biomass and refuse (25, 36, 37). Various mixtures of silica (SiO_2) and alumina (Al_2O_3) have been used in biomass gasification only recently, so the

opportunity exists for intensive research. Although metallic oxides are considered to be good catalysts, alkali carbonates are generally more economical and slightly more efficient.

Methods Used in Obtaining Pyrolysis Data

Pyrolysis of carbonaceous material has been studied by many researchers using different experimental methods and ways of analyzing their data. Some of these methods are:

A. Thermal Analysis

The two most common methods used in thermal analysis are differential thermal analysis (DTA) and thermogravimetry (TG). Other known methods include evolved gas detection, thermomechanical analysis, and differential scanning calorimetry.

The differential thermal analysis (DTA) technique has been used to study reaction kinetics. It involves the measuring of change in enthalpy of the constituents of the sample as a function of temperature. In addition, the temperature difference between the sample under study and a chosen standard sample is measured. The following problems have limited the widespread use of this method (38, 39):

i) the temperature difference makes interpretation of reaction kinetic data from a DTA curve a difficult task,

ii) parameters such as sample size, composition of the atmosphere used, and the nature of the reaction being studied could affect the DTA curve.

Blazek (40) did a review of the use of thermogravimetric (TG) techniques in studying reaction kinetics by isothermal and non-isothermal methods. The isothermal or static method entails the determination of any weight change as a function of time, at constant temperature. Certain disadvantages (41, 42) exist in using this technique. They include the following:

i) many experimental runs are required in order to complete a data set,

ii) the effect of heating rates cannot be studied,

iii) a time lapse occurs before the sample attains the required temperature, and during this period the reactions have proceeded to a certain extent,

iv) a buoyant effect is produced when the cold sample is subjected to extremely high temperature.

The dynamic or non-isothermal method involves the determination of the weight change as a function of time while the temperature increases linearly. The following advantages of the non-isothermal method have been reported by Wendlant (42):

i) since only one sample is used, less data is required,

ii) kinetic parameters can be estimated over the entire temperature range in a continuous manner.

The most serious disadvantage of the dynamic method is that the reaction mechanisms cannot be studied (40, 42). Therefore, kinetic parameters estimated from data using the dynamic method are pertinent to only that particular set of experimental conditions.

B. Flow Techniques

These methods involve the use of several different types of flow reactors such as fluidized bed, free fall, packed bed and entrained flow reactors. There are many advantages as well as disadvantages associated with using flow techniques. Flow reactors can be used to study the effect of particle size, residence time, product quality, and heat and mass transfer in feedstock particles. Although this technique is closer to the pilot plant stage, a flow reactor requires complex mathematical analysis of heat and mass transfer equations (18).

Pyrolysis Models

There are many published reports on kinetic models for pyrolysis of carbonaceous materials (1, 5-10, 16-18, 43-47). Most of the investigation was done using DTA and TGA methods. The evaluation of kinetic parameters from thermogravimetric curves has been the topic of many research papers (46-53). These papers have proposed a fairly large number of analytical methods for obtaining kinetic parameters

from TGA and DTA curves. Consequently, the results have been conflicting kinetic data plus a wide range of kinetic parameters.

Most reported kinetic models are based on either the weight of the sample (feedstock) or the decomposable weight. This is so, because it is impossible to identify all the individual chemical reactions which occur during the thermal decomposition of cellulosic materials. The models of Stamm (5) and van Krevelen (9) are frequently used by other researchers in describing their data.

Tran and Rai (8) developed a kinetic model for the pyrolysis of Douglas fir bark. They defined the conversion of solid feed to gaseous and liquid product in terms of fractional weight loss and on a catalyst-free basis as:

$$X = \frac{W_0 - W}{W_0} \qquad (3)$$

They assumed that the apparent activation energy is dependent on the extent of the reaction, because pyrolysis occurs through many steps where the molecules of the feedstock are changed physically and chemically. The presence of many concurrent and consecutive reactions during pyrolysis makes it impossible to single out an activation energy for any particular reaction. From their experimental data, the apparent activation energy was found to be a direct function of conversion, that is,

$$E = E_0 + aX \tag{4}$$

where E_0 is the activation energy at X = 0 and a is a constant which measures the sensitivity of E with respect to X. Furthermore, they proposed the following n^{th} order kinetic equation to describe the rate of weight loss of the bark during pyrolysis:

$$-\frac{1}{W_0}\frac{dW}{dt} = k_0 e^{-E/RT} f(W)^n \tag{5}$$

where f(W) is a function of the residue and can be written as:

$$f(W)^n = (W/W_0)^n \tag{6}$$

n is the order of reaction, k_0 is the frequency factor as described by Arrhenius' law, R is the universal gas constant, and T is the absolute temperature at which the pyrolysis reaction occurs. Tran and Rai (8) used the dynamic TGA and graphical techniques to obtain values for the apparent activation energy, the frequency factor, the reaction rate constant, and the order of reaction. In general, their results compared fairly well with values obtained by other investigators using different feedstocks as well as other experimental set-ups.

Conclusions

In this section, the kinetics of pyrolysis, the effects of heating rate, particle size and catalysts on the

gasification of carbonaceous materials have been reviewed. Furthermore, some of the methods used for obtaining and analyzing pyrolytic data were discussed. The literature review has given rise to the following conclusions:

1) The kinetic parameters such as the reaction rate constant and the apparent activation energy for pyrolysis of carbonaceous materials have been investigated by various workers at different particle sizes and temperatures, but the reported results in the literature show great inconsistency.

2) Factually, the carbon content in carbonaceous materials becomes relatively less and less as the pyrolysis reaction proceeds, and also different reactions occur sequentially as well as simultaneously during the pyrolysis step.

3) Catalysts can be used to increase gas yields and alter gas composition in the pyrolysis-gasification of carbonaceous materials. The alkali carbonates, particularly K_2CO_3, seem to be the most effective catalysts. Nickel appears to be an excellent catalyst for gasification reactions. However, special attention should be given to the relative recovery methods and costs for any potential catalyst.

4) The dynamic thermogravimetric technique when compared to the static method appears to be a simpler and less time consuming approach. The data obtained from the dynamic

method is adequate for the estimation of various kinetic parameters.

5) If a thermal analysis technique is used to obtain kinetic parameters, then there should be verification of the resulting kinetic model with data obtained from a flow reactor to establish the accuracy of the proposed model.

CHAPTER III
EXPERIMENTAL

A. Description of Apparatus

The pyrolysis of Douglas fir bark was carried out in the apparatus schematically shown in Figure 2. The dynamic weight loss data which were obtained provided the information needed to evaluate some kinetic parameters, such as reaction rate constant and activation energy.

The apparatus may be divided into three sections:

i) Feed

ii) Reaction Assembly

iii) Control Section

i) Feed Section

Nitrogen was used to produce the inert atmosphere required for pyrolysis. The gas was obtained from a high pressure cylinder passed through a filter and a drying tube packed with drierite (Fisher Cat. No. C-140) and then through two flowmeters (tube and float series 601, Matheson Co.). The gas lines for nitrogen also had two needle valves which kept the gas at atmospheric pressure. These stainless steel, micrometer control valves are manfactured by Nupro Company, part number SS2SG with 0.08 cm orifice. They are supplied by Ottawa Valve and Fitting Company.

There were also two 50.8 cm standard cleanout mercury manometers (Merian Instrument Company, Cleveland, Ohio) which indicated the pressure of nitrogen entering the

reactor and thermogravimetric balance. One end of each manometer was opened to the atmosphere while the other was connected to the line leading to either the top or the bottom of TGB - and - reactor assembly.

ii) Reactor Assembly

This section of the apparatus consisted of a thermogravimetric balance (TGB), hangwire and sample bucket, reactor and furnace.

The TGB (supplied by Mettler Instruments, Zurich, Switzerland) had features which provided direct weight loss data during the bark pyrolysis. A block diagram of the TGB is shown in Figure 3. The beam scanner (5) records the beam deflection which occurred during weighing. It controlled the control amplifier (6). The latter generated a current proportional to the weight in the moving coil of the compensation system (2) by way of the range selector switch (7). The current generated a magnetic opposing force, which kept the beam at rest in the case of minimum deflection.

The hangwire suspending the sample bucket had a 60.0 cm length and a diameter of 0.03 cm. The bucket was 1.2 cm in diameter and 1.0 cm deep. Both items were made of quartz (Vandernof, glassblower, NRC, Ottawa).

The control socket of the TGB was modified into a quartz reactor 72 cm long and 4.0 cm O.D. It had two side

Schematic Diagram of Experimental Apparatus

Symbol	Item
F	Furnace
LTP	Linear Temperature Programmer
M	Manometer
NV	Needle Valves
N_2	Nitrogen Supply
QR	Quartz Reactor
R	Rotameter
S	Sample Bucket
TC	Thermocouple
TGB	Thermogravimetric Balance
V	Two-way Valves for Flow Control

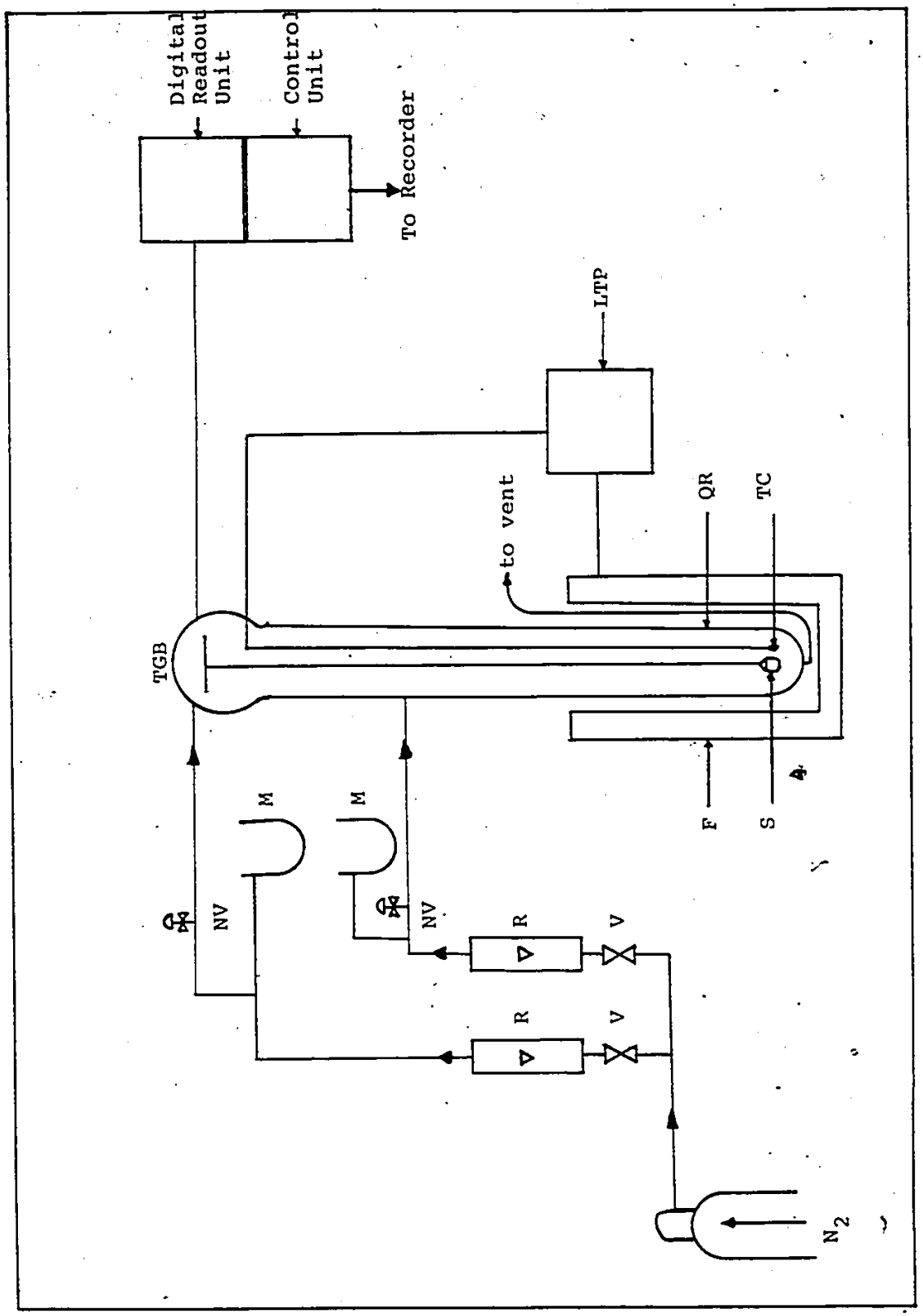

Figure 2 - Schematic Diagram of the Apparatus

Legend for Block Diagram of TGB (Figure 3)

1	Weighing system
2	Magnetic compensation system
3	Pan brake
4	Power supply
5	Inductive beam scanning
6	Control amplifier
6a	Control for pan brake
7	Range selector
8	Measuring amplifier
9	Taring and zero point
10	Analog output signal

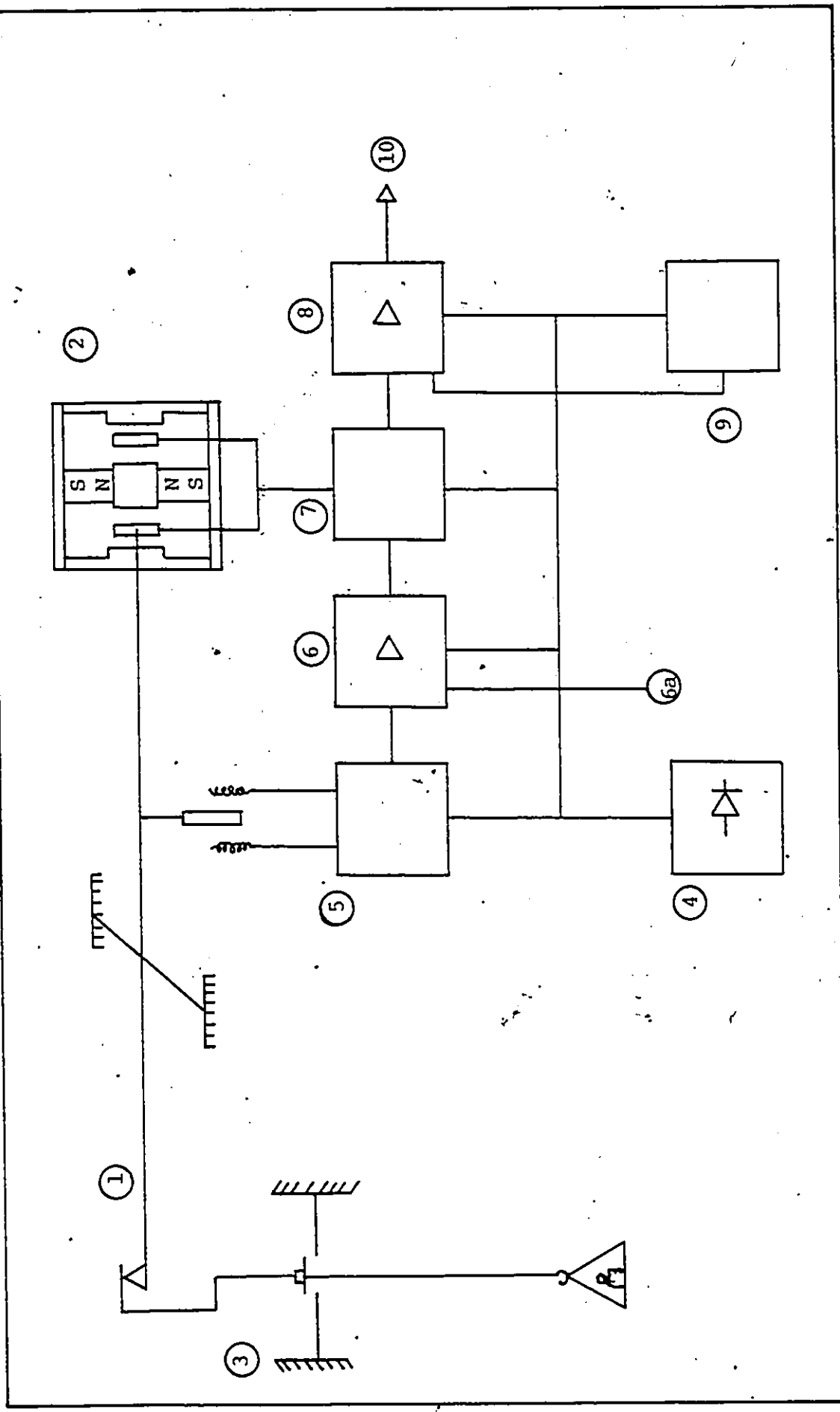

Figure 3 - Block Diagram of TGB

openings for the entry of nitrogen and the exit of the gaseous pyrolytic products (plus nitrogen). The top of the reactor was clamped to the TGB.

In order to heat the reactor, a Lindberg type furnace was used. It had two vertically split half circle heating units (2 K.W.). A paste of asbestos powder mixed with water was applied to the outside of the heating elements for insulation. The asbestos was slowly dried to prevent cracking. The wires of the furnace were connected to the power and control section of the set-up.

iii) Control Section

The TGB had a control unit. This was used for calibration and taring purposes. A strip chart recorder (Series B-5000, Houston Instrument, Austin, Texas) was connected to the 10 volts analog output of the control unit. The output signal in millivolts was transferred to the recorder.

A digital readout unit (Mettler ME 22) was placed on top of and connected to the control unit. The recorder and the digital readout unit gave the sample weight at any particular time.

A temperature programmer/controller (Model PC-6011) was supplied by the Valley Forge Instrument Company, Phoenixville, Pa. The programmer could be operated isothermally or used to maintain a change of temperature at a

"precise" rate. The heating rate could be varied from 5-50°C/min. It had a controlled service outlet to provide power to the furnace, and required only one connection to the power line to operate the entire system. A large dial indicated the temperature set point, program process, and maximum temperature limit.

A chromel versus alumel (Type K) thermocouple was inserted into the quartz reactor, close to but not touching the suspended sample bucket. The leads of the thermocouple were connected to the terminals marked "SENSOR" at the rear of the programmer, observing the polarity as marked. The thermocouple was supplied by Thermoelectric Canada Ltd., Brampton, Ontario.

B. Calibration of Equipment

It was necessary to tare and calibrate the thermogravimetric balance before any experimental run. The power switch was turned on for the recorder, the control and digital readout units of the TGB. About 15 minutes was allowed for the warming up of the instruments. A zero reading for the TGB was obtained by using the taring knob on the control unit. This was done with the hangwire, sample bucket and the reactor in place. Simultaneously, the recorder was adjusted to give a corresponding zero reading. A 10 mg calibrating ring was hung from the TGB. The readout unit and recorder should display readings of 10 mg and 10 mV,

respectively. On removing the calibrating rings, zero readings should be obtained. If the zero point is incorrect, the taring and calibration steps are repeated.

The thermocouple (Type K) was calibrated using a mercury thermometer, a potentiometer and a controller-heater-reactor assembly. The heater and controller were used to obtain isothermal conditions in a stainless steel reactor. The thermometer and the thermocouple were tied together and suspended in the reactor. The leads of the thermocouple were connected to the millivolt potentiometer. A plot of the thermometer reading versus the E.M.F. of the potentiometer is shown in Figure 4.

Temperature profiles were obtained for the LTP at heating rates of 15 and 50 degrees Celsius per minute. These were done to ascertain the actual temperature in the quartz reactor when the LTP was set a specified heating rate. The data are found in Appendix A.

C. Experimental Procedure

The following steps were performed for each run:

i) The TGB was tared and calibrated simultaneously with the analog recorder.

ii) The sample was placed in the bucket which was then suspended by the hangwire in the reactor.

iii) The reactor assembly was then purged with nitrogen to remove air from the entire system. This was done

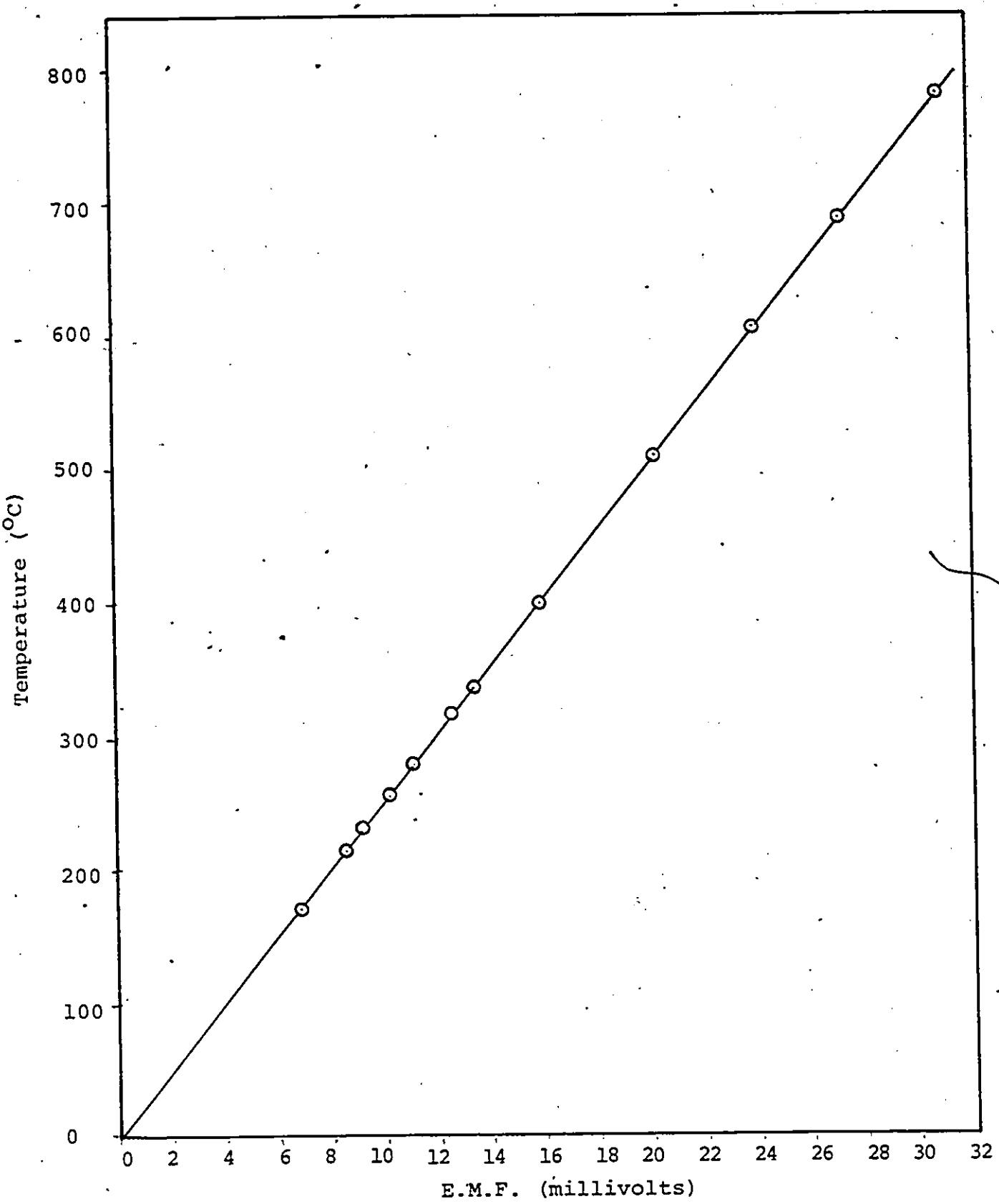

Figure 4 - Calibration Curve for the Thermocouple of the LTP

for about half an hour. Furthermore, the assembly was checked for any leaks.

iv) The LTP was set in the isothermal mode at 20°C as the starting temperature. A period of 30 minutes was allowed for thermal equilibrium.

v) The flowrate of nitrogen through the system was set at 150 ml/min after the purging step. A bubble-meter at the outlet was used to determine the correct flowrate.

vi) The needle valves were adjusted (if necessary) to obtain atmospheric pressure in the system.

vii) A heating rate and the heating limit (800°C) were selected on the LTP.

viii) The recorder's chart speed motor was turned on simultaneously with the LTP in the "rise to hold" mode of operation.

