LOW TEMPERATURE PYROLYSIS OF

WOOD WASTE MATERIALS

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SUMMARY

The pyrolysis of jack pine bark, jack pine sawdust, and cellulose powder has been studied by thermogravimetric (TG), and isothermal weight-loss methods in both inert and oxidizing atmospheres. The effects of particle size, solvent extraction, and a number of additives on the low temperature pyrolysis of jack pine bark have also been examined.

Samples were analysed by low-temperature gas adsorption and the bark characterized by infrared spectroscopy. Residues were analysed for CHN contents and structural changes which occurred on heating were examined by scanning electron microscopy.

The TG characteristics of bark were affected only slightly by particle size, solvent extraction, and additives. Isothermal decomposition data for bark and sawdust were similar and closely resembled established kinetic expressions associated with inorganic decomposition reactions controlled by diffusion processes. The data for cellulose were described by at least two kinetic stages with the second or principal region resembling a standard kinetic expression for a phase-boundary controlled reaction.

The pyrolysis data were found to fit a reaction rate compensation curve, often associated with oxidation processes but more generally with heterogeneous catalytic reactions.

The compensation curve also relates the kinetic parameters found by other workers for a large variety of wood-derived materials.

1. OBJECTIVES OF THE PRESENT STUDY

The objectives of the present study were to observe the nature of the kinetics of pyrolysis, to examine the effects of heat treatment on the products of pyrolysis, and to observe the effects of selected additives on the pyrolysis of wood waste materials. The main emphasis was placed upon the bark and sawdust of jack pine, Pinus banksianna, Lamb, which is extensively used by the forest products industry in Northern Ontario. Cellulose, the main constituent of wood wastes, was considered separately for comparison.

1.1. Note on units

The units and symbols adopted in this thesis are those most currently in use throughout the North American Continent by practising workers in this field as well as the professional, technological and scientific journals which deal with and record reports on work of this nature. Although the use of units from the S. I. system entirely would have had many obvious advantages, it was felt necessary to abide with the present practice specifically of the sponsors of the project and generally of the Canadian applied science community.

2. INTRODUCTION

2.1. Prologue

The direct combustion of wood was probably one of the first sources of energy discovered by man. Much later, the dry distillation of wood was a source of a number of useful products in early periods of industrialization. Wood as a raw material has since been replaced by coal and petroleum.

Due to the increasing price of fossil fuels in recent years, wood, a renewable resource, is presently receiving considerable attention as an alternative source of chemicals and energy. The value of wood wastes as a source of fuels was recognized as early as 1929: "The development of a practical and economic means of converting wood waste into motor fuels has a deeper significance than the immediately important factor of conservation--it provides a source of motor fuels for the future which is under the direct control of man" (Morrell, Egloff 1929).

It is estimated that in Canada there are more than 10^9 ft^3 of wood waste produced annually (Prakash, Murray 1972), while statistics for the United States indicate over 3.10^9 ft^3 of wood residues and from 7 to 20.10^6 tons of bark residues (Shafizadeh, Chin 1975). The trend today in the forest products industry is towards more complete utilization of a single tree. However, there remain areas of high

concentrations of wood waste materials; for example, the areas where logging operations are carried out.

As an energy source, wood has been utilized by direct combustion, carbonization, and liquefaction or gasification. Controlled pyrolysis of cellulosic materials may be considered as a possibility for the chemical conversion of waste to fuel. This not only includes wood wastes, but also agricultural, municipal and industrial wastes. A number of descriptions of such pyrolitic processing of wastes are currently available (Wolfson, Beckman, Walters, Bennett 1969; Sanner, Ortuglio, Walters, Wolfson 1970; Appell, Wender, Miller 1970; Schlesinger, Sanner 1973).

Wood is a complex material consisting primarily of the polymers cellulose, lignin, and the hemicelluloses. Although the elemental composition of wood materials is almost constant (49.5%C, 6.3%H, 44.2%O (Prakash, Murray 1972)), wood composition varies not only from species to species, but also within a single tree, in terms of its three main constituents.

The simplest constituent is cellulose, a regular, repeating condensation polymer of β -D-glucose containing the 1:4-β-glycosidic bond linkage (1). Lignin is a complex polymer, the exact structure of which is not known, but the basic unit is the phenylpropane group (2). Hemicellulose polymers commonly contain a number of sugars, including

D-glucopyranose (3), D-xylopyranose (4), and D-mannopyranose
(5), as their structural units.

Bark is used as a general term to indicate all
tissues outside the cambium, Figure 1. A detailed descrip-
tion of the anatomy of jack pine bark is outside the scope
of this study, however, such a description has been given
by Chang (1954). Also shown in Figure 1 is a general
schematic of the cell structure of wood.

2.2. Thermal decomposition of wood and related products

A number of reviews of the thermal decomposition of
wood are available in the literature (Browne 1958; MacKay
1966; Schaffer 1966; Beall, Eickner 1970). Most of the
previous work has been aimed at determining the activation
energy and frequency factor necessary to characterize the
kinetics of weight loss, and therefore the rate of decomposi-
tion. The following review has been divided into sections
according to the experimental methods used.

2.2.1. Transient heat balance techniques

This method involves measurement of the temperature
of a wood specimen which is exposed to external heating
under controlled conditions. The temperature profile thus
obtained is used to solve a heat conduction equation which
includes a heat source term to cover sample self-heating.

(1)

(2) R = H, OCH₃

(3)   (4)   (5)
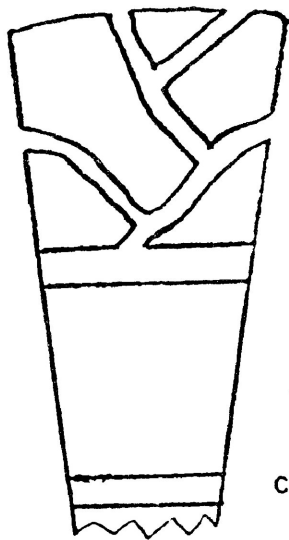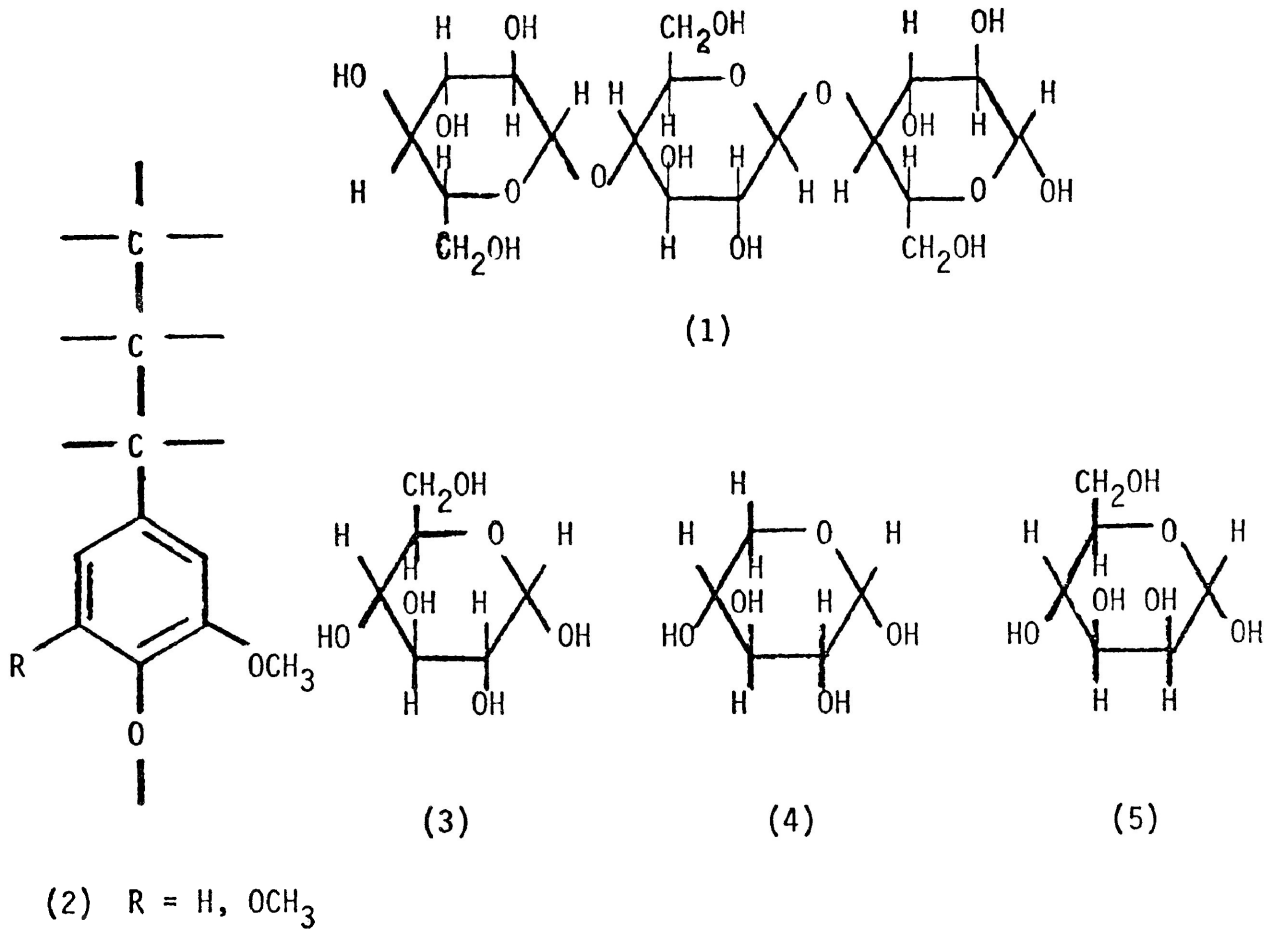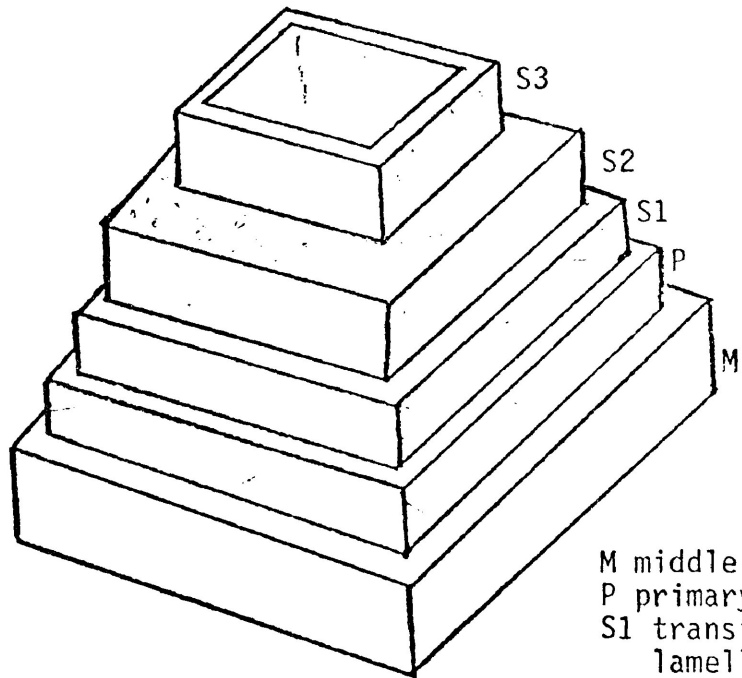
(6) mature bark   (7) wood cell

M middle lamella
P primary wall
S1 transition
    lamella
S2 secondary wall
S3 tertiary wall

Figure 1 Schematic representation of wood constituents.

Generally, the heat source term has the form, $q \frac{dW}{dt}$, where

q is the heat of decomposition (cal.g^{-1}), W is the weight

of volatile or reactable constituents (g.cm^{-3}), and t is

the time.

Bamford, Crank, and Malan (1946) studied the

ignition of wood and determined a numerical value for q from

the observed sudden temperature increase at 600 K. The rate

of weight change of the decomposable components was assumed

to obey first order kinetics where the rate constant, k,

was temperature-dependent in an Arrhenius sense. The rate

was therefore given as:

$$- \frac{dW}{dt} = A \ e^{-Ea/RT} \ W \qquad (1)$$

and values of A and Ea, the only unknowns remaining in the

heat conduction equation, were taken to describe a tempera-

ture/time curve to fit the experimental data.

Bowes (1956) measured the rate of heat evolution

(q = cal.g-min^{-1}) in a number of species of wood raspings in

air over the temperature range 473 to 573 K. The logarithm

of the rate of heat evolution was plotted against T^{-1} in the

Arrhenius fashion to produce the values for Ea and ln A

given in Table 1.

Akita (1959) solved a heat conduction equation

using a heat source term of the form:

$$q \frac{dW}{dt} = q \ k \ (\ W_t - W_\infty \ ) \qquad (2)$$

where W_t is the weight of reactant at time t $(g.cm^{-3})$ and

W_∞ is the residue weight of reactant. Roberts and Clough

(1962) obtained both weight/time and temperature/time data

for cylindrical beech samples in an increasing temperature

environment in nitrogen. Weight loss data were represented

by a first order expression to yield values for apparent

activation energy, Ea, and pre-exponential factor, A.

Using these values, a heat balance equation was then applied

to find a value for q.

Havens (1969) described the pyrolysis of wood as a

transient, multidimensional heat transfer problem. A

constant rate of heat absorption per unit weight of material

decomposed in nitrogen was observed and the char front

temperature was thought to be as low as 623 K. Roberts

(1970) noted that cracking occurred at 573 to 593 K on

pyrolysis of wood in air and that the network of cracks

produced on the surface would propagate into the wood with

the pyrolysis wave (Roberts 1971). A sharp transition in

pyrolysis was expected to occur at the plane where macro-

scopic structure failure began. An autocatalytic effect

which could affect kinetic constants according to position

in the pyrolysis zone was described.

Heat effects in wood pyrolysis may also be examined

by means of differential thermal analysis (DTA) and dif-

ferential scanning calorimetry (DSC). The experimental

procedure will not be discussed here since descriptions of these techniques may be found in textbooks on thermal analysis. (For example, "Differential Thermal Analysis", R. C. Mackenzie (ed) (1972), or "Thermal Analysis Volume 1", R. F. Schwenker, P. D. Garn (1969).)

Results obtained from DTA and DSC studies on wood pyrolysis are often confusing and seemingly contradictory. These results are influenced by the conditions of removal of primary products and the repression of oxidation and condensation reactions (Domburg, Sergeeva, Koshik, Kozmal 1969). The primary condensation of wood components caused by dehydration occurs at 453 to 473 K and is exothermic. The endothermic glucosidic bond cleavage of xylan begins at 493 K and the basic decomposition of the hemicelluloses ends before 553 K. The splitting off of aliphatic chains from lignin occurs as an endothermic effect at 513 K, while the basic bond breaking mechanism in lignin at 613 K, endothermic, may be compensated by the exothermic condensation of the primary products of carbohydrate decomposition. The cellulose component is expected to depolymerize over a narrow temperature range to produce an endotherm at 623 K. However, if the primary products cannot escape readily, then exothermic secondary reactions may occur (Arseneau 1971).

2.2.2. Isothermal techniques

In these studies, a specimen is positioned in a constant temperature environment and some physical parameter is monitored as a function of time. Most investigations to date concerning the pyrolysis of wood products deal with isothermal weight-change determinations which involve the measurement of sample weight loss. It is usually assumed that either the sample attains furnace temperature instantaneously, or that during the time required for the sample to reach thermal equilibrium with the furnace, there is no significant weight loss.

Generally, a first order rate expression has been utilized with the rate constant temperature dependent in an Arrhenius fashion:

$$- \frac{dW}{dt} = k \ W^n = Ae^{-Ea/RT} \ W^n \qquad (3)$$

where W is the sample weight and the other symbols have their usual significance.

If wood pyrolysis is assumed to be a first order process, (n = 1), then equation (3) upon rearrangement and integration becomes:

$$\ln W = k \ t \ + \ \ln W_0 \qquad (4)$$

where W_0 is the initial sample weight. A plot of ln W against time, t, should give a straight line of slope k for each temperature, and an Arrhenius plot of lnk against T^{-1} would yield a straight line of slope -Ea/R and intercept lnA.

This method was used by Stamm (1959) to interpret data for pine, fir, and spruce wood as well as Douglas fir sawdust and its constituents. Experiments were carried out in air or under molten metal with intermittent weighing over the temperature range 367 to 573 K for the wood specimens and 383 to 493 K for the sawdust samples. However, the accuracy of these results has been questioned by Brown (1972).

Martin (1956) studied the ignition of cellulosic materials and expressed the kinetics as the sum of two elementary reactions:

$$ - \frac{dW}{dt} = (k_1 \, A_1 \, e^{-Ea_1/RT} + k_2 \, A_2 \, e^{-Ea_2/RT}) \, W \qquad (5) $$

A slow pyrolysis reaction, and therefore k_1, was thought to predominate at low temperatures, and a fast pyrolysis reaction was thought to predominate > 673 K. Browne (1958) described the kinetics of wood pyrolysis as reasonably first order and probably diffusion controlled.

The rate of wood pyrolysis in air was described as slow < 473 K, becoming rapid > 543 K at pressures from atmospheric to 2 Torr by Akita (1959). Over the temperature range 423 to 673 K, the rate of isothermal pyrolysis was described as a summation of the rates of thermal decomposition of the constituents of wood:

$$ \frac{dN}{dt} = \sum_i k_i \, (N_{\infty \, i} - N_i) \qquad (6) $$

where N is the total number of moles of gas evolved at time t, N_i is the number of moles of gas evolved at time t by the i'th constituent, $N_{\infty i}$ is the total number of moles evolved by the i'th constituent, and k_i is the rate constant for the i'th constituent. Equation (6) was expressed as the sum of three terms representing cellulose, lignin and hemicellulose, each of which was said to fit first order kinetic models. In the Arrhenius plot for both cellulose and wood, two distinct linear regions were observed with an inflection point corresponding to 613 K. The data are summarized in Table 1. It should be noted that this model precludes the possibility of any synergetic or competing secondary reactions among wood components.

Tang (1960) found a point of inflection at 603 K in the Arrhenius plots obtained from the pyrolysis of ponderosa pine. The activation energy was observed to decrease with increasing sample thickness for veneers and dowels. The numerical results were later questioned because of the excessive weight loss which occurred before thermal equilibrium was attained (Tang, Neill 1964).

Eickner (1962) indicated that wood pyrolysis studies conducted at the U. S. Forest Products Laboratory were described by the first order expression:

$$- \ln (1 - W/W_d) = k t \qquad (7)$$

where W is the weight loss at time t, and W_d is the final

weight loss. However, he noted that such plots often exhibited more than one linear region. Wood pyrolysis was later described as the sum of two reaction schemes occurring consecutively at each point within the wood matrix (Tinney 1965). Each mechanism was believed to have its own kinetic constants and heat of reaction with the transition from one to the other occurring at a certain value of local density. A unique kinetic investigation by Wright and Hayward (1951) involved measuring the pressure change in a closed system under nitrogen during wood pyrolysis at temperatures of 773, 973, and 1173 K. For sample cubes, the rate constant was found to be proportional to their specific surface area and to the furnace temperature. The rate constant was evaluated from the expression:

$$[100 (1 - P/P_\infty)]^{0.5} = k\ t \qquad (8)$$

where P is the pressure at time t, and P_∞ is the final pressure. Pyrolysis was envisioned as occurring in a re-action zone or shell which advances inwards from the surface, where the rate of advance is higher along the wood grain than across the grain. The rate was thought to be related to an internal heat transfer effect.

2.2.3. Dynamic thermogravimetry (TG)

In this method, sample weight is monitored con-tinuously in a linearly-increasing temperature environment

where the surrounding atmosphere may be controlled. This technique has been used mostly in observing the effects of additives and fire retardants on wood pyrolysis.

Browne and Tang (1962) indicated that the diffusion of heat into the sample interior and the escape of volatile products would enter into the over-all process. In nitrogen and under vacuum, wood veneer began to lose weight at 493 K. At 523 K the weight loss amounted to 3.7% and at 673 K the loss was 76%. The extent to which an additive lowered the temperature at which the major weight loss started was observed to depend more upon the nature of the additive than on its quantity. Later, fire retardant additives were classified according to their effect upon the TG curve of native wood (Browne, Tang 1963).

Tang (1967) extracted kinetic parameters from TG studies by making pseudo-first order Arrhenius plots directly from the data. His results are summarized in Table 1. The additives studied decreased the temperature at which weight loss began, increased weight loss < 623 K, and pro-duced more char at temperatures > 623 K. The Arrhenius plots exhibited a break in kinetics for wood, cellulose, and lignin.

Heinrich and Kaesche-Krischer (1962) indicated that plots of rates of weight loss against temperature exhibited three distinct maxima for beech sawdust in vacuum. They

concluded that the decomposition could not be treated as a
first order process. Havens (1969) noted that rate of
weight loss curves for oak and pine wood in nitrogen showed
two maxima, but he did not extract kinetic parameters.

Brown (1972) indicated that pine and oak each
showed a single activation energy, Table 1, although a
change in reaction order was observed. Hirata (1974)
described the pyrolysis of Japanese cedar in vacuum as a
composite of its components. The Arrhenius plot showed a
break at 588 K and kinetics were analysed by the equation:

$$\ln \left(- \frac{d \ln W}{dT} \right) = \ln A/\phi - E/RT \qquad (9)$$

where W is the weight of decomposable material at time t
and ϕ is the heating rate. Below 588 K, the rate was thought
to be controlled by decomposition of lignin and hemicellu-
loses while > 588 K, it was controlled by cellulose and
lignin decomposition. These results are presented in
Table 1.

2.2.4. Spectroscopic techniques

The main problem in the study of the pyrolysis of
wood products using modern instrumental analysis is that of
sample preparation and handling. When these problems are
solved, spectroscopic techniques may produce more evidence
concerning the chemical reactions of pyrolysis than can be
obtained solely by thermal analysis methods.

Chow (1972) observed the IR spectral characteristics of white spruce microsections over the temperature range 373 to 513 K in air and nitrogen. As the temperature was increased, the intensity of the 6.2 μm band, indicating the absorption of carbonyl and ester groups, was observed to decrease initially and then increase at a greater rate. The decrease was due to loss of these groups while the increase was ascribed to oxidative carboxylation which was thought to be more temperature dependent than de-esterification. Activation energies for pyrolysis were calculated from the decreases in intensity of the 3 μm hydroxyl band based upon first order Arrhenius plots. The results are given in Table 1.

Chow (1972) also studied the pyrolysis of Douglas fir and red alder barks < 212 μm particle size by observing the UV spectra of water-soluble extractives. First order kinetic plots yielded the activation energies given in Table 1. The decrease with T over the range 473 to 593 K of the UV absorbance at 280 nm of the extracts was attributed to condensation reactions of the extracts and the loss of volatile components. These results indicated the existence of the polymerization of phenolic substances in bark. The IR spectra of the extracts showed that the intensity of the 9.6 μm carbohydrate absorption band of heated samples was 30 to 50% lower than that of the air-dried bark. The low

water solubility was attributed to dehydration and cross-
linking reactions.

A number of Russian investigators have studied the
pyrolysis of wood products using electron paramagnetic
resonance (EPR) spectroscopy. Ivanov et al (1970) noted
that the thermal initiation of free radicals in wood occurred
at temperatures well below that of the exothermic thermal
decomposition reactions and as low as 393 K. EPR curves
differed between species and good correlation was achieved
between both pH and temperature of heat treatment, with the
process of initiation of free radicals. Levin, Barabush, and
Sidorov (1971) observed that the EPR signal intensity in the
pyrolysis of Siberian larch bark over the range 403 to 973 K
depended upon the temperature of treatment. Increased EPR
signal intensity and increased condensation products were
related to the formation of free radicals. At temperatures
> 773 K, recombination of radicals prevailed, followed by
the formation of condensed rings and crosslinking (Levin,
Barabush 1971).

The electron spin resonance (ESR) spectra of the
residues obtained by vacuum pyrolysis of Douglas fir were
studied by Nanassy and Fung (1975). The activation energy
for the formation of unpaired spin was 105 $Kj.mol^{-1}$ in the
range 673 to 873 K. Both unpaired spin producing and
reducing mechanisms were observed for wood pyrolysis. A

Table 1   Kinetic parameters for the pyrolysis of wood materials.

SAMPLE	ATMOSPHERE	Ea (Kj.mol^{-1})	ln A (min^{-1})	TREATMENT	REFERENCE
wood slab	air	139	24.2	transient	Bamford, Crank, Malan
oak	air	97	20.9	transient	Bowes
whitewood	"	105	23.3	"	"
beech	"	120	26.8	"	"
mahogany	"	127	29.3	"	"
cedar	"	130	28.7	"	"
iroko	"	138	30.4	"	"
beech	nitrogen	105, 63	21.7, 11.4	transient	Roberts, Clough
Japanese cypress	air	109, 96	--	isothermal	Akita
ponderosa pine	vacuum	96, 226	16.8, 42.8	dynamic TG	Tang
cellulose	"	146, 234	26.7, 44.6	"	"
lignin	"	88, 38	13.8, 4.0	"	"
white pine	nitrogen	207	37.4	dynamic TG	Brown
oak	"	238	44.6	"	"
cellulose	vacuum	165, 112	21.0	dynamic TG	Hirata
lignin	"	146	29.1	"	"
hemicellulose	"	119	24.1	"	"
Douglas fir bark	air	54	8.6	spectroscopic	Chow
red alder bark	"	67	12.1	"	"
white spruce	air or	50	--	"	"
extracted white spruce	nitrogen	84	--	"	"

solid cylindrical specimen and sawdust gave identical spin
concentrations at 573 K. Increasing spin concentration was
related to increasing mass loss while constant or decreasing
concentration was related to no change in mass loss.
Recently, the unpaired spin concentration was observed to
be greater in flame-retardant treated wood (Nanassy, Fung
1976). The flame retardant ammonium dihydrogen ortho-
phosphate was shown to act as a deoxygenation agent in wood
pyrolysis.

2.2.5. Pyrolytic products

In an investigation of the various reaction processes
of coal and a discussion of coalification, van Krevelen
(1950) outlined the principal reactions of pyrolysis of
cellulose and lignin from a graphical-statistical analysis
of pyrolysis residues:

$$(C_6H_{10}O_5)_{12} + O \longrightarrow (C_{36}H_{26}O_{13})\underset{O}{\diagup\diagdown}(C_{36}H_{26}O_{13})$$

cellulose   lignite

$$+ 17\ H_2O \tag{10}$$

$$(C_{10}H_{12}O_4) + O \longrightarrow (C_{36}H_{26}O_{13})\underset{O}{\diagup\diagdown}(C_{36}H_{26}O_{13})$$

lignin

$$+ 8\ CH_4 + 6\ H_2O \tag{11}$$
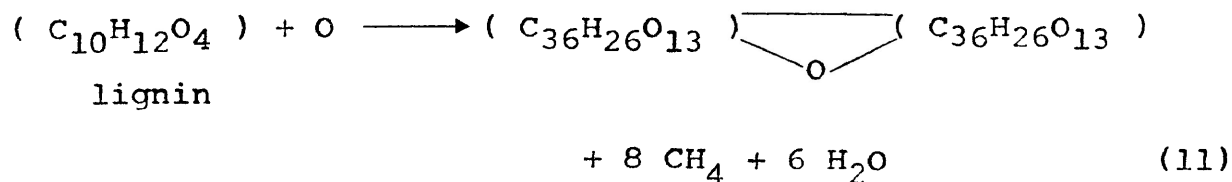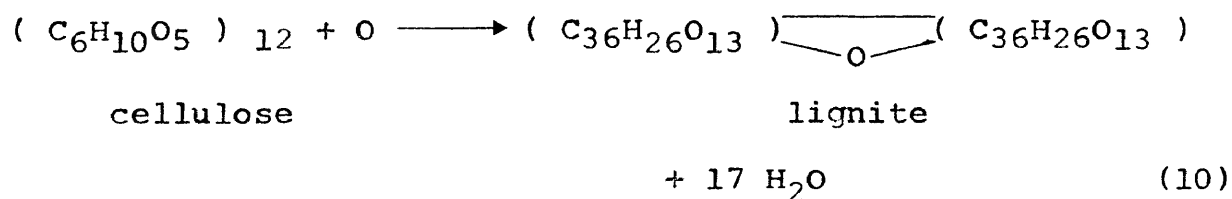
Mitchell, Seborg, and Millett (1953) noted that
variations in heating conditions affected the chemical

composition of the pyrolysis products of Douglas fir. Greater weight loss and greater dimensional changes were observed in a closed system while more CO_2 was evolved from an open system. Stamm (1959) indicated that the extent of decomposition would be greater in air due to oxidation, and greater in a closed system due to the accumulation of acid and the catalysis of hydrolysis reactions.

A review by Browne (1958) described four zones of pyrolysis defined by temperature as shown:

Zone	Temperature (K)	Gaseous products
A	< 473	H_2O, CO_2 (trace)
B	473 to 553	H_2O, CO_2, CO (trace)
C	573 to 773	CO_2, H_2O, CO, CH_4, H_2
D	> 773	CO, H_2, CO_2, H_2O

The products of pyrolysis were found to vary with temperature, pressure, time, sample geometry, and environment.

Havens (1969) noted that the initial products of decomposition must pass from their point of origin to the wood surface to escape. In an increasing temperature environment, therefore, the products pass through a higher temperature char layer where heat exchange and secondary reactions could occur. Roberts (1971) stated that secondary reactions would be completed at a distance of 8 mm from the point of origin of the primary products and that these

reactions would be particularly important < 593 K. Because
no systematic differences were observed in the measured
heat of reaction under nitrogen or oxygen, he postulated
that reactions between pyrolysis products and atmospheric
oxygen did not occur in the interior of a pyrolizing wood
specimen. Kanury (1972) concluded that the thickness of
the char layer, and therefore the resistance to removal of
primary pyrolysis products, increased with time. This would
serve to increase the possible effects of any secondary
reactions while the formation of cracks and fissures would
reduce these effects.

Several workers have investigated changes in the
anatomy of wood with heat treatment (Fengel 1966; Knudson,
Williamson 1971; McGinnes, Kandeel, Szopa 1971). In all
cases, embrittlement and some structural changes of the wood
tissues were observed while a wood-like appearance was
retained. Although no study of the anatomical changes
occurring in wood bark with heat treatment has been noted in
the literature, similar results might be expected.

Schlesinger, Sanner, and Wolfson (1973) have listed
the products of pyrolysis of pine bark at 1173 K. One ton
of bark produced 20,154 ft^3 gas, 5.5 gal. tar and oil, 29.4
gal. aqueous, and 630 lb residue. Later, O'Mara (1974)
studied the pyrolysis of wood in a National Bureau of
Standards smoke chamber coupled to a gas chromatograph.

The generation of CO was found to be almost constant throughout, while the CO_2/CO ratio decreased, then increased. Moisture had no effect upon the rate, it merely produced an induction period. Physical factors which influence the rate of thermal decomposition were thought to be more important in CO generation than the chemical composition of the wood. The production of CO_2 was dependent upon the concentration of atmospheric oxygen. Also in 1974, Beall, Blankenhorn, and Moore showed that the weight loss observed in the pyrolysis of yellow poplar could be expressed as the sum of the weight loss for the individual constituents-- cellulose, lignin, and hemicellulose.

2.2.6. Cellulose pyrolysis

While cellulose may be described as a simple repeating condensation polymer of β -D-glucose, the mechanism of cellulose pyrolysis is complex and it must be noted that a mechanistic description of the pyrolysis of pure cellulose may not necessarily be extrapolated to the pyrolysis of cellulose in a wood matrix.

An isothermal weight-loss study of the pyrolysis of cellulose in nitrogen by Lipska and Parker (1966) described an initial rapid reaction followed by a linear region where the rate of decay was constant (zero order) up to a 70% weight loss and a first order decomposition of the char

thereafter to yield 15% residue. After the weight loss reached 70%, only an insignificant amount of residual cellulose was left. Chatterjee and Conrad (1966) observed the pyrolysis of cotton cellulose in helium and found a complex reaction up to 40% weight loss followed by a first order decomposition. These experiments were not entirely isothermal, as the sample was heated at 3 K.min^{-1} to the desired temperature and then held constant. This would allow a considerable weight loss to occur in some cases before isothermal conditions were attained.

Fung (1969) described the initial pyrolysis of cellulose paper as occurring by first order random chain scission where the degree of polymerization (DP) was rapidly reduced to 200. Ramiah (1970) derived kinetic parameters from isothermal studies in vacuum using the first order expression:

$$\ln (1 - \alpha) = k\, t \qquad (12)$$

where α was defined as the weight loss at time t over the final weight loss. The final weight loss was taken as the loss after 4 h when a sample was heated at the maximum temperature of pyrolysis. Two competitive reactions in cellulose pyrolysis were described by Arseneau (1971). Dehydration at temperatures as low as 483 K was thought to produce anhydrocellulose which would yield char eventually, and the depolymerization of non-reacted cellulose would yield

levoglucosan as the major product at temperatures > 543 K.
Kosik, Luzakova and Reiser (1972) described three re-
actions in cellulose pyrolysis--thermoxidation, dehydration
and the formation of glucosans. In the presence of oxygen,
the DP was observed to decrease rapidly down to 160.- Both
thermal oxidation and dehydration were described as dif-
fusion controlled and occurring primarily in the non-
crystalline regions. The low temperature pyrolysis was
explained by the theory of peroxidic free radical formation
followed by splitting of the β -glycosidic linkage (Church
1965; Kosik, Micko, Domansky 1969).

The pyrolysis of cellulose at 524 K was studied by
Basch and Lewin (1973) in air and vacuum. Results in vacuum
substantiated the mechanism of Chatterjee and Conrad (1966)
and the rapid initial weight loss was attributed to cross-
linking reactions. Studies in air indicated first order
kinetics where the rate of diffusion of oxygen into the
cellulose structure was thought to play a significant role.
Weight loss in air was greater than that in vacuum.

Cellulose powder pyrolysis in nitrogen was observed
to produce a residue of 12% with a maximum rate at 633 K
(Shafizadeh, Fu 1973). Pyrolytic reactions were thought to
produce a variety of products through concurrent and con-
secutive reactions.

Kinetic parameters for cellulose pyrolysis in

nitrogen have been derived using the Avrami-Erofeev expression:

$$[- \ln (1 - \alpha)]^{1/2} = k \ t \qquad (13)$$

and hence explained by the model reaction of random nucleation and nucleus growth in cylindrical particles (Dollimore, Holt 1973). Evidence suggesting the cylindrical nature of cellulose fibrils was also presented.

Using TG, Kumagai and Ohuchi (1974) found a two-stage Arrhenius plot for cellulose pyrolysis based upon first order kinetics. The maximum rate of weight loss occurred at a higher temperature in nitrogen compared to results in air.

Activation energies for cellulose pyrolysis are summarized in Table 2. Generally, apparent activation energies found by isothermal techniques are significantly lower than those derived by TG.

3. EXPERIMENTAL

3.1. Materials

3.1.1. Gases

Certified nitrogen and helium, and compressed air were used as supplied by Canadian Liquid Air Limited. For gas analysis studies, a calibrated gas mixture containing CO, CO_2, H_2, and CH_4 in helium was obtained from the same supplier.

Table 2   Kinetic parameters for the pyrolysis of cellulose.

SAMPLE	ATMOSPHERE	ACTIVATION ENERGY $(KJ.mol^{-1})$	TREATMENT	REFERENCE
paper	nitrogen	176	isothermal	Lipska, Parker.
cotton	helium	initiation 227	isothermal and	Chatterjee,
		propogation 138	dynamic	Conrad
ball-milled	helium	initiation 314	isothermal and	Chatterjee,
		propogation 155	dynamic	Conrad
paper	vacuum	148	isothermal	Fung
avicel	vacuum	146	isothermal	Ramiah
avicel	vacuum	initial 251 final 163	dynamic	Ramiah
powder	nitrogen	initial 151 final 190	dynamic	Arseneau
powder	nitrogen	144	isothermal	Dollimore, Holt
avicel	air	270	dynamic	Kumagai, Ohuchi
avicel	nitrogen	initial 201 final 290	dynamic	Kumagai, Ohuchi
paper	air	initial 182 final 487	dynamic	Kumagai, Ohuchi
paper	nitrogen	initial 214 final 457	dynamic	Kumagai, Ohuchi

3.1.2. Additives

The following reagent-grade chemicals were used as supplied: $NaCl$, $CaCl_2$, $MgCl_2$, NH_4Cl, $FeCl_2$, $FeCl_3$, $CuCl_2$, $NiCl_2$, MnF_2, $MnCl_2$, $Mn Br_2$, MnI_2, $ZnF2$, $ZnCl_2$, $ZnBr_2$, ZnI_2, $NaHPO_4$, $(NH_4)_2 HPO_4$, $NaHSO_4$ and $(NH_4) HSO_4$.

3.1.3. Jack pine bark

Bark was stripped from jack pine (Pinus banksiana, Lamb), which had been cut in the Lakehead University Woodlot in Fowler and Jacques Townships, Thunder Bay District. The trees, 80 to 150 years old, were those commonly used in the pulp and paper industry in this area. The bark was hand screened to remove wood traces, washed with distilled water, and then dried in air at 333 K for 60 h. The bark was shredded in a high-speed blender and separated by sieving using U. S. Standard Sieve Series - 30, 40, and 70 mesh - to give a range of particle size; > 600 μm, 600 to 425 μm, 425 to 212 μm, and < 212 μm.

Samples used in thermogravimetric studies were subsequently dried in vacuum (10^{-2} Torr) at 333 K for 1 h and stored in a desiccator in sealed containers.

3.1.4. Extracted bark

Portions of jack pine bark, < 212 μm, were treated to remove extraneous materials by continuous extraction with

an ethanol/benzene mixture (2:1 $^V/_V$) for 4 h followed by
extraction with ehtanol for 4 h (ASTM D 1105 - 56).
Samples were then dried and stored as described previously.

3.1.5. Bark containing additives

Portions of native and extracted bark, < 212 µm,
were treated with various additives. The additive,
approximately 20 mg, was mixed with 300 mg bark and 5 ml
of distilled water. The mixture was then stirred for 10
min to give a homogeneous slurry. The slurry was then left
for 24 h before being dried at 338 K for 72 h and finally
the sample was heat treated at 333 K for 1 h at 10^{-2} Torr.

(It has been observed that similar preparations
using water soluble additives produced an alteration of wood
pyrolysis without excessive weight loss from the additives
themselves (Tang 1967; Tang, Eickner 1968).)

3.1.6. Jack pine sawdust

Jack pine sawdust was collected from repeated cuts
through a single jack pine tree section approximately 13 cm
in diameter. The sawdust was sieved and dried as described
previously.

3.1.7. Cellulose

Whatman column chromedia CF 1 fibrous cellulose

powder (maximum 0.015% ash) was obtained from W. R. Balston Limited, and used as supplied.

3.2. Apparatus and procedure

3.2.1. Thermobalance

A Stanton-Redcroft Thermobalance, model HT-SF, was used in thermal analysis experiments. The balance had an automatic weight-loading assembly to extend the weight range in steps of 20 mg to a 200 mg maximum. A vertical sample support column was connected to the back pan of the balance as shown in the schematic diagram, Figure 2. A servo-driven capacity-follower device was used to transmit beam movement to the recording mechanism, while the beam was controlled by a conventional air damping arrangement.

Sample temperatures were monitored on a Leeds and Northrup recorder from a platinum/platinum-rhodium (13%) thermocouple positioned within the sample support, Figure 2. A correction was applied for the thermocouple cold junction at room temperature. The recorder was calibrated using a Honeywell Portable Potentiometer over the range 0 to 10 mV. The accuracy of the sample temperature measuring arrangement was therefore limited by the accuracy in reading the recorder chart which amounted to $\pm$ 1 K over the temperature region of interest.

Samples were heated by a 37.5 mm bore platinum/

rhodium-wound furnace which was mounted vertically and could be raised or lowered around the sample support. A silica sheath allowed a flowing gas to surround the sample continuously. Furnace temperature was controlled by a platinum/platinum-rhodium (13%) thermocouple located between the furnace wall and silica sheath. The furnace could be operated isothermally at a pre-selected temperature with a proportional controller, or in a dynamic mode in which case the furnace temperature was increased linearly at a rate of 7 $K.min^{-1}$.

Nitrogen or compressed air was passed through a drying column, 3.5 cm diameter by 40 cm consisting of self-indicating silica gel and calcium sulphate, before entering the furnace.

A saturator immersed in a water bath controlled by a Sargent-Welch Thermocontroller to $\pm$ 0.5 K was used to introduce water vapour to the flowing gas stream. The gas stream was maintained at 373 K between the saturator and the furnace by an external winding of thermal tape.

3.2.2. Isothermal technique

A small-capacity low-profile platinum crucible, 10 mm diameter by 5 mm, was used to hold 40 mg samples. In the loading procedure, the preweighed specimen was balanced on the back pan of the thermobalance with the sample support and
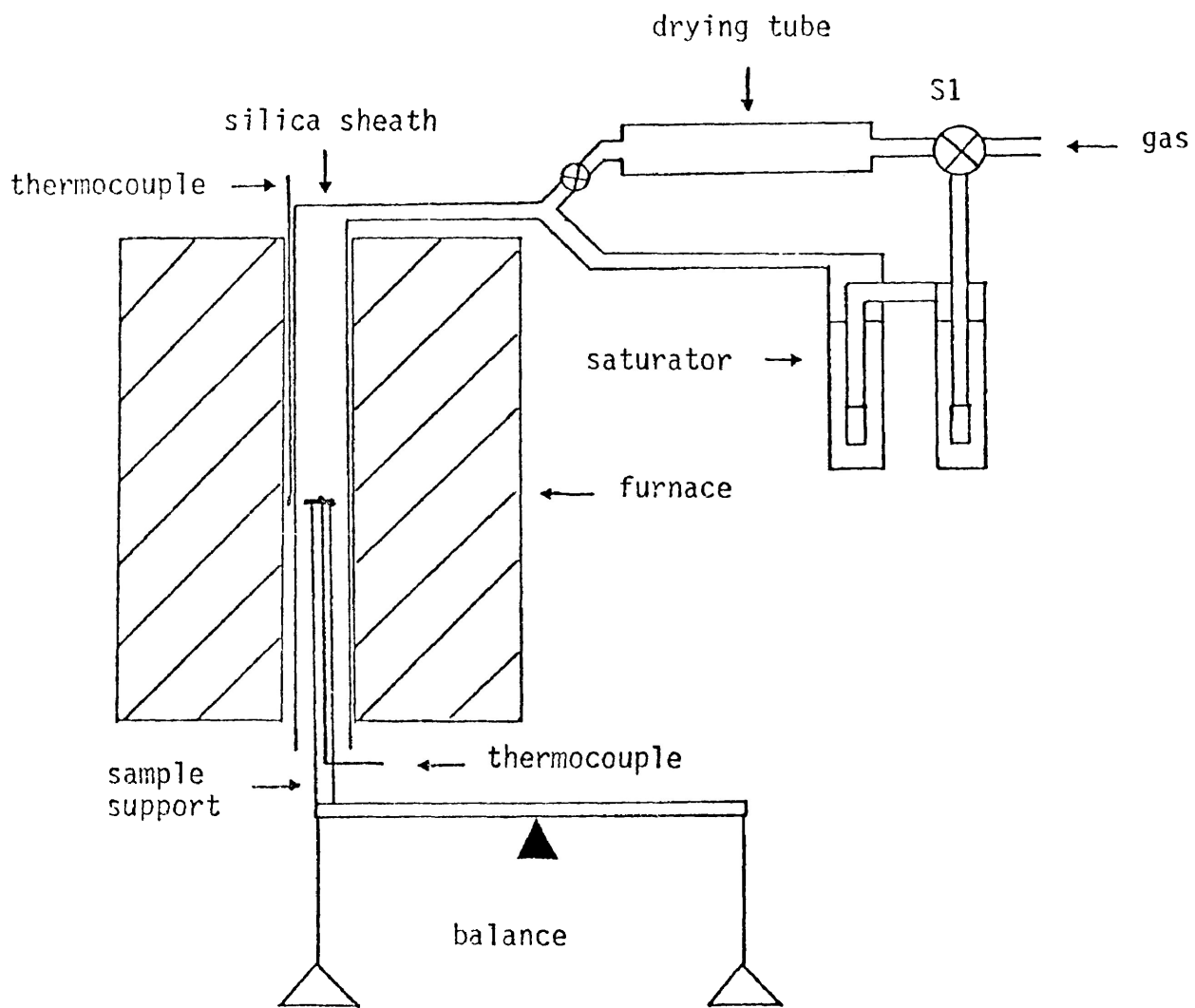
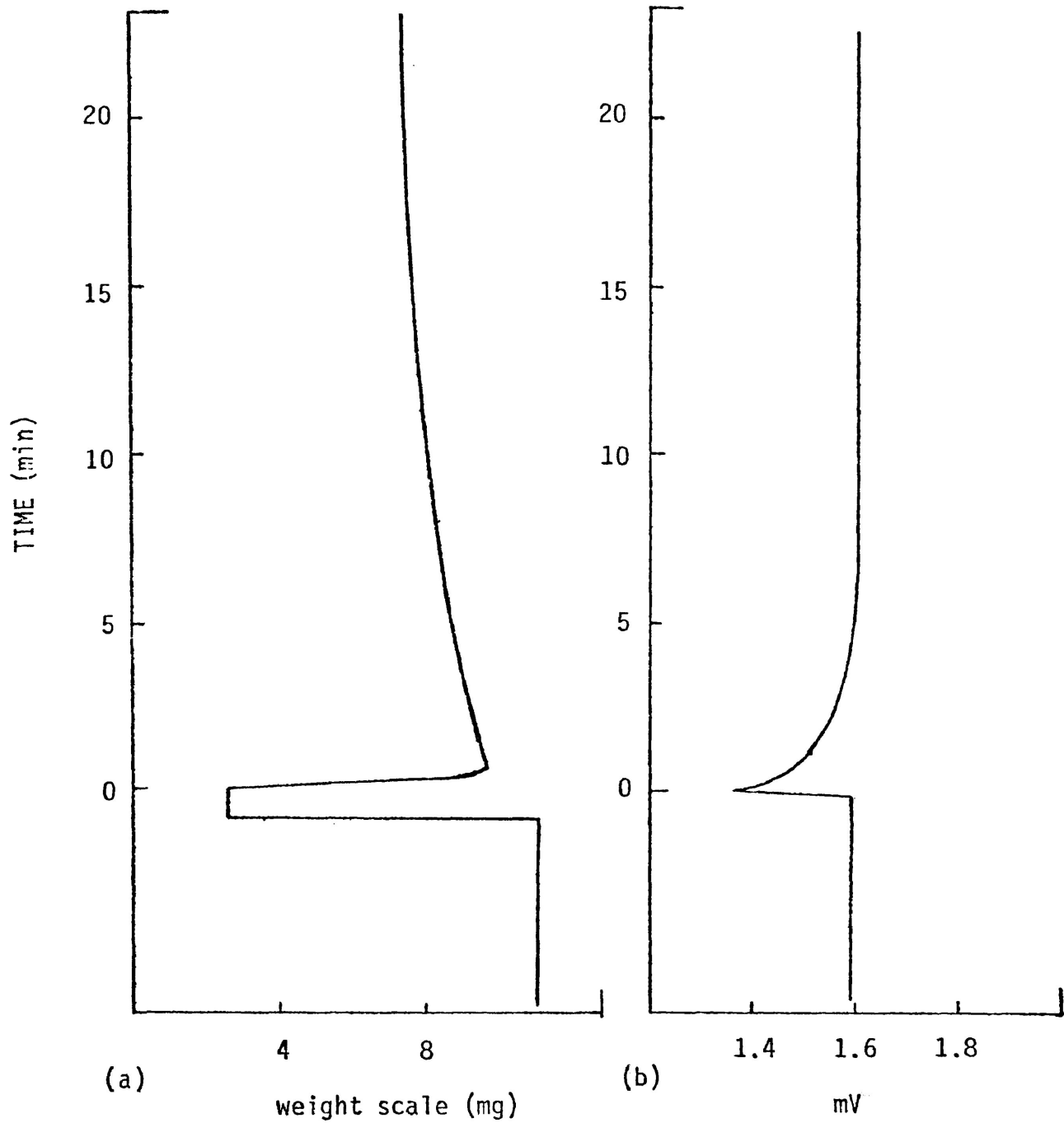Figure 2   Schematic of thermobalance assembly.

Figure 3 Typical chart recordings of sample weight (a) and temperature (b) versus time.

furnace preheated to a selected temperature for 20 min with a gas flow. The specimen was then quickly transferred to the sample support. The time delay between removing the sample from the back pan and placing it in the furnace was 30 sec. The specimen attained thermal equilibrium with the furnace in 4 min. The sample temperature rose to within 15 K instantaneously, and to within 3 K of the selected treatment temperature in 2 min. Typical chart recordings of sample weight and temperature versus time are given in Figure 3.

In all experiments, a flowing gas atmosphere was maintained at 230 ml.min^{-1} (NTP).