As the temperature of the furnace rises, the reactor is heated, the weight loss data of the sample are obtained from the strip chart of the recorder.

ix) At the limit (800°C) the heating is continued for 5 minutes more. After this time the LTP is turned off. The recorder is stopped. Nitrogen is allowed to continue passing through the system to vent the product gas.

D. Samples and Chemicals

The Douglas fir bark was obtained from the Eastern Forest Products Laboratory, Ottawa, Ontario. The bark was powdered, screened, and then dried for 30 minutes. The powdered bark was stored in a dessicator. Table 3 shows an example of analyses done on two samples of the powdered bark.

Catalyzed bark was prepared by the impregnation method. The bark and a solution of the catalyst were mixed together. Then this mixture was oven dried (at 100°C) to form catalyzed bark of a particular percentage by weight (of catalyst). The compounds used as catalysts were supplied by the Fischer-Scientific Co., New Jersey, U.S.A. The nitrogen used was obtained from Liquid Carbonic, Ottawa, Canada.

CHAPTER IV

RESULTS

The dynamic or non-isothermal method was used to obtain the experimental data during this investigation. However, the temperature rise indicated by the LTP was non-linear. This was determined by the temperature profiles obtained for the LTP at heating rates of 15 and 50 degrees Celsius per minute (see Tables 4 and 5).

The effect of various variables, namely, heating rates, particle size, nitrogen flow rate, and catalysts on the conversion of Douglas fir bark to gaseous products were studied.

Conversion (X) was defined in terms of fractional weight loss and on a catalyst-free basis as:

$$X = \frac{W_0 - W}{W_0} .$$

Tables 6 and 7 show the results of using heating rates of 15 and 50°C/min, respectively. Figure 5 is a plot of conversion versus time (temperature) for the two heating rates. It is observed that a heating rate of 50°C/min when compared to one of 15°C/min gave higher levels of conversion and in a shorter period of time. Hence, the higher heating rate was used for the rest of the experimental runs.

The effect of particle size on conversion was studied in the size range 75-710 microns using a heating rate of 50°C/min. The data are shown in Tables 8-16. The plots

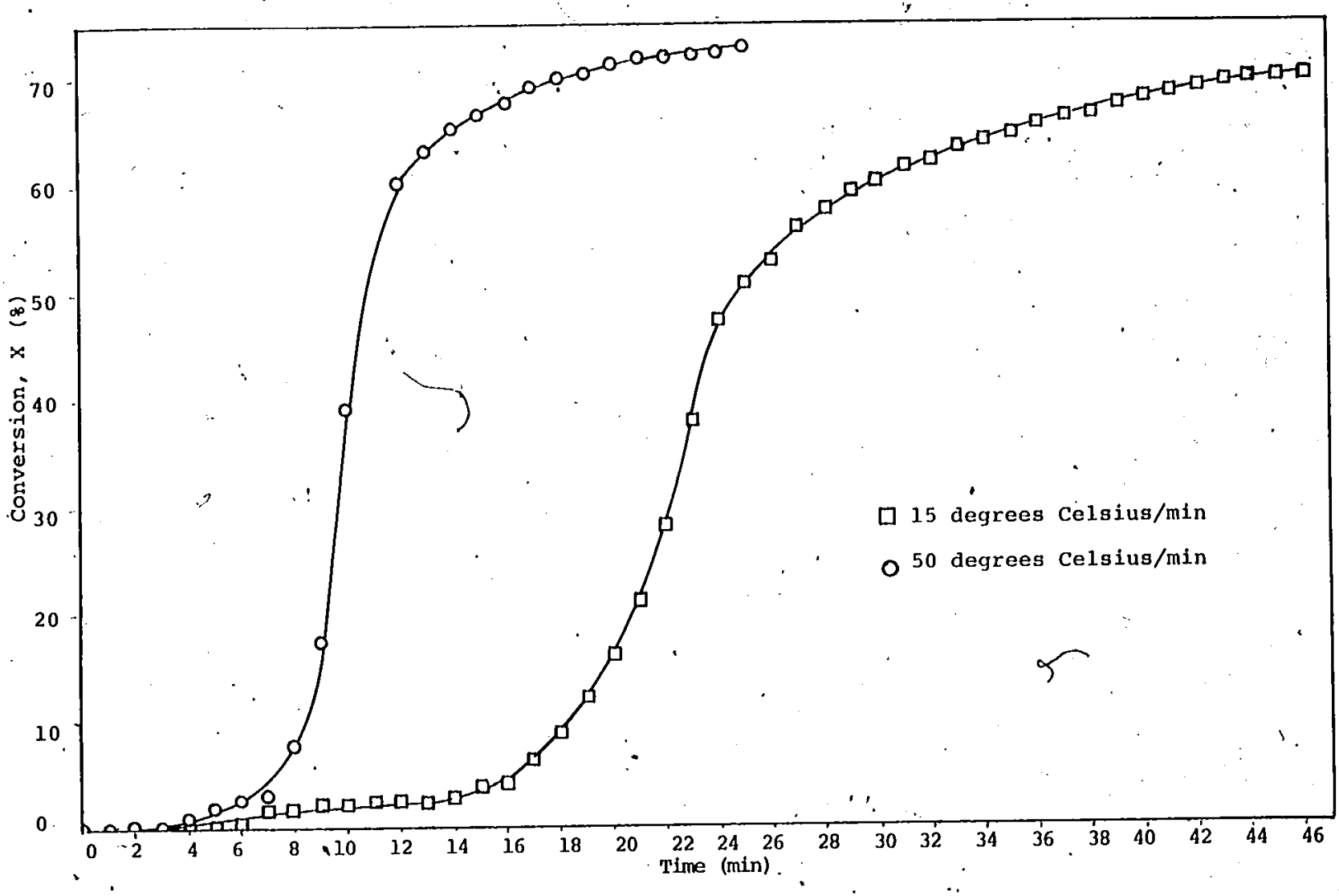

Figure 5 - The Effect of Heating Rate on the Conversion of Douglas Fir Bark

of conversion against time (temperature) with particle size as a parameter are shown in Figures 6 and 7. A particle size of 150 microns gave the highest levels of conversion, therefore, it was used for the mass transfer and catalytic studies.

To investigate the effect of mass transfer on conversion, experiments were done using different flowrates of nitrogen in the reactor. Tables 17-20 show the data obtained. Figure 8 depicts the plot of conversion versus time (temperature) with nitrogen flow rate as a parameter.

The effect of catalysis on the conversion of bark was investigated using the carbonates, chlorides of potassium and sodium, the nitrate of nickel and potassium hydroxide. Tables 21-31 are the results of the catalytic studies. Figures 9-13 are plots of conversion against time (temperature) with the parameter being percentage (by weight) of catalyst.

The experimental data for the non-catalyzed and catalyzed pyrolysis of bark revealed that the rate of weight loss ($-dW/dt$) varied with time (temperature), refer to Tables 8-16 and 21-31. Figures 14 and 15 show examples of plots of $-dW/dt$ versus time (temperature) for noncatalyzed and catalyzed samples.

All the data are given in Appendix B.

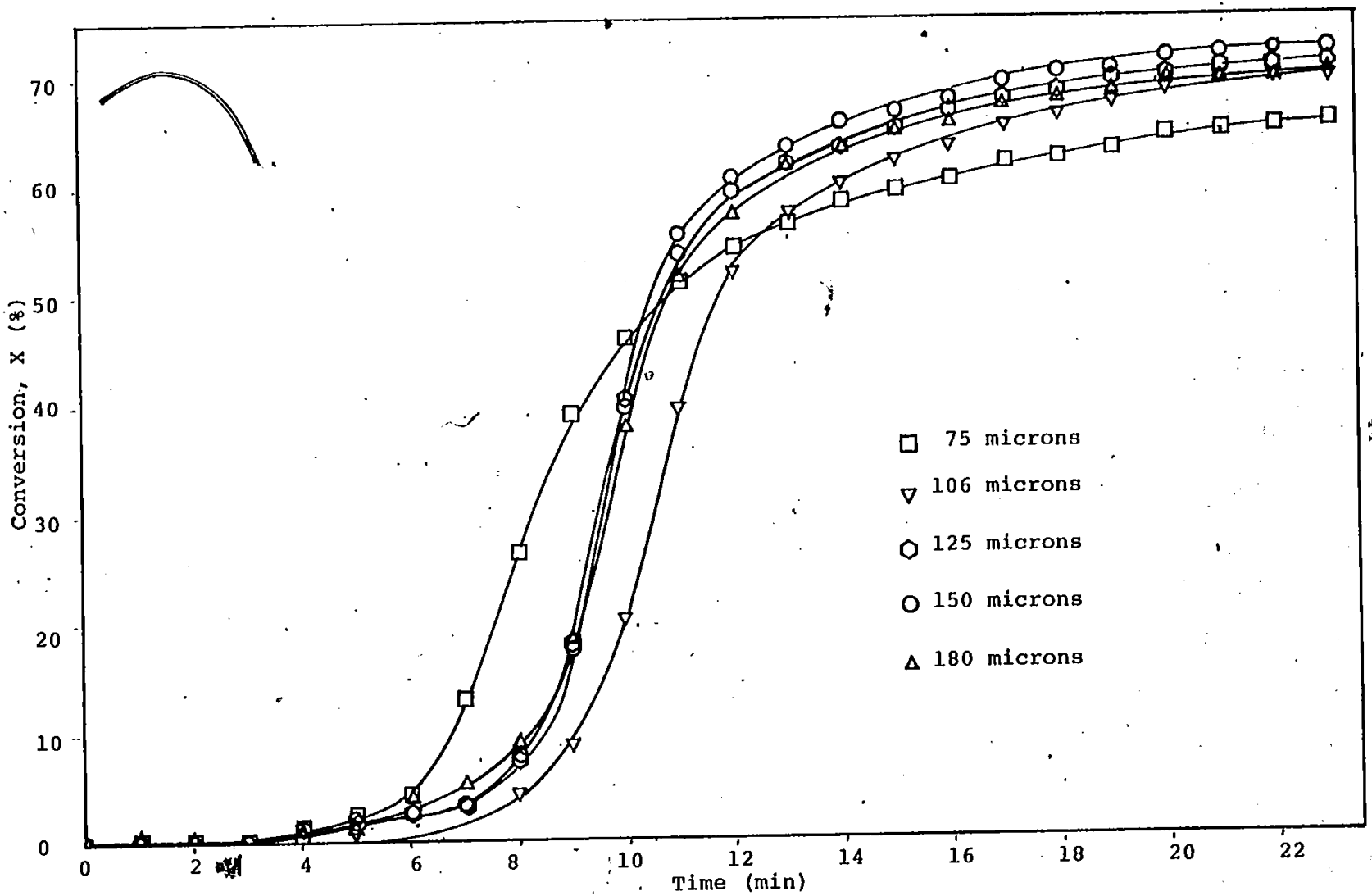

Figure 6 - The Effect of Particle Size on the Conversion of Non-catalyzed Douglas Fir Bark

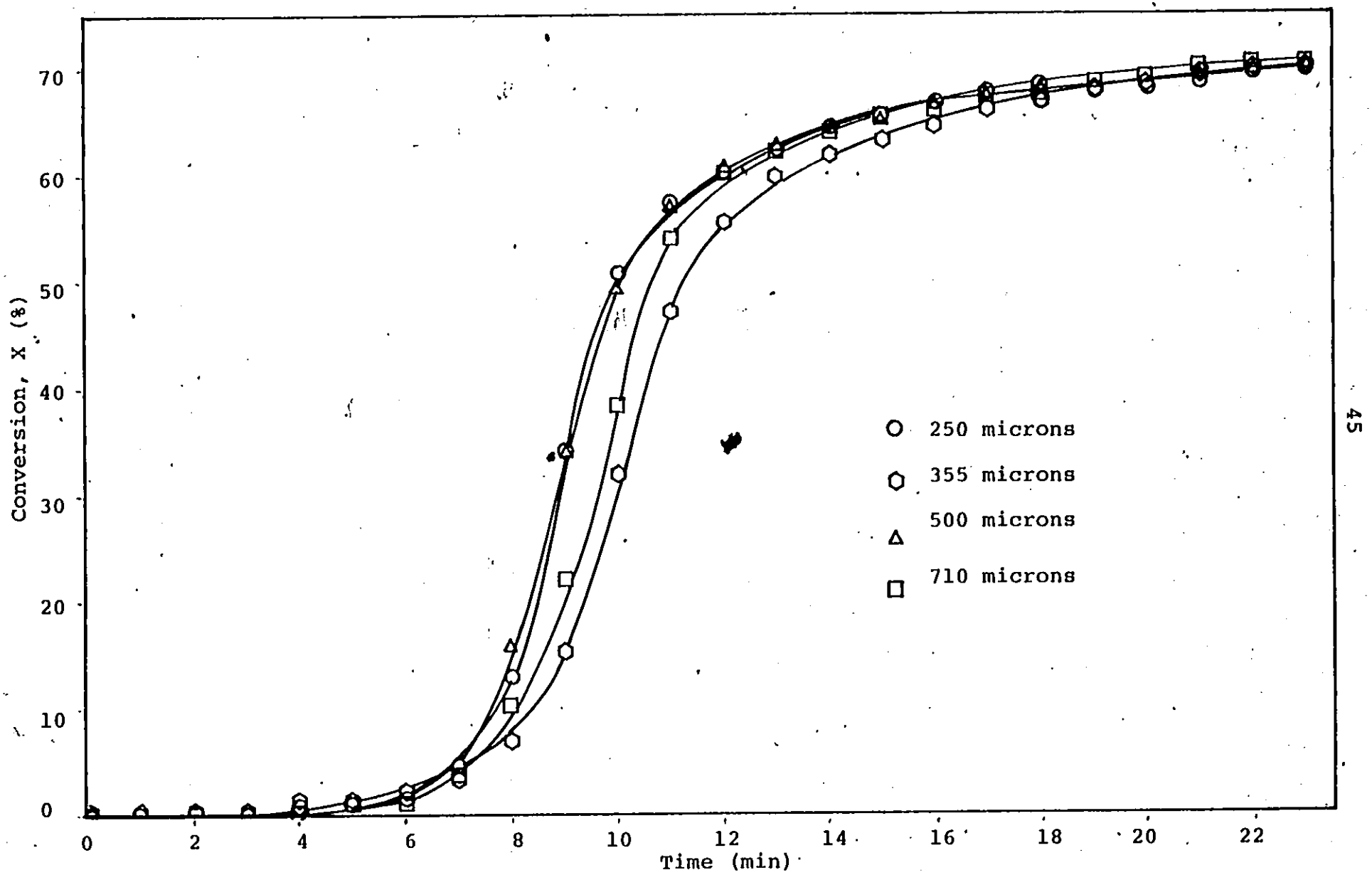

Figure 7 - Effect of Particle Size on the Conversion of Non-catalyzed Douglas Fir Bark

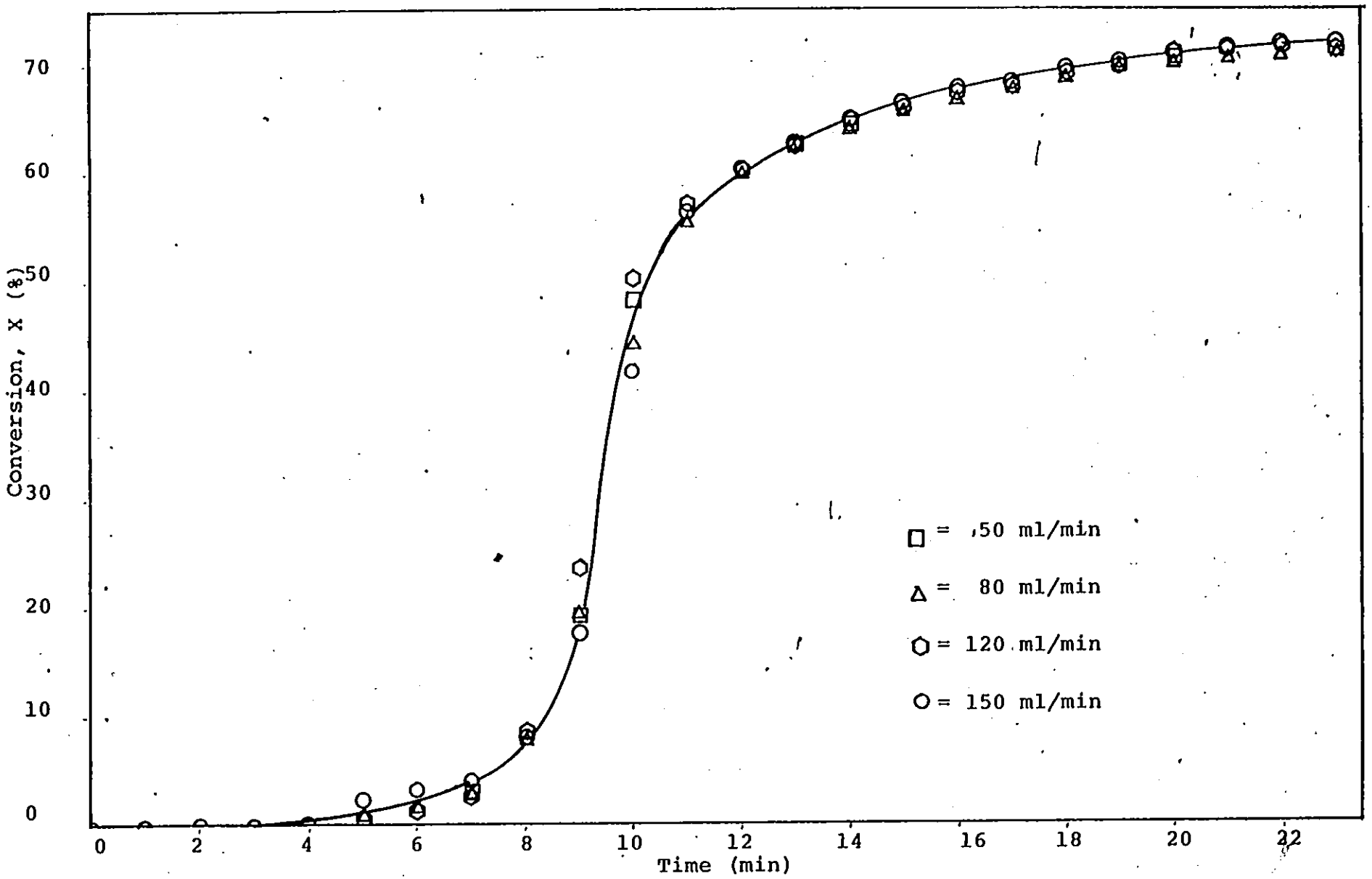

Figure 8 - Conversion vs Time (temp) with Varying Flowrates of Sweep-gas as Parameter