3.2.3. Dynamic thermogravimetric technique

A conical alumina crucible, 8 mm in height, 15 mm top diameter and 9 mm bottom diameter, was used to contain the 40 mg samples. This crucible was better suited for TG studies as some samples appeared to cause pitting of a similar platinum crucible at high temperatures. The procedure employed was to balance the specimen on the sample support in the furnace at room temperature in a flowing atmosphere at 230 ml.min^{-1} (NTP), to achieve a straight base line, and flush the furnace assembly. The thermobalance was then programmed to reach 1273 K (approximately 2.5 h).

For those runs in an atmosphere of nitrogen plus

water vapour, the saturator was placed into the line by means of stopcock S1, Figure 2, when the sample temperature had reached 383 K. This procedure prevented condensation on the sample support at low temperatures.

3.2.4. Analysis of gaseous products

A stainless steel high pressure apparatus, Figure 4, was used in conjunction with a Beckman GC-5 gas chromatograph (GC) to perform gas analysis studies on the gaseous effluents from jack pine bark. The main body of the apparatus was fabricated from 5 cm o.d. stainless steel tubing, total length 60 cm, in two sections mated with a copper gasket.

The top section housed a calibrated quartz spring which would have allowed for the determination of sample weight loss measurements. In the bottom section, viewing windows were installed with rubber gaskets and a copper cooling coil was placed just below these windows. A stainless steel sample bucket allowed the use of 100 mg samples. All gas lines were stainless steel tubing, 3 mm diameter, connected by Swagelok fittings. An in-line glass wool plug was installed at the gas outlet.

A moveable resistance-wound furnace could be raised around the assembly as required. The temperature was controlled by a chromel/alumel thermocouple which was positioned
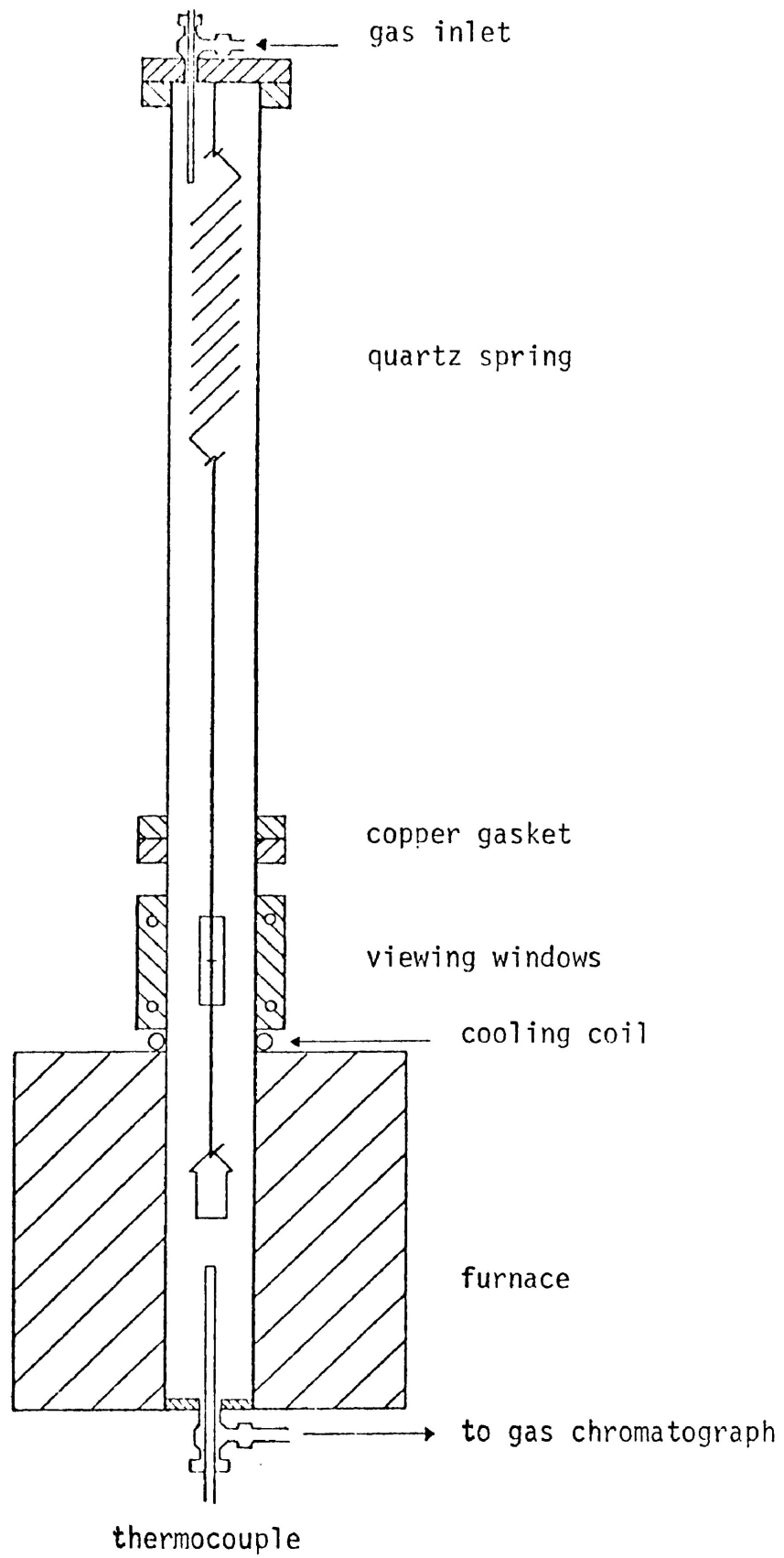
Figure 4   Schematic of high pressure apparatus.

directly below the sample bucket and connected to a Thermo-electric 400 proportional controller.

The gas chromatograph utilized "Carbosieve B" columns which were run at 383 K with a helium flow rate of 30 ml.min^{-1} (NTP). The effluent gases were analysed by a thermal conductivity detector (TCD) and traces were recorded on a Beckman 10" recorder.

Samples were weighed into the sample bucket, placed in the apparatus, and dried overnight in helium (6.5 atmospheres) at 373 K. A GC trace was then obtained by flushing the gas sample through a sample loop. The apparatus was flushed with helium for 30 min and then pressurized again. The temperature was raised to a preselected value, and when sample weight remained constant a further GC trace was obtained. The apparatus was then purged and pressurized in preparation for the next temperature increment.

3.2.5. Photomicrographs

Bark samples were characterized by scanning electron microscopy (SEM) using a Cambridge Stereoscan 600. Samples were coated with a thin layer of gold by a standard flash evaporation technique at 10^{-4} Torr. Pictures were taken with a 35 mm or Polaroid camera attached to the CRT screen. Residues obtained by heat-treatment of jack pine bark, < 212 μm, over the temperature range 473 to 609 K in

nitrogen were also observed. These samples were attached to the SEM specimen holder by double-sided tape.

A standard 12 mm diameter copper specimen holder was modified to allow the observation of the effects of heat upon larger bark samples, approximately 5 x 3 x 1 mm. Three steel pins were inserted and bark samples impaled on these. Samples were observed at room temperature initially, and again after pyrolysis at selected temperatures and atmospheres on the thermobalance. An aluminum dowel with a central hole was used as a holder to mount the specimens on the sample support in the furnace assembly. Isothermal weight-change determinations were carried out as described earlier.

Before heat treatment, samples could be observed at 1.5 KV and magnification 50 to 100 X without coating, however, after pyrolysis, the specimens had to be coated with gold for observation purposes.

3.2.6. Surface area measurements

The technique involves the measurement of the amount of gas necessary to form a monomolecular layer on a solid surface. From the number of molecules adsorbed and the area occupied by each molecule, the surface area of the solid can be determined.

The following general BET equation was used (Brunauer,

Emmett, Teller 1938):

$$\frac{P}{V \ (\ P_O \ - \ P \ )} \ = \ \frac{1}{Vm \ C} \ + \ \frac{(\ C \ - \ 1 \ ) \ P}{Vm \ C \ P_O} \qquad (14)$$

where V is the total volume of gas adsorbed per gram of material at measured pressure P, Vm is the monolayer volume, P_O is the saturation pressure of the adsorbate gas at liquid nitrogen temperature, and C is a constant which depends upon the heats of adsorption and liquefaction of the gas.

The adsorbate krypton was used in a Pyrex apparatus, Figure 5. Approximately 10 mg of sample was weighed into the sample holder which was then positioned on the apparatus and evacuated at 10^{-4} Torr overnight at 383 K. Krypton was admitted to Va and the pressure in this space was measured on the McLeod gauge. The gas was then admitted into the sample container which was immersed in liquid nitrogen. After equilibrium was achieved, approximately 20 min, the pressure was again measured and the volume of krypton adsorbed was then calculated in the usual way (Gregg, Sing 1967).

3.2.7. Residue analysis

Samples were analysed for carbon, hydrogen and nitrogen using a Perkin Elmer model 240 Elemental Analyser. The technique involved the complete combustion of a sample (1.5 to 3.5 mg) in pure oxygen followed by analysis by difference for N_2, CO_2, and H_2O using thermal conductivity
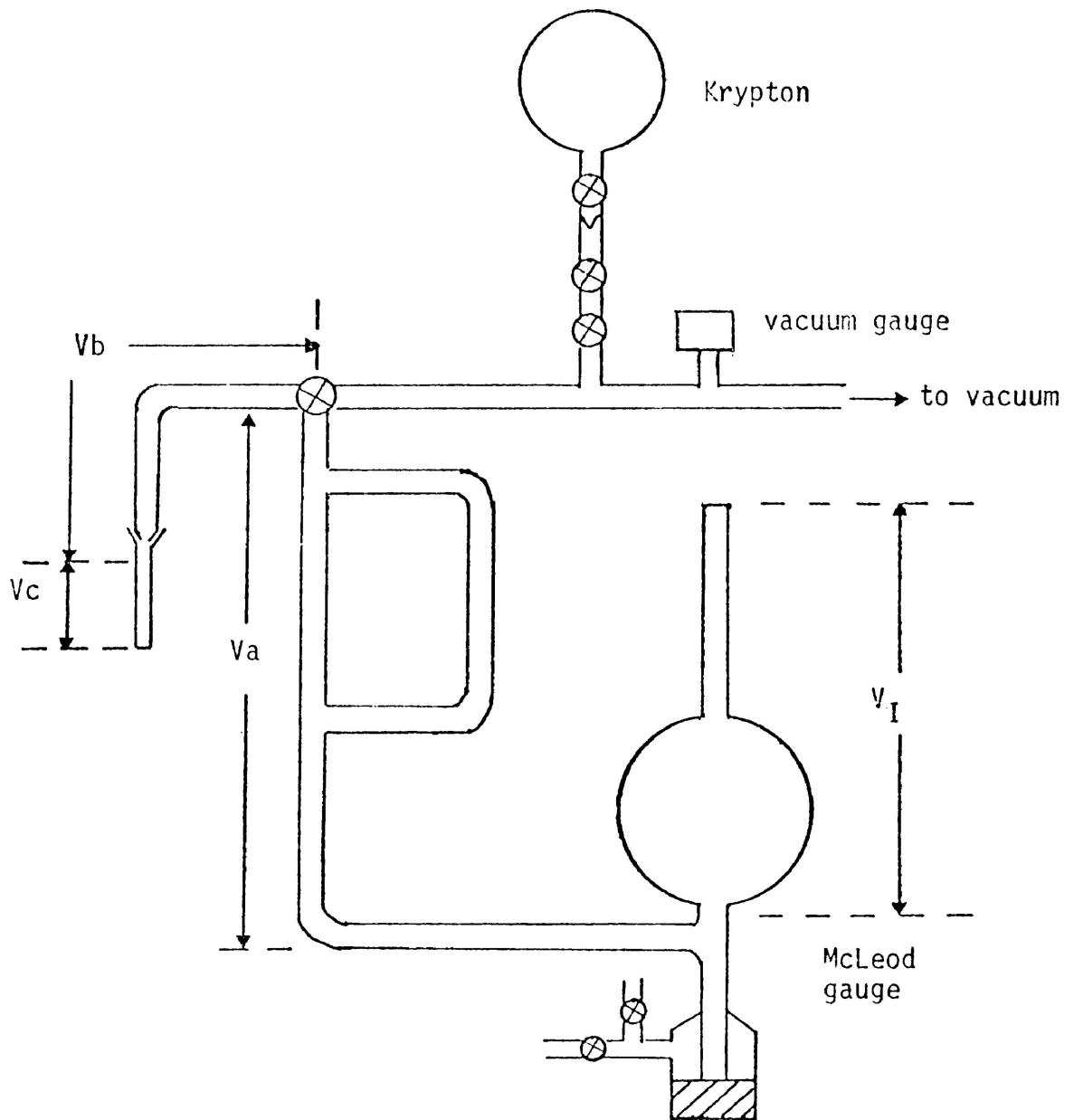
Figure 5   Krypton BET apparatus; Va = 13.6 ml, Vb = 1.855 ml,
Vc = 0.865 ml, V_I = 47.37 ml.

cells.

Various residues produced in the isothermal weight loss studies were analysed for %C, %H, and %N.

3.2.8. Infrared analysis

Jack pine bark specimens were prepared by grinding a mixture of bark with dry KBr (1% w/w) in an agate mortor. Pellets were prepared in a 1.27 cm die using a hydraulic press.

Infrared spectra were recorded on a Beckman 1R 12 Spectrophotometer. The instrument was operated in the double beam mode with a pellet of pure KBr positioned in the reference beam. Calibration of the instrument was checked against a standard polystyrene film.

3.2.9. Ash analysis

The ash obtained from jack pine bark was analysed by a Phillips X-ray Fluorescence Spectrometer, PW 1540 XRF. A chromium anode tube, FA 100/3, was supplied by a generator, PW 1130, at 50 kV and 30 ma and the x-rays were analysed by a scintillation detector (LiF). The instrument was capable of indicating the K_α radiation of elements from Z = 19 to Z = 56 where these elements were present at > 10 ppm.

The ash content of jack pine bark and sawdust were determined by heating samples at 873 K in a muffle furnace

in air (ASTM D1102-56).

4. RESULTS

4.1. Isothermal pyrolysis of jack pine bark

4.1.1. Dry nitrogen

Isothermal weight-change determinations using 40 mg samples of bark, < 212 μm, were carried out in flowing dry nitrogen at temperatures from 480 to 609 K. The results are presented as weight percent loss versus time of heating, Figure 6. The figure shows an initial period of rapid weight loss followed by a period of deceleration and slow approach to constant weight loss values. The final weight loss of a sample at any temperature was defined from a plot of weight loss against reciprocal time (t^{-1}) where the final loss was obtained by linear extrapolation to $t^{-1} = 0$, as shown in Figure 6 (see, for example; Dollimore, Holt 1973).

Generally, isothermal weight-change studies may be analysed according to an equation of the type:

$$F (\alpha) = k t \qquad (15)$$

where α is the fraction reacted and $F (\alpha)$ represents some function of α. To this end, the data for each temperature were plotted in the standard kinetic form, Figure 7 (Sharp, Brindley, Achar 1966), as degree of decomposition, α, against reduced time, $t/t_{0.5}$, where α is given by the weight loss at time t divided by the final weight loss and

$t_{0.5}$ is the time when $\alpha = 0.5$. When plotted in this way, these data fitted a common curve.

In order to derive values for the rate constants of the reactions, tests were carried out on the applicability of established kinetic expressions to describe the rate data (Appendix 2). Figure 8 indicates that derived plots of $\ln [-\ln (1 - \alpha)]$ versus $\ln t$ gave straight lines with an average slope of 0.5 for values of α from 0.1 to 0.9. Hence, the decomposition could be described by a type of Avrami-Erofeev expression (Avrami 1941; Erofeev 1946) originally derived for a nucleation and growth process, namely:

$$[- \ln (1 - \alpha)]^{1/n} = k_1 t \qquad (16)$$

where n is a positive number and k_1 is the reaction rate constant. Upon substitution for $n = 0.5$, equation (16) becomes:

$$[- \ln (1 - \alpha)]^2 = k_1 t. \qquad (17)$$

Values of k_1 were obtained from the linear plots of $[- \ln (1 - \alpha)]^2$ against time, Figure 9, and the temperature coefficient for activation, Tc, was calculated from the slope of an Arrhenius plot in the usual way. Since wood bark is a complex matrix of organic materials of unknown molecular weight, the effects of temperature on the reaction rates should preferably be quoted as a "temperature co-efficient" (Tc) rather than "activation energy". The kinetic
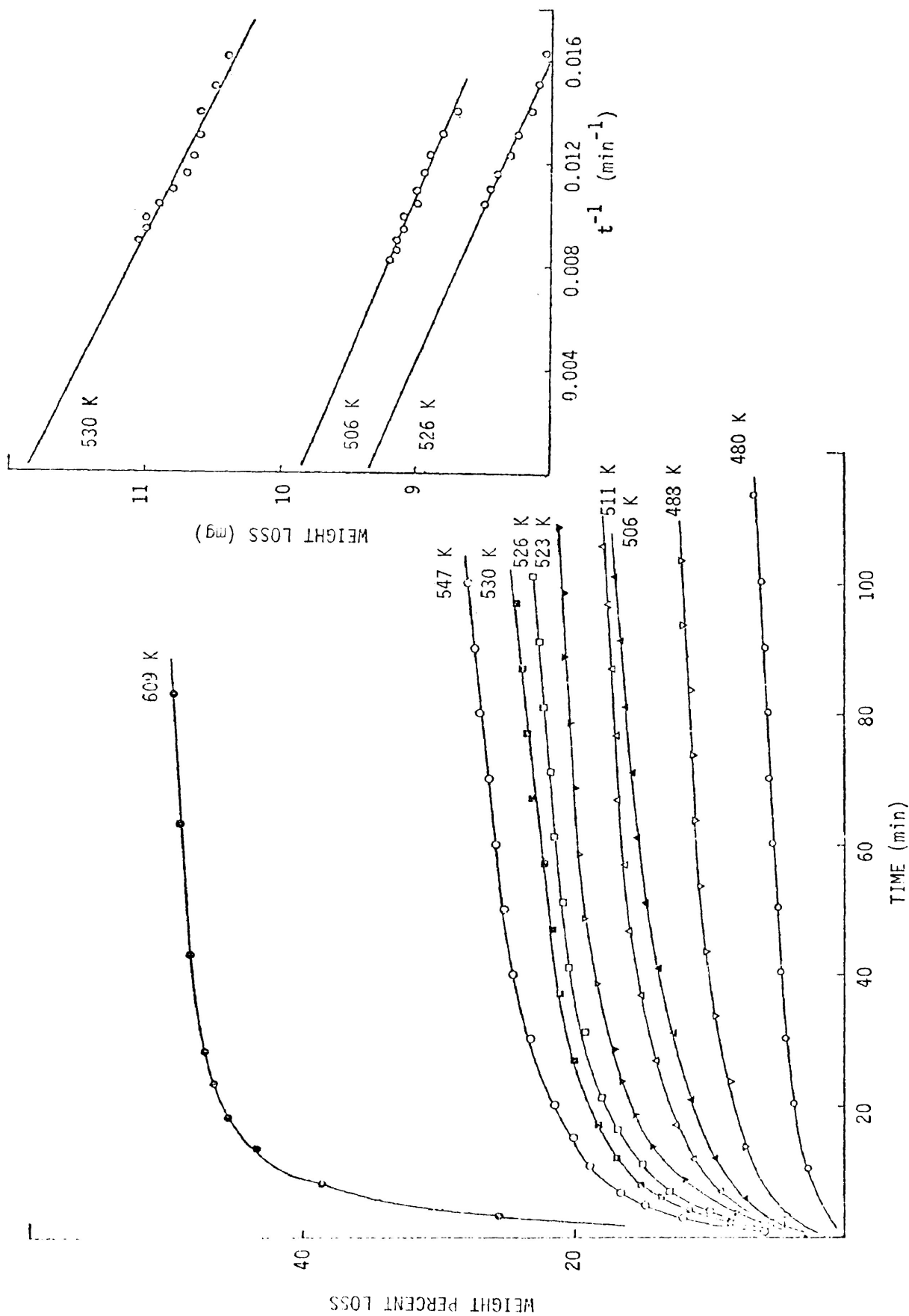
Figure 6 The thermal decomposition of jack pine bark in nitrogen. Inset: Plot of weight loss versus reciprocal time.
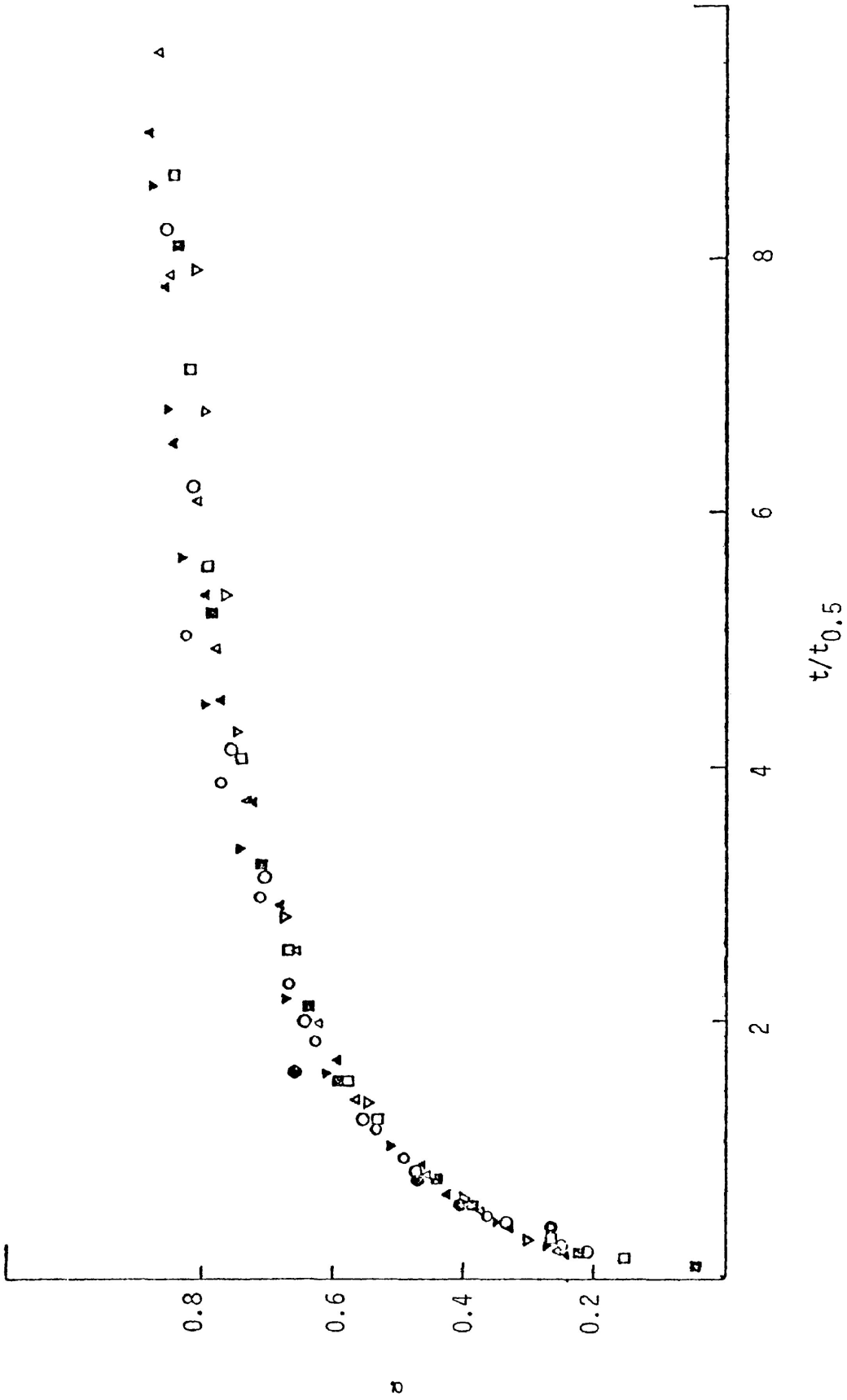
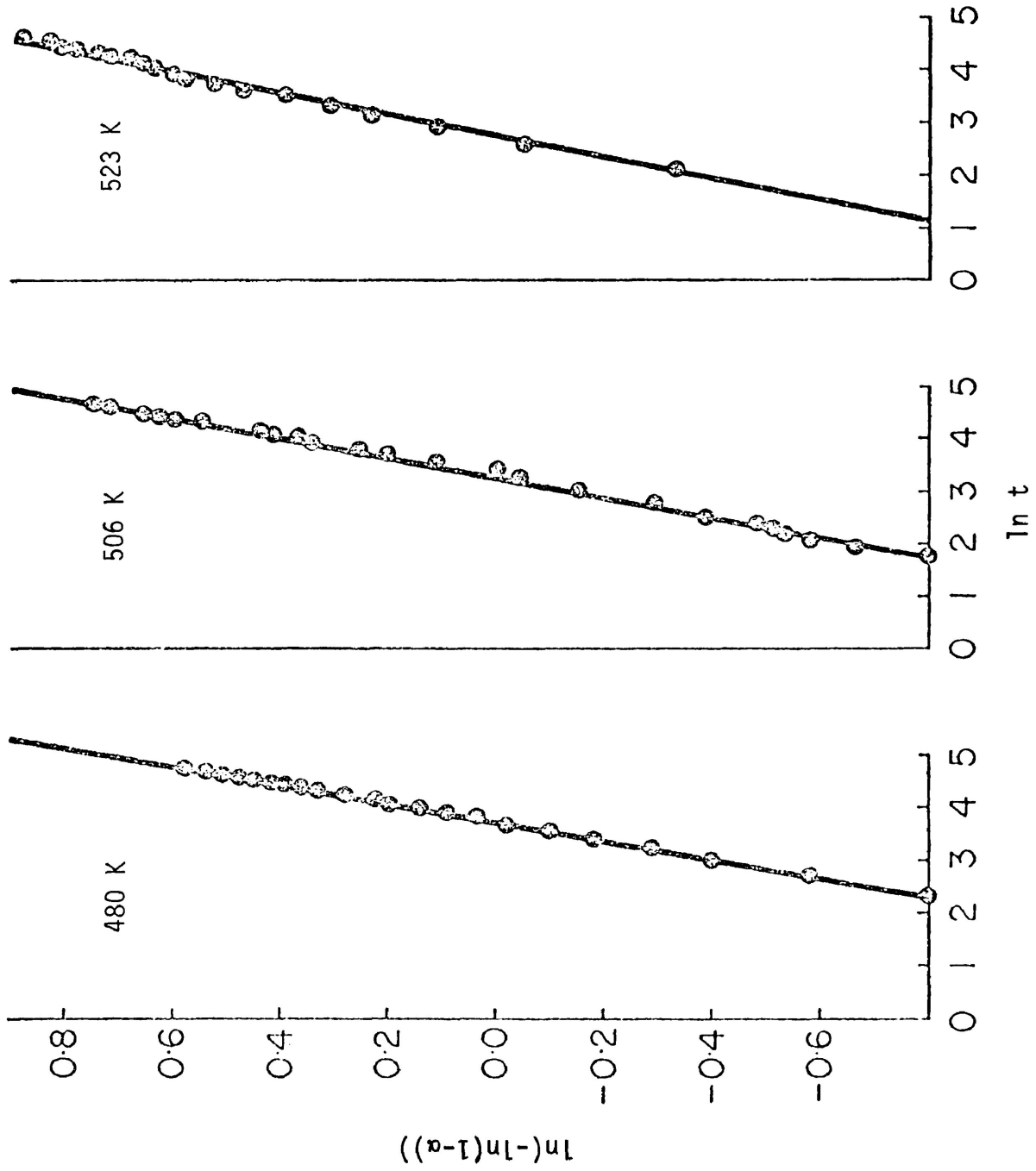Figure 7 Reduced time plot of the isothermal decomposition of jack pine bark.