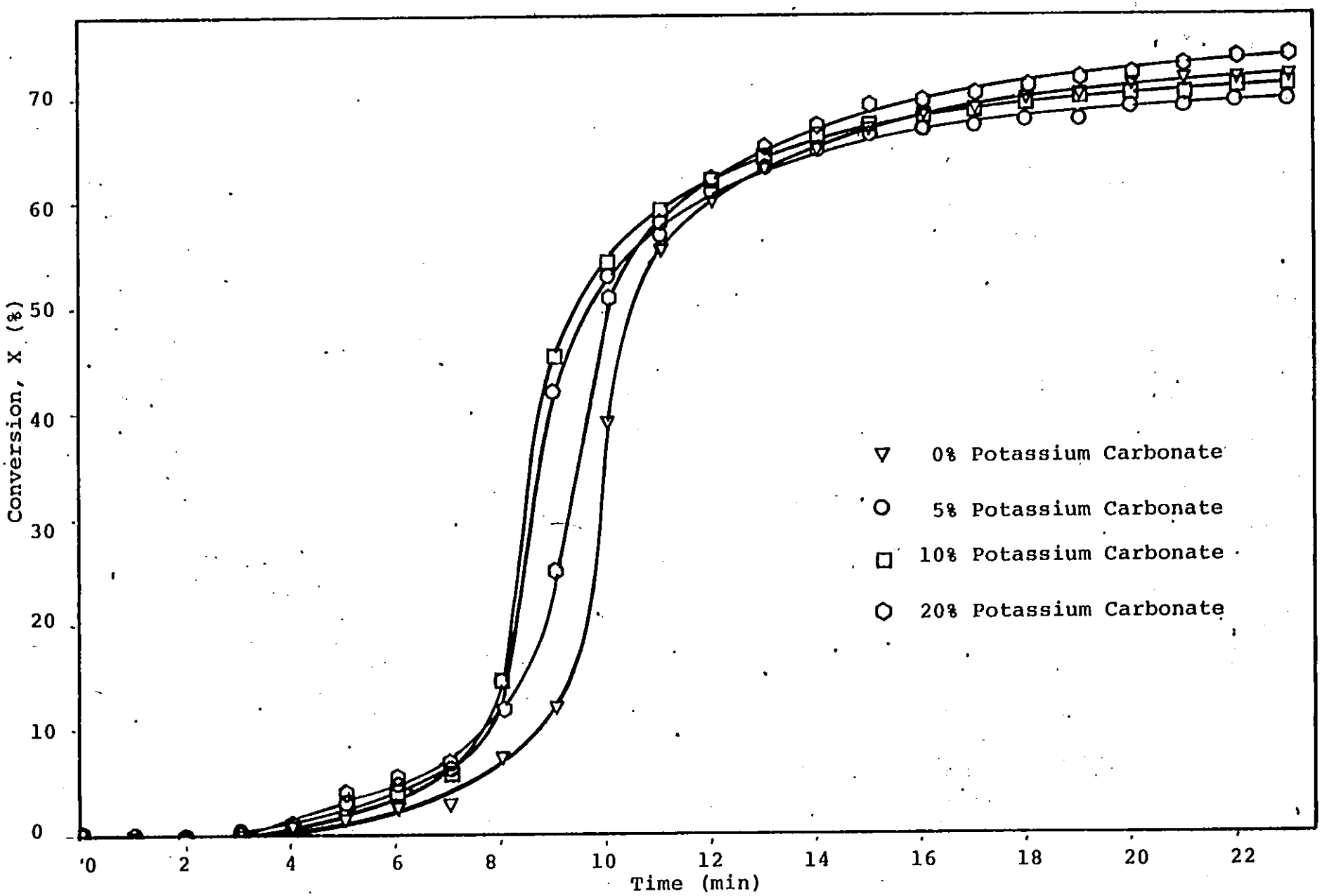

Figure 9 - The Effect on Conversion of Potassium Carbonate at Varying Weight Percentages

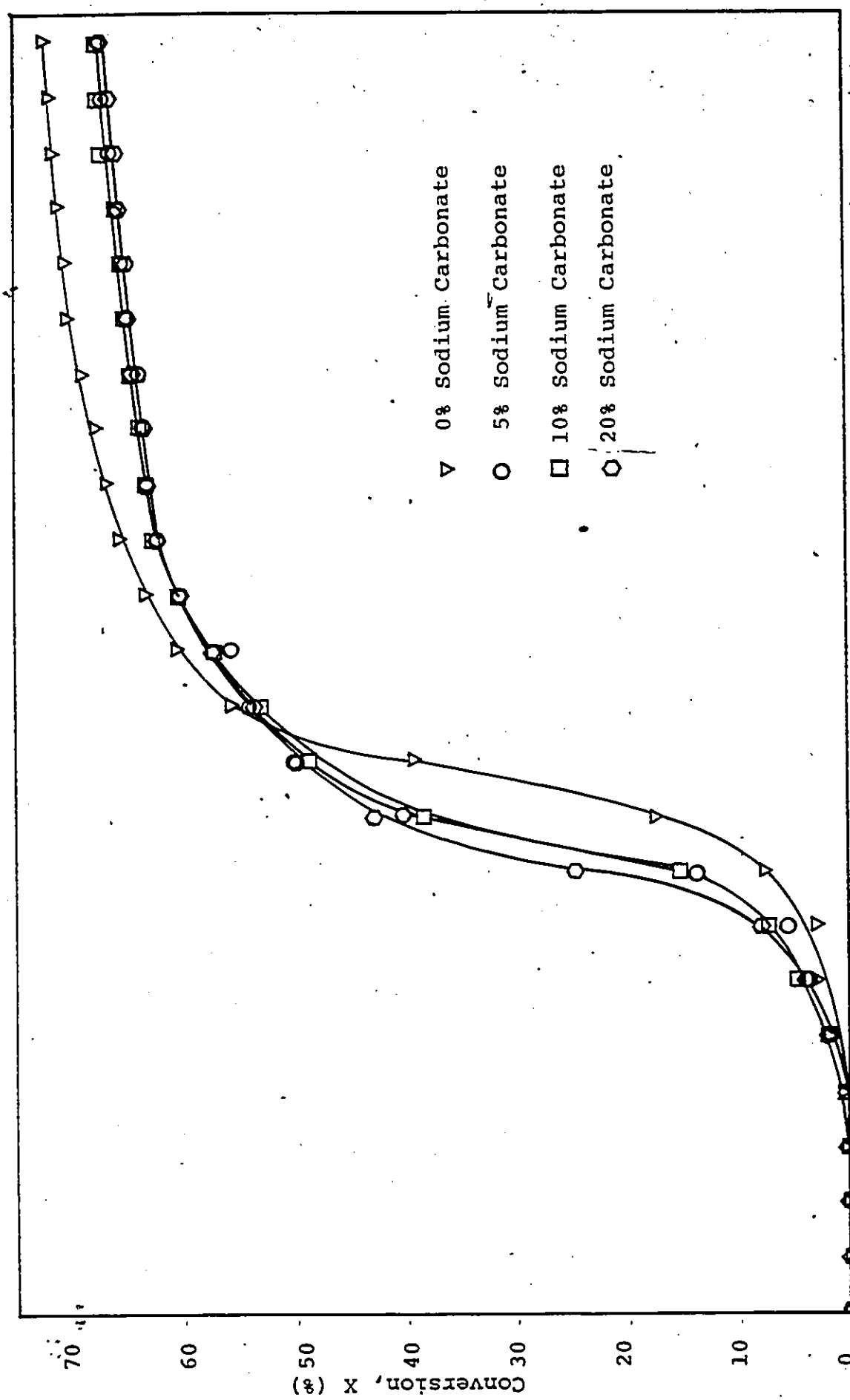

Figure 10 - The Effect on Conversion of Sodium Carbonate at Varying Weight Percentages

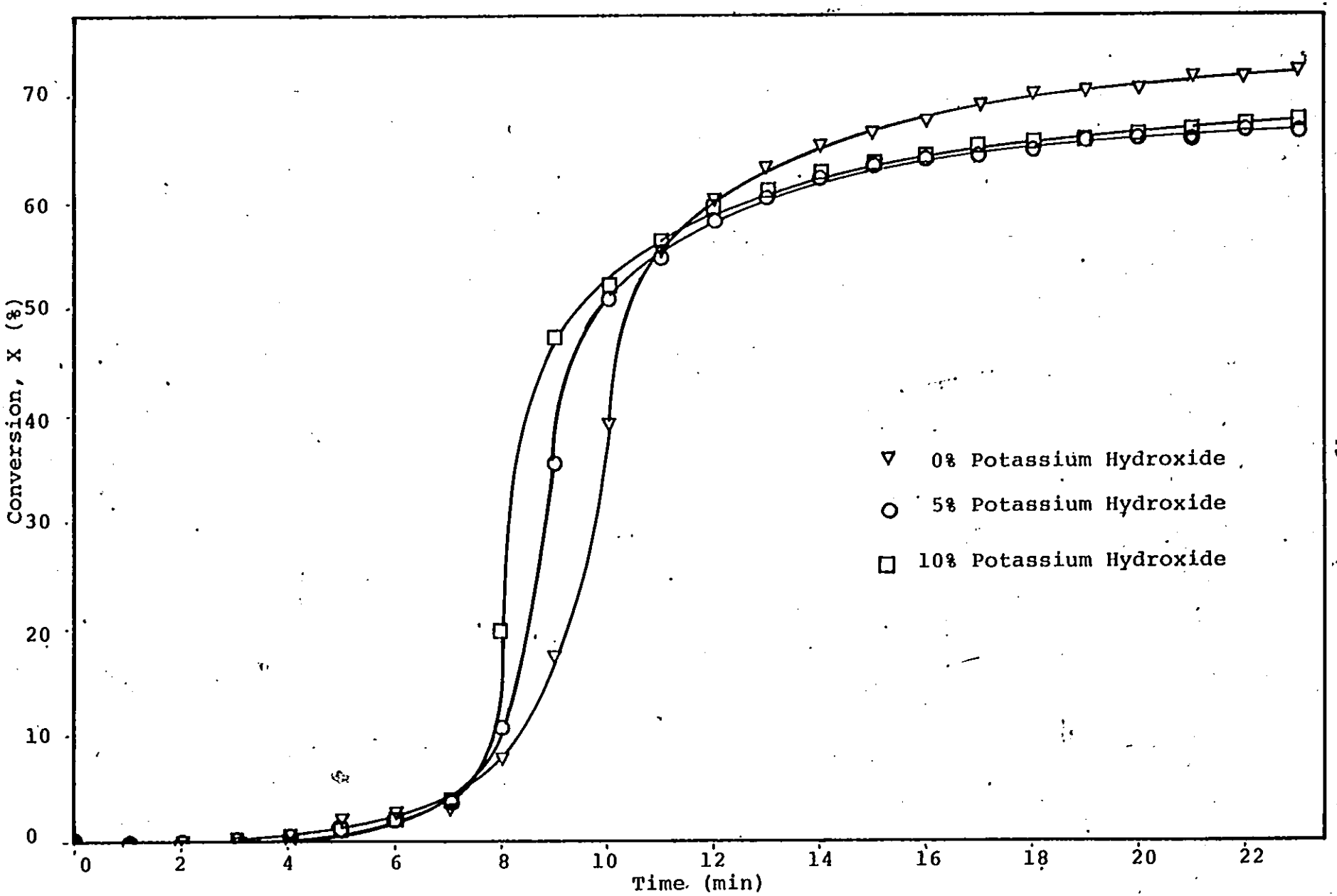

Figure 11 - The Effect on Conversion of Potassium Hydroxide at Varying Weight Percentages

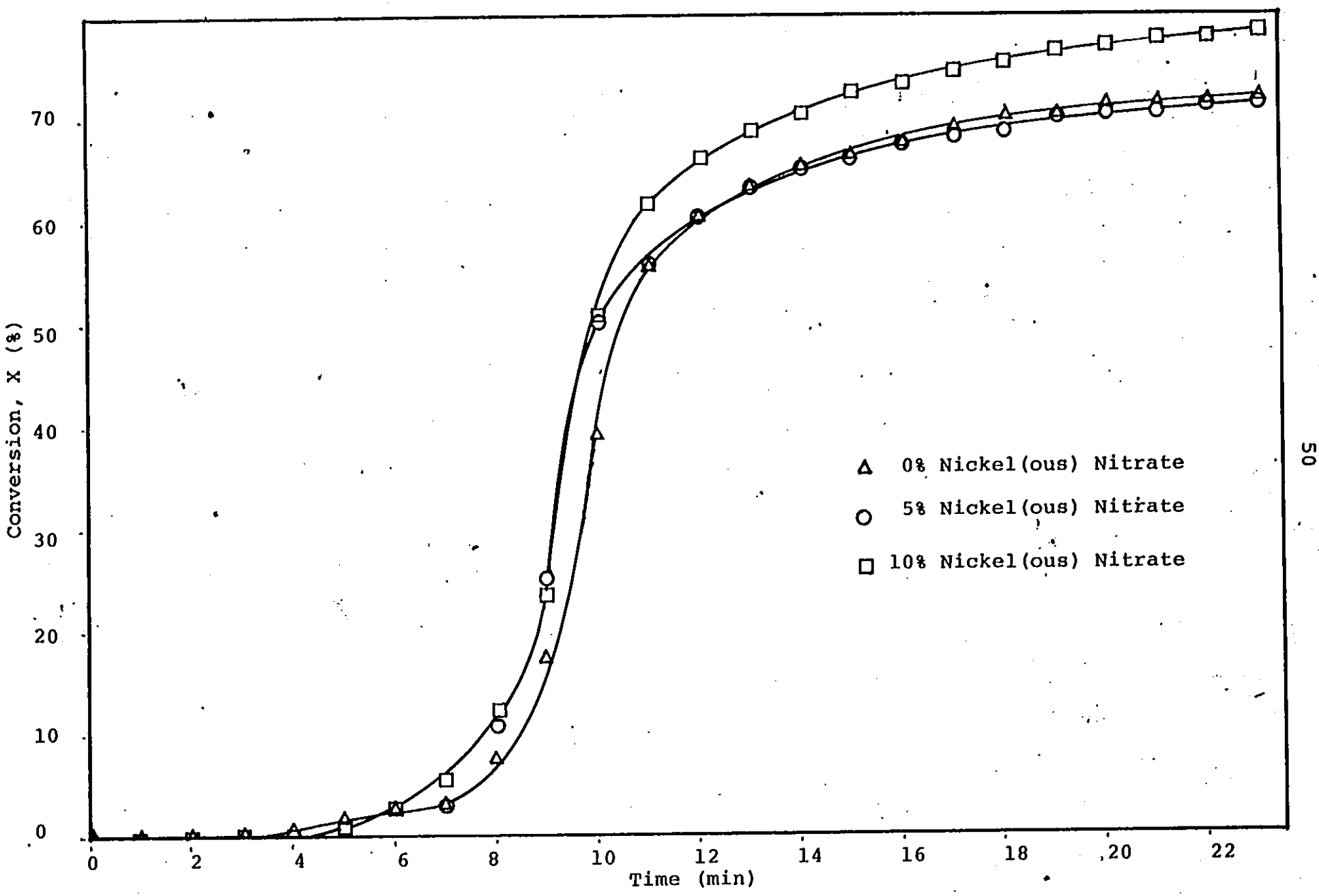

Figure 12 - The Effect on Conversion of Nickel(ous) Nitrate at Varying Weight Percentages

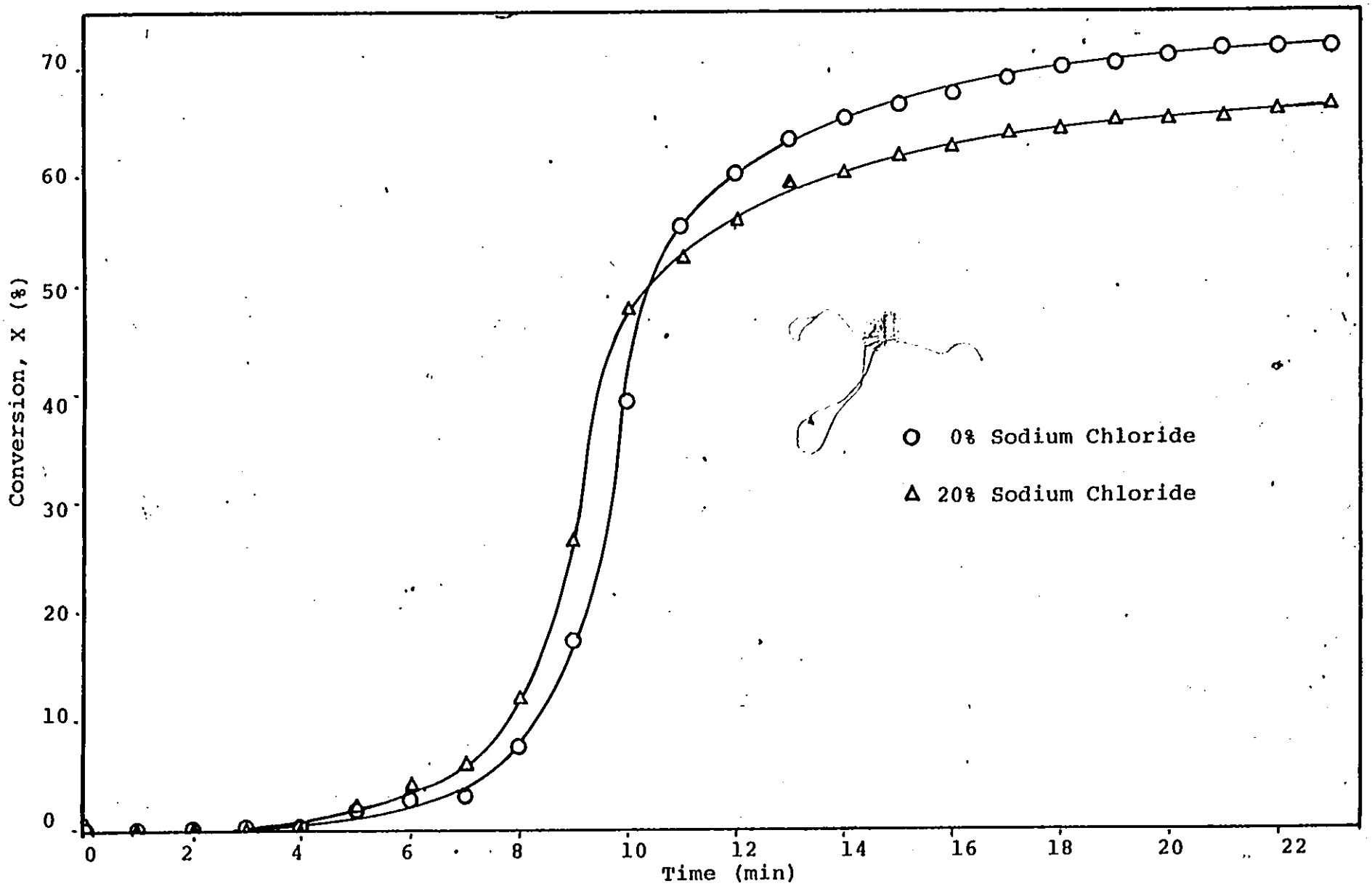

Figure 13 - The Effect on Conversion of Sodium Chloride at Varying Weight Percentages

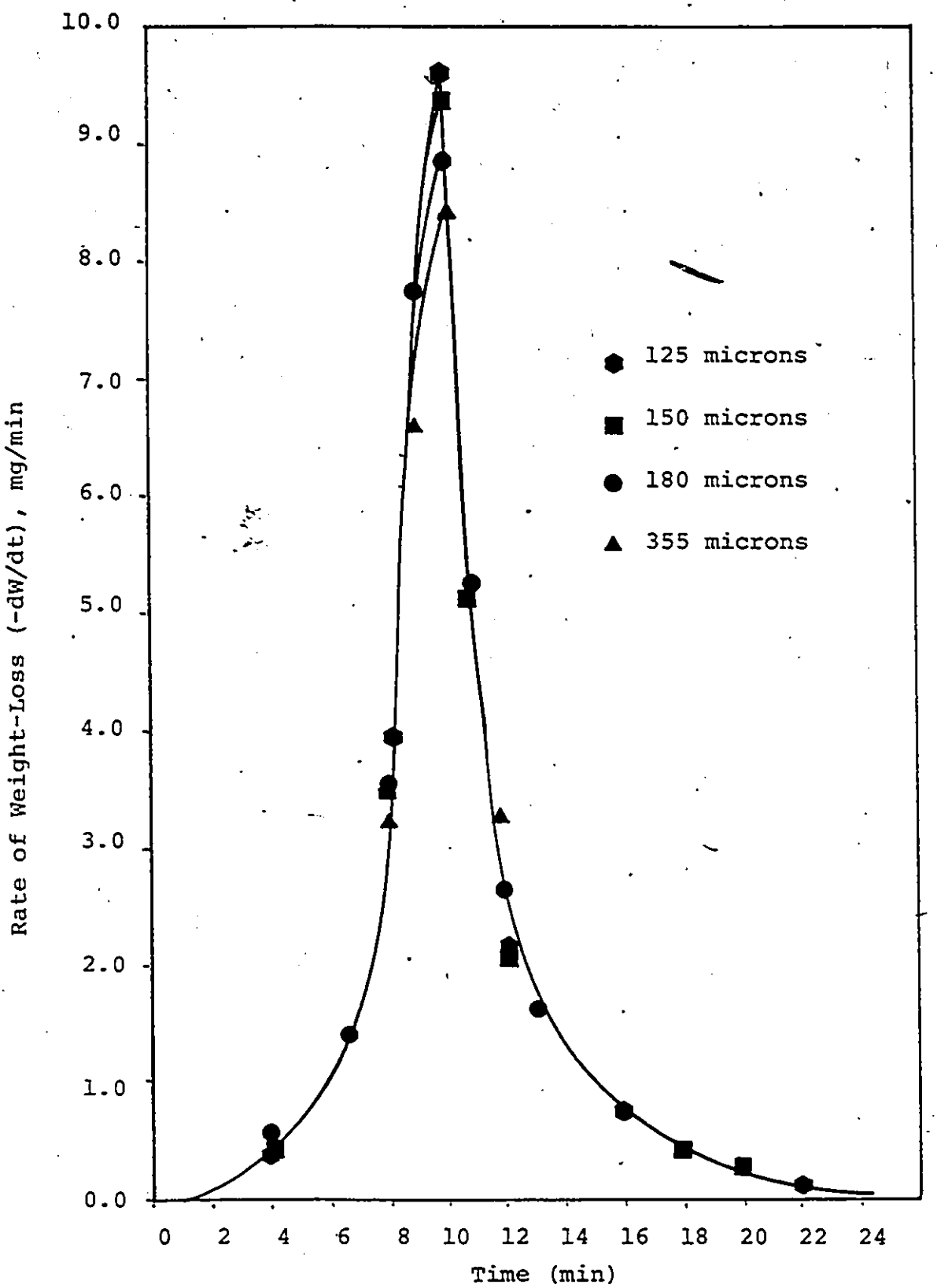

Figure 14 - Rate of Weight-loss for Various Particle Sizes of Non-catalyzed Douglas Fir Bark

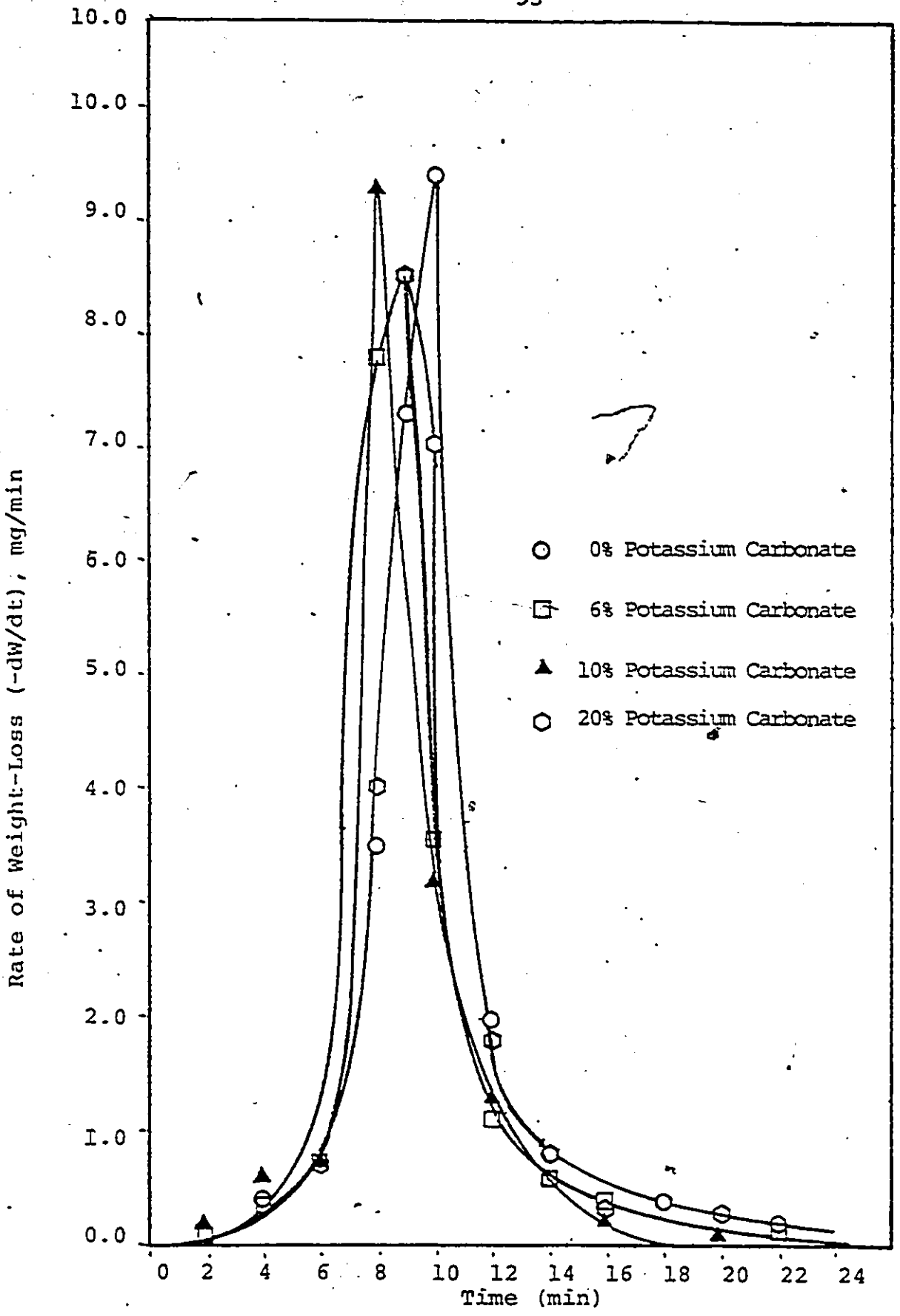

Figure 15 - Rate of Weight-loss for Catalyzed Bark at Varying Weight Percentages of Potassium Carbonate

CHAPTER V

DISCUSSION OF RESULTS

In this section, the effect of various operating variables on the pyrolysis of Douglas fir bark will be discussed. The development of a kinetic model based on the experimental data will be presented.

A. Effect of Heating Rate

Tables 6-7 and Figures 5 are the results of the effect of heating rate on the pryolysis of bark. For the lower heating rate, there was slow weight loss especially in the temperature range 220-500°C. Lower levels of conversion were obtained throughout the heating range (20-800°C) while using the lower heating rate.

These results are supported by other investigators (4, 12, 13). For slow heating rates, the decomposition occurs in an orderly manner, resulting in the formation of stable molecules. These molecules being richer in carbon converge toward the more stable hexagonal structure of graphite carbon. Hence, the reactivity of the carbon is decreased resulting in lower levels of conversion and less rapid weight loss during slow heating rate processes.

At the higher heating rate, higher temperatures were required in order to achieve a specified weight loss or level of conversion. Similar behaviour has been observed (14, 15, 16) during the decomposition of other carbonaceous material.

B. Effect of Particle Size

In this study, the particles used were in the size range from 75 to 710 microns. The data in Tables 8-16 and the plots in Figures 6 and 7 show no appreciable difference in the results obtained for any particular particle size. However, particles of 150 microns showed slightly higher levels of conversion in the latter stages of the pyrolytic reaction. Conversion of the wood bark was highest for the smallest particle size (75 microns) during the earliest phase of the pyrolysis. This trend was reversed as the reaction proceeded. It would seem likely that the smallest particle size became agglomerated particles. Because of this agglomeration, the effective particle size would be increased thus lowering the conversion.

For particles with a radius of less than 0.1 cm, the rate of pyrolysis is controlled by chemical reactions (17). This information was used to choose the particle size range used in this project. It could possibly explain the lack of any clear pattern in the results obtained.

A random selection of duplicate runs was done for some of the particle sizes. The reproducibility of the experimental data was reasonably good, since the deviation in any set of duplicate runs was less than 5%. Tables 33-36 show this trend.

C. Mass Transfer Effect

Nitrogen flow rates of 50, 80, 120, and 150 ml/min were used to study mass transfer effect on the pyrolysis of bark.

The results in Tables 17-20 and Figure 8 seem to indicate that there is little or no mass transfer effect at these flow rates. This agrees with the findings of Berkowitz (54). He reported that using activation energy as an indication of mass transfer effect, it was found that at 150 ml/min gas flow rate the effect of mass transfer is minimized.

D. Effect of Catalysts

Catalysts play a major role in conventional hydrocarbon processing, but their application to conversion of carbonaceous material to gases or liquids has not been intensively investigated except in the conversion of coal to synthetic fuels. In principle, catalysts will accelerate or retard chemical reactions, thus enabling selectivity of products in chemical processes. A literature review has shown that certain compounds acting as catalysts are capable of beneficially influencing the gasification of carbonaceous materials.

The chemical compounds used as catalysts in this project were potassium carbonate, sodium carbonate, nickel(ous) nitrate, potassium hydroxide and sodium chloride. The effectiveness of these catalysts were determined at varying concentrations (i.e. weight percentages). The results of these studies are shown in Tables 21-31 and Figures 9-13. The data reveal that in the time interval 7-12 minutes and the temperature range 270-500°C, the greatest amount of thermal decomposition or pyrolytic conversion occurred. Table 32 shows some of the results of the pyrolysis for catalyzed and non-catalyzed bark in this time period and temperature range.

Table 32

COMPARISON DATA SHOWING THE RELATIVE EFFECTIVENESS OF THE CATALYSTS

Time (min)	Type of Catalyst (% by weight)	K_2CO_3	Na_2CO_3	KOH	$Ni(NO_3)_2$	NaCL	None	Temperature (^oC)
		(% conversion						
7.0	6.0						3.0	216
	5.0	6.2	5.2	3.9	4.2			
	10.0	5.7		5.7	5.3			
	20.0	7.0	7.6			5.8		
8.0	0.0						7.5	320
	5.0	14.5	13.7	10.7	10.7			
	10.0	14.5	15.1	19.6	12.2			
	20.0	11.6	24.5			12.0		
9.0	0.0			-	-			372
	5.0	42.0	40.0	35.5	25.2		17.2	
	10.0	45.3	38.2	47.6	23.5			
	20.0	25.0	43.0	-	-	26.4		
10.0	0.0						55.4	460
	5.0	58.1	54.0	54.7	56.7			
	10.0	59.0	52.8	56.2	61.5			
	20.0	57.0	53.4			52.4		
12.0	0.0						60.2	500
	5.0	61.0	55.5	57.8	60.5			
	10.0	61.7	-	59.3	66.0			
	20.0	62.0	57.1	-		55.8		

The overall results indicate that small amounts (5% by weight) of potassium and sodium carbonates seem to be the most effective of the catalysts. However, a clear ranking of the catalyst effectiveness was not possible. Other investigators (18, 23, 24, 25, 26, 27) have confirmed the effectiveness of the alkali carbonates as excellent catalysts for the pyrolysis of biomass. Others (8, 32, 45, 55, 56) have reported that these carbonates prevent the carbon of the feedstocks from forming stable structures by various proposed mechanisms. Hence, these additives lowered the pyrolytic temperature required to continue the reaction. The data in Table 32 show that, in general, a higher temperature is required for the non-catalyzed bark to attain the same level of conversion as the catalyzed bark. Therefore, the catalysts have the effect of lowering the operating temperatures resulting in greater thermal efficiency. The catalysts greatly improve the conversion of bark to gaseous products and also increase the reaction rates.

E. Kinetic Analysis of Experimental Data

Thermogravimetric analysis (TGA) has become increasingly useful in investigations of the pyrolysis and combustion behaviour of solids. If, for example, some powdered bark is heated in an inert atmosphere at a linearly programmed (or non-linear) rate, a record of its weight as a function of time produces a curve such as that shown in Figure 16.

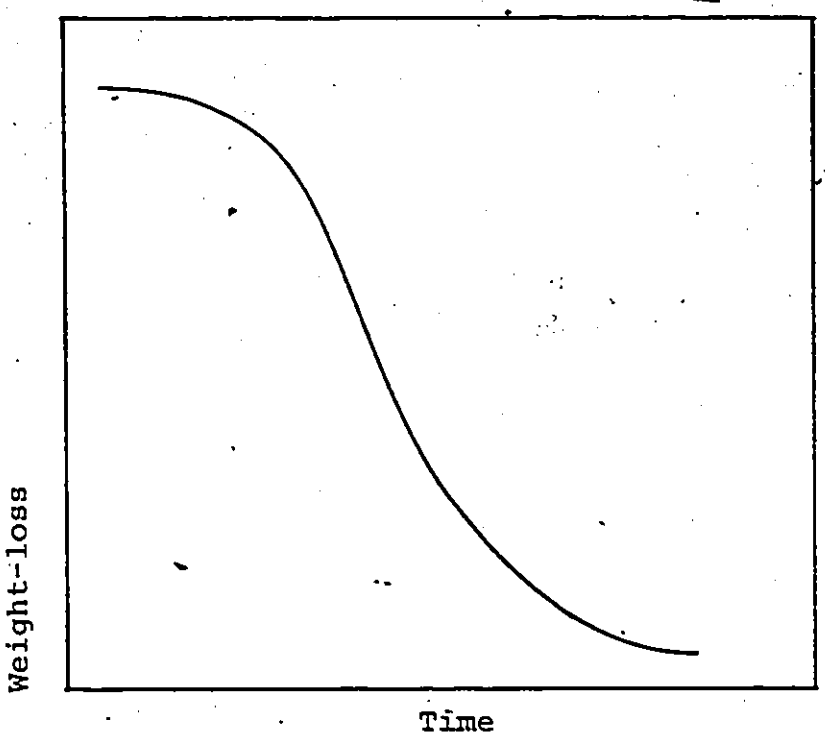

Figure 16 - Typical Thermogram of Solid Pyrolysis

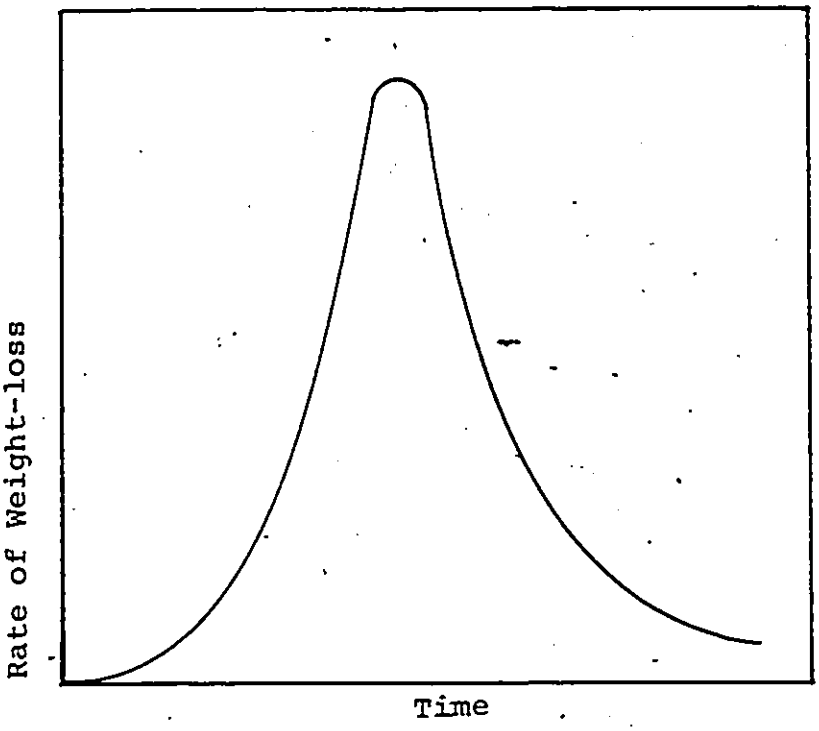

Figure 17 - Typical Rate of Weight-loss vs Time Curve for Solid Pyrolysis

These data can be utilized to determine the kinetic parameters such as activation energy and order of these reactions.

Differentiating the curve in Figure 16 gives the results shown in Figure 17. It is shown that, the decomposition occurs at a very slow rate until a critical temperature region is reached. Then the pyrolysis rate increases very rapidly to a maximum, after which, as the sample further decomposes, the rate drops even more rapidly. This behaviour is characteristic of a large number of decomposition reactions, e.g., pyrolysis, and a significant number of methods have been proposed for obtaining the kinetic parameters of such reactions from the recorded thermogram (Figure 16) or its derivative (Figure 17). The proposed models differ in their complexity and in the precision of the results which may be obtained. Hence, there have been large variations in the values of the kinetic parameters which have been determined from TG curves. Extreme caution is necessary to evaluate and interpret such results.

Model Development

From the experimental weight-loss data it was possible to determine the rate of weight-loss with increasing time (temperature). The computer program used for the calculations was DGT3 in the Scientific Subroutine Package

of IBM. Tables 6-31 are the results of the computations.

Figures 14 and 15 show plots of the rate of weight-loss versus time for the non-catalyzed and catalyzed Douglas fir bark, respectively. These curves are similar to that of Figure 17. They show that the initial pyrolysis reaction occurs at a slow rate until a critical temperature is attained. Then the rate increases very rapidly to a maximum, after this, with further decomposition, the rate drops more rapidly.

The initial weight of any sample of Douglas fir bark consists of the weights of the volatile materials and the char. In mathematical form, this can be written as

$$W_0 = W_{v0} + W_c \tag{7}$$

At any time t, the weight of the sample is

$$W = W_v + W_c \tag{8}$$

Assuming a first-order thermal decomposition of the volatile materials, then at time t

$$W_v = W_{v0}e^{-kt} \tag{9}$$

But from Arrhenius' law, the rate constant is

$$k = Ae^{-E/RT} \tag{10}$$

Hence, the weight of the sample at time t becomes

$$W = W_{v0} e^{-(Aexp-E/RT)t} + W_c \quad (11)$$

On assuming an n^{th} order reaction for the pyrolysis of the volatile materials, the weight of a sample at time t is given as

$$W^{-n+1} = W_{v0}^{-n+1} + (n-1)kt + W_c \quad (12)$$

where $n \neq$ (see Appendix C).

Equations 11 and 12 represent the two proposed models which were used to estimate the kinetic parameters from the experimental data. This was achieved by using the Box-Modified Gauss method and the computer program NONLIN from the WATFIV library (see Appendix C).

Estimation of Parameters

The literature review (3, 7, 8, 10, 16, 18) on the pyrolysis of carbonaceous materials has shown that many investigators report this process as a first or second order thermal decomposition. This would seem to indicate that for the pyrolysis of Douglas fir bark, the experimental data should be fitted to a first or second order model. Therefore, models with first, second, as well as fractional order of reaction were tried for the experimental data.

Residual analyses were done on the data for each run to determine which model gave the most adequate fit to the experimental results. Table 35 shows the values of the sum of squares of the residuals which were obtained

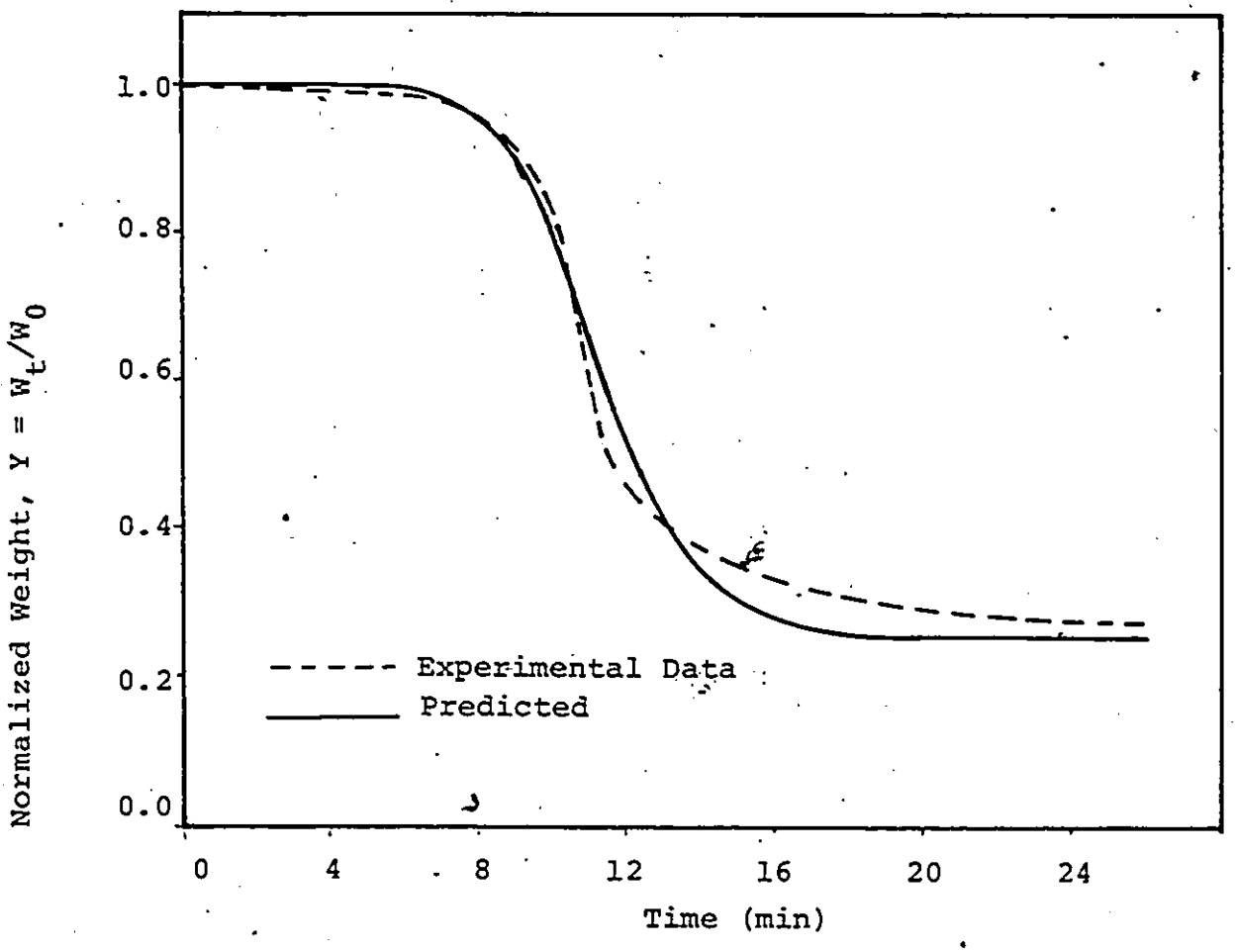

Figure 18 - Thermogram for Non-catalyzed bark pyrolysis (n=1)

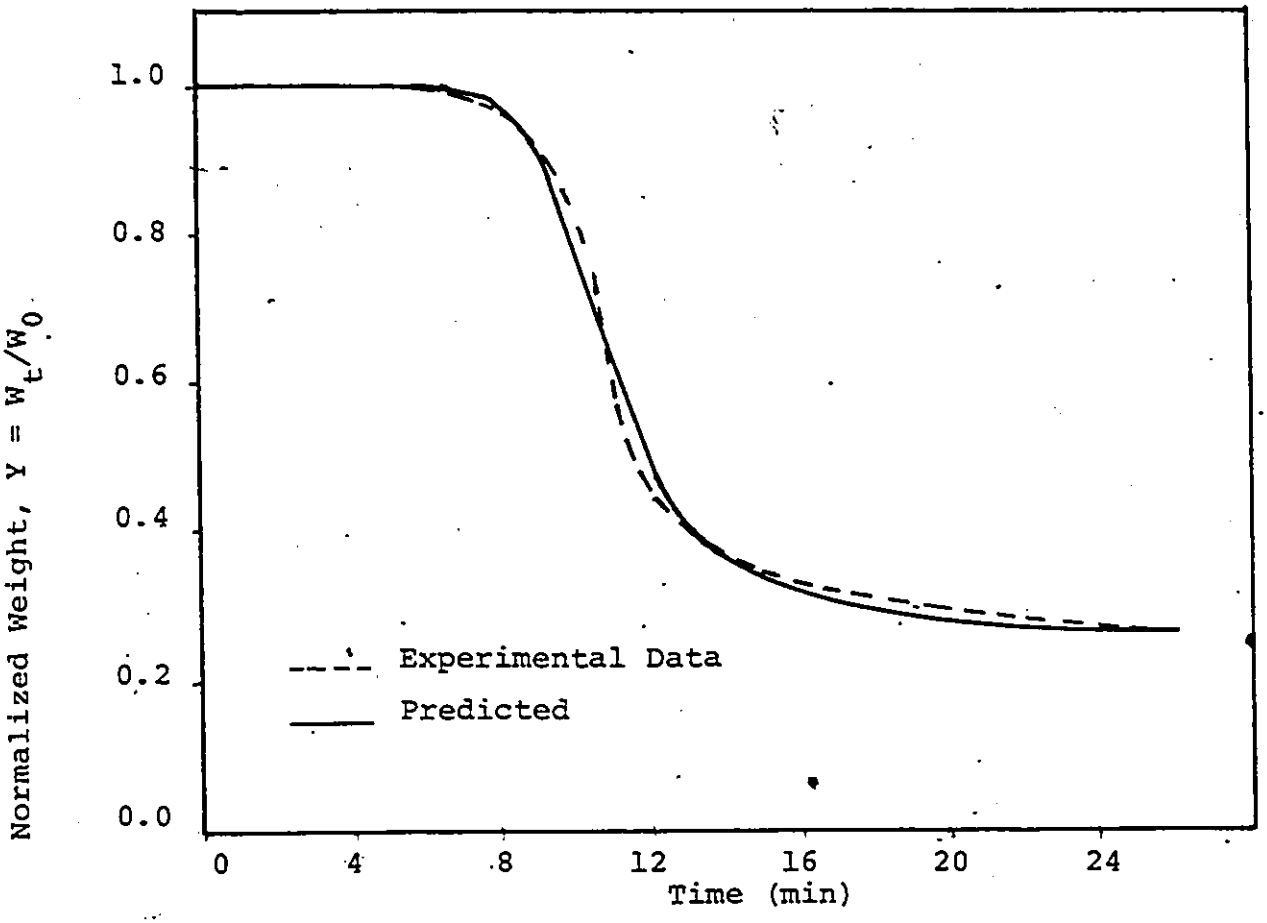

Figure 19 - Thermogram for Non-catalyzed Bark Pyrolysis (n=2)