Figure 8 Typical plots of $\ln(-\ln(1-\alpha))$ versus $\ln t$ for the pyrolysis of jack pine bark.
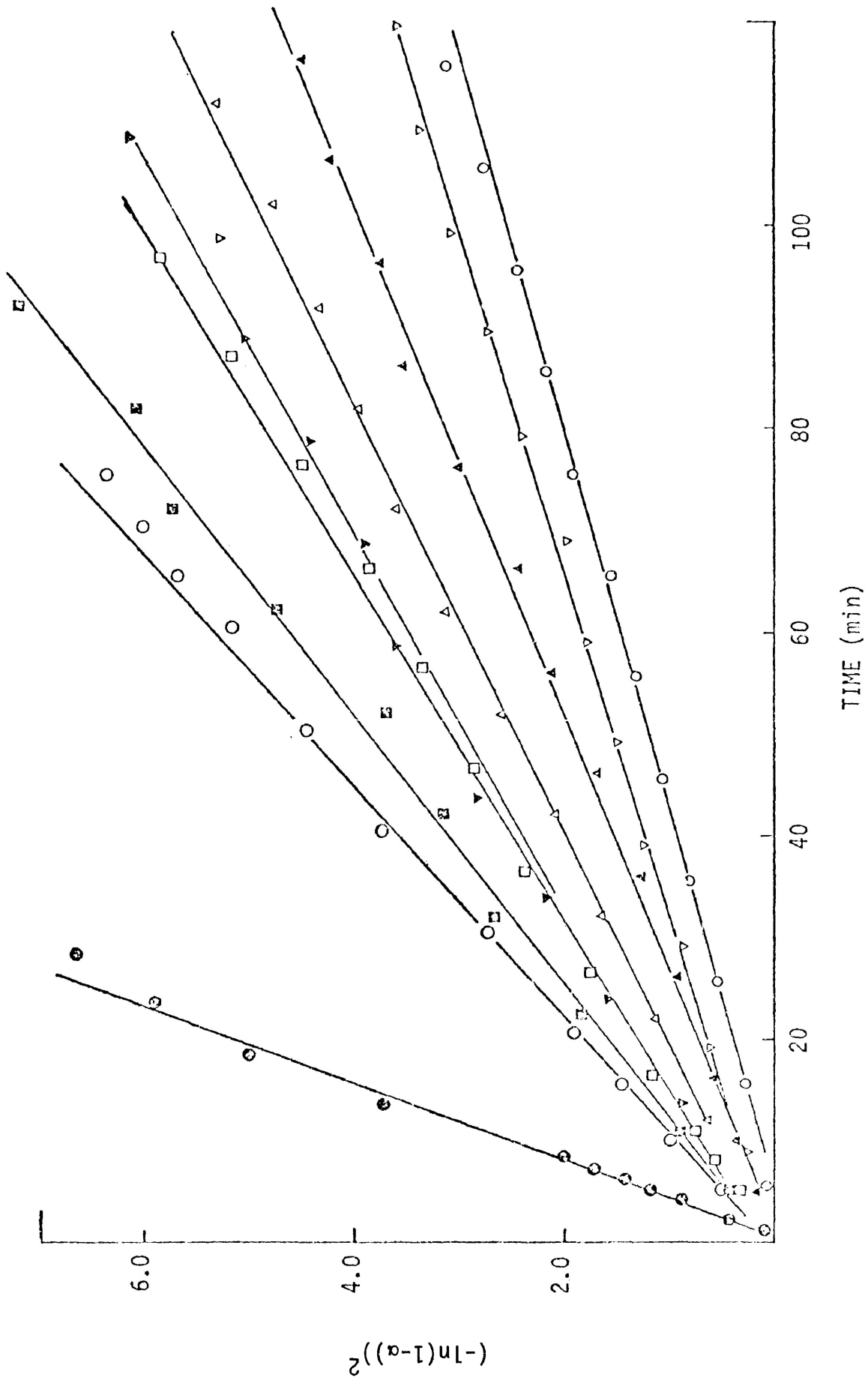
Figure 9 Kinetics of decomposition of jack pine bark in nitrogen.

data are summarized in Table 3, and for the purpose of comparisons only, derived numerical values of the pre-exponential factor, A, and "apparent activation energy", Ea, have been included.

Buoyancy corrections were determined for isothermal experiments by using 40 mg samples of dead-burned alumina. Over the temperature region 493 to 594 K, all samples exhibited an apparent weight loss amounting to 0.2 mg when transferred from the back pan of the balance into the furnace. It was noted that such small corrections would have little or no effect upon the interpretation of the data.

Linear plots with an average slope of k = 1.0 were also obtained for the pyrolysis of jack pine bark when the results were plotted as ln [α / (1 - α)] versus ln t. These findings indicate that the results should fit a modified type of Prout-Tompkins equation (Prout, Tompkins 1946) of the form:

$$\alpha \ / \ (\ 1 - \alpha \ ) = k_2 \ t \qquad\qquad (18)$$

Plots of α / (1 - α) versus time for jack pine bark pyrolysis were reasonably linear for values of α from 0.2 to 0.8. Calculation of the rate constant, k_2, allowed the temperature coefficient for activation to be calculated from an Arrhenius plot. This value of Tc, $5.57 \ . \ 10^3 \ K^{-1}$, is in good agreement with that obtained using equation (17), $5.16 \ . \ 10^3 \ K^{-1}$. Because the experimental data fitted equation

(17) over a wider range of α values, and because the reduced time curve obtained from equation (17) provided a better fit to the experimental curve, only the kinetic parameters for pyrolysis calculated from this expression are given in Table 3.

4.1.2. Air

The kinetics of pyrolysis of jack pine bark, < 212 μm, in flowing air were obtained by isothermal weight-change determinations over the temperature region 479 to 563 K. Plots of weight percent loss against time, Figure 10, exhibited a rapid initial loss followed by a slow approach to constant final weight similar to those found for pyrolysis in nitrogen. Final weight loss values were obtained by extrapolation. The percent weight loss observed in air was approximately twice that found in nitrogen.

When plotted in the standard kinetic form, α versus $t/t_{0.5}$, Figure 11, these data fit the same common curve as that for bark pyrolysis in nitrogen.

The working kinetic expression for decomposition in air was therefore described by equation (17) and the rate constant, k_1, was obtained from linear plots of $[- \ln (1 - \alpha)]^2$ against t, Figure 12. Kinetic parameters were again derived from an Arrhenius plot and these are summarized in Table 3.
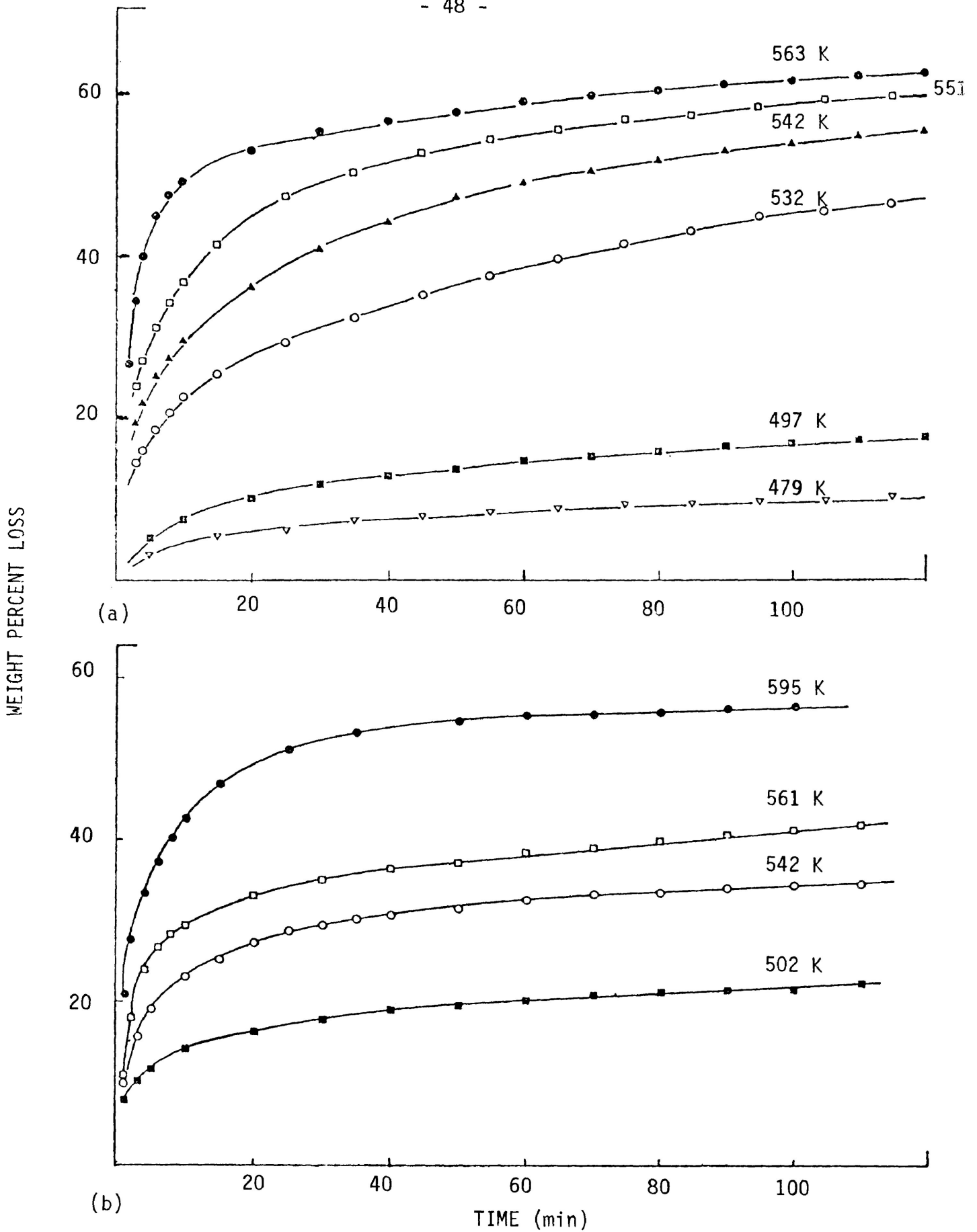
Figure 10   The thermal decomposition of jack pine bark
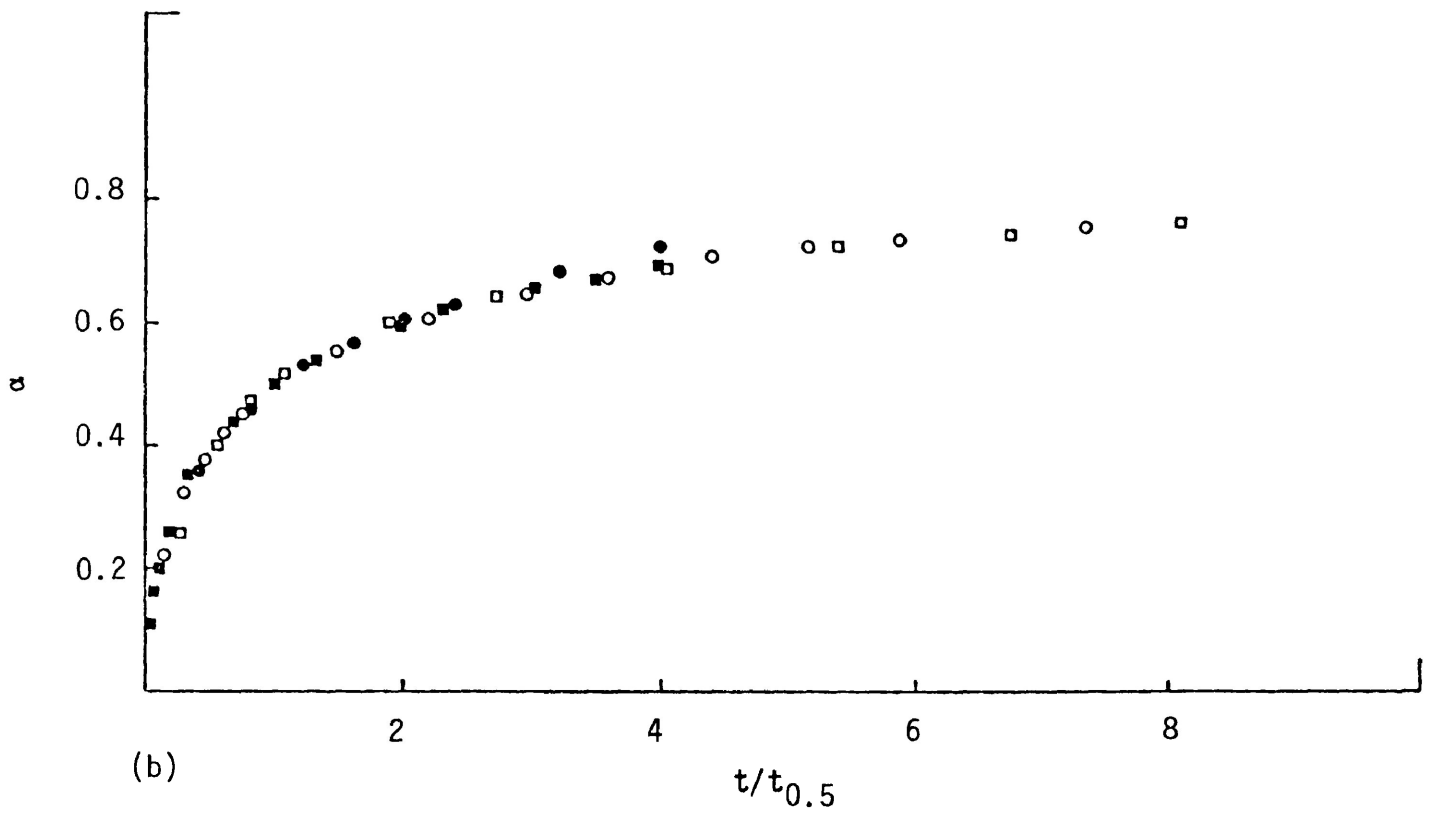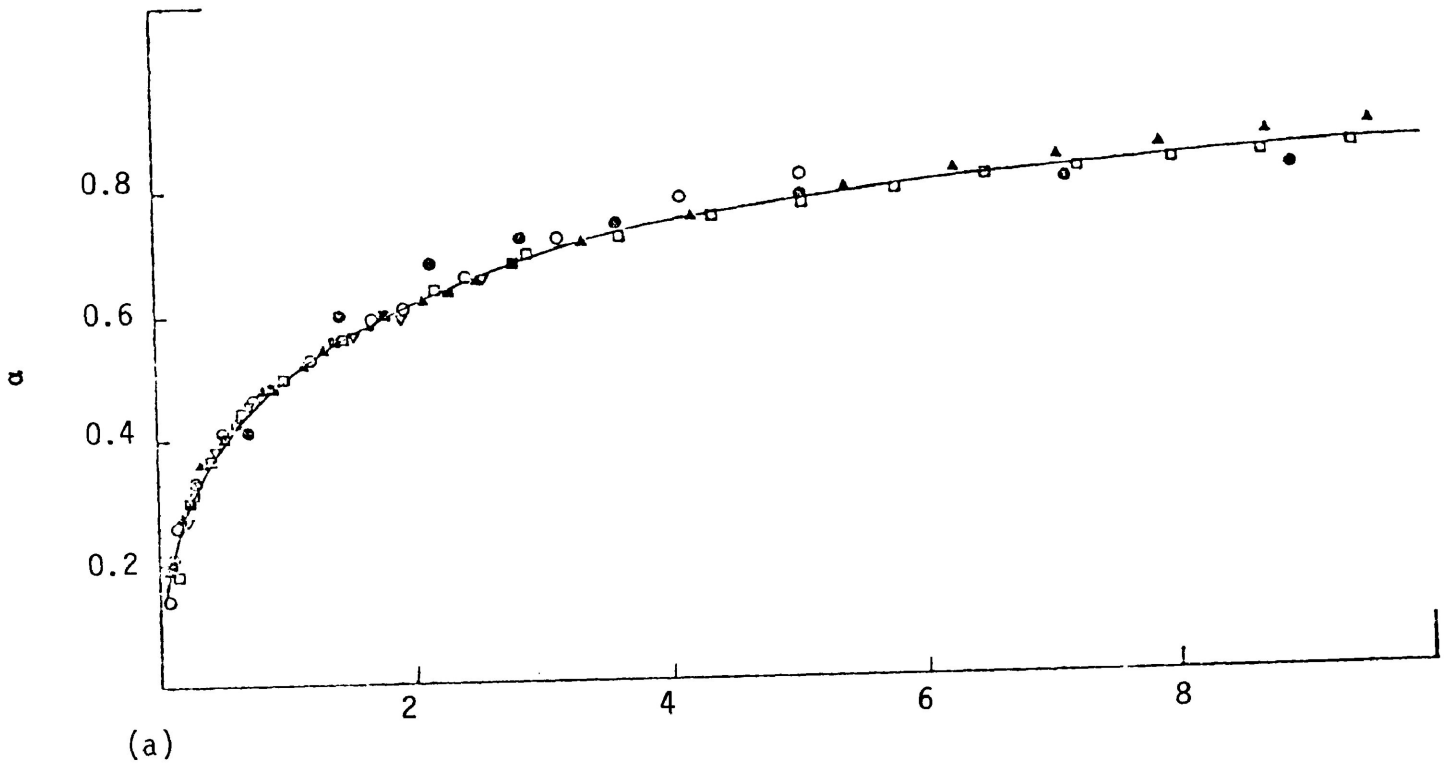in air (a), and in nitrogen + H_2O (b).

Figure 11   Reduced time plot of the isothermal decomposition
of jack pine bark in air (a), and in nitrogen + H_2O (b).
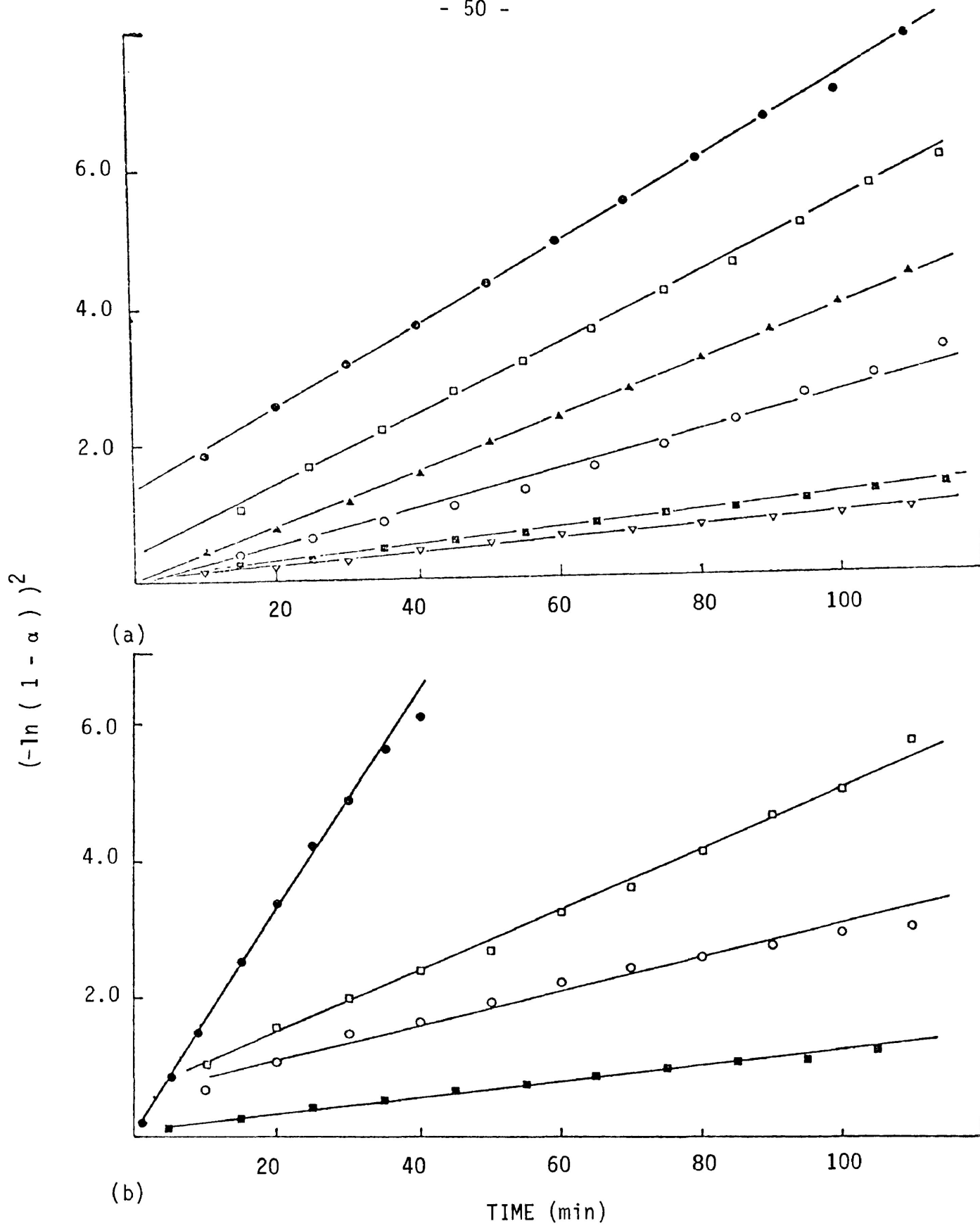
Figure 12   Kinetics of decomposition of jack pine bark
in air (a), and in nitrogen + H_2O (b).

Table 3 Kinetic parameters for the pyrolysis of jack pine bark   212 um.