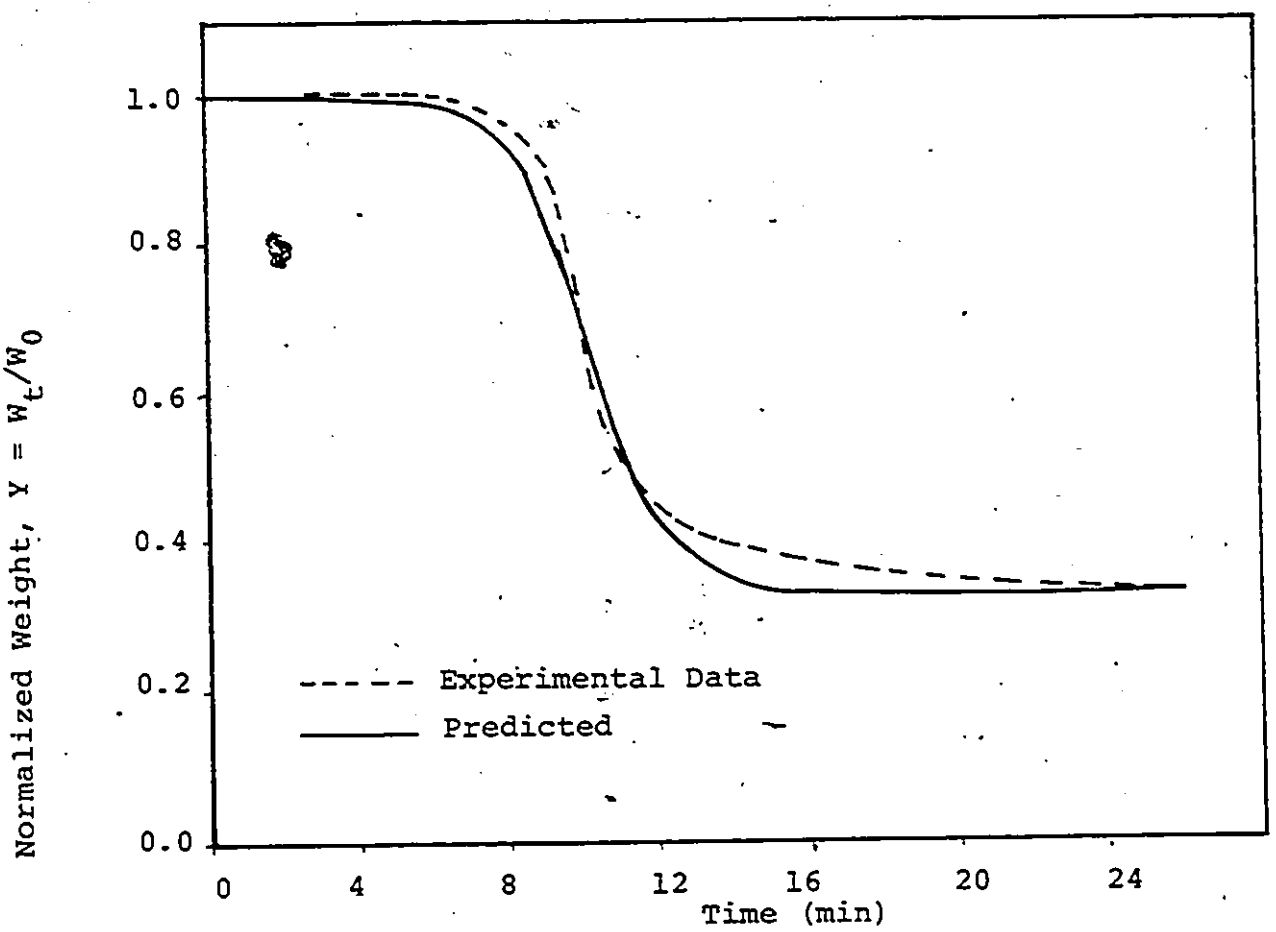

Figure 20 - Thermogram for Catalyzed Bark Pyrolysis (5% KOH); (n=1)

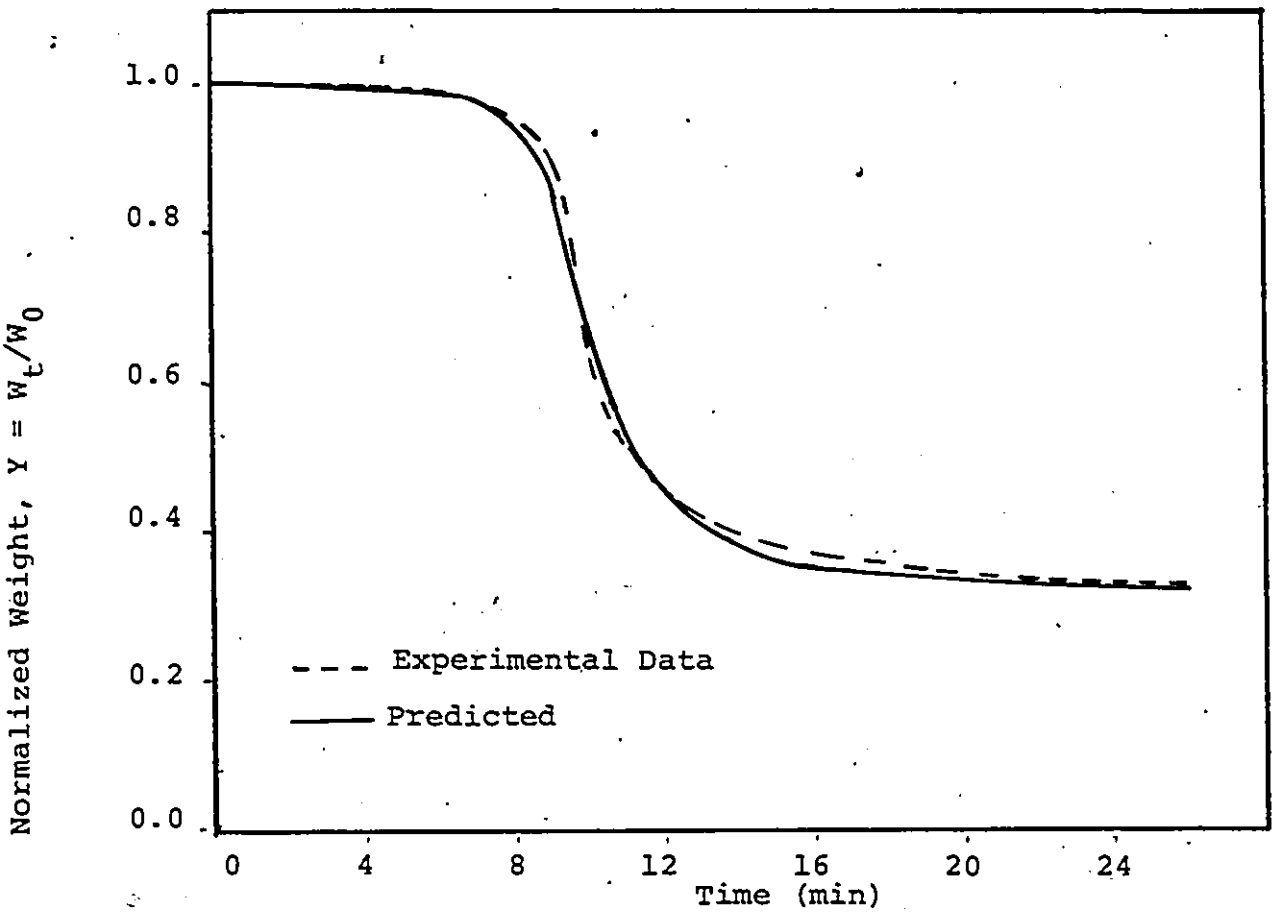

Figure 21 - Thermogram for Catalyzed Bark Pyrolysis (5% KOH); (n=2)

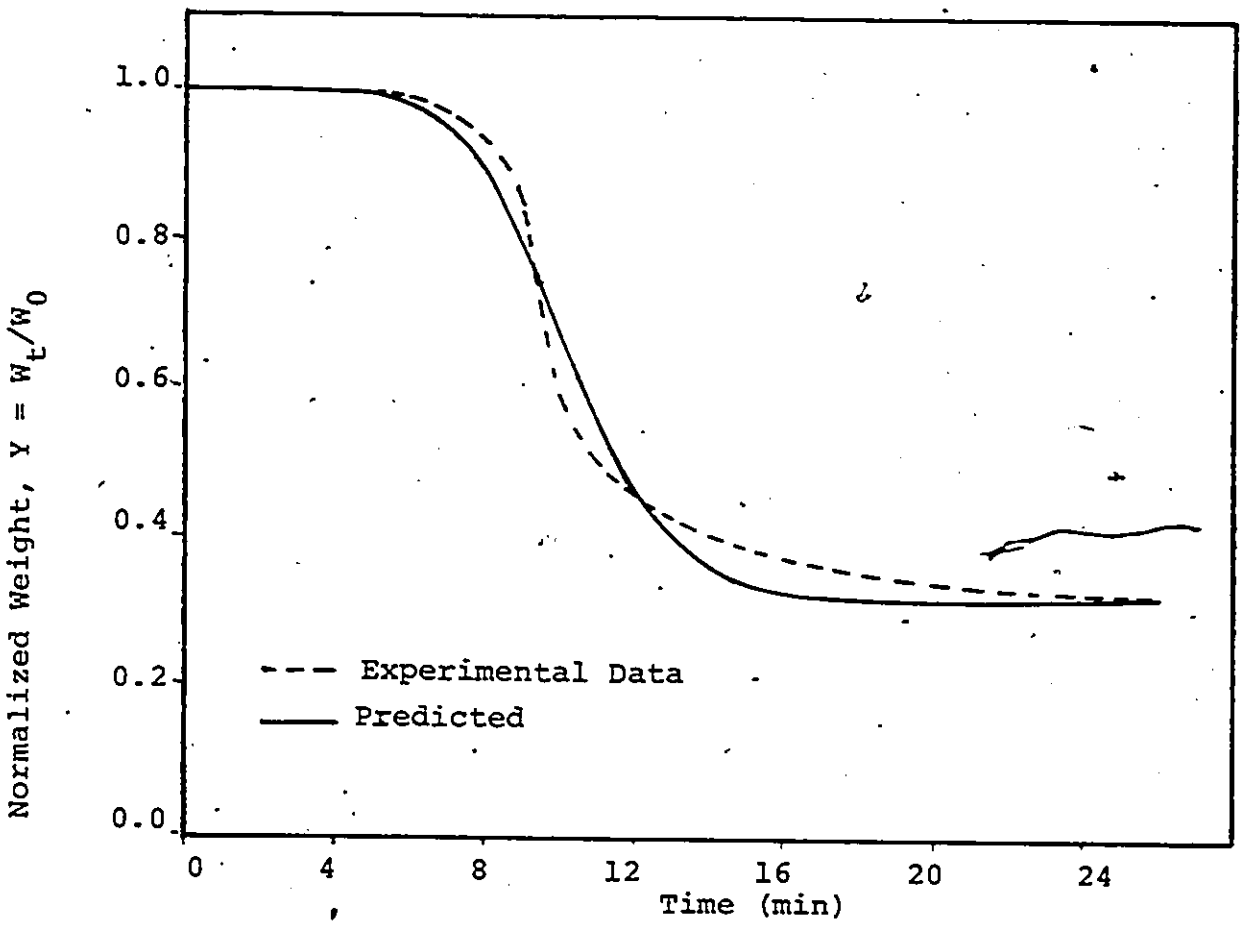

Figure 22 - Thermogram for Catalyzed Bark Pyrolysis (5% Sodium Carbonate) (n=1)

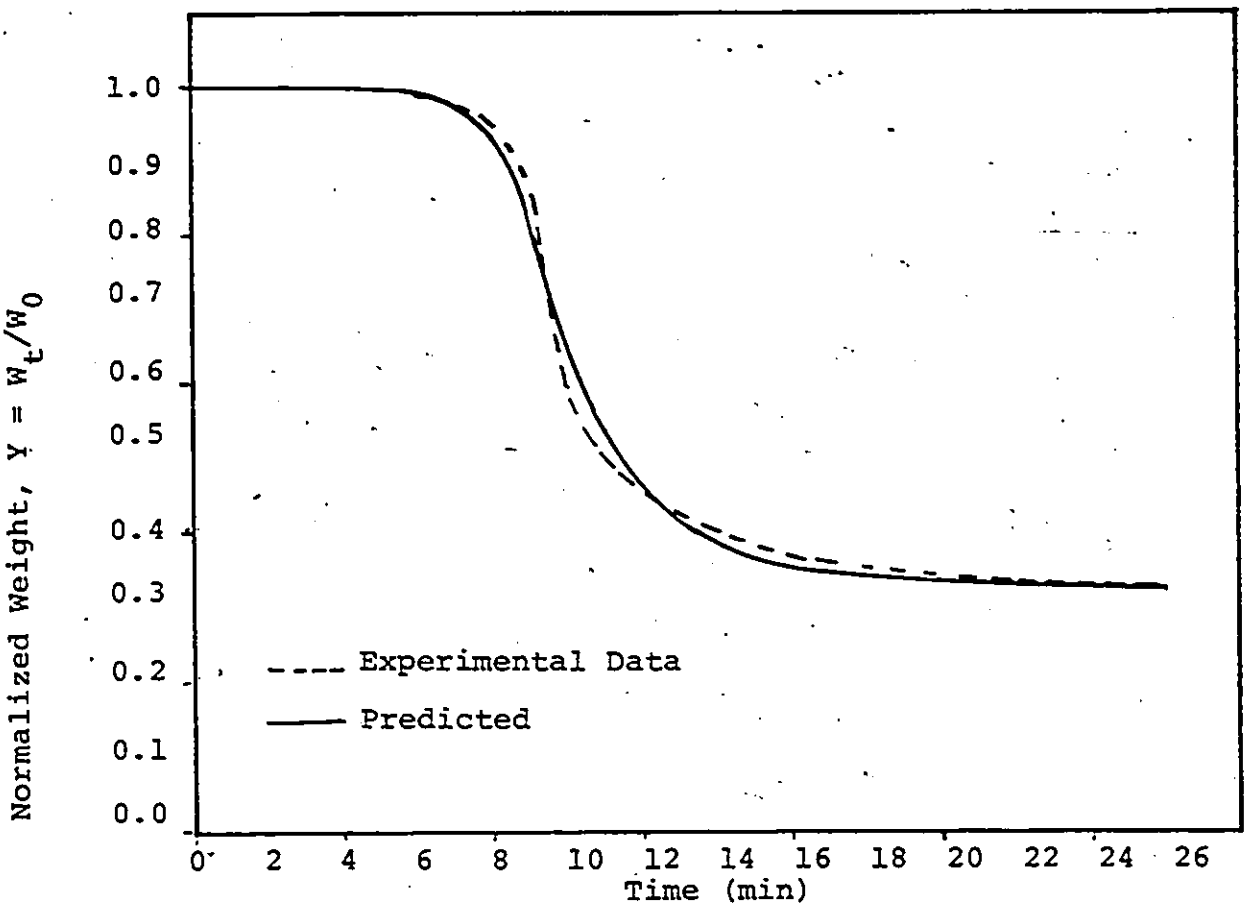

Figure 23 - Thermogram for Catalyzed Bark Pyrolysis (5% Sodium Carbonate); (n=2)

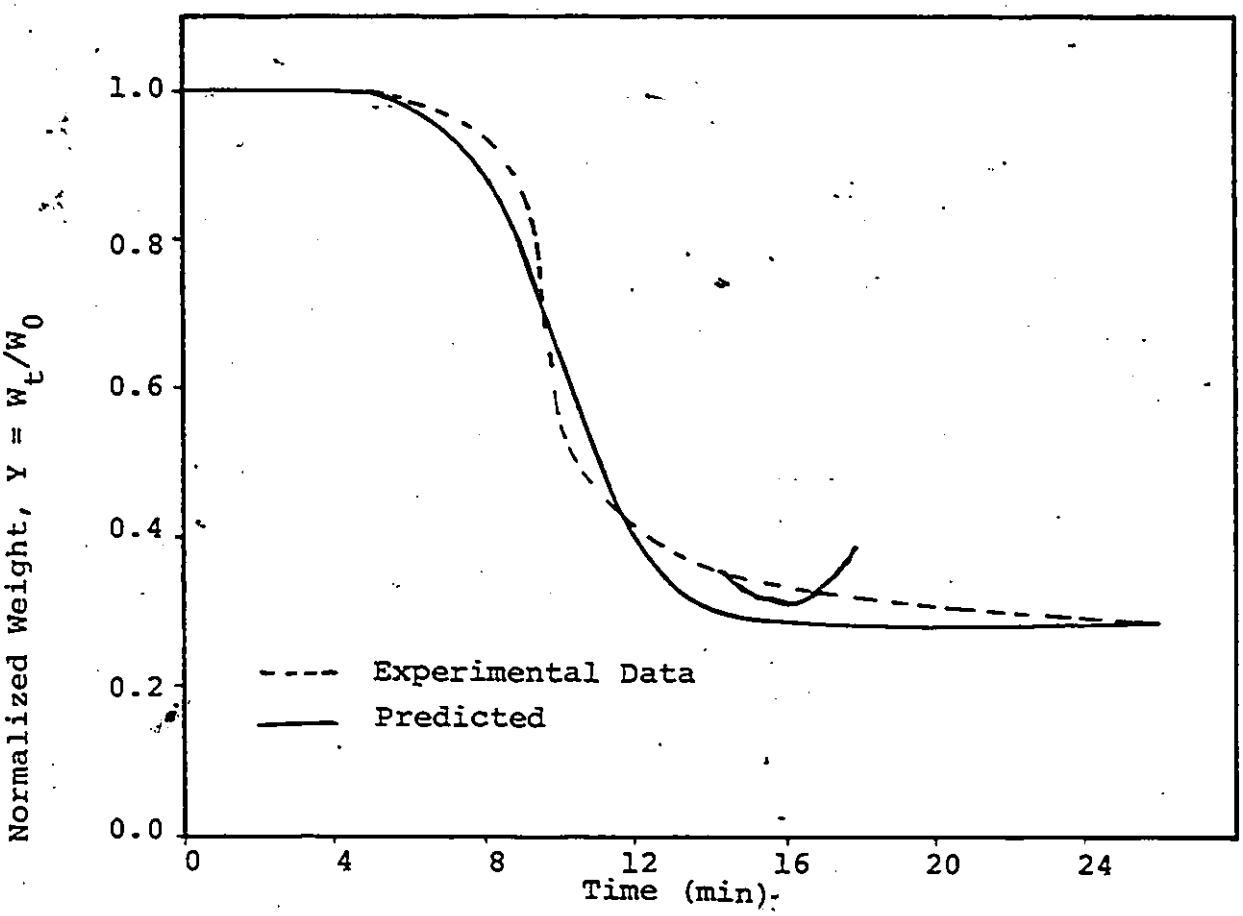

Figure 24 - Thermogram for Catalyzed Bark Pyrolysis (10% Potassium Carbonate); (n=1)

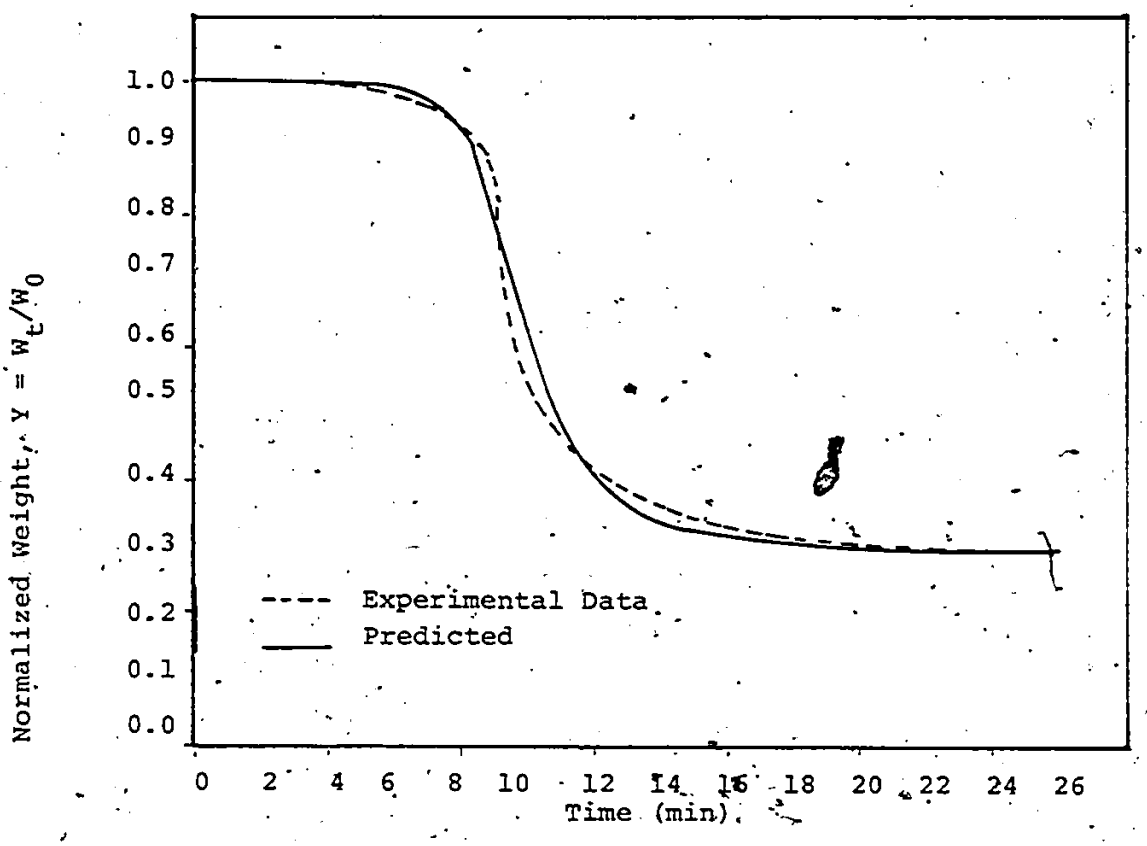

Figure 25 - Thermogram for Catalyzed Bark Pyrolysis (10% Potassium Carbonate); (n=2)

from the analyses. The results show that there is a decrease in the sum of squares of the residuals as the order of reaction is increased from one to two. Based on the trend shown in these results, it was concluded that a second order model gave the "best" fit to the experimental data. Figures 18-23 are plots of the predicted and actual values of the normalized weight (W_t/W_0) versus time for both the first and second models. These plots confirm that the second order model is a "better" fit for the data. Hence, from equation (12) with n=2, the results of this study on the pyrolysis of Douglas fir bark can be represented by the following model

$$W = \frac{W_{v0}}{1 + W_{v0}kt} + W_c \qquad (13)$$

Table A contains the kinetic parameters which were estimated from equation (13).

The value of the activation energy was found to be 15.3 kcal/gmole for the non-catalyzed bark, while for the catalyzed bark the activation energy varied from 9.0 to 15.0 kcal/gmole. The values of the activation energy were smaller for the catalyzed bark than for the non-catalyzed bark. This is to be expected since catalysts such as the alkali carbonates prevent the carbon of the sample from forming a stable structure, thereby decreasing the amount of energy required for the decomposition.

Table A

APPARENT KINETIC PARAMETERS FOR PYROLYSIS OF DOUGLAS FIR BARK FROM THE EXPERIMENTAL DATA

Sample Sample	Frequency Factor $(mgmin)^{-1}$	Activation Energy (kcal/gmole)
NON-CATALYZED	3.1×10^7	15.3
5% Na_2CO_3	0.84×10^7	12.3
22% Na_2CO_3	0.07×10^7	9.0
6% K_2CO_3	3.6×10^7	14.1
11% K_2CO_3	2.0×10^7	13.3
20% K_2CO_3	0.5×10^7	12.4
5% KOH	6.7×10^7	15.1
10% KOH	1.5×10^7	12.7
6% $Ni(NO_3)_2$	2.3×10^7	14.3
10% $Ni(NO_3)_2$	1.9×10^7	14.3

Order of reaction: n=2 for both non-catalyzed and catalyzed samples.

The frequency factor was 3.0×10^7 $(mgmin)^{-1}$ for the non-catalyzed bark and varied from 0.1×10^7 to 6.7×10^7 $(mgmin)^{-1}$ for the catalyzed bark.

The values for the activation energy and the frequency factor obtained from this study are lower than most and different from those reported in the literature (see Table 2). This is not unusual since the investigators have followed varying techniques and approaches in interpreting their TG data in order to estimate the kinetic parameters. All the investigators (cited in Table 2) except Tran have used feedstocks other than Douglas fir bark. Therefore, only the results of Tran can be compared with those of this study.

Tran (8) based his model on the assumption that the activation energy is a linear function of the conversion and that there were linear heating rates during pyrolysis of his samples. His proposed model was

$$-\frac{1}{W_0}\frac{dW}{dt} = k_0 e^{-E/RT}\left(\frac{W}{W_0}\right)^n \qquad (14)$$

In terms of conversion equation (8) becomes

$$\frac{dX}{dt} = k_0 e^{-E/RT}(1-X)^n \qquad (15)$$

Tran's results are found in Table B. They show that the activation energy is

Table B

KINETIC PARAMETERS FOR PYROLYSIS OF DOUGLAS FIR BARK FROM TRAN'S DATA

		Non-Catalyzed Bark			Catalyzed Bark	
		90% Confidence Limit			90% Confidence Limit	
		Lower	Upper		Lower	Upper
E_0 kcal/mol	24.92	24.02	24.57	24.50	23.50	25.21
a kcal/mol	34.12	33.50	34.73	20.56	18.96	22.15
k_0 min^{-1}	1.3×10^{10}	1.02×10^{10}	1.61×10^{10}	3.23×10^{10}	0.16×10^{10}	6.57×10^{10}
n order of reaction	1.0	1.67	1.35	2.0	(-5.0)	(9.0)

$$E = 24.3 + 34.1 X \text{ kcal/gmole}$$

for the non-catalyzed bark, and

$$E = 24.5 + 20.6 X \text{ kcal/gmole}$$

for the catalyzed bark. The order of reaction was one and two for the non-catalyzed and catalyzed bark, respectively.

Although the feedstock was Douglas fir bark for Tran's and this project, there are differences in the results. Tran's values for the activation energy and frequency factor are higher than those obtained in this study (refer to Tables A and B). This is to be expected since he has assumed that the activation energy is a linear function of conversion. Hence, with increasing conversion the activation energy also increases. He has also considered the total mass of the sample in the analysis of the decomposition data. In this study each sample was treated as consisting of volatile materials (about 70% by weight) and char. Tran in his analysis included the char as an integral part of the weight at any time during the pyrolysis. As time increases, the effect of char becomes more predominant because he is considering the pyrolysis rate to be proportional to the total weight of the sample. This study is based on the dependence of the pyrolysis rate on the weight of the decomposable material. This approach was taken since the kinetic rate of gaseous evolution should depend on the volatile matter.

It should be reiterated that the pyrolysis of carbonaceous materials proceeds through a complex series of consecutive and competing reactions (3), hence the estimated values of the kinetic parameters from weight-loss data have been conflicting and varied.

In conclusion, the large variations in the values of the kinetic parameters calculated from TG curves make it necessary to evaluate such results. Although TGA curves offer an extremely effective short cut to the accumulation of considerable kinetic data, they must be treated with great caution if they are not to add more confusion than enlightenment.

CHAPTER VI

CONCLUSIONS, RECOMMENDATIONS AND SUMMARY

Thermogravimetry has been used to study the effects of certain variables on the pyrolytic conversion of Douglas fir bark. In addition, a kinetic model was proposed for the pyrolysis process. The following conclusions about the pyrolysis of bark have resulted from this study:

1) Higher levels of conversion and rapid decomposition were obtained with a higher heating rate.
2) In the range 75-710 microns, conversion was not appreciably influenced by varying the particle size.
3) For nitrogen flowrates of 50 to 150 ml/min, conversion levels did not differ significantly. This would indicate an absence of mass transfer effect.
4) Catalysts such as potassium and sodium carbonates, as well as potassium hydroxide were effective in increasing the conversion and rate of decomposition of the bark.
5) For the non-catalyzed and catalyzed bark, the following kinetic model was proposed:

$$W = \frac{W_{v0}}{1 + W_{v0}kt} + W_c$$

The order of reaction, n, was found to be two for both the non-catalyzed and catalyzed bark samples.

6) TGA provides an extremely effective method of accumulating considerable amounts of reproducible kinetic data but the treatment of such data requires great caution in their interpretation.

Recommendations

These recommendations are proposed as possible guidelines for future investigations:

a) A linear temperature programmer capable of higher heating rates is required. The LTP should have a thermocouple which has been calibrated with the unit.

b) A suitable and highly sensitive unit for the continuous analysis of the product gas should be included in the apparatus. This would provide additional data for mass balance and heating value calculations.

c) The proposed model could be further refined by taking a distribution of the activation energy and then estimating the kinetic parameters. This would be a more realistic approach.

Summary

It has been estimated (Eastern Forest Products Laboratory Bulletin) that approximately six million tonnes of bark are produced each year in Canada by the wood processing industry. Less than one-half is put to any use and the balance is either incinerated or dumped as

landfill. Bark has been used as a source of energy for many years in some forest industries, e.g., in the pulp and paper industry bark is used to generate process steam and power.

The rate of depletion of petroleum and natural gas reserves plus the high costs of these fuels have resulted in greater attention being given to conversion of wood wastes (e.g., bark) to clean, convenient fuels. Pyrolysis is a useful technique for recovering energy from wood residuals and other plant materials. Substantial amounts of kinetic data will be required for the selection of the proper design and construction of reactors for pyrolysis and other conversion processes. TGA provides the tool for the treatment and interpretation of the pyrolysis data.

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APPENDICES

APPENDIX A

1. Analyses of powdered Douglas fir bark.
2. Data for temperature profiles with the LTP set at heating rates of 15°C/min and 50°C/min.

Table 3

ANALYSES OF POWDERED DOUGLAS FIR BARK

Parameter Assayed	Sample Description: 125 µm (I) Orig.	Dup.	Trip	Avg. Val.	150 µm (II) Orig.	Dup.	Trip	Avg. Val.	Specifications of Standard
Energy Equivalent of Calorimeter, Cal/^{o}C	2410	-	-	-	-	-	-	-	2402
Moisture Content of Sample (wt %)	1.4	1.6	-	1.5	0.44	0.43	-	0.44	
Cal.Val.(Wet Basis) of Sample, Cal/g	4836	4847	-	4842	5003	5005	-	5004	
Cal.Val.(Dry Basis), Cal/g	4910	4920	-	4915	5025	5027	-	5026	
Cal.Val.(Wet Basis), BTU/lb	8705	8725	-	8715	9005	9009	-	9007	
Cal.Val.(Dry Basis), BTU/lb	8838	8856	-	8847	9045	9049	-	9047	9015 9112
Elemental Analysis of Sample									
- wt% H	6.10	6.04	6.23	6.12	6.26	6.02	6.45	6.24	
- wt% C	51.97	52.41	52.30	52.22	52.28	52.22	52.04	52.18	
- wt% O	41.25	40.91	40.81	41.00	40.84	41.14	40.87	40.96	
- wt% Ash	0.68	0.64	0.66	0.66	0.62	0.62	0.64	0.62	
Elemental Analysis of Standard									
- wt%	5.28								5.26
- wt% C	63.13								63.16
- wt% O	31.59								31.58

Table 4

TEMPERATURE PROFILE DATA FOR PROGRAMMER AT 15°C/MIN

Time (min)	Programmer Temperature (°C)	Actual Temperature (°C)
0.0	20	20
1.0	35	20
2.0	50	24
3.0	65	44
4.0	80	74
5.0	95	100
6.0	110	120
7.0	125	124
8.0	140	138
9.0	155	162
10.0	170	184
11.0	185	200
12.0	200	214
13.0	215	230
14.0	230	250
15.0	245	276
16.0	260	288
17.0	275	306
18.0	290	326
19.0	305	344
20.0	320	356
21.0	335	372
22.0	350	394
23.0	365	414
24.0	380	428
25.0	395	448
26.0	410	462
27.0	425	480
28.0	440	500
29.0	455	520
30.0	470	536
31.0	485	548
32.0	500	564
33.0	515	584
34.0	530	600
35.0	545	616
36.0	560	632
37.0	575	648
38.0	590	668
39.0	605	682
40.0	620	696
41.0	635	740
42.0	650	740
43.0	665	752
44.0	680	772
45.0	695	788
46.0	710	804

Table 5

TEMPERATURE PROFILE DATA FOR PROGRAMMER AT 50°C/MIN

Time (min)	Programmer Temperature (°C)	Actual Temperature (°C)
0.0	20	20
1.0	70	30
2.0	120	40
3.0	170	76
4.0	220	120
5.0	270	168
6.0	320	216
7.0	370	268
8.0	420	320
9.0	470	372
10.0	520	420
11.0	570	460
12.0	620	500
13.0	670	540
14.0	72-	568
15.0	770	600
16.0	800	628
17.0		664
18.0		688
19.0		716
20.0		742
21.0		768
22.0		786
23.0		800
24.0		822
25.0		844

APPENDIX B

PYROLYSIS DATA

Tables 6- 7 - Heating rate effect

Tables 8-16 - Particle size effect

Tables 17-20 - Mass transfer effect

Tables 21-32 - Catalytic studies

Tables 33-36 - Replicate data for particle size effect

Table 37 - Residual analysis data

Table 6

WEIGHT-LOSS AND CONVERSION FOR BARK
AT HEATING RATE = 15°C/MIN

Particle Size:
150 microns

Flowrate Nitrogen:
150 ml/min

Time (min)	Weight (mg)	Conversion (%)	Rate of Weight-Loss -(mg/min)
0.0	50.1	0.0	0.0
1.0	50.1	0.0	0.0
2.0	50.1	0.0	0.0
3.0	50.1	0.0	0.0
4.0	50.1	0.0	0.1
5.0	49.9	0.4	0.2
6.0	49.8	0.6	0.3
7.0	49.3	1.6	0.3
8.0	49.2	1.8	0.2
9.0	49.0	2.2	0.1
10.0	49.0	2.2	0.1
11.0	48.9	2.4	0.1
12.0	48.9	2.4	0.0
13.0	48.9	2.4	0.1
14.0	48.7	2.8	0.4
15.0	48.2	3.8	0.4
16.0	48.0	4.2	0.6
17.0	47.0	6.2	1.1
18.0	45.8	8.6	1.5
19.0	44.1	12.0	1.9
20.0	42.1	16.0	2.3
21.0	39.6	21.0	3.1
22.0	36.0	28.1	4.3
23.0	31.1	38.0	4.8
24.0	26.5	47.1	3.2
25.0	24.7	50.7	1.5
26.0	23.5	53.0	1.3
27.0	22.2	55.7	1.1
28.0	21.3	57.5	0.8
29.0	20.6	59.0	0.7
30.0	19.9	60.3	0.7
31.0	19.2	61.7	0.5
32.0	19.0	62.1	0.4
33.0	18.4	63.3	0.5
34.0	18.0	64.1	0.3
35.0	17.8	64.5	0.4

Table 6 (continued)

WEIGHT-LOSS AND CONVERSION FOR BARK
AT HEATING RATE = 15°C/MIN

Particle Size:
150 microns

Flowrate Nitrogen:
150 ml/min

Time (min)	Weight (mg)	Conversion (%)	Rate of Weight-Loss -(mg/min)
36.0	17.2	65.7	0.4
37.0	17.0	66.1	0.2
38.0	16.8	66.5	0.3
39.0	16.4	67.3	0.4
40.0	16.0	68.1	0.3
41.0	15.9	68.3	0.2
42.0	15.7	68.7	0.3
43.0	15.4	69.3	0.3
44.0	15.2	69.7	0.2
45.0	15.1	70.0	0.1
46.0	15.0	70.1	0.1

Table 7

WEIGHT-LOSS AND CONVERSION FOR BARK
AT HEATING RATE = 50°C/MIN

Particle Size: 150 microns
Flowrate Nitrogen: 150 ml/min

Initial Weight: 49.3 mg
Weight Residue: 13.4 mg

Time (min)	Weight (mg)	Conversion (%)	Rate of Weight-Loss -(mg/min)
0.0	49.3	0.0	0.0
1.0	49.3	0.0	0.0
2.0	49.3	0.0	0.1
3.0	49.2	0.2	0.2
4.0	49.0	0.6	0.4
5.0	48.4	1.8	0.5
6.0	48.0	2.6	0.3
7.0	47.8	3.0	1.2
8.0	45.6	7.5	3.5
9.0	40.8	17.2	7.8
10.0	30.0	39.1	9.4
11.0	22.0	55.4	5.2
12.0	19.6	60.2	2.0
13.0	18.1	63.3	1.3
14.0	17.1	65.3	0.8
15.0	16.5	66.5	0.6
16.0	16.0	67.5	0.6
17.0	15.3	69.0	0.5
18.0	15.0	70.0	0.4
19.0	14.6	70.4	0.4
20.0	14.2	71.2	0.3
21.0	14.0	71.6	0.1
22.0	14.0	71.6	0.2
23.0	13.8	72.0	0.2
24.0	13.6	72.4	0.2
25.0	13.4	72.8	0.2

Table 8

DECOMPOSITION DATA FOR PARTICLE SIZE = 75 MICRONS.

Flowrate Nitrogen: 150 ml/min
*Heating Rate: 50°C/min

Initial Weight: 50.0 mg
Weight Residue: 17.0 mg

Time (min)	Weight (mg)	Conversion (%)	Rate of Weight-Loss -(mg/min)
0.0	50.0	0.0	0.0
1.0	50.0	0.0	0.0
2.0	50.0	0.0	0.1
3.0	50.0	0.2	0.4
4.0	49.2	1.4	0.6
5.0	48.6	2.6	0.7
6.0	47.8	4.2	2.6
7.0	43.4	13.0	5.5
8.0	36.8	26.3	6.5
9.0	30.5	39.0	4.9
10.0	27.0	46.0	3.0
11.0	24.5	51.0	2.0
12.0	23.1	53.7	1.3
13.0	22.0	56.0	1.1
14.0	21.0	58.0	0.8
15.0	20.4	59.1	0.7
16.0	19.7	60.5	0.7
17.0	19.0	62.0	0.5
18.0	18.8	62.3	0.4
19.0	18.3	63.5	0.4
20.0	18.0	64.3	0.3
21.0	17.8	64.7	0.2
22.0	17.6	65.0	0.2
23.0	17.5	65.5	0.2
24.0	17.2	65.7	0.2
25.0	17.0	66.0	0.1

* Programmer's rate

Table 9

DECOMPOSITION DATA FOR PARTICLE SIZE = 106 MICRONS

*Heating Rate: 50 °C/min
Flowrate Nitrogen: 150 ml/min

Initial Weight: 5-.2 mg
Weight Residue: 15.1 mg

Time (min)	Weight (mg)	Conversion (%)	Rate of Weight-Loss -(mg/min)
0.0	51.2	0.0	0.0
1.0	51.2	0.0	0.0
2.0	51.2	0.0	0.0
3.0	51.2	0.0	0.0
4.0	51.2	0.0	0.2
5.0	50.9	0.6	0.6
6.0	50.0	2.3	0.7
7.0	49.5	3.3	0.5
8.0	49.0	4.3	1.4
9.0	46.8	8.6	4.0
10.0	41.0	19.9	7.8
11.0	31.2	39.1	8.1
12.0	24.8	51.6	4.6
13.0	22.0	57.0	2.1
14.0	20.7	59.6	1.2
15.0	19.6	61.7	0.9
16.0	18.9	63.1	0.8
17.0	18.0	64.8	0.7
18.0	17.5	65.8	0.7
19.0	16.7	67.4	0.7
20.0	16.2	68.4	0.4
21.0	16.0	68.8	0.2
22.0	15.9	68.9	0.2
23.0	15.6	69.5	0.3
24.0	15.3	70.1	0.3
25.0	15.1	70.5	0.1

Table 10

DECOMPOSITION DATA FOR PARTICLE SIZE = 125 MICRONS

Flowrate Nitrogen: 150 ml/min
*Heating Rate: 50°C/min

Initial Weight: 53.5 mg
Weight Residue: 15.4 mg

Time (min)	Weight (mg)	Conversion (%)	Rate of Weight-Loss -(mg/min)
0.0	53.5	0.0	0.0
1.0	53.5	0.0	0.0
2.0	53.5	0.0	0.0
3.0	53.5	0.0	0.3
4.0	53.0	0.9	0.4
5.0	52.7	1.5	0.5
6.0	52.1	2.6	0.4
7.0	51.9	3.0	1.3
8.0	49.6	7.3	4.0
9.0	44.0	17.8	8.8
10.0	32.0	40.2	9.6
11.0	24.8	53.6	5.0
12.0	22.0	58.9	2.2
13.0	20.5	61.7	1.2
14.0	19.7	63.2	0.8
15.0	18.9	64.7	0.9
16.0	18.0	66.4	0.8
17.0	17.4	67.5	0.5
18.0	17.0	68.2	0.3
19.0	16.8	68.6	0.4
20.0	16.3	69.5	0.4
21.0	16.0	70.1	0.2
22.0	15.9	70.3	0.1
23.0	15.8	70.5	0.2
24.0	15.5	71.0	0.2
25.0	15.4	71.2	0.2

Table 11

DECOMPOSITION DATA FOR PARTICLE SIZE = 150 MICRONS

*Heating Rate: 50°C/min
Flowrate Nitrogen: 150 ml/min

Initial Weight: 53.1 mg
Weight Residue: 14.8 mg

Time (min)	Weight (mg)	Conversion (%)	Rate of Weight-Loss -(mg/min)
0.0	53.1	0.0	0.0
1.0	53.1	0.0	0.0
2.0	53.1	0.0	0.1
3.0	53.0	0.2	0.2
4.0	52.8	0.6	0.6
5.0	51.9	2.3	0.8
6.0	51.2	3.6	0.5
7.0	51.0	4.0	1.1
8.0	49.0	7.7	3.6
9.0	43.8	17.5	9.0
10.0	31.0	41.6	10.3
11.0	23.2	56.3	5.0
12.0	21.0	60.5	1.8
13.0	19.6	63.1	1.2
14.0	18.6	65.0	0.8
15.0	18.0	66.1	0.8
16.0	17.1	67.8	0.6
17.0	16.8	68.4	0.3
18.0	16.1	69.7	0.4
19.0	16.0	70.0	0.3
20.0	15.5	71.0	0.4
21.0	15.2	71.4	0.2
22.0	15.1	71.6	0.1
23.0	15.0	71.8	0.1
24.0	14.9	72.0	0.1
25.0	14.8	72.1	0.1

Table 12

DECOMPOSITION DATA FOR PARTICLE SIZE = 180 MICRONS

Flowrate Nitrogen: 150 ml/min
Heating Rate: 50°C/min

Initial Weight: 54.0 mg
Weight Residue: 16.0 mg

Time (min)	Weight (mg)	Conversion (%)	Rate of Weight-Loss -(mg/min)
0.0	54.0	0.0	0.0
1.0	54.0	0.0	0.0
2.0	54.0	0.0	0.0
3.0	54.0	0.0	0.1
4.0	53.8	0.4	0.6
5.0	52.8	2.2	1.0
6.0	51.9	3.9	0.8
7.0	51.2	5.2	1.4
8.0	49.2	8.9	3.6
9.0	44.1	18.3	7.8
10.0	33.7	37.6	8.9
11.0	26.4	51.1	5.3
12.0	23.2	57.0	2.7
13.0	21.1	61.0	1.6
14.0	20.0	63.0	1.0
15.0	19.2	64.4	0.7
16.0	18.7	65.4	0.6
17.0	18.0	66.7	0.6
18.0	17.6	67.4	0.4
19.0	17.2	68.1	0.3
20.0	17.0	68.5	0.2
21.0	16.8	69.0	0.1
22.0	16.8	69.0	0.3
23.0	16.2	70.0	0.4
24.0	16.0	70.4	0.1
25.0	16.0	70.4	0.1