ATMOSPHERE	T (K)	$t_{0.5}$ (min)	SLOPE $\ln(-\ln(1-\alpha))$ VERSUS $\ln t$	RATE CONSTANT $(k.10^{-2}\ min^{-1})$	Tc $(.10^3\ K^{-1})$	A (min^{-1})	Ea $(Kj.mol^{-1})$
in nitrogen	480	22.0	0.57 ± 0.01	2.66 ± 0.06			
	488	13.8	0.47 ± 0.02	2.78 ± 0.19			
	506	12.4	0.52 ± 0.01	4.09 ± 0.08	5.16 ± 0.56		
	511	8.5	0.49 ± 0.01	4.68 ± 0.16		$1.13.10^3$	
	523	8.6	0.50 ± 0.03	5.33 ± 0.30			43
	526	6.5	0.51 ± 0.03	5.82 ± 0.26			
	530	5.2	0.49 ± 0.02	7.62 ± 0.45			
	547	4.9	0.52 ± 0.03	8.25 ± 0.23			
	609	3.3	0.57 ± 0.11	24.93 ± 1.84			
in air	479	45.0	0.49 ± 0.02	0.85 ± 0.05			
	497	39.0	0.48 ± 0.01	1.14 ± 0.02	6.58 ± 0.89		
	532	20.8	0.49 ± 0.02	2.91 ± 0.14		$7.19.10^3$	
	542	12.0	0.48 ± 0.01	3.84 ± 0.08			55
	551	6.9	0.51 ± 0.03	5.08 ± 0.11			
	563	2.8	0.54 ± 0.12	5.93 ± 0.17			
in nitrogen plus water vapour	502	30.0	0.46 ± 0.02	1.12 ± 0.06			
	542	6.8	0.42 ± 0.03	3.74 ± 0.38	8.12 ± 0.64		
	561	3.7	0.42 ± 0.06	5.87 ± 0.78		$1.18.10^5$	
	595	2.5	0.46 ± 0.01	14.25 ± 0.71			68

Isothermal heat treatment at temperatures in excess
of 563 K produced a very rapid weight loss which could not
be followed with the present thermobalance.

4.1.3. Nitrogen plus water vapour

A similar kinetic study of the pyrolysis of jack
pine bark, < 212 μm, was conducted in nitrogen saturated
with water vapour (15.5 Torr) at temperatures from 502 to
595 K. The results were very similar to those obtained from
weight-change determinations in flowing air as shown in
Figures 10, 11, and 12.

Kinetic parameters were derived from an Arrhenius
plot, and are summarized in Table 3.

The error for 95% confidence interval is indicated in
Table 3 (Appendix 1).

4.1.4. The effects of $FeCl_3$ and $ZnCl_2$

Isothermal weight-change determinations were carried
out on jack pine bark, < 212 μm, with additions of $ZnCl_2$
(3.9% W/W), and $FeCl_3$ (2.4% W/W). These experiments were
conducted in flowing dry nitrogen over the temperature range
485 to 599 K.

Plots of weight percent loss versus time, Figure 13,
were similar to those obtained for native bark. Final weight
loss was extrapolated as before and excellent agreement was

obtained between that value and the observed final value for the additives at 599 K ($\pm$ 1%).

The standard kinetic plots were identical for both samples at all temperatures, and were coincident with that obtained for native bark. Plots of ln [- ln (1 - α)] against time produced an average slope of 0.5. The rate constant was therefore described by the expression:

$$k = [- \ln (1 - \alpha)]^2 / t \, . \qquad (19)$$

The kinetic parameters are shown in Table 4.

The temperature coefficient for activation for bark plus $ZnCl_2$, $5.12 \cdot 10^3 \ K^{-1}$, was similar to that obtained for native bark, while that for bark plus $FeCl_3$, $6.34 \cdot 10^3 \ K^{-1}$, was slightly higher.

4.1.5. Extracted bark

Isothermal pyrolysis studies were conducted on extracted bark, < 212 μm, in flowing dry nitrogen over the region 485 to 595 K. Plots of weight percent loss against time are given in Figure 14. As with the previous samples, these plots indicated a rapid initial weight loss and a slow approach to constant weight.

The standard kinetic plot was identical to that for native bark and kinetic analysis was performed using equation (17). An Arrhenius plot gave a value for the temperature coefficient of activation of $7.88 \cdot 10^3 \ K^{-1}$. The kinetic
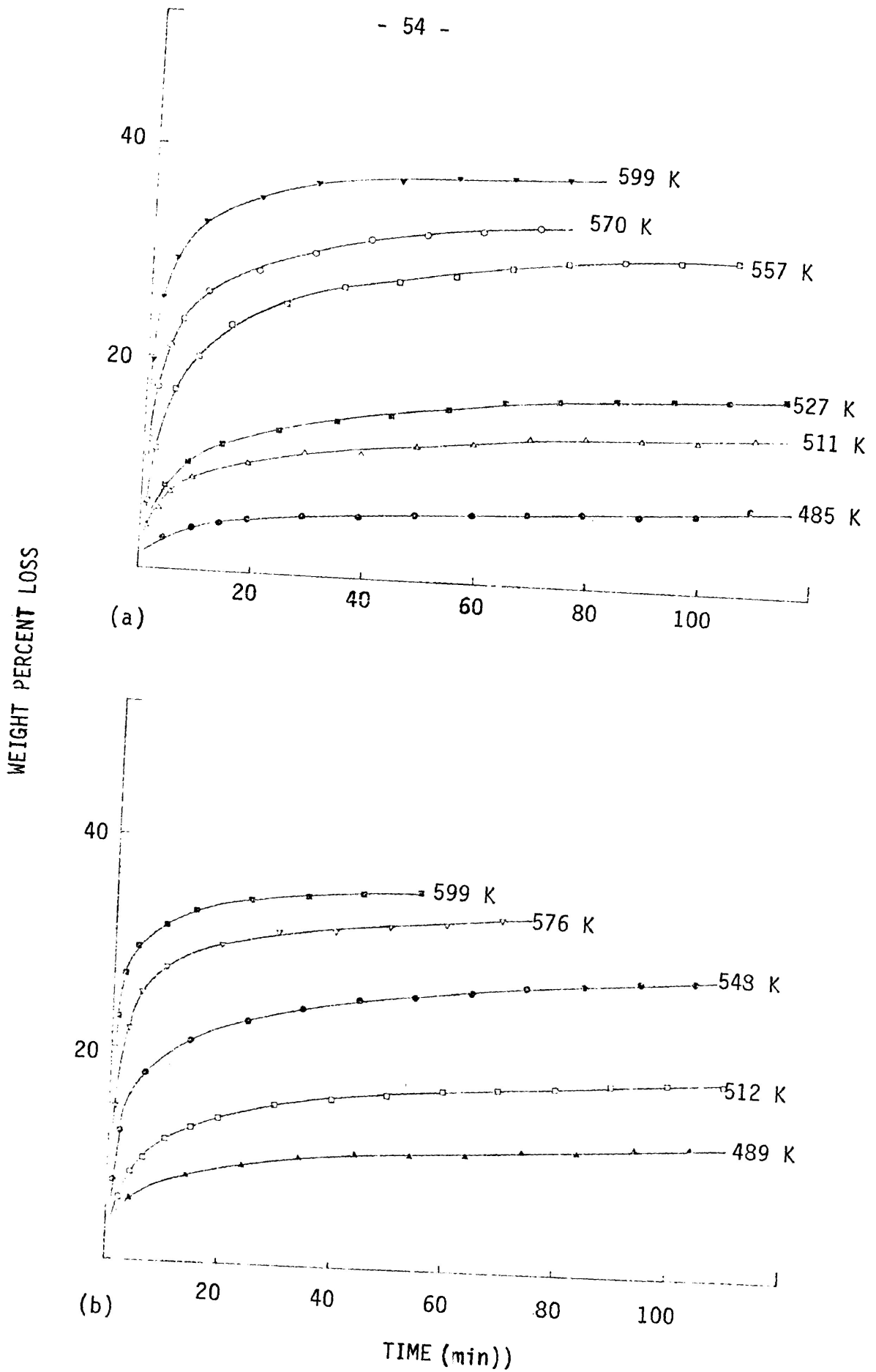
Figure 13   The thermal decomposition of jack pine bark containing
32.4% $FeCl_3$ (a) and 3.9% $ZnCl_2$ (b).

Table 4 Kinetic parameters for the pyrolysis of native jack pine bark containing additives and extracted bark in nitrogen.

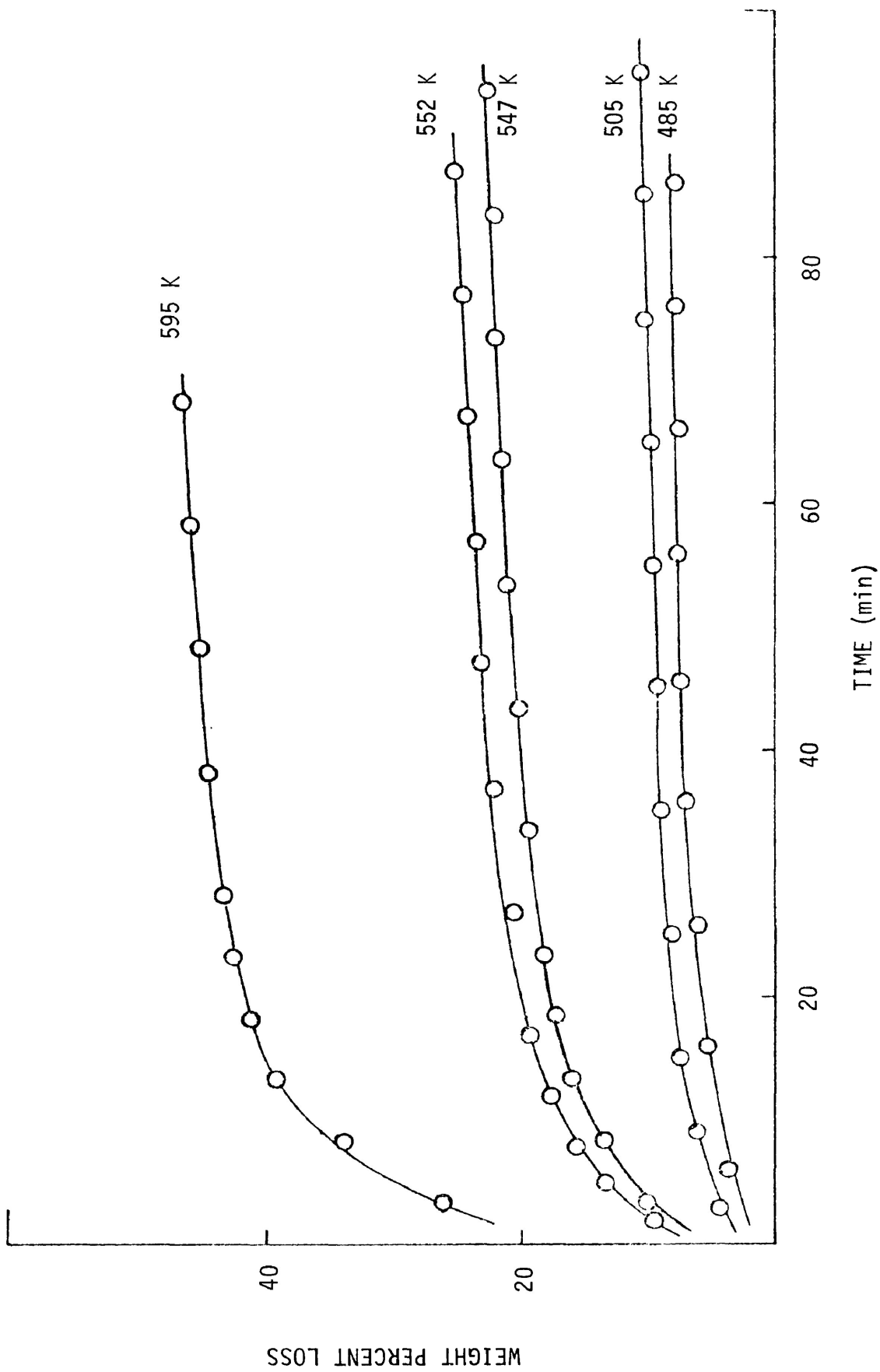| TREATMENT	T (K)	$t_{0.5}$	SLOPE $\ln(-\ln(1-\alpha))$ VERSUS $\ln t$	RATE CONSTANT $(k.10^{-2}\ min^{-1})$	T_c $(.10^3\ K^{-1})$	A (min^{-1})	E_a $(Kj.mol^{-1})$
+ ZnCl$_2$	489	10.0	0.41 ± 0.02	3.22 ± 0.21			
(3.9%)	512	6.5	0.47 ± 0.02	4.97 ± 0.17	5.12 ± 0.84		
	548	3.7	0.43 ± 0.02	8.85 ± 0.49		$1.10.10^3$	
	576	1.4	0.39 ± 0.03	14.18 ± 1.01			43
	599	0.8	0.32 ± 0.02	23.33 ± 3.48			
+ FeCl$_3$	485	18.0	0.45 ± 0.04	1.79 ± 0.10			
(2.4%)	511	8.6	0.48 ± 0.02	4.40 ± 0.27			
	527	8.6	0.48 ± 0.02	5.00 ± 0.22	6.34 ± 0.90		
	557	4.0	0.54 ± 0.04	10.67 ± 0.34		$9.08.10^3$	
	570	2.1	0.40 ± 0.04	12.65 ± 0.58			53
	599	1.0	0.39 ± 0.05	23.68 ± 3.39			
solvent	485	31.0	0.44 ± 0.02	0.86 ± 0.15			
extracted	505	11.4	0.39 ± 0.02	2.24 ± 0.19			
	525	11.8	0.52 ± 0.02	3.84 ± 0.22	7.88 ± 1.25		
	547	9.3	0.43 ± 0.02	6.54 ± 0.29		$1.11.10^5$	
	552	5.5	0.51 ± 0.02	8.37 ± 0.36			65
	595	3.2	0.50 ± 0.03	16.10 ± 2.66			

Figure 14 The thermal decomposition of extracted jack pine bark in nitrogen.

parameters are summarized in Table 4.

4.1.6. Particle size effects

Isothermal weight-change determinations were carried out on native jack pine bark of various particle sizes—212 to 425 μm, 425 to 600 μm, and > 600 μm—in nitrogen over the temperature region 486 to 598 K. Plots of weight percent loss versus time are given in Figures 15, 16, and 17.

The mathematical interpretation of data from this study was identical to that described previously for bark, < 212 μm, in nitrogen. The kinetic parameters are given in Table 5. The temperature coefficient for activation was observed to decrease with increasing particle size.

4.2. Analysis of gaseous products

The gaseous products of pyrolysis in helium of jack pine bark, < 212 μm, were determined at temperatures from 373 to 623 K. Average relative peak heights values for CO, CO_2, CH_4, and H_2O are given in Table 6.

Typical gas chromatographic traces are presented in Figure 18. These results indicate that at temperatures < 523 K the most prevalent product was H_2O, with some CO_2 and CO. The production of CH_4 began > 523 K and no H_2 was observed < 623 K.
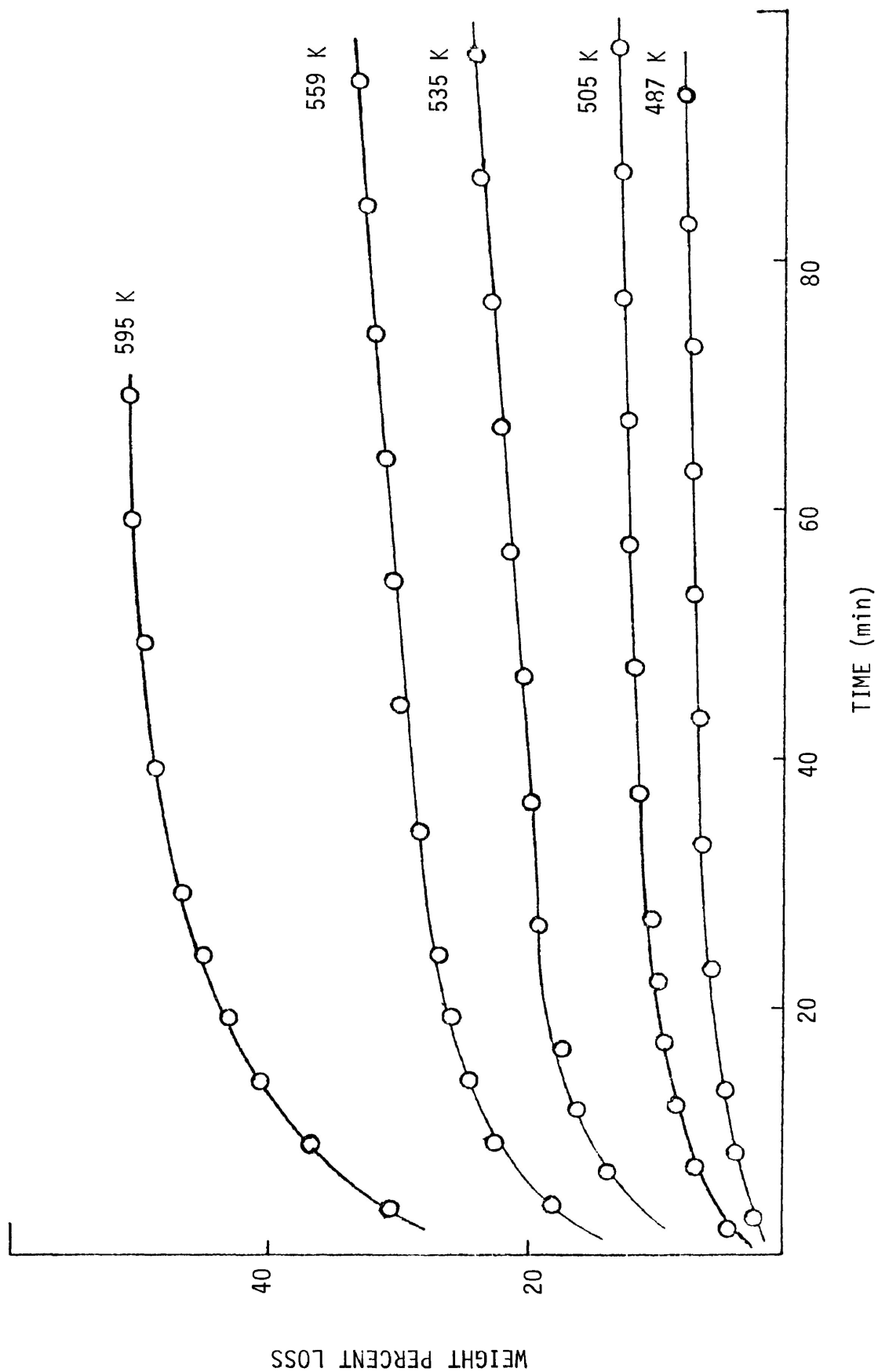
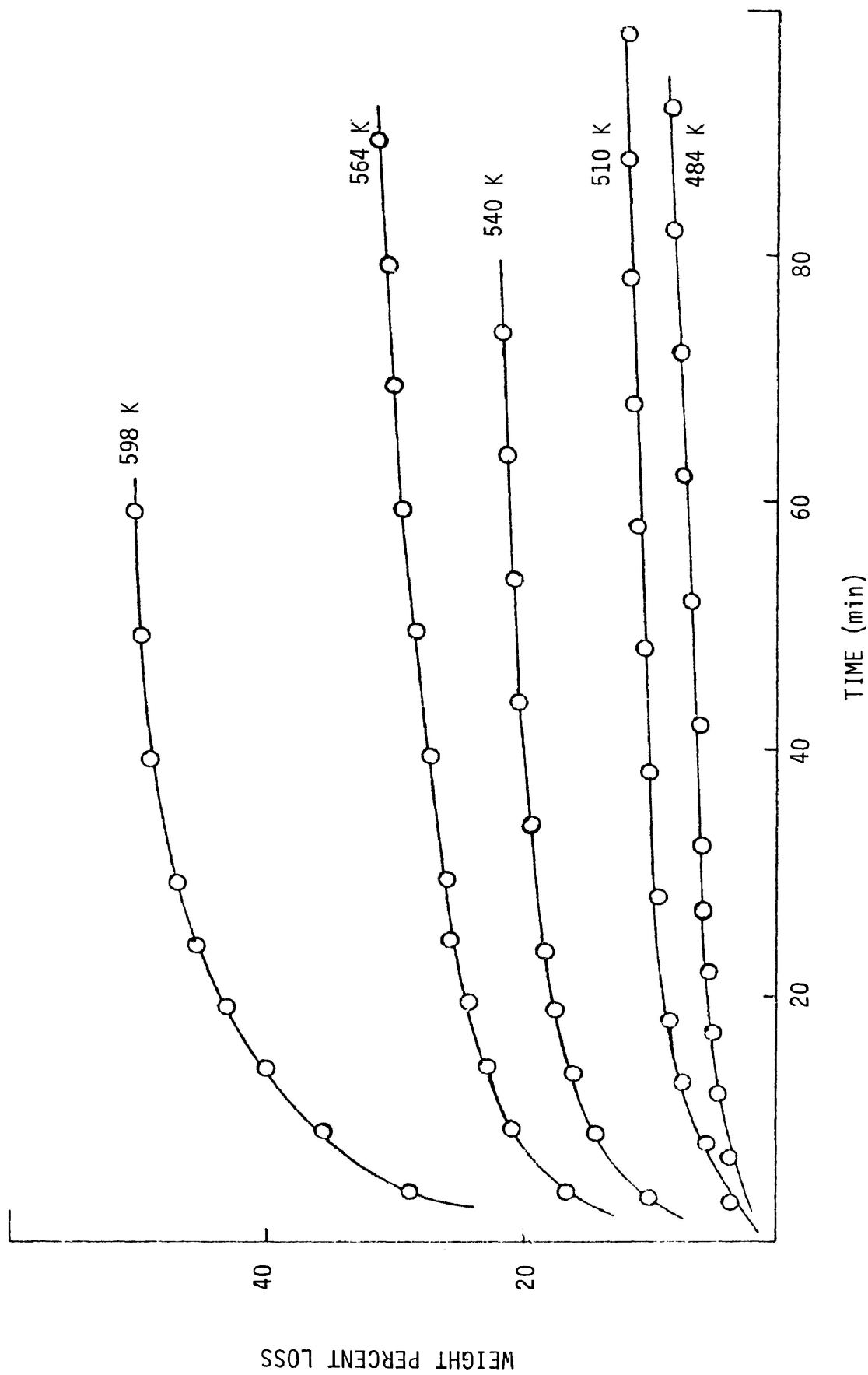Figure 15 The thermal decomposition of jack pine bark, 212 to 425 μm.

Figure 16   The thermal decomposition of jack pine bark, 425 to 600 μm.
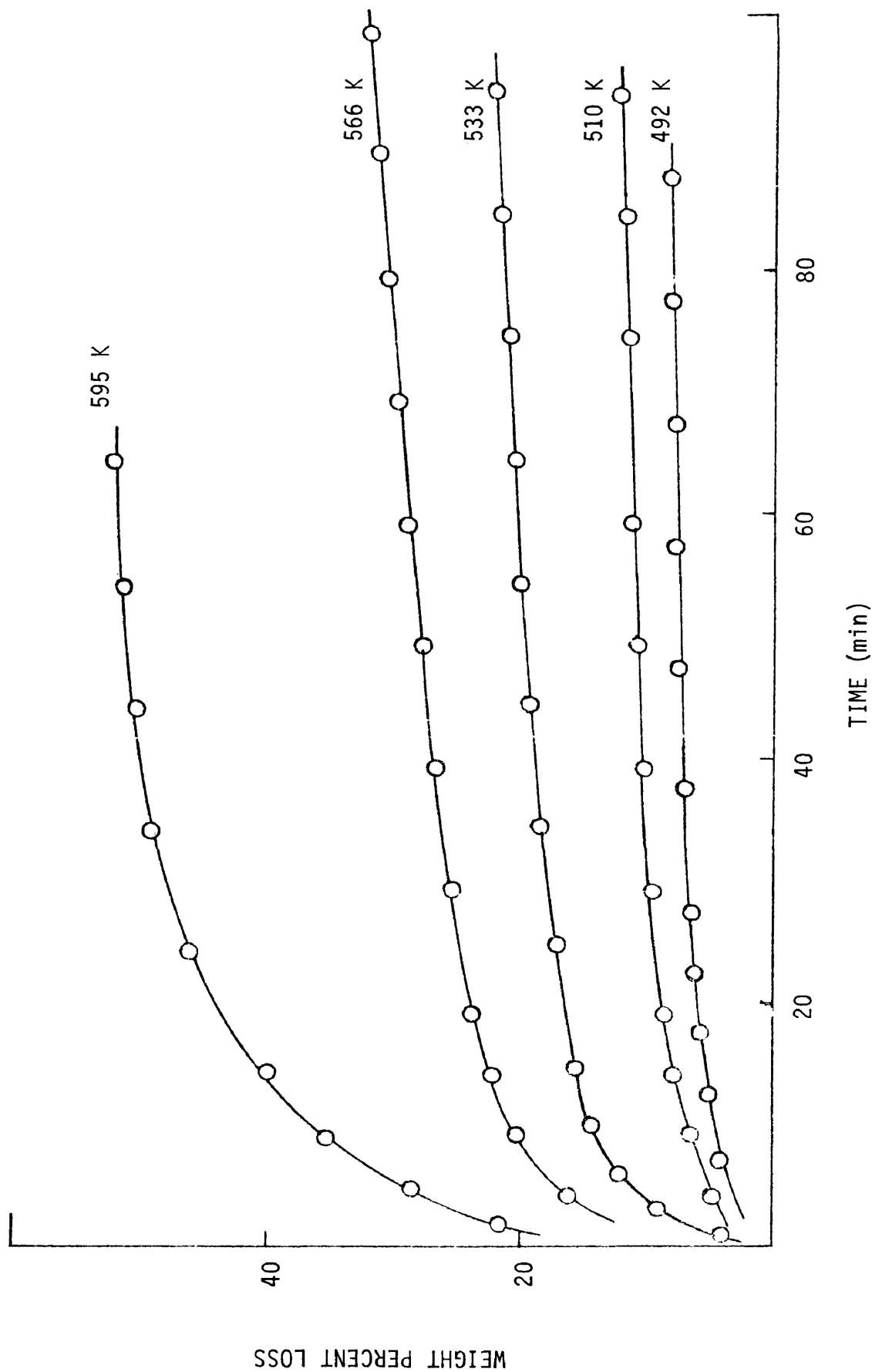
Figure 17 The thermal decomposition of jack pine bark, > 600 μm.