Table 13

DECOMPOSITION DATA FOR PARTICLE SIZE = 250 MICRONS

Flowrate Nitrogen: 150 ml/min
Heating Rate: 50°C/min

Initial Weight: 50.2 mg
Weight Residue: 14.9 mg

Time (min)	Weight (mg)	Conversion (%)	Rate of Weight-Loss -(mg/min)
0.0	50.2	0.0	0.0
1.0	50.2	0.0	0.0
2.0	50.2	0.0	0.0
3.0	50.2	0.0	0.1
4.0	50.0	0.4	0.2
5.0	49.9	0.6	0.2
6.0	49.5	1.4	1.0
7.0	48.0	4.4	3.0
8.0	43.8	12.7	7.4
9.0	33.2	34.0	9.5
10.0	24.8	50.6	5.9
11.0	21.4	57.4	2.5
12.0	19.9	60.4	1.2
13.0	19.0	62.2	1.0
14.0	18.0	64.0	0.9
15.0	17.3	65.5	0.6
16.0	16.9	66.3	0.6
17.0	16.2	67.7	0.5
18.0	16.0	68.0	0.2
19.0	15.8	68.5	0.2
20.0	15.6	69.0	0.3
21.0	15.2	70.0	0.3
22.0	15.0	70.1	0.2
23.0	14.9	70.3	0.1
24.0	14.9	70.3	0.0
25.0	14.9	70.3	0.0

Table 14

DECOMPOSITION DATA FOR PARTICLE SIZE = 355 MICRONS

Flowrate Nitrogen: 150 ml/min
Heating Rate: 50°C/min

Initial Weight: 52.8 mg
Weight Residue: 16.0 mg

Time (min)	Weight (mg)	Conversion (%)	Rate of Weight-Loss -(mg/min)
0.0	52.8	0.0	0.0
1.0	52.8	0.0	0.0
2.0	52.8	0.0	0.1
3.0	52.6	0.4	0.2
4.0	52.4	0.8	0.3
5.0	52.0	1.5	0.3
6.0	51.8	1.9	0.4
7.0	51.2	3.0	1.3
8.0	49.2	6.8	3.2
9.0	44.8	15.2	6.6
10.0	36.0	31.8	8.4
11.0	28.0	47.0	6.2
12.0	23.6	55.3	3.3
13.0	21.4	59.5	1.7
14.0	20.2	61.7	1.1
15.0	19.3	63.4	0.7
16.0	18.8	64.4	0.7
17.0	18.0	65.9	0.6
18.0	17.6	66.7	0.5
19.0	17.1	67.6	0.4
20.0	16.9	68.0	0.2
21.0	16.7	68.4	0.4
22.0	16.2	69.3	0.4
23.0	16.0	69.7	0.1
24.0	16.0	69.7	0.0
25.0	16.0	69.7	0.0

Table 15

DECOMPOSITION DATA FOR PARTICLE SIZE = 500 MICRONS

Flowrate Nitrogen: 150 ml/min
*Heating Rate: 50°C/min
Initial Weight: 53.3 mg
Weight Residue: 16.1 mg

Time (min)	Weight (mg)	Conversion (%)	Rate of Weight-Loss -(mg/min)
0.0	53.3	0.0	0.0
1.0	53.3	0.0	0.0
2.0	53.3	0.0	0.0
3.0	53.3	0.0	0.1
4.0	53.1	0.4	0.2
5.0	52.9	0.8	0.3
6.0	52.5	1.5	0.7
7.0	51.5	3.4	3.8
8.0	45.0	15.6	8.3
9.0	35.0	34.3	9.0
10.0	27.0	49.3	6.1
11.0	22.8	57.2	3.0
12.0	21.1	60.4	1.4
13.0	20.0	62.5	1.0
14.0	19.2	64.0	0.7
15.0	18.6	65.0	0.6
16.0	18.0	66.2	0.5
17.0	17.6	67.0	0.5
18.0	17.1	68.0	0.3
19.0	17.0	68.1	0.2
20.0	16.8	68.5	0.3
21.0	16.5	69.0	0.3
22.0	16.2	69.6	0.2
23.0	16.2	69.6	0.1
24.0	16.1	70.0	0.1
25.0	16.1	70.0	0.1

Table 16

DECOMPOSITION DATA FOR PARTICLE SIZE = 710 MICRONS

Flowrate Nitrogen: 150 ml/min
Heating Rate: 50°C/min

Initial Weight: 52.8 mg
Weight Residue: 15.8 mg

Time (min)	Weight (mg)	Conversion (%)	Rate of Weight-Loss -(mg/min)
0.0	52.8	0.0	0.0
1.0	52.8	0.0	0.0
2.0	52.8	0.0	0.0
3.0	52.8	0.0	0.0
4.0	52.8	0.0	0.2
5.0	52.5	0.6	0.3
6.0	52.2	1.1	0.8
7.0	51.0	3.4	2.5
8.0	47.2	10.6	5.0
9.0	41.2	22.0	7.3
10.0	32.6	38.3	8.4
11.0	24.4	53.8	5.7
12.0	21.2	60.0	2.2
13.0	20.0	62.1	1.1
14.0	19.1	63.8	0.9
15.0	18.2	65.5	0.6
16.0	18.0	66.0	0.5
17.0	17.2	67.4	0.5
18.0	17.0	68.0	0.3
19.0	16.6	68.6	0.3
20.0	16.4	68.8	0.3
21.0	16.0	70.0	0.2
22.0	16.0	70.0	0.1
23.0	15.8	70.1	0.1
24.0	15.8	70.1	0.1
25.0	15.8	70.1	0.1

Table 17

CONVERSION AND WEIGHT-LOSS DATA FOR
NITROGEN FLOWRATE = 50 ml/min

Particle Size: 150 microns
*Heating Rate: 50°C/min

Initial Weight: 52.0 mg
Weight Residue: 15.0 mg

Time (min)	Weight (mg)	Conversion (%)	Rate of Weight-Loss -(mg/min)
0.0	52.0	0.0	0.0
1.0	52.0	0.0	0.0
2.0	52.0	0.0	0.0
3.0	52.0	0.0	0.1
4.0	51.9	0.2	0.4
5.0	51.2	1.5	0.5
6.0	50.9	2.1	0.5
7.0	50.3	3.3	1.9
8.0	47.2	9.2	5.2
9.0	40.0	23.1	10.1
10.0	27.0	48.1	8.5
11.0	23.0	55.8	3.1
12.0	20.9	60.0	1.7
13.0	19.6	62.3	1.1
14.0	18.8	63.8	0.8
15.0	18.0	65.4	0.7
16.0	17.4	66.5	0.5
12.0	17.0	67.3	0.6
18.0	16.3	68.7	0.5
19.0	16.0	69.2	0.2
20.0	15.9	69.4	0.2
21.0	15.6	70.0	0.3
22.0	15.3	70.6	0.2
23.0	15.2	70.8	0.2
24.0	15.0	71.2	0.1
25.0	15.0	71.2	0.1

Table 18

CONVERSION AND WEIGHT-LOSS DATA FOR
NITROGEN FLOWRATE = 80 ml/min

Particle Size: 150 microns
*Heating Rate: 50°C.min

Initial Weight: 52.0 mg
Weight Residue: 15.0 mg

Time (min)	Weight (mg)	Conversion (%)	Rate of Weight-Loss -(mg/min)
0.0	52.0	0.0	0.0
1.0	52.0	0.0	0.0
2.0	52.0	0.0	0.0
3.0	52.0	0.0	0.1
4.0	51.9	0.2	0.4
5.0	51.3	1.3	0.5
6.0	51.0	2.0	0.4
7.0	50.6	2.7	1.5
8.0	48.0	7.7	4.3
9.0	42.0	19.2	9.5
10.0	29.0	44.2	9.4
11.0	23.2	55.4	4.0
12.0	21.0	60.0	1.7
13.0	19.8	62.0	1.0
14.0	19.0	63.5	0.9
15.0	18.0	65.4	0.7
16.0	17.6	66.2	0.5
17.0	17.0	67.3	0.6
18.0	16.5	68.3	0.5
19.0	16.0	69.2	0.4
20.0	15.8	69.6	0.2
21.0	15.6	70.0	0.2
22.0	15.5	70.2	0.3
23.0	15.0	71.2	0.3
24.0	15.0	71.2	0.0
25.0	15.0	71.2	0.0

Table 19

CONVERSION AND WEIGHT-LOSS DATA FOR
NITROGEN FLOWRATE = 120 ml/min

Particle Size: 150 microns
Heating Rate: 50°C/min

Initial Weight: 52.3 mg
Weight Residue: 15.0 mg

Time (min)	Weight (mg)	Conversion (%)	Rate of Weight-Loss -(mg/min)
0.0	52.3	0.0	0.0
1.0	52.3	0.0	0.0
2.0	52.3	0.0	0.0
3.0	52.3	0.0	0.1
4.0	52.2	0.2	0.2
5.0	52.0	0.6	0.4
6.0	51.5	1.5	0.5
7.0	51.0	2.5	1.8
8.0	48.0	8.2	5.5
9.0	40.0	23.5	11.0
10.0	26.0	50.3	8.8
11.0	22.4	52.2	2.8
12.0	20.5	60.8	1.6
13.0	19.2	63.3	1.1
14.0	18.4	64.8	0.7
15.0	17.8	66.0	0.6
16.0	17.2	67.1	0.5
17.0	16.9	67.7	0.5
18.0	16.3	68.8	0.5
19.0	16.0	69.4	0.3
20.0	15.8	70.0	0.3
21.0	15.5	70.4	0.3
22.0	15.3	70.7	0.2
23.0	15.1	71.1	0.2
24.0	15.0	71.3	0.1
25.0	15.0	71.3	0.1

Table 20

CONVERSION AND WEIGHT-LOSS DATA FOR
NITROGEN FLOWRATE = 150 ml/min

Particle Size: 150 microns
*Heating Rate: 50°C/min
Flowrate Nitrogen: 150 ml/min

Initial Weight: 50.0 mg
Weight Residue: 14.0 mg

Time (min)	Weight (mg)	Conversion (%)	Rate of Weight-Loss -(mg/min)
0.0	50.0	0.0	0.0
1.0	50.0	0.0	0.0
2.0	50.0	0.0	0.1
3.0	49.2	0.4	0.5
4.0	49.4	1.2	0.5
5.0	48.9	2.2	0.4
6.0	48.6	2.8	1.4
7.0	46.1	7.8	4.7
8.0	39.2	21.6	10.3
9.0	25.5	49.0	9.0
10.0	21.2	57.6	3.2
11.0	19.2	61.6	1.6
12.0	18.0	64.0	1.1
13.0	17.1	65.8	0.8
14.0	16.5	67.0	0.6
15.0	16.0	68.0	0.5
16.0	15.5	69.0	0.5
17.0	15.0	70.0	0.3
18.0	14.9	70.2	0.1
19.0	14.8	70.4	0.2
20.0	14.5	71.0	0.3
21.0	14.3	71.4	0.2
22.0	14.2	71.6	0.2
23.0	14.0	72.0	0.1
24.0	14.0	72.0	0.0
25.0	14.0	72.0	0.0

Table 21

DATA FOR 5% POTASSIUM CARBONATE (BY WEIGHT) AS CATALYST

Particle Size: 150 microns
*Heating Rate: 50°C/min
Flowrate Nitrogen: 150 ml/min

Initial Weight: 46.3 mg
Weight Residue: 16.0 mg

Time (min)	Weight (mg)	Conversion (%)	Rate of Weight-Loss -(mg/min)
0.0	46.3	0.0	0.0
1.0	46.3	0.0	0.0
2.0	46.3	0.0	0.1
3.0	46.1	0.5	0.2
4.0	45.9	0.9	0.6
5.0	45.0	3.0	0.9
6.0	44.2	4.8	0.7
7.0	43.6	6.2	2.1
8.0	40.0	14.5	7.8
9.0	28.1	42.0	8.5
10.0	23.0	53.5	3.6
11.0	21.0	58.1	1.6
12.0	19.8	61.0	1.1
13.0	18.8	63,2	0.9
14.0	18.0	65.0	0.6
15.0	17.7	65.7	0.4
16.0	17.3	66.6	0.4
17.0	17.0	67.3	0.2
18.0	16.9	67.6	0.2
19.0	16.7	68.0	0.3
20.0	16.4	69.0	0.3
21.0	16.2	69.2	0.2
22.0	16.1	69.4	0.1
23.0	16.0	69.6	0.1
24.0	16.0	69.6	0.0
25.0	16.0	69.6	0.0

Table 22.

DATA FOR 10% POTASSIUM CARBONATE (BY WEIGHT) AS CATALYST

Particle Size: 150 microns
Heating Rate: 50°C/min
Flowrate Nitrogen: 150 ml/min

Initial Weight: 52.8 mg
Weight Residue: 19.2 mg

Time (min)	Weight (mg)	Conversion (%)	Rate of Weight-Loss -(mg/min)
0.0	52.8	0.0	0.0
1.0	52.8	0.0	0.0
2.0	52.8	0.0	0.2
3.0	52.5	0.6	0.3
4.0	52.2	1.3	0.6
5.0	51.4	3.0	0.6
6.0	51.0	3.8	0.7
7.0	50.1	5.7	2.5
8.0	46.0	14.5	9.3
9.0	31.5	45.3	9.3
10.0	27.4	54.1	3.2
11.0	25.2	59.0	1.8
12.0	23.8	61.7	1.3
13.0	22.7	64.1	1.0
14.0	21.9	65.8	0.8
15.0	21.2	67.2	0.5
16.0	21.0	67.7	0.2
17.0	20.8	68.1	0.3
18.0	20.4	69.0	0.4
19.0	20.1	69.6	0.2
20.0	20.0	70.0	0.1
21.0	19.9	70.0	0.2
22.0	19.7	70.4	0.3
23.0	19.4	71.1	0.3
24.0	19.2	71.5	0.3
25.0	19.2	71.5	0.1

Table 23

DATA FOR 20% POTASSIUM CARBONATE (BY WEIGHT) AS CATALYST

Particle Size: 150 microns
*Heating Rate: 50°C/min
Flowrate Nitrogen: 150 ml/min

Initial Weight: 54.0 mg
Weight Residue: 21.4 mg

Time (min)	Weight (mg)	Conversion (%)	Rate of Weight-Loss -(mg/min)
0.0	54.0	0.0	0.0
1.0	54.0	0.0	0.0
2.0	54.0	0.0	0.0
3.0	54.0	0.0	0.3
4.0	53.5	1.2	0.8
5.0	52.4	3.7	1.0
6.0	51.6	5.6	0.7
7.0	51.0	7.0	1.3
8.0	49.0	11.6	4.0
9.0	43.2	25.0	8.5
10.0	32.0	51.0	7.0
11.0	29.5	57.0	2.4
12.0	27.3	62.0	1.8
13.0	25.9	65.0	1.2
14.0	25.0	67.1	0.8
15.0	24.3	69.0	0.5
16.0	24.0	69.4	0.3
17.0	23.7	70.1	0.3
18.0	23.4	71.0	0.4
19.0	23.0	71.8	0.3
20.0	22.8	72.2	0.3
21.0	22.6	73.0	0.3
22.0	22.2	73.6	0.3
23.0	22.0	74.1	0.2
24.0	21.8	74.5	0.2
25.0	21.4	75.5	0.2

Table 24

DATA FOR 5% SODIUM CARBONATE (BY WEIGHT) AS CATALYST

Particle Size: 150 μm
*Heating Rate: 50°C/min
Flowrate Nitrogen: 150 ml/min

Initial Weight: 53.1 mg
Weight Residue: 19.0 mg

Time (min)	Weight (mg)	Conversion (%)	Rate of Weight-Loss - (mg/min)
0.0	53.1	0.0	0.0
1.0	53.1	0.0	0.0
2.0	53.1	0.0	0.0
3.0	53.1	0.0	0.1
4.0	53.0	0.2	0.4
5.0	52.3	1.6	0.7
6.0	51.6	3.0	0.9
7.0	50.5	5.2	2.7
8.0	46.2	13.7	8.8
9.0	33.0	40.0	9.1
10.0	28.0	50.0	3.5
11.0	26.0	53.7	1.5
12.0	25.1	55.5	1.6
13.0	22.9	60.0	1.6
14.0	22.0	61.7	0.8
15.0	21.3	63.0	0.5
16.0	21.0	63.6	0.2
17.0	20.9	63.8	0.3
18.0	20.4	64.8	0.5
19.0	20.0	65.6	0.3
20.0	19.9	65.8	0.2
21.0	19.6	66.4	0.3
22.0	19.3	67.0	0.3
23.0	19.1	67.4	0.2
24.0	19.0	67.6	0.1
25.0	19.0	67.6	0.1

Table 25

DATA FOR 10% SODIUM CARBONATE (BY WEIGHT) AS CATALYST

Particle Size: 150 microns
*Heating Rate: 50°C/min
Flowrate Nitrogen: 150 ml/min

Initial Weight: 63.0 mg
Weight Residue: 20.1 mg

Time (min)	Weight (mg)	Convention (%)	Rate of Weight-Loss -(mg/min)
0.0	53.0	0.0	0.0
1.0	53.0	0.0	0.0
2.0	53.0	0.0	0.0
3.0	53.0	0.0	0.2
4.0	52.6	0.8	0.5
5.0	52.0	2.1	0.8
6.0	51.0	4.2	0.9
7.0	50.0	7.8	2.5
8.0	45.8	15.1	7.4
9.0	34.8	38.2	7.9
10.0	30.0	48.2	3.5
11.0	27.8	52.8	3.0
12.0	26.0	56.5	1.6
13.0	24.3	60.2	1.5
14.0	23.2	62.5	0.7
15.0	23.0	63.0	0.2
16.0	22.8	63.3	0.4
17.0	22.2	64.6	0.4
18.0	22.0	65.0	0.1
19.0	22.0	65.0	0.2
20.0	21.6	66.0	0.4
21.0	21.2	67.0	0.3
22.0	21.0	67.1	0.2
23.0	20.9	67.3	0.3
24.0	20.4	68.3	0.4
25.0	20.1	69.0	0.2

Table 26

DATA FOR 20% SODIUM CARBONATE (BY WEIGHT) AS CATALYST

Particle Size: 150 microns
*Heating Rate: 50°C/min
Flowrate Nitrogen: 150 ml/min

Initial Weight: 52.3 mg
Weight Residue: 24.0 mg

Time (min)	Weight (mg)	Conversion (%)	Rate of Weight-Loss -(mg/min)
0.0	52.3	0.0	0.0
1.0	52.3	0.0	0.0
2.0	52.3	0.0	0.1
3.0	52.2	0.2	0.2
4.0	52.0	0.7	0.2
5.0	51.8	1.2	0.6
6.0	50.8	3.7	1.3
7.0	49.2	7.6	4.3
8.0	42.3	24.5	7.2
9.0	34.8	43.0	5.1
10.0	32.1	50.0	2.2
11.0	30.5	53.4	1.6
12.0	29.0	57.1	1.3
13.0	28.0	60.0	1.0
14.0	27.0	62.0	0.6
15.0	26.8	62.5	0.3
16.0	26.5	63.2	0.3
17.0	26.2	64.0	0.3
18.0	26.0	64.5	0.1
19.0	26.0	64.5	0.1
20.0	25.9	65.0	0.3
21.0	25.5	65.7	0.4
22.0	25.2	66.4	0.3
23.0	25.0	67.0	0.3
24.0	24.6	68.0	0.5
25.0	24.0	69.3	0.7

Table 27

DATA FOR 5% POTASSIUM HYDROXIDE (BY WEIGHT) AS CATALYST

Particle Size: 150 microns
*Heating Rate: 50°C/min
Flowrate Nitrogen: 150 ml/min

Initial Weight: 51.0 mg
Weight Residue: 18.6 mg

Time (min)	Weight (mg)	Conversion (%)	Rate of Weight-Loss -(mg/min)
0.0	51.0	0.0	0.0
1.0	51.0	0.0	0.0
2.0	51.0	0.0	0.0
3.0	51.0	0.0	0.1
4.0	50.9	0.2	0.4
5.0	50.3	1.4	0.5
6.0	50.0	2.1	0.6
7.0	49.1	3.9	2.1
8.0	45.8	10.7	7.7
9.0	33.8	35.5	9.7
10.0	26.4	50.8	4.7
11.0	24.5	54.7	1.7
12.0	23.0	57.8	1.3
13.0	21.9	60.1	1.0
14.0	21.0	62.0	0.7
15.0	20.5	63.0	0.5
16.0	20.1	63.7	0.3
17.0	19.9	64.2	0.3
18.0	18.6	64.8	0.3
19.0	19.3	65.4	0.3
20.0	19.0	66.0	0.2
21.0	19.0	66.0	0.1
22.0	18.8	66.4	0.1
23.0	18.8	66.4	0.1
24.0	18.6	67.0	0.1
25.0	18.6	67.0	0.1

Table 28

DATA FOR 10% POTASSIUM HYDROXIDE (BY WEIGHT) AS CATALYST

Particle Size: 150 microns
*Heating Rate: 50°C/min
Flowrate Nitrogen: 150 ml/min

Initial Weight: 51.0 mg
Weight Residue: 19.8 mg

Time (min)	Weight (mg)	Conversion (%)	Rate of Weight-Loss -(mg/min)
0.0	51.0	0.0	0.0
1.0	51.0	0.0	0.0
2.0	51.0	0.0	0.0
3.0	51.0	0.0	0.1
4.0	50.9	0.2	0.2
5.0	50.6	0.9	0.5
6.0	50.0	2.2	1.1
7.0	48.4	5.7	4.0
8.0	42.0	19.6	9.6
9.0	29.3	47.3	7.4
10.0	27.2	52.0	2.1
11.0	25.2	56.2	1.7
12.0	23.8	59.3	1.2
13.0	22.9	61.2	0.8
14.0	22.3	62.5	0.5
15.0	22.0	63.2	0.4
16.0	21.5	64.3	0.4
17.0	21.2	65.0	0.3
18.0	21.0	65.4	0.2
19.0	20.9	65.6	0.2
20.0	20.6	66.2	0.2
21.0	20.5	66.4	0.2
22.0	20.2	67.1	0.3
23.0	20.0	67.5	0.1
24.0	20.0	67.5	0.1
25.0	19.8	68.0	0.3