Table 5   Kinetic parameters for the pyrolysis of jack pine bark
of various particle sizes in nitrogen.

PARTICLE SIZE (μm)	T (K)	SLOPE $\ln(-\ln(1-\alpha))$ VERSUS lnt	RATE CONSTANT $(k.10^{-2} \, min^{-1})$	Tc $(.10^3 \, K^{-1})$	A (min^{-1})	Ea $(Kj.mol^{-1})$
	487	0.47 ± 0.02	3.17 ± 0.20			
212	505	0.46 ± 0.01	4.30 ± 0.19	3.83 ± 1.07		
to	535	0.42 ± 0.02	6.98 ± 0.42		83.9	
425	559	0.42 ± 0.03	7.65 ± 0.57			32
	595	0.47 ± 0.03	14.19 ± 0.53			
	486	0.41 ± 0.04	2.02 ± 0.15			
425	510	0.53 ± 0.02	4.20 ± 0.12	3.79 ± 1.86		
to	540	0.46 ± 0.02	5.76 ± 0.26		59.1	
600	564	0.46 ± 0.03	7.58 ± 0.66			31
	598	0.54 ± 0.02	13.54 ± 0.65			
	492	0.43 ± 0.01	3.13 ± 0.15			
	510	0.49 ± 0.01	4.38 ± 0.12	3.74 ± 0.89		
600	533	0.44 ± 0.01	5.18 ± 0.22		61.6	
	566	0.44 ± 0.03	7.94 ± 0.77			31
	595	0.53 ± 0.03	12.41 ± 0.28			

Table 6   Average relative peak heights of the
           gaseous products of pyrolysis of jack
           pine bark, <   212 µm, in helium.

Peak height

T (K)	CO	CO_2	CH_4	H_2O
448	1	10.9	0	38.9
473	3.2	25.4	0	44.8
513	14.6	50.0	0	95.2
523	49.4	174.0	0.4	196.0
543	23.3	56.2	0	95.2
573	43.2	75.4	0.8	122.6
603	61.0	88.0	2.3	97.6
623	75.7	104.4	3.9	101.0

A standard gas sample containing CO (0.105%), CO_2 (0.104%), H_2 (0.10%), and CH_4 (0.105%) with helium making up the balance was used to calibrate the thermal conductivity detector in measuring product ratios using their relative peak heights. The following ratios were obtained from the standard sample: CO_2/CO = 0.573, CH_4/CO = 0.570. The water peak was not used in the description of product ratios due to the difficulty in assessing the relative amount present.

The results are shown in Figure 19 as ln (product ratio) versus temperature. The ratio CO_2/CO was observed to decrease from 19.0 at 448 K to 2.2 at 623 K while the ratio CH_4/CO was observed to increase from 0.01 at 523 K to 0.10
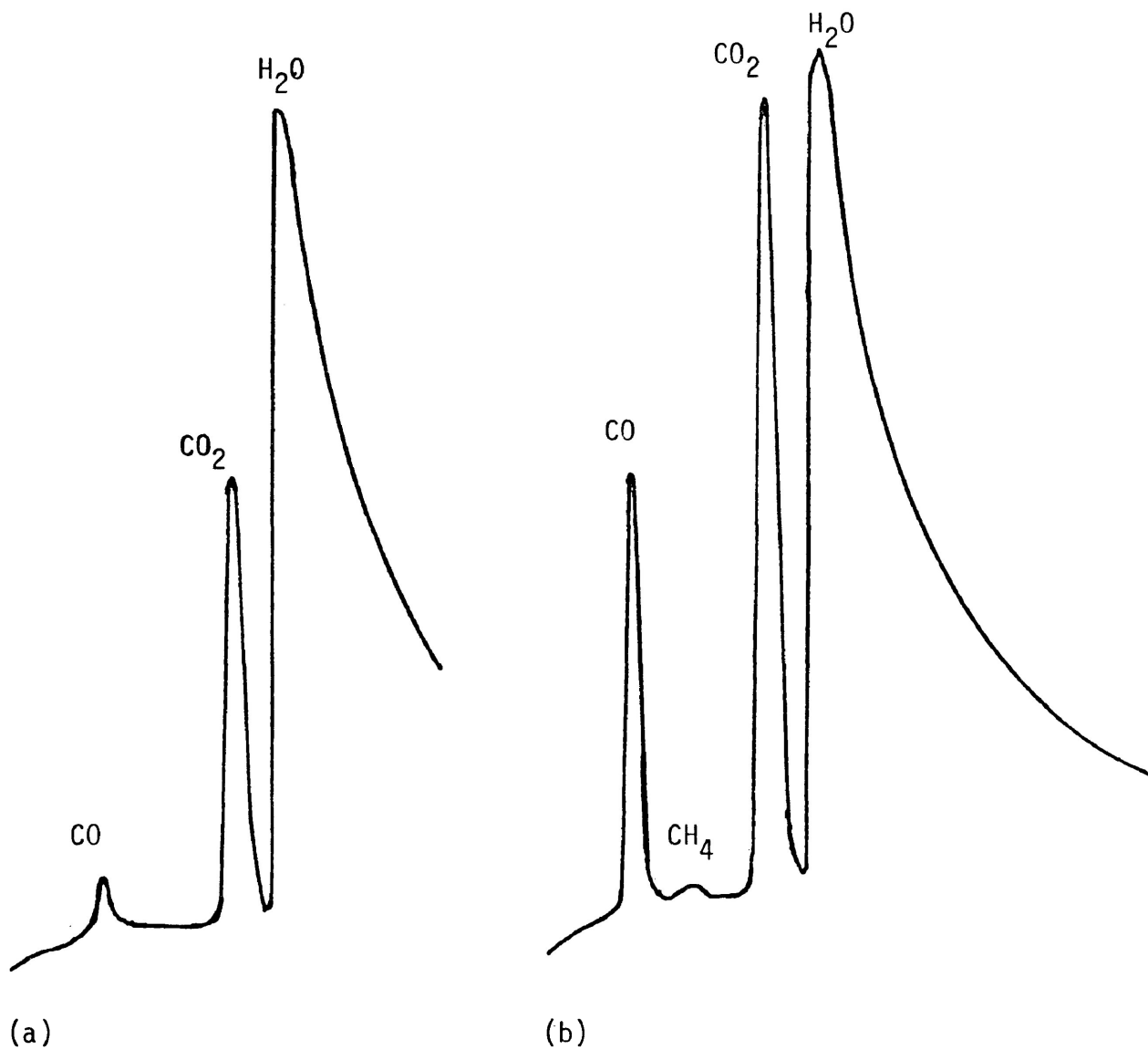
Figure 18   Typical GC traces from jack pine bark pyrolysis
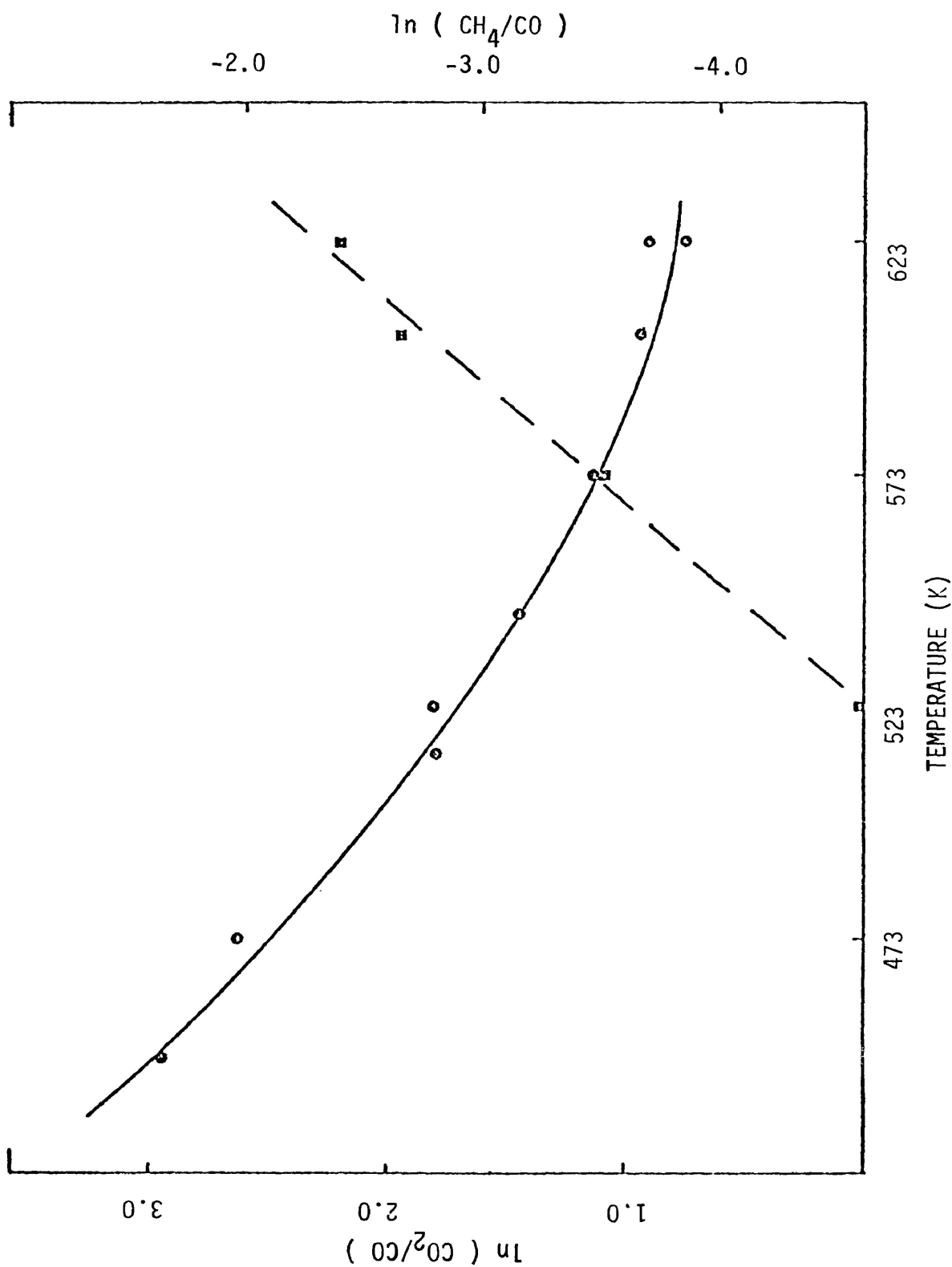   at 473 K (a), and 573 K (b).

Figure 19   Logarithmic plot of the gaseous product ratios for the pyrolysis of jack pine bark in an inert atmosphere.

at 623 K.

Only H_2O was observed from the heat treatment of bark at 373 K. The H_2O peak appeared to decrease in size with increasing temperature relative to that of CO.

4.3. Photomicrographs

Native jack pine bark, < 212 μm, was examined by scanning electron microscopy and found to consist of irregularly-shaped particles, Figure 20. The colour change to the characteristic black of charcoal was visibly apparent after pyrolysis in nitrogen at temperatures from 480 to 609 K. Few structural changes were observed on pyrolysis. Bark particles appeared to have a smoother surface after heat treatment and there appeared to be progressive cracking or separation of layers along the fibre axis.

Few anatomical features could be identified because of the destructive nature of the sample preparation procedure. No significant differences were observed between pyrolysed bark samples and those treated with $FeCl_3$ or $ZnCl_2$, or by the extraction process.

Treatment of larger bark particles in nitrogen at 576 K produced little structural alteration, Figure 21. The separation of layers along the fibre axis, however, was more apparent. Pyrolysis in air (560 K) produced similar results.

Photomicrographs of native jack pine sawdust,
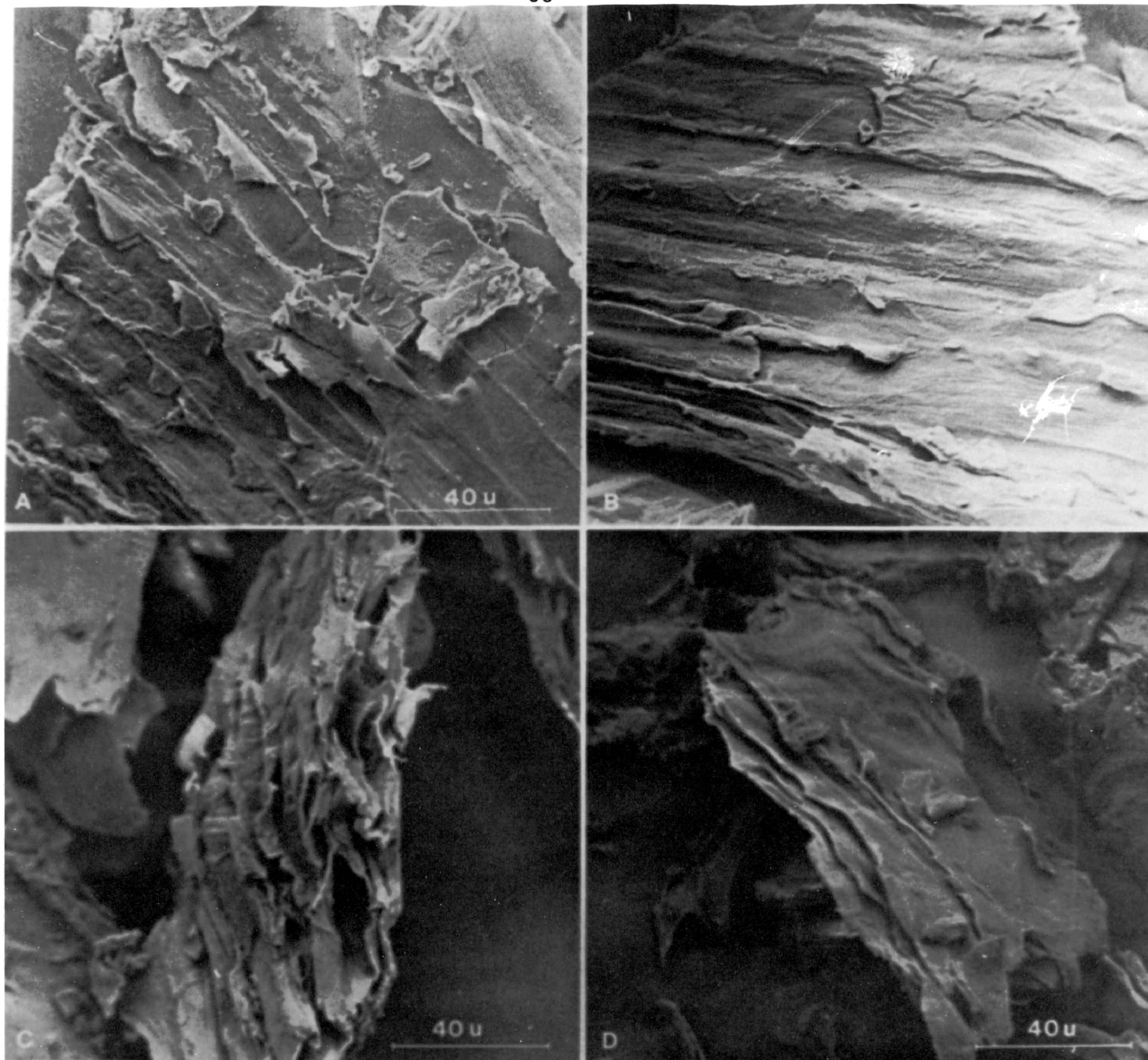
Figure 20   Scanning electron micrographs of jack pine bark after
various treatments.   A. The addition of $FeCl_3$.
B. Pyrolysis in nitrogen at 523 K.   C. Pyrolysis in nitrogen
at 547 K.   D. Pyrolysis in nitrogen at 609 K.

(a)
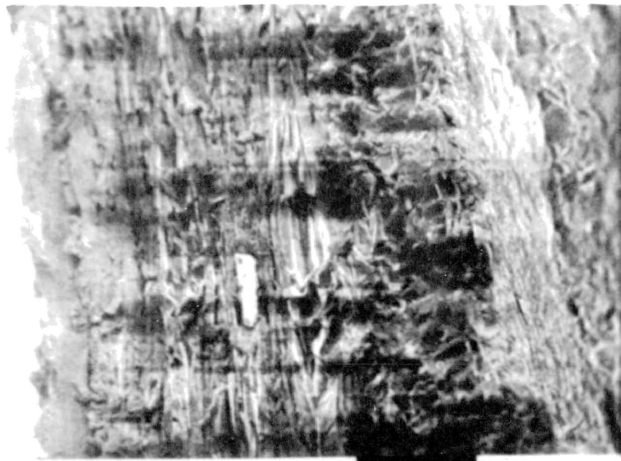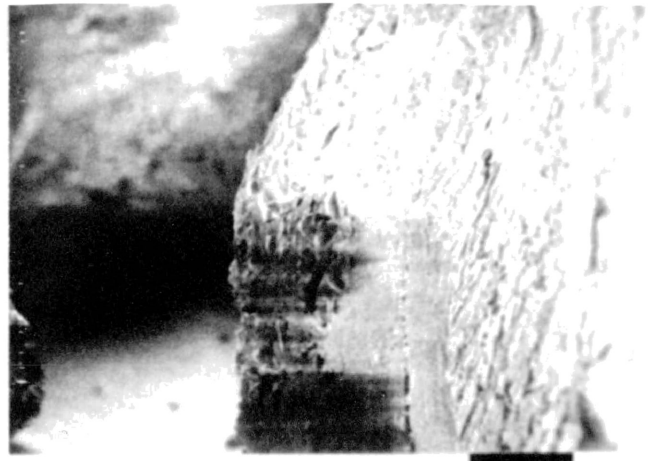
(b)

Figure 21   Scanning electron micrographs of native jack pine bark (a), and bark after heat treatment in nitrogen at 576 K (b).

(a)
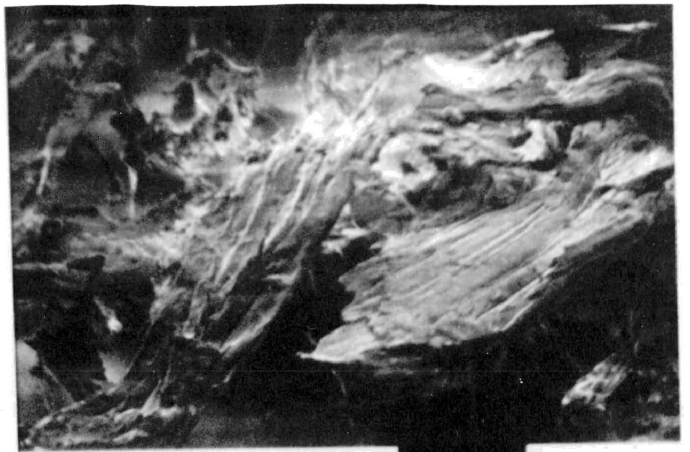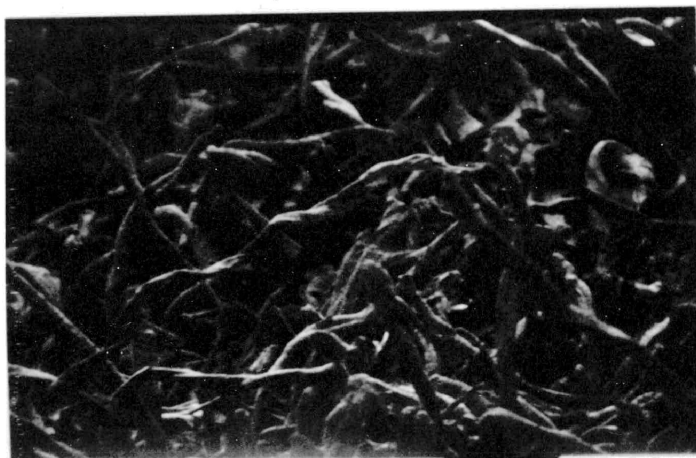
(b)

Figure 22   Scanning electron micrographs of native jack pine
sawdust (a), and cellulose powder (b).

< 212 µm, and cellulose were also obtained, Figure 22.
The sawdust exhibited a more fibrous-like structure, com-
pared to bark, however no simple or well-defined geometric
shape was apparent. The cellulose sample consisted of
long, twisted cylindrical particles, approximately 20 µm
in diameter.

4.4. Isothermal pyrolysis of jack pine sawdust

Isothermal weight-change determinations were conducted
using jack pine sawdust, < 212 µm, in flowing nitrogen (535
to 603 K) and in air (523 to 566 K). When plotted as weight
percent loss against time, Figure 23, the results obtained
in a nitrogen atmosphere were similar to those obtained for
bark. Again, an initial rapid rate of loss was followed by
a slow approach to constant weight loss values. Results in
air showed greater weight loss over the time period (2 h)
with an initially rapid rate followed by an almost linear
rate of loss in the region 20 to 50% loss and a slow approach
to constant weight.

The final weight loss was obtained by extrapolation.
In air this loss was approximately 70% and constant, while
in nitrogen the final loss increased with temperature.