Table 29

DATA FOR 5.6% NICKEL(OUS) NITRATE AS CATALYST

Particle Size: 150 microns
*Heating Rate: 50°C/min
Flowrate Nitrogen: 150 ml/min

Initial Weight: 52.7 mg
Weight Residue: 15.0 mg

Time (min)	Weight (mg)	Conversion (%)	Rate of Weight-Loss -(mg/min)
0.0	52.7	0.0	0.0
1.0	52.7	0.0	0.0
2.0	52.7	0.0	0.1
3.0	52.6	0.2	0.1
4.0	52.5	0.4	0.3
5.0	52.0	1.3	0.6
6.0	51.3	2.7	0.8
7.0	50.5	4.2	2.1
8.0	47.1	10.7	5.5
9.0	39.5	25.2	10.3
10.0	26.5	50.0	8.3
11.0	23.0	56.7	2.8
12.0	21.0	60.5	1.7
13.0	19.7	63.0	1.1
14.0	18.8	64.7	0.9
15.0	18.0	66.2	0.6
16.0	17.6	67.0	0.5
17.0	17.0	68.2	0.4
18.0	16.8	68.5	0.5
19.0	16.1	70.0	0.4
20.0	16.0	70.1	0.2
21.0	15.8	70.4	0.3
22.0	15.5	71.0	0.2
23.0	15.4	71.2	0.2
24.0	15.1	71.8	0.2
25.0	15.0	72.0	0.0

Table 30

DATA FOR 10% NICKEL(OUS) NITRATE AS CATALYST

Particle Size: 150 microns
*Heating Rate: 50°C/min
Flowrate Nitrogen: 150 ml/min

Initial Weight: 52.0 mg
Weight Residue: 15.0 mg

Time (min)	Weight (mg)	Conversion (%)	Rate of Weight-Loss -(mg/min)
0.0	52.0	0.0	0.0
1.0	52.0	0.0	0.0
2.0	52.0	0.0	0.0
3.0	52.0	0.0	0.0
4.0	52.0	0.0	0.2
5.0	51.6	0.9	0.5
6.0	51.0	2.1	1.1
7.0	49.5	5.3	2.4
8.0	46.3	12.2	4.3
9.0	41.0	23.5	9.0
10.0	28.3	50.6	8.9
11.0	23.2	61.5	3.6
12.0	21.1	66.0	1.7
13.0	19.9	68.6	1.1
14.0	19.0	70.5	1.0
15.0	18.0	72.6	0.7
16.0	17.7	73.3	0.5
17.0	17.1	74.6	0.5
18.0	16.7	75.4	0.5
19.0	16.1	76.7	0.4
20.0	16.0	77.0	0.2
21.0	15.7	77.6	0.3
22.0	15.5	78.0	0.3
23.0	15.2	78.6	0.3
24.0	15.0	79.1	0.1
25.0	15.0	79.1	0.1

Table 31

DATA FOR 20% SODIUM CARBONATE (BY WEIGHT) AS CATALYST

Particle Size: 150 microns
*Heating Rate: 50°C/min
Flowrate Nitrogen: 150 ml/min

Initial Weight: 52.0 mg
Weight Residue: 24.3 mg

Time (min)	Weight (mg)	Conversion (%)	Rate of Weight-Loss -(mg/min)
0.0	52.0	0.0	0.0
1.0	52.0	0.0	0.0
2.0	52.0	0.0	0.0
3.0	52.0	0.0	0.1
4.0	51.9	0.2	0.5
5.0	51.0	2.4	0.8
6.0	50.3	4.1	0.7
7.0	49.6	5.8	1.7
8.0	47.0	12.0	4.3
9.0	41.0	26.4	7.4
10.0	32.2	47.6	5.4
11.0	30.2	52.4	1.7
12.0	28.8	55.8	1.3
13.0	27.6	59.0	0.9
14.0	27.0	60.1	0.7
15.0	26.2	62.0	0.5
16.0	26.0	62.5	0.4
17.0	25.5	63.7	0.4
18.0	25.2	64.4	0.3
19.0	25.0	65.0	0.2
20.0	24.9	65.1	0.1
21.0	24.8	65.4	0.2
22.0	24.6	66.0	0.3
23.0	24.3	66.6	0.2
24.0	24.3	66.6	0.0
25.0	24.3	66.6	0.0

Table 33

REPLICATE RUN FOR PARTICLE SIZE = 500 MICRONS

Flowrate Nitrogen: 150 ml/min
*Heating Rate: 50°C/min

Initial Weight: 50.6 mg
Weight Residue: 15.0 mg

Time (min)	Weight (mg)	Conversion (%)	Rate of Weight-Loss (mg/min)
0.0	50.6	0.0	0.0
1.0	50.6	0.0	0.0
2.0	50.6	0.0	0.0
3.0	50.6	0.0	0.3
4.0	50.1	1.0	0.5
5.0	49.6	2.0	0.4
6.0	49.3	2.6	0.9
7.0	47.9	5.3	3.1
8.0	43.1	14.8	6.5
9.0	35.0	30.8	8.1
10.0	27.0	46.6	6.5
11.0	22.0	56.5	3.5
12.0	20.0	60.5	1.5
13.0	19.0	62.5	1.0
14.0	18.0	64.4	0.8
15.0	17.4	65.6	0.5
16.0	17.0	66.4	0.5
17.0	16.5	67.4	0.5
18.0	16.0	68.4	0.4
19.0	15.8	68.8	0.1
20.0	15.6	69.2	0.1
21.0	15.3	69.8	
22.0	15.2	70.0	
23.0	15.0	70.4	
24.0	15.0	70.4	
25.0	15.0	70.4	

Table 34

REPLICATE RUN FOR PARTICLE SIZE = 150 MICRONS

Flowrate Nitrogen: 150 ml/min
*Heating Rate: 50°C/min

Initial Weight: 49.6 mg
Weight Residue: 13.0 mg

Time (min)	Weight (mg)	Conversion (%)	Rate of Weight-Loss -(mg/min)
0.0	49.6	0.0	0.0
1.0	49.6	0.0	0.0
2.0	49.6	0.0	0.1
3.0	49.4	0.4	0.4
4.0	48.9	1.4	0.8
5.0	47.8	3.0	0.7
6.0	47.4	4.2	0.8
7.0	46.2	6.9	2.9
8.0	41.8	15.7	6.9
9.0	32.4	34.7	9.5
10.0	22.9	53.8	6.3
11.0	19.9	60.0	2.5
12.0	18.0	63.7	1.4
13.0	17.1	65.5	0.8
14.0	16.5	66.7	0.8
15.0	15.6	68.5	0.7
16.0	15.0	69.8	0.4
17.0	14.8	70.2	0.5
18.0	14.0	71.8	0.5
19.0	13.9	72.0	0.2
20.0	13.7	72.4	0.2
21.0	13.6	72.6	0.2
22.0	13.4	73.0	0.2
23.0	13.2	73.4	0.2
24.0	13.0	73.8	0.1
25.0	13.0	73.8	0.0

Table 35

REPLICATE RUN FOR PARTICLE SIZE = 125 MICRONS

Flowrate Nitrogen: 150 ml/min
*Heating Rate: 50°C/min

Initial Weight: 52.0 mg
Weight Residue: 15.0 mg

Time (min)	Weight (mg)	Conversion (%)	Rate of Weight-Loss -(mg/min)
0.0	52.0	0.0	0.0
1.0	52.0	0.0	0.0
2.0	52.0	0.0	0.0
3.0	52.0	0.0	0.2
4.0	51.6	0.8	0.5
5.0	51.0	1.9	0.6
6.0	50.5	3.0	1.0
7.0	49.0	5.8	3.6
8.0	43.4	16.5	9.0
9.0	31.0	40.4	9.9
10.0	23.6	54.6	5.0
11.0	21.0	59.6	2.0
12.0	19.6	62.3	1.1
13.0	18.8	63.8	0.8
14.0	18.0	65.4	0.9
15.0	17.1	67.1	0.7
16.0	16.6	68.1	0.5
17.0	16.1	69.0	0.4
18.0	15.8	69.6	0.3
19.0	15.5	70.2	0.2
20.0	15.4	70.4	0.2
21.0	15.1	71.0	0.1
22.0	15.0	71.2	0.7
23.0	15.0	71.2	0.1
24.0	15.0	71.2	0.1
25.0	15.0	71.2	0.1

Table 36

REPLICATE RUN FOR PARTICLE SIZE = 75 MICRONS

Flowrate Nitrogen: 150 ml/min
*Heating Rate: 50°C/min

Initial Weight: 53.2 mg
Weight Residue: 19.0 mg

Time	Weight	Conversion	Rate of Weight-Loss
0.0	53.2	0.0	0.0
1.0	53.2	0.0	0.0
2.0	53.2	0.0	0.0
3.0	53.2	0.0	0.1
4.0	53.0	0.4	0.6
5.0	52.0	2.3	0.7
6.0	51.6	3.0	1.4
7.0	49.2	7.5	4.4
8.0	42.8	19.5	7.2
9.0	34.9	34.4	6.3
10.0	30.2	43.2	4.0
11.0	27.0	49.2	2.5
12.0	25.3	52.4	1.5
13.0	24.1	54.7	1.1
14.0	23.0	56.8	0.8
15.0	22.0	58.6	0.6
16.0	21.4	59.8	0.6
17.0	20.8	60.9	0.4
18.0	20.3	61.8	0.3
19.0	20.0	62.4	0.4
20.0	19.8	62.9	0.4
21.0	19.3	63.7	0.2
22.0	19.0	64.3	0.1
23.0	19.0	64.3	0.0
24.0	19.0	64.3	0.0
25.0	19.0	64.3	0.0

Table 37

RESIDUAL ANALYSIS DATA FOR VARYING ORDER OF REACTION

Order (n)	1.0	1.2	1.5	1.6	1.8	2.0
	Sum of squares of the residuals					
No Catalyst	0.28×10^{-1}	0.23×10^{-1}	0.17×10^{-1}	0.15×10^{-1}	0.12×10^{-1}	0.10×10^{-1}
5% K_2CO_3	0.22×10^{-1}	0.18×10^{-1}	0.14×10^{-1}	0.13×10^{-1}	0.11×10^{-1}	0.096×10^{-1}
10% K_2CO_3	0.32×10^{-1}	0.28×10^{-1}	0.22×10^{-1}	0.2×10^{-1}	0.17×10^{-1}	0.15×10^{-1}
20% K_2CO_3	0.32×10^{-1}	0.27×10^{-1}	0.21×10^{-1}	0.19×10^{-1}	0.17×10^{-1}	0.15×10^{-1}
5% Na_2CO_3	0.29×10^{-1}	0.28×15^{-1}	0.17×10^{-1}	0.16×10^{-1}	0.13×10^{-1}	0.11×10^{-1}
20% Na_2CO_3	0.36×10^{-1}	0.29×10^{-1}	0.2×10^{-1}	0.18×10^{-1}	0.14×10^{-1}	0.11×10^{-1}
5% KOH	0.22×10^{-1}	0.18×10^{-1}	0.13×10^{-1}	0.12×10^{-1}	0.097×10^{-1}	0.08×10^{-1}
10% KOH	0.22×10^{-1}	0.2×10^{-1}	0.2×10^{-1}	0.19×10^{-1}	0.16×10^{-1}	0.13×10^{-1}
5.6% $Ni(NO_3)_2$	0.29×10^{-1}	0.24×10^{-1}	0.17×10^{-1}	0.16×10^{-1}	0.13×10^{-1}	0.11×10^{-1}
10% $Ni(NO_3)_2$	0.32×10^{-1}	0.23×10^{-1}	0.17×10^{-1}	0.15×10^{-1}	0.12×10^{-1}	0.11×10^{-1}

APPENDIX C

1. Derivation for n^{th} Order Reaction
2. Programs used for computations
   a) program used to obtain conversion and rate of weight-loss data
   b) program used for estimating the kinetic parameters from the proposed model with n=2
   c) computation of the kinetic parameters (A and E) using the program NONLIN.

Derivation for n^{th} Order Reaction

Consider an n^{th} order reaction for the rate of weight-loss of a sample of bark, then

$$-\frac{dW}{dt} = kW^n$$

$$-\frac{dW}{W^n} = k\,dt$$

$$-\frac{W^{-n+1}}{-n+1}\Bigg|_{W_0}^{W_t} = kt$$

$$W_t^{-n+1} - W_0^{-n+1} = (n-1)kt$$

$$\therefore W_t^{-n+1} = W_0^{-n+1} + (n-1)kt$$

Valid for $n \neq 1$ and n where

$$k = Ae^{-E/RT}$$

a) Program used to obtain conversion and rate of weight-loss data for catalyzed and non-catalyzed bark

FORTRAN IV G LEVEL 21

```
1           DIMENSION W(100),TEMP(100),TIME(100),
            Z(100),X(100),ZZ(100)
2     5     CONTINUE
3           READ(5,100) J,W0,RH,DP,CATP
4           WRITE(6,203) J,W0,RH,CATP
5     203   FORMAT(/23X,'NO OF OBS=',13,5X,'INITIAL WEIGHT=',
            F5,2,5X,'HEATING RATE='F5,2,5X,'CATALYST.
            PERC*',F5.2)
6           NDIM=J
7     101   FORMAT(20F4,1)
8           READ(5,101)(W(I),I=1,J)
9           WCAT=(CATP*W0/100.
10          DO 6 T=1,J
11          X(I)=(W0=W(I))/(W0=WCAT)*100
12          TIME(I)=1.*I=1.
13          IF(I,GE,17) GO TO 7
14          TEMP(I)=20.+(I=1)*RH
15          GO TO 6
16    7     TEMP(I)=800.
17    6     CONTINUE
18          CALL DGT3(TIME, W,Z,NDIM,IER)
19          WRITE(6,33) IER
20          WRITE(6,204) DP
21    204   FORMAT(50X,'PART. SIZE',F6.2)
22          WRITE(6,201)
23    33    FORMAT(//50X'IER='13)
24    201   FORMAT(/15X'TIME',10X,'W',15X,'TEMP',15X,
            'Z',12X,'X')
25          WRITE(6,202) (TIME(I),W(I),TEMP(I),
            TEMP(I),Z(I),X(I),I=1,J)
26    202   FORMAT(//2X,5F15.4)
27          GO TO 5
28    100   FORMAT(I2,4F10.4)
29          STOP
30          END
```

b) Program used for estimating the kinetic parameters

```
     *JOB  SF339372,NIDHI,PAGES=50,TIME=500
1          DIMENSION X(2,420),Y(100),THETA(10),FMT(20),MT(300
2          COMMON/DATA/X,Y,THETA,MITER,IWRITE,EPS,LAMBDA
3          COMMON/DIM/ NVAR,NPAR,NDATA,NVND,NPNP,NPND
4          COMMON/WEIGHT/W(100),IWATE
5          COMMON TITLE(20)
6          COMMON/COMF/A,B,WR
7          REAL*4 LAMBDA
8     1    FORMAT(20A4)
9     2    FORMAT(4F10.4)
10         READ(5,1) TITLE
11         NPAR=2
12         NVAR=2
13         EPS=0.0
14         IWRITE=0
15         MITER=0
16         LAMBDA=0.
17         IWATE=0
18         J=26
19    77   READ(5,2) (THETA(I),I=1,NPAR)
20         READ(5,9)(MT(I),I=1,J)
21    9    FORMAT(26I3)
22    12   FORMAT(20F4.1)
23         NDATA=J
24         DO 3 I=1,J
25         X(1,I)=(I-1)*1./60.
26    3    CONTINUE
27         DO 4 I=1,J
28         TB=700.
29         MT(I)=MT(I)+273.
30         X(2,I)=(MT(I)-TB)/MT(I)
31    4    CONTINUE
32    70   READ(5,21)W0,WR,PER,CA,TA,LY,ST
33    21   FORMAT(3F4.3,4A4)
34         WRITE(6,126) W0,WR,PER,CA,TA,LY,ST
35    126  FORMAT(/50X,2E12.3,5X,F10.2,4A4)
36         WCAT=W0*PER/100.
37         W0=W0=WCAT
38         READ(5,12)(Y(I),I=1,J)
39         DO 15 I=1,J
40         Y(I)=Y(I)-WCAT
41         Y(I)=Y(I)/WC
42    15   CONTINUE
43         WR=WR-WCAT
```

```
      WR=WR/WO
      A=1.-WR
      CALL NONLIN(1)
      A2=THETA(1)*EXP(THETA(2))
      E1=THETA(2)*TB
      WRITE(6,127) A2,E1
127   FORMAT(//50X,'A1=',E12.3,5X,'E1=',E12.3)
      GO TO 70
      RETURN
      END
      SUBROUTINE DERIV(Z,THETA,X,P,DELT,TPD,D)
      COMMON/DIM/ NVAR,NPAR,NDATA, NVND,NPNP,NPND
      COMMON/WEIGHT/W(100),IWATE
      COMMON/COMP/A,B,WR
      DIMENSION Z(NVND),D(NPND),X(NVAR),P(NPAR),
     THETA(NPAR),DELT(NPAR)
      DIMENSION TFD(NPAR)
      M1=-NVAR
      M3=-NPAR
      DO 100 KK=1,NDATA
      M1=M1+NVAR
      M3=M3+NPAR
      DO 101 J=1,NVAR
      M2=M1+J
      X(J)=Z(M2)
101   CONTINUE
      AA=EXP(THETA(2)*X(2))
      A1=1.+A*X(1)*THETA(1)*AA
      P(1)=-A*X(1)*AA/A1/A1 *A
      P(2)=P(1)*THETA(1)*X(2)
      DO 132J=1,NPAR
      N4=M3+J
      D(M4)=P(J)*W(KK)
132   CONTINUE
100   CONTINUE
      RETURN
      END
      SUBROUTINE RESID (Z,THETA,Y,NOP,X,DELY,SS)
      COMMON/WEIGHT/W(100),IWATE
      COMMON/DIM/ NVAR,NPAR,NDATA,NVND,NPNP,NP
      COMMON/COMP/A,B,WR
      DIMENSION Z(NVND),Y(NDATA),DELY(NDATA),
     THETA(NPAR),X(NVAR)
      FORMAT(5X,I5,5X,3E20.5)
      FORMAT('1',20X,'RESIDUAL ANALYSIS',/,6X,'RUN
     NUMBER',13X,'PREDIC',
     112X, 'ACTUAL',13X,'RESIDUAL',/)
      IF(NDP.EQ.3) WRITE(6,2)
      M1=NVAR
      SS=0.
```

```
90          DD 100 I=1,NDATA
91          IF(IWATE.EQ.0) W(I)=1.0
92          M1=M1+NVAR
93          DO 101 J=1,NVAR
94          M2=M1+J
95          N(J)=Z(M2)
96    101   CONTINUE
97          F=WR+1./(A*X(1)*THETA(1)*EXP(THETA(2)*X(2))+1.) *A
98          DELY(I)=Y(I)-F
99          IF(NOP.EQ.3) WRITE(6,1)(,F,Y(I),DELY(I)
100         DELY(I)=DELY(I)*W(I)
101         SS=SS+(DELY(I)**2)
102   100   CONTINUE
103         RETURN
104         END
```

c) Computation of the kinetic parameters (A and E) using NONLIN

In order to calculate the kinetic parameters (A and E) the program NONLIN was used. This program incorporated the use of the Box-Modified Gauss method of parameter estimation. It computes two parameters θ_1 and θ_2, from which A and E were evaluated.

From the proposed kinetic model one can define a function (F) for the predicted weight of the sample (at any time) in terms of time, temperature, the actual weight, θ_1 and θ_2. Mathematically this can be written as:

$$F = f(\theta_1, \theta_2, \text{time, temp, actual weight})$$

In the computer program the function is given as:

$$F = W_r + \frac{1}{A\,[A \times (1)\theta_1,\ e^{\theta_2 \times (2)} + 1]}$$

Initial values of θ_1, and θ_2 were given to NONLIN to calculate the predicted value for F. This value for F was then compared to the actual weight as measured during the experiment. The sum of squares (SS) were calculated and compared to E (0.001). The iteration was terminated, if SS is less than or equal to E. If SS was greater than (or not equal to) E, new estimates of the θ's were calculated from using the term lambda specified in the NONLIN program. This iteration is repeated until convergence occurs for the SS and the θ's.

The final values for θ_1, and θ_2 were then used to calculate A and E: where $A = \theta_1\ e^{\theta_2}$

and $E = \theta_2\ T_B$

APPENDIX D

This section offers a brief discussion of some of the problems encountered in this study. Some of the limitations of the TG technique used will also be presented.

The major problems associated with this project were related to the experimental set-up. The solution of these problems brought this study to completion.

Experimental problems - these included:

(a) ordering and obtaining a linear temperature programmer (LTP) from a supplier in the United States. It took one-and-a-half years for the order to filled.

(b) the LTP did not function as the manufacturers specified. The programmed heating rates were non-linear. This necessitated calibrating the instrument with a standard type K thermocouple. It is recommended that attempts be made to calibrate any LTP and thermocouple in an experimental set-up.

(c) selecting a suitable material for the hangwire and the sample bucket. Initially, the hangwire was platinum but it did not hang vertically due to coiling. Other matarials, such as stainless steel, were also tried but they also proved inadequate. Finally quartz was chosen and another obstacle was overcome.

(d) installing a small potentiometer between the TGB and the analog recorder, so that both instruments could be calibrated simultaneously. This was very important since all the data to be collected were to be printed on the strip chart of the recorder.

These are just some of the many experimental difficulties which occurred in this study.

Limitations of the technique:

It must be emphasized that the TG technique used in this study is one of several methods used to generate data from which kinetic parameters can be estimated. However, these kinetic parameters estimated from the data are pertinent to only the particular set of experimental conditions. Hence, such parameters should not be regarded as "universal" but as apparent constants estimated from a set of experimental data.

The other limitations involve:

(a) the actual temperature of the sample could not be accurately monitored during the pyrolytic decomposition. The thermocouple would have to be placed in the sample (and in the bucket). This was physically impossible.

(b) there is some time lag between the temperature of the sample and the inert medium during increased heating. The lag would be greater when using high heating rates.

Regardless of the limitations of the technique, TGA does generate considerable data which could indicate the values of some kinetic parameters relative to the set of experimental conditions.