These data were then plotted in the standard kinetic
form, Figure 24. The results obtained in nitrogen followed
a similar curve which was identical to that found for jack
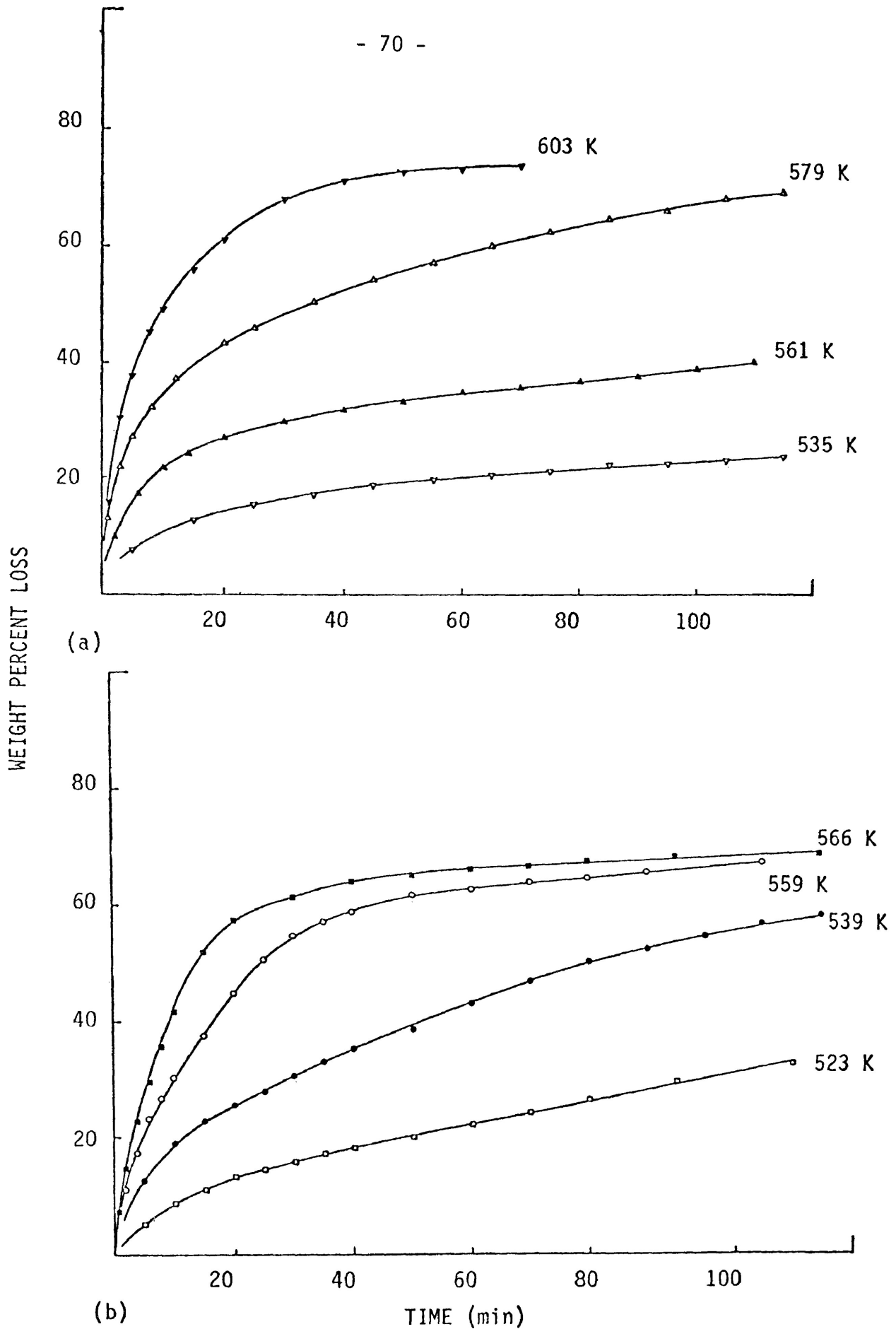
Figure 23 The thermal decomposition of jack pine sawdust
in nitrogen (a), and in air (b).
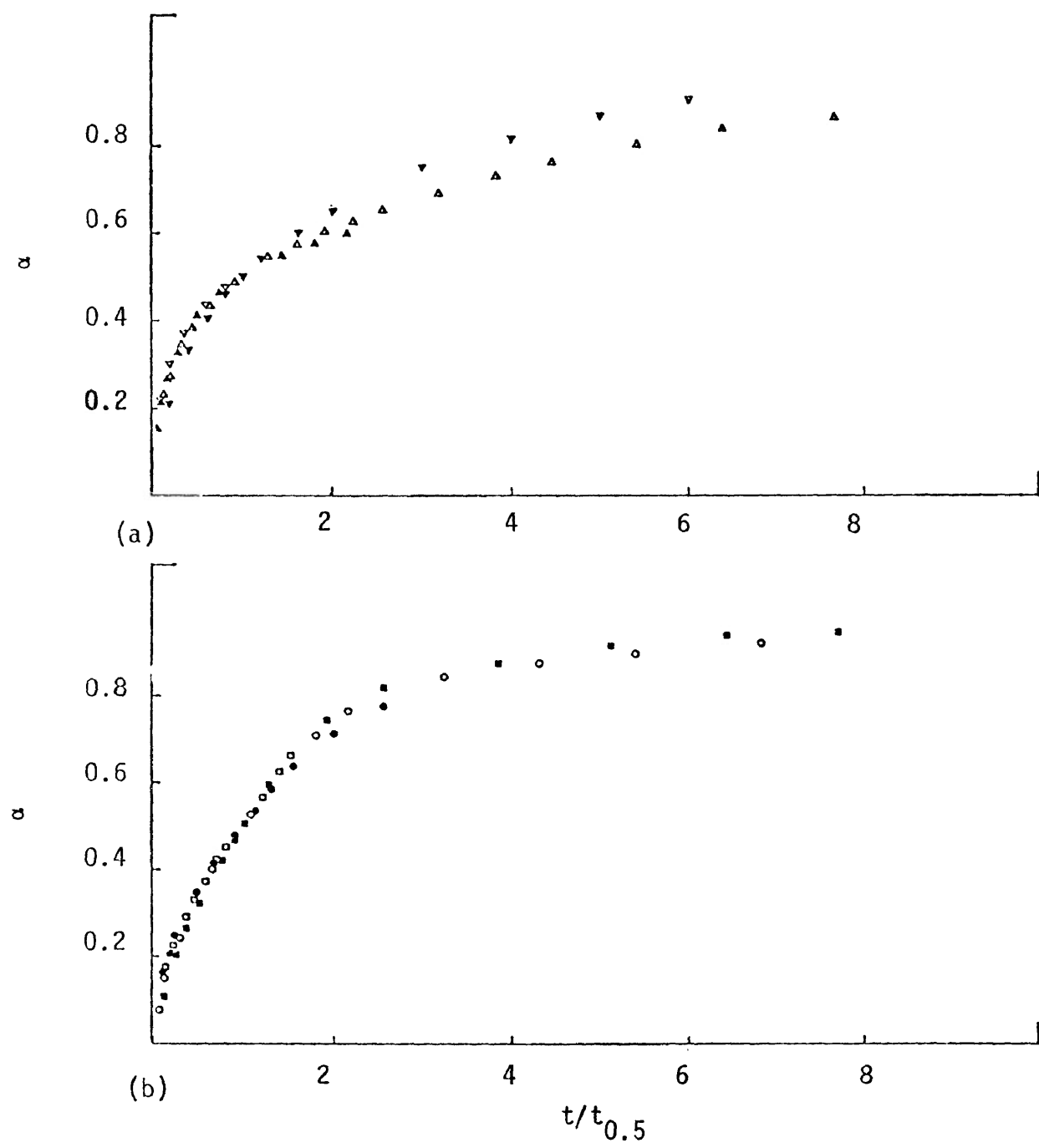
Figure 24   Reduced time plot of the isothermal decomposition
of jack pine sawdust in nitrogen (a), and in air (b).
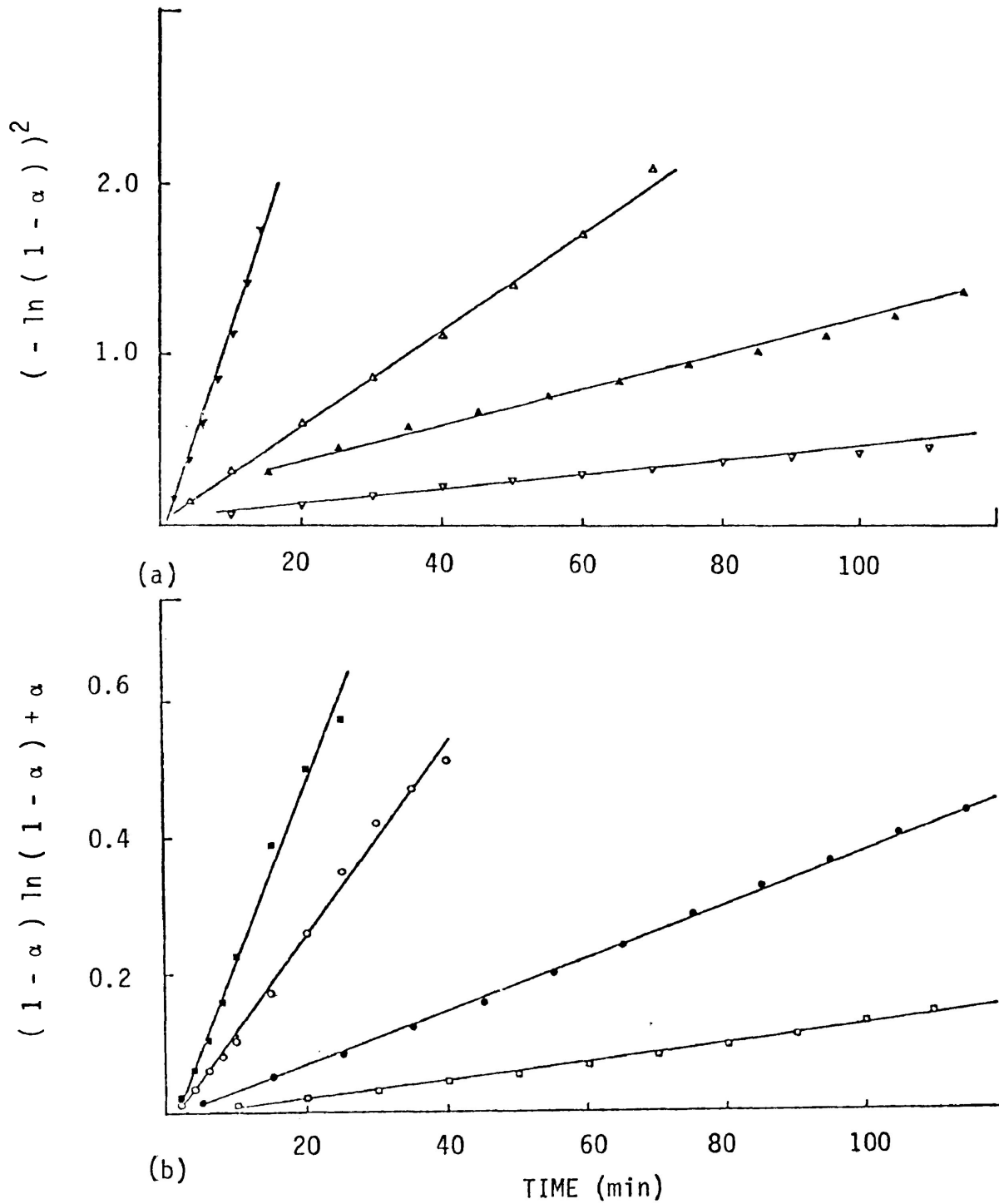
Figure 25   Kinetics of decomposition of jack pine sawdust
in nitrogen (a), and in air (b).
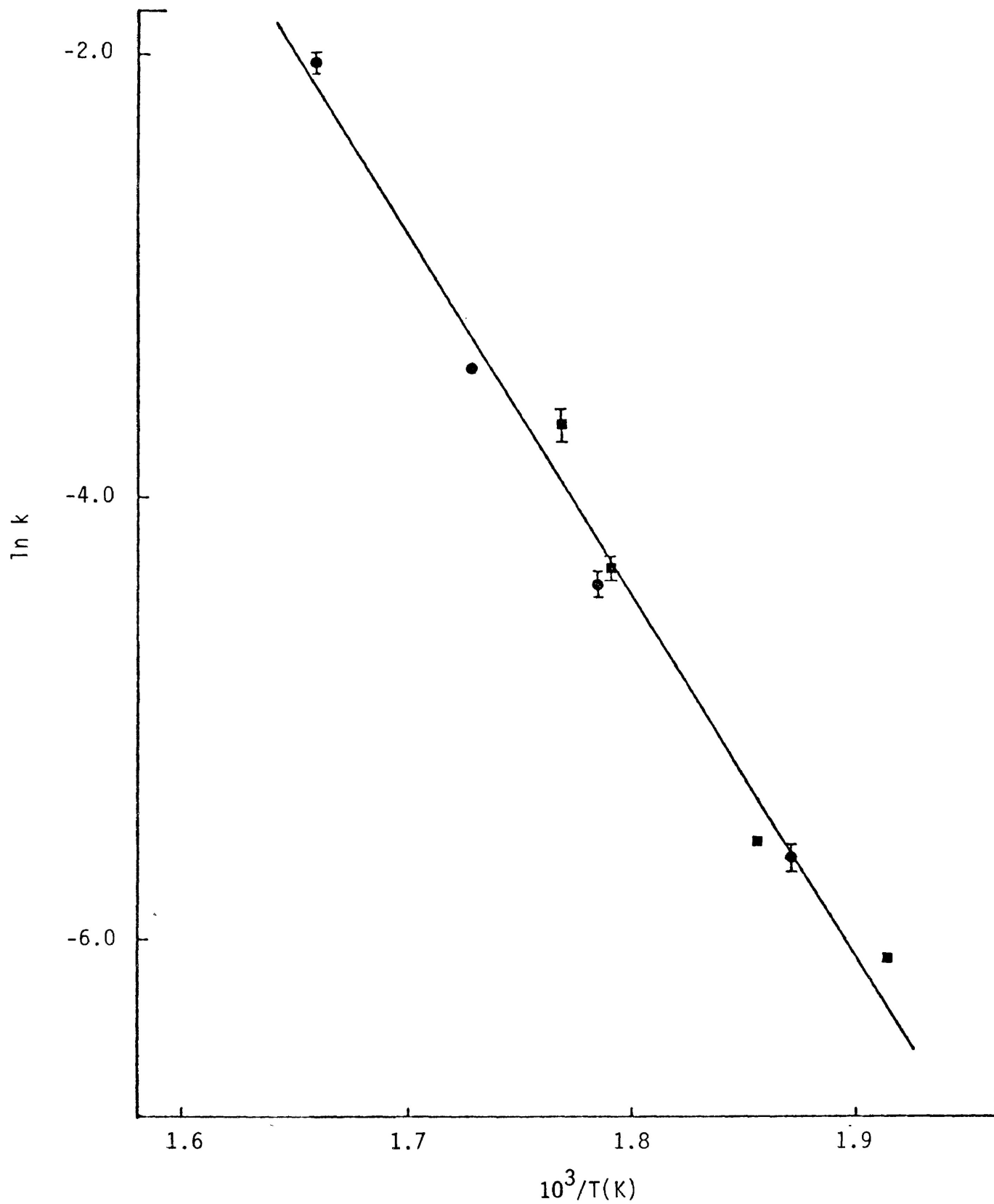
Figure 26   Arrhenius plot for the thermal decomposition
of jack pine sawdust in nitrogen (●), and in air (■).

Table 7 Kinetic parameters for the pyrolysis of jack pine sawdust < 212 μm.

TREATMENT	T (K)	SLOPE $\ln(-\ln(1-\alpha))$ VERSUS lnt	RATE CONSTANT $(k.10^{-2} min^{-1})$	Tc $(.10^3 K^{-1})$	A (min^{-1})	Ea $(Kj.mol^{-1})$
in nitrogen $(k = k_1)$	535	0.41 ± 0.02	0.36 ± 0.02			
	561	0.46 ± 0.02	1.23 ± 0.03	17.62 ± 1.85		
	579	0.49 ± 0.01	3.27 ± 0.10			
	603	0.63 ± 0.02	13.06 ± 0.59		$6.37.10^{11}$	
in air $(k = k_d)$	523	0.70	0.14 ± 0.01			
	539	0.67	0.38 ± 0.01			147
	559	0.73	1.34 ± 0.07			
	566	0.71	2.55 ± 0.19			

pine bark pyrolysis. The kinetics were therefore described by equation (17) and plots of $[- \ln (1 - \alpha)]^2$ against time were linear up to $\alpha = 0.85$, Figure 25.

The reduced time curve for sawdust pyrolysis in air most closely resembled that for a two-dimensional diffusion-controlled reaction into a cylinder of radius r (Holt, Cutler, Wadsworth 1962). The kinetics could therefore be described by the equation:

$$(1 - \alpha) \ln (1 - \alpha) + \alpha = (k/r^2) t . \qquad (20)$$

Plots of the left-hand side of equation (20) against time, Figure 25, were linear for values of $\alpha < 0.8$ and the slope of this line was taken as the rate constant k_d where $k_d = k/r^2$. The Arrhenius plot, Figure 26, produced a single line for data obtained from both nitrogen and air atmospheres, and the results are summarized in Table 7. The value for Tc was determined to be $17.62 . 10^3$ K^{-1} for sawdust pyrolysis.

4.5. Isothermal pyrolysis of cellulose

Isothermal weight-change determinations were carried out on cellulose powder in flowing nitrogen (571 to 614 K) and air (548 to 599 K). Plots of weight percent loss versus time, Figure 27, showed a linear response to approximately 5% loss followed by a rapid loss and a slow approach to constant weight. At all temperatures this final loss was 88% in nitrogen and 84% in air. An apparent instantaneous

weight loss was observed with all samples to decrease as the treatment temperature was increased. In both atmospheres, this apparent loss ranged from 1.20 to 0.35 mg. Similar effects have been observed elsewhere (Basch, Lewin 1973) and are probably related to buoyancy and gas/ solid equilibria phenomena. In this study however, such effects were so negligible in comparison to the real weight changes that no corrections were applied. The initial specimen weight was obtained by an extrapolation of the initial linear region of weight loss to zero time.

When plotted in the standard kinetic form, Figure 28, the results showed significant scatter. The general shape of the curves, however, resembled those which would be described by an Avrami-Erofeev expression of the form:

$$[- \ln (1 - \alpha)]^{1/n} = k\ t \qquad (21)$$

where n is 2 or 3.

Plots of $\ln [- \ln (1 - \alpha)]$ against $\ln t$ were therefore constructed, Figure 29, to verify the use of such an expression. These plots clearly indicate an initial linear relationship with a slope of 1.0 at values of α < 0.05, followed by a gentle curve over the region of α from 0.05 to 0.85. Hence, kinetic parameters were not derived from equation (21).

As an alternative method, cellulose pyrolysis was described in two regions--an initial region of constant rate

of loss (up to 5%), and a second region covering the major
weight loss. Reduced time curves for this second region
were obtained by considering the point of inflection on the
weight percent loss/time curve as the origin. These
standard kinetic plots exhibited significantly less scatter
and were identical for results in both air and nitrogen
atmospheres, Figure 30. When compared to known standard
kinetic plots, the data were observed to fit the curve
derived from the expression:

$$[1 - (1 - \alpha)^{0.5}] = (u/r) t. \qquad (22)$$

This equation was derived by considering a reaction rate con-
trolled by the movement of an interface at constant velocity
u for a disk or cylinder, of radius r, reacting from the
edge inward (Sharp, Brindley, Achar 1966).

The rate constant K_b, given by u/r, was obtained
from the slope of the linear plots of $[1 - (1 - \alpha)^{0.5}]$
against time, Figure 31. Values for the temperature co-
efficient and pre-exponential factor were derived from
Arrhenius plots, Figure 32.

Kinetic parameters were obtained for the initial
region using a zero order rate expression:

$$dW/dt = k_a \qquad (23)$$

where W is the weight percent loss at time t. Plots of
weight percent loss versus time gave rise to straight lines
of slope k_a, and Arrhenius plots gave the kinetic parameters
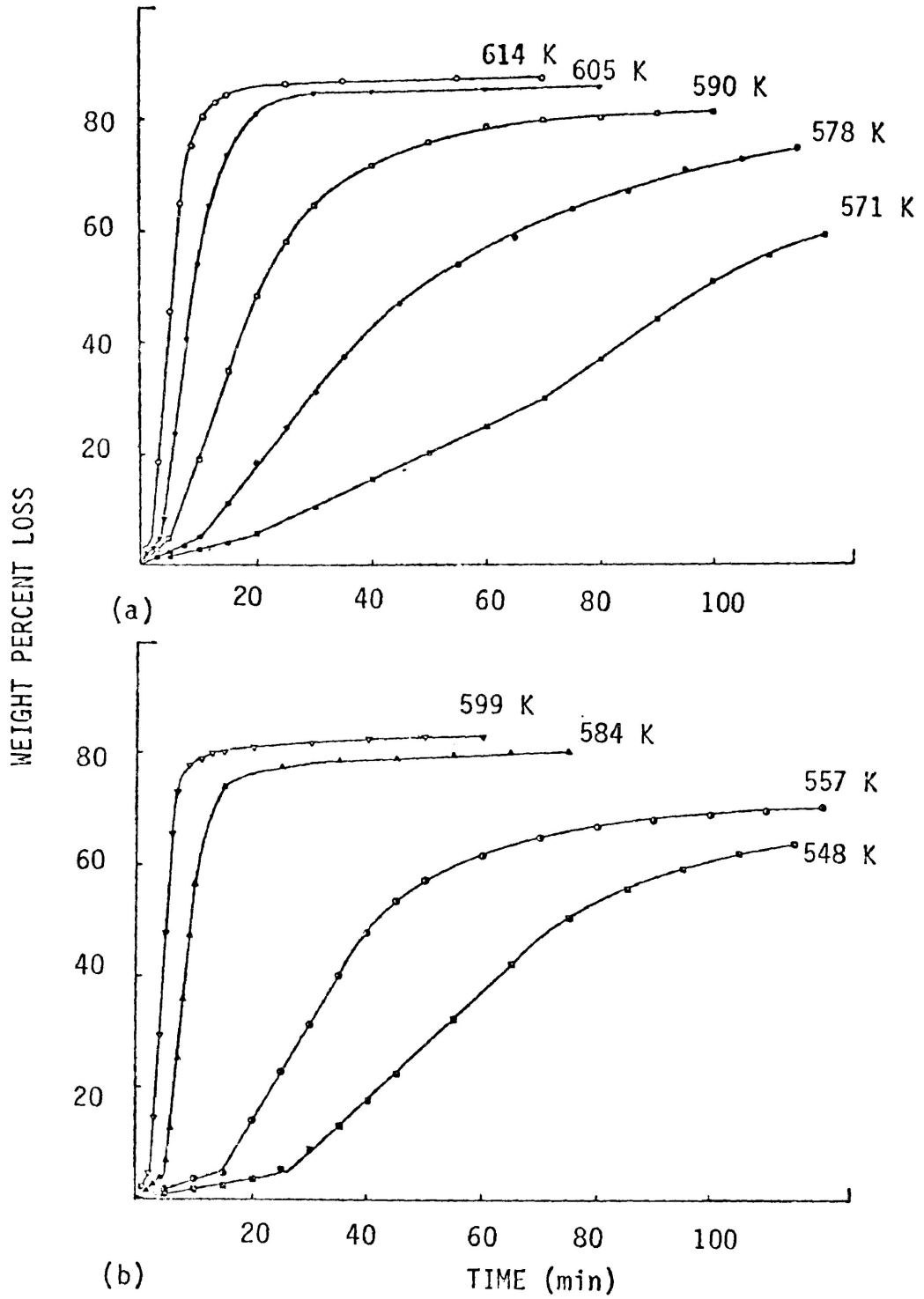
Figure 27   The thermal decomposition of cellulose
in nitrogen (a), and in air (b).
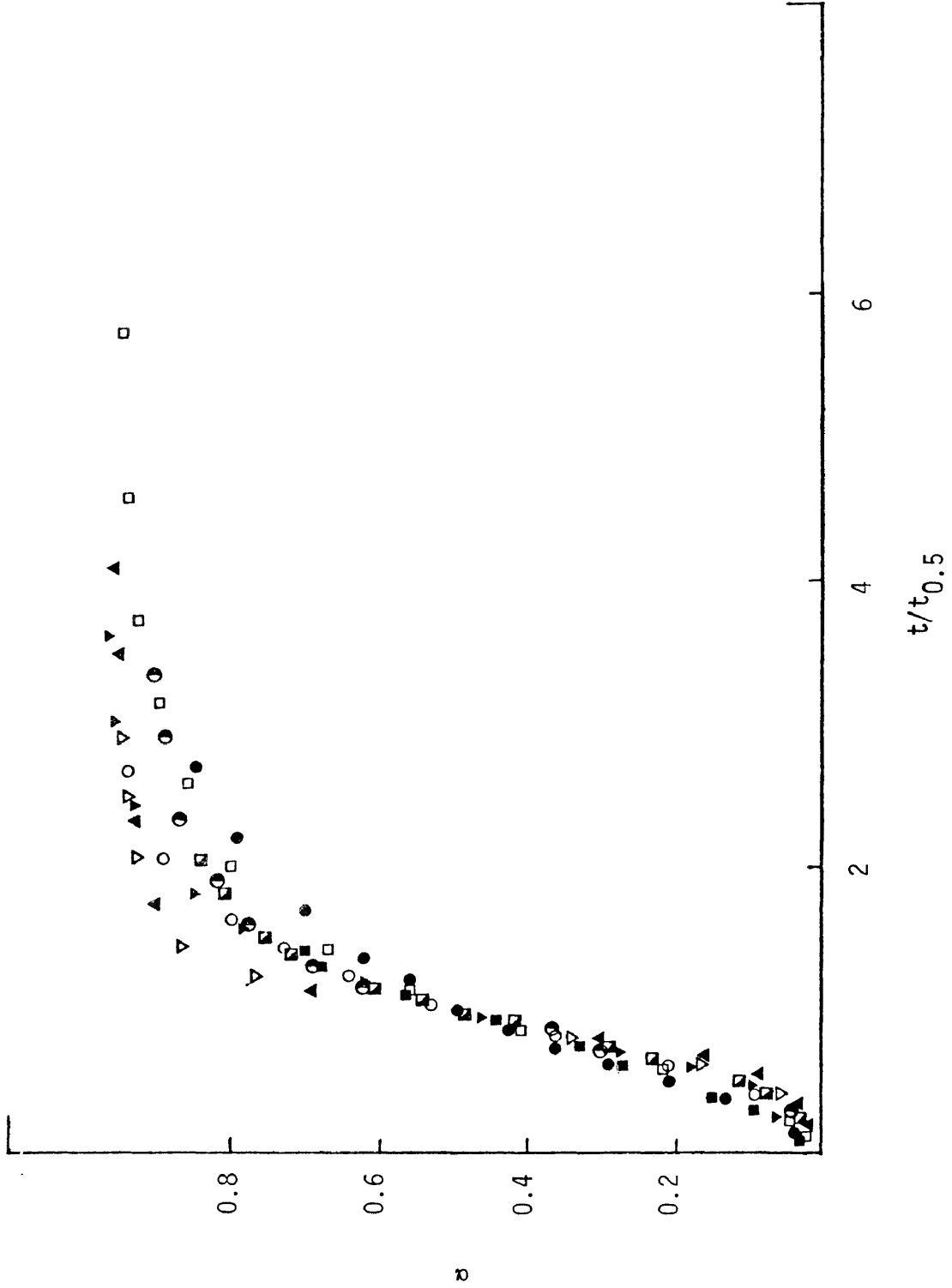
Figure 28   Reduced time plot of the isothermal decomposition of cellulose.
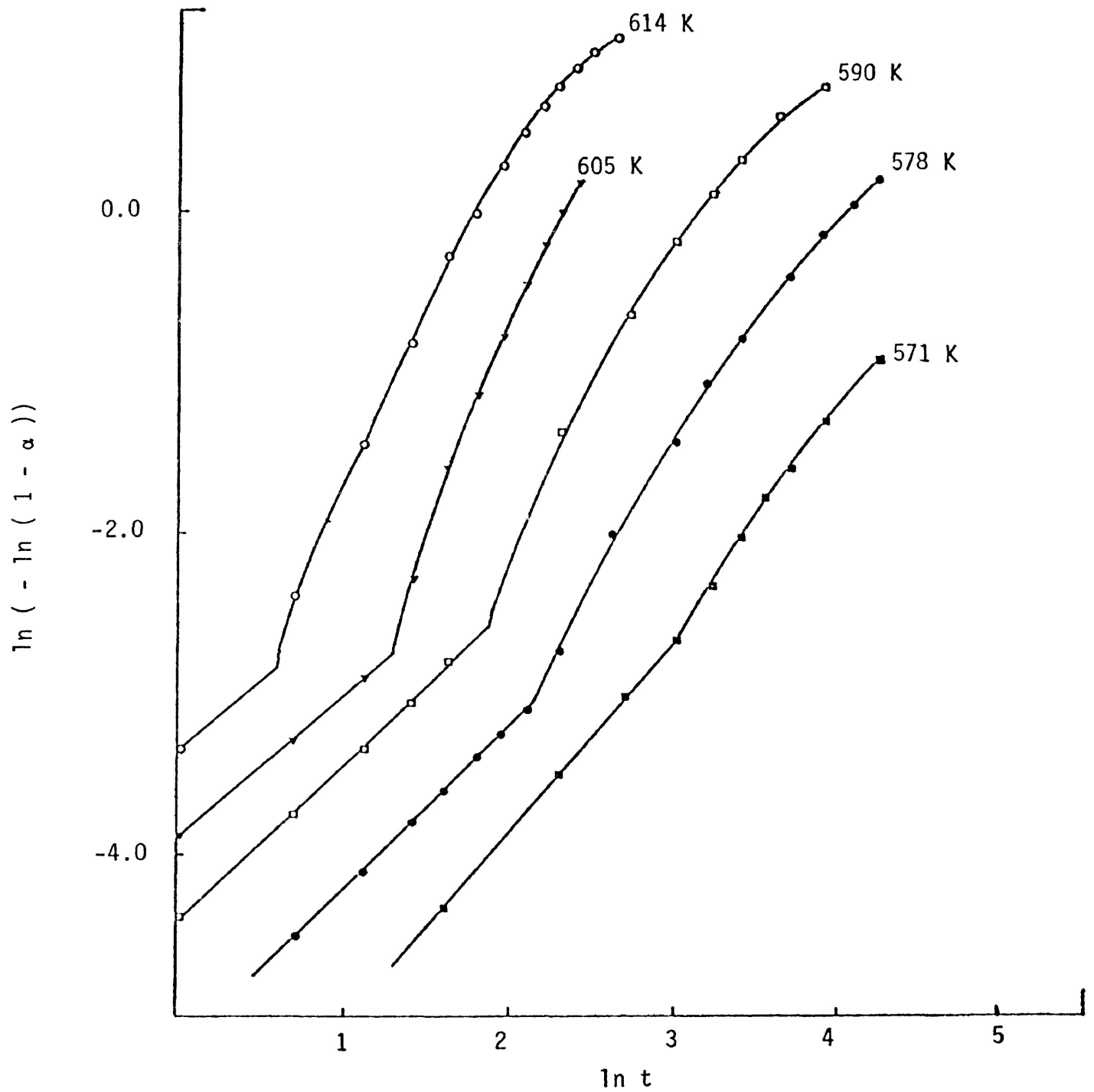
Figure 29   Plots of ln (- ln (1 - α)) versus ln t for cellulose pyrolysis in nitrogen.
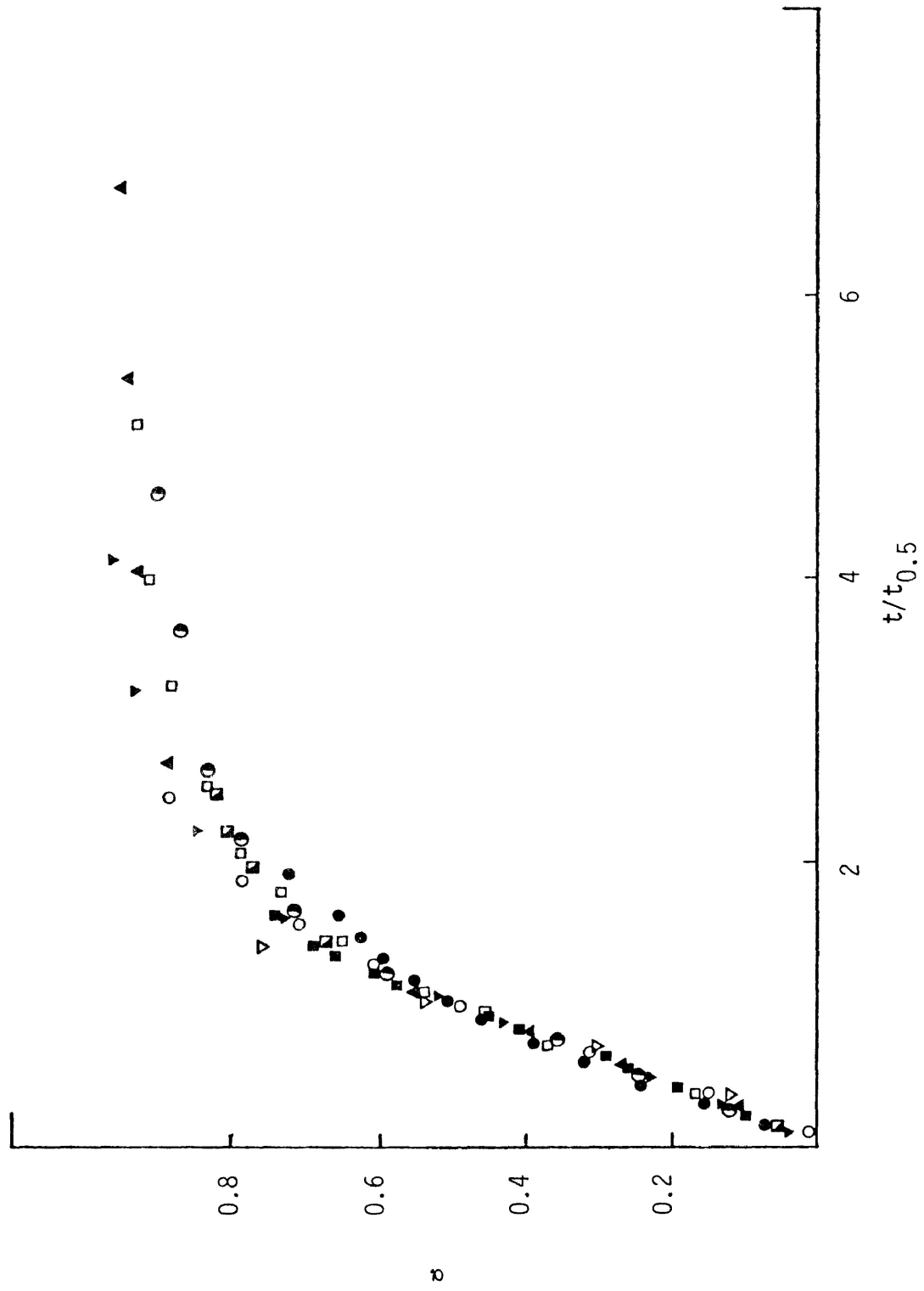
Figure 30   Reduced time plot of the isothermal decomposition of cellulose, second region.
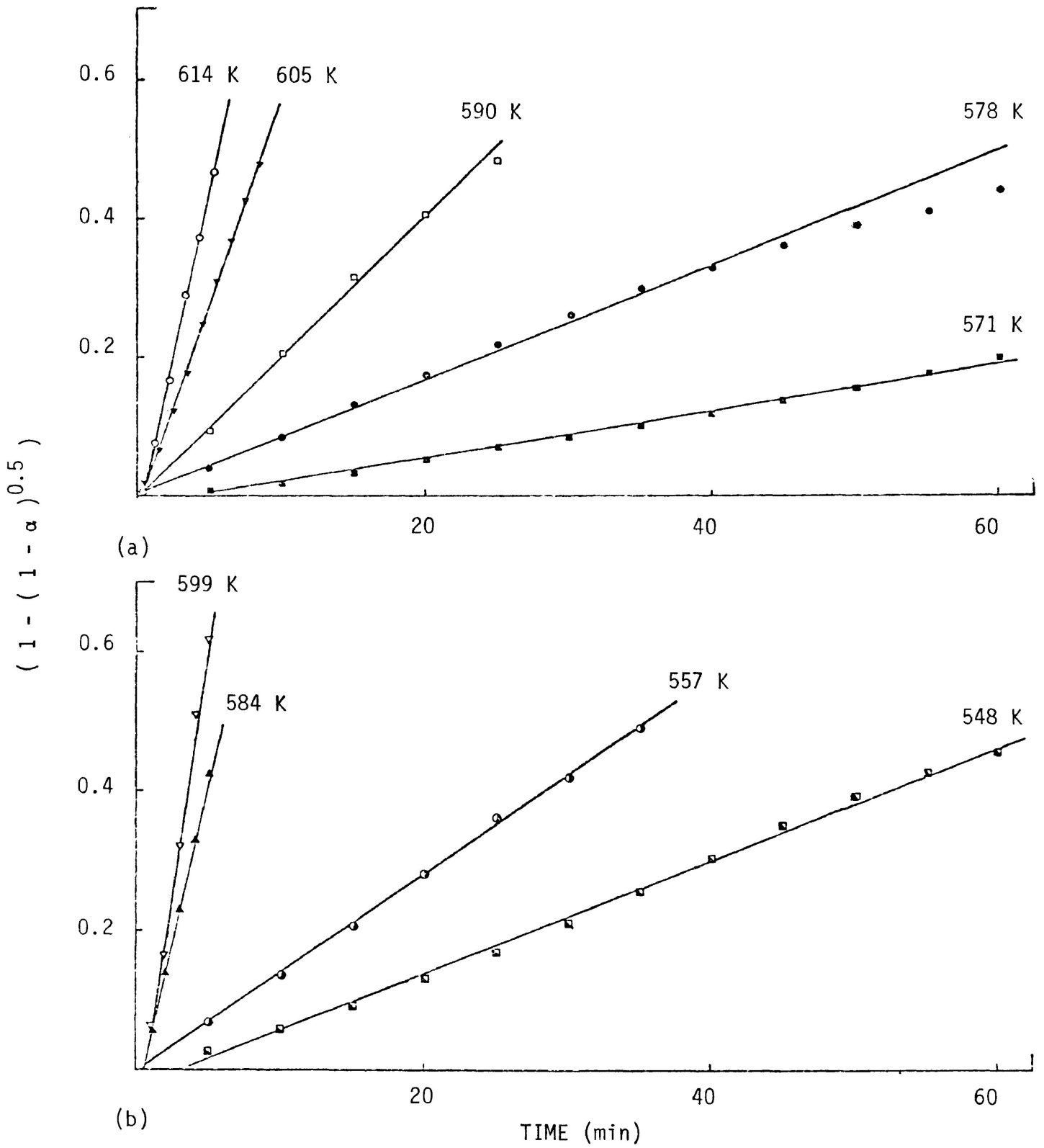
Figure 31   Kinetics of decomposition of cellulose in nitrogen (a),and
in air (b).
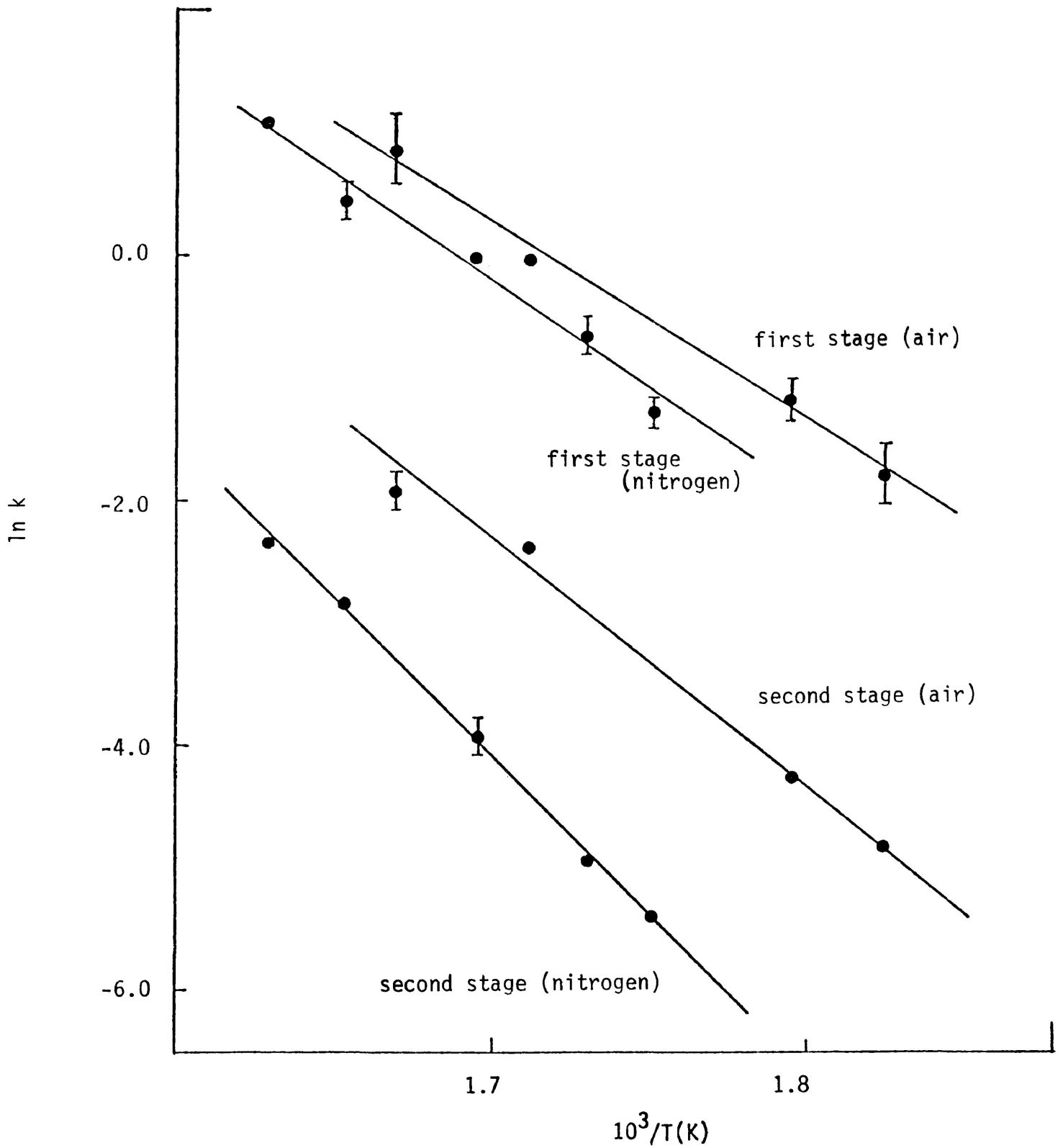
Figure 32 Arrhenius plots for the thermal decomposition of cellulose.

Table 8   Kinetic parameters for the pyrolysis of cellulose.

TREATMENT	T (K)	RATE CONSTANT $(k.10^{-2} \text{ min}^{-1})$	Tc $(.10^3 \text{ K}^{-1})$	A (min^{-1})	Ea (Kj.mol^{-1})
first stage in nitrogen $(k = k_a)$	571	27.9 ± 3.6			
	578	52.2 ± 8.2	17.89 ± 5.06		
	590	99.4 ± 5.0		$1.28.10^{13}$	
	605	156.3 ± 23.0			149
	614	301 --			
first stage in air $(k = k_a)$	548	16.62 ± 5.0			
	557	30.84 ± 5.82	16.43 ± 4.44		
	584	95.8 ± 6.12		$1.82.10^{12}$	
	599	238.0 ± 88.0			137
second stage in nitrogen $(k = k_b)$	571	0.45 ± 0.03			
	578	0.71 ± 0.06	25.52 ± 2.54		
	590	1.98 ± 0.34		$1.13.10^{17}$	
	605	5.89 ± 0.16			212
	614	9.41 ± 0.86			
second stage in air $(k = k_b)$	548	0.80 ± 0.03			
	557	1.40 ± 0.10	19.55 ± 6.75		
	584	9.26 ± 0.64		$2.55.10^{13}$	
	599	14.64 ± 2.62			163
second stage in nitrogen (equation 24)	571	1.23 ± 0.09			
	578	1.75 ± 0.06	26.47 ± 3.66		
	590	4.63 ± 0.45		$1.51.10^{18}$	
	605	16.79 ± 0.82			220
	614	27.33 ± 1.91			
second stage in air (equation 24)	548	1.77 ± 0.12			
	557	3.15 ± 0.31	21.81 ± 4.78		
	584	23.97 ± 1.69		$3.43.10^{15}$	
	599	47.07 ± 14.45			181

which are summarized in Table 8.

The second region of cellulose pyrolysis may also be described by the usual first order expression applicable to unimolecular decay processes:

$$[- \ln (1 - \alpha)] = k\, t. \qquad (24)$$

Such an expression may be derived from equation (21) setting $n = 1.0$. Plots of $\ln [- \ln (1 - \alpha)]$ against $\ln t$ produced reasonably straight lines of slope 1.0. Kinetic parameters derived using equation (24) are also presented in Table 8. When plotted in the standard kinetic form, the data more closely resembled the reduced time curve derived from equation (22).

4.6. Surface areas

Gas adsorption data obtained from the BET apparatus were analysed with the aid of the APL program "KRBET" (Appendix 1). Typical plots of $P/V(P_o - P)$ versus P/P_o are shown in Figure 33 and the results are summarized in Table 9. The area occupied by one molecule of krypton on a solid surface was taken as $19.5\ \overset{o}{A}{}^2$ (Gregg, Sing 1967).

4.7. Residue analysis

4.7.1. Jack pine bark < 212 μm

Results obtained from the previously-described weight-change determinations were plotted as final weight
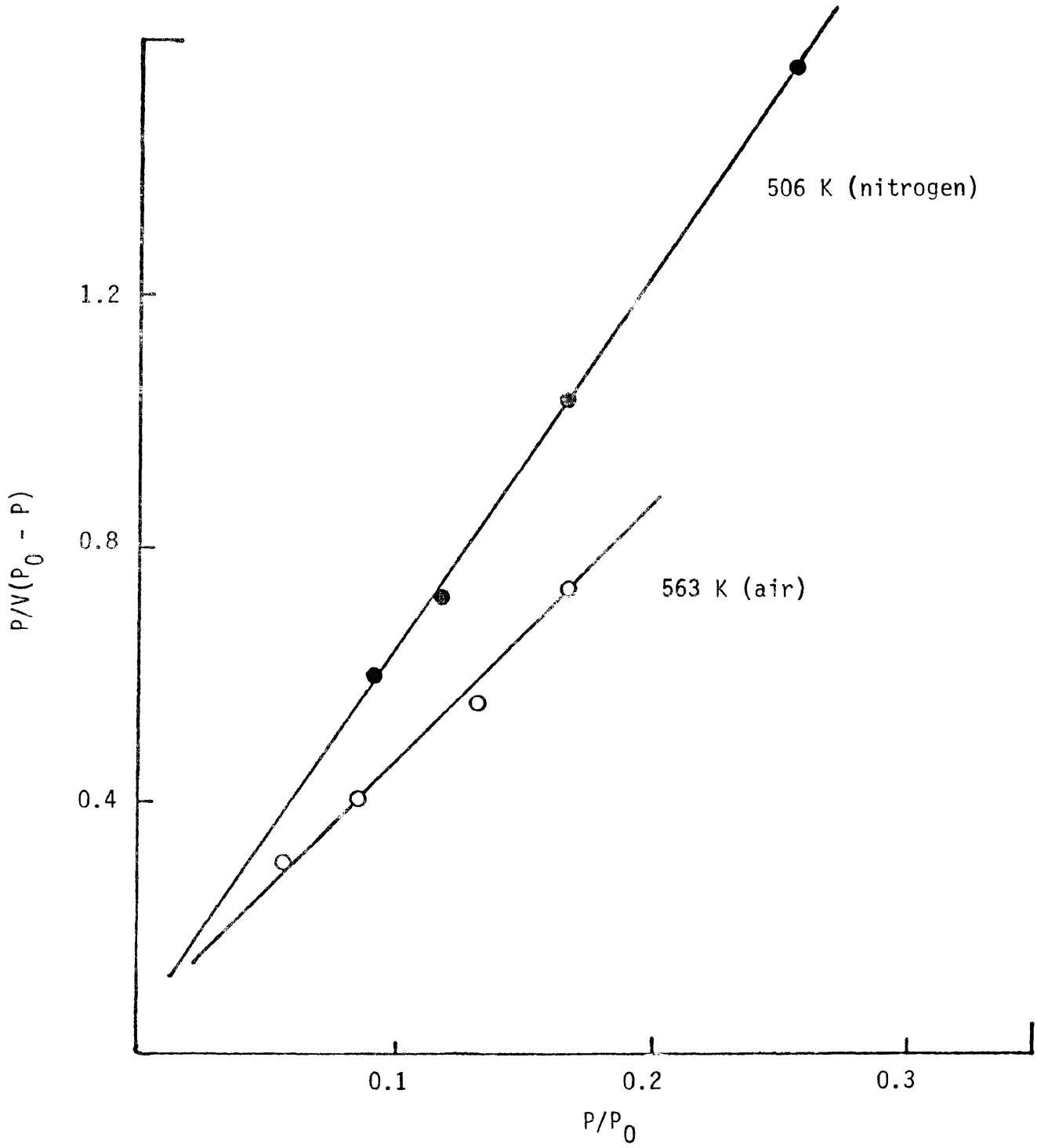
Figure 33 Typical Krypton surface area plots.

Table 9 Surface areas.

SAMPLE	NATIVE BARK				EXTRACTED BARK	HEAT TREATED BARK < 212 um				SAWDUST	CELLULOSE
						AIR		NITROGEN			
	>600 μm	600 to 425 μm	425 to 212 μm	<212 μm	<212 μm	507 K	563 K	506 K	572 K	< 212 μm	
SURFACE AREA ($m^2 \cdot g^{-1}$)	0.10	0.15	0.20	0.30	0.50	1.50	1.40	0.90	1.20	0.50	0.45

percent loss versus temperature, Figure 34. This graph shows that regardless of bark pretreatment, the weight percent loss determined from pyrolysis in nitrogen exhibits a linear relationship with temperature which is described approximately by the equation:

$$W_f = 0.3 \, T - 134 \qquad (25)$$

where W_f is the final weight percent loss and T is the temperature of treatment (K). This equation was derived from results obtained for the pyrolysis of jack pine bark in nitrogen over the temperature region 473 to 623 K.

Also shown in Figure 34 are the results obtained for bark pyrolysis in air. An initial linear relationship between final weight percent loss and temperature of treatment, 473 to 510 K, is followed by a rapid increase in rate and then a slow approach to 66% loss at 563 K. Treatment at temperatures greater than 563 K yielded mostly ash.

The results of treatment of bark in nitrogen plus water vapour appear to follow the linear relationship observed for pyrolysis in dry nitrogen. The data obtained from residue elemental analysis are presented in Tables 10 and 11.

4.7.2. Jack pine sawdust < 212 μm

Results obtained for jack pine sawdust indicate that the final weight percent loss increased with treatment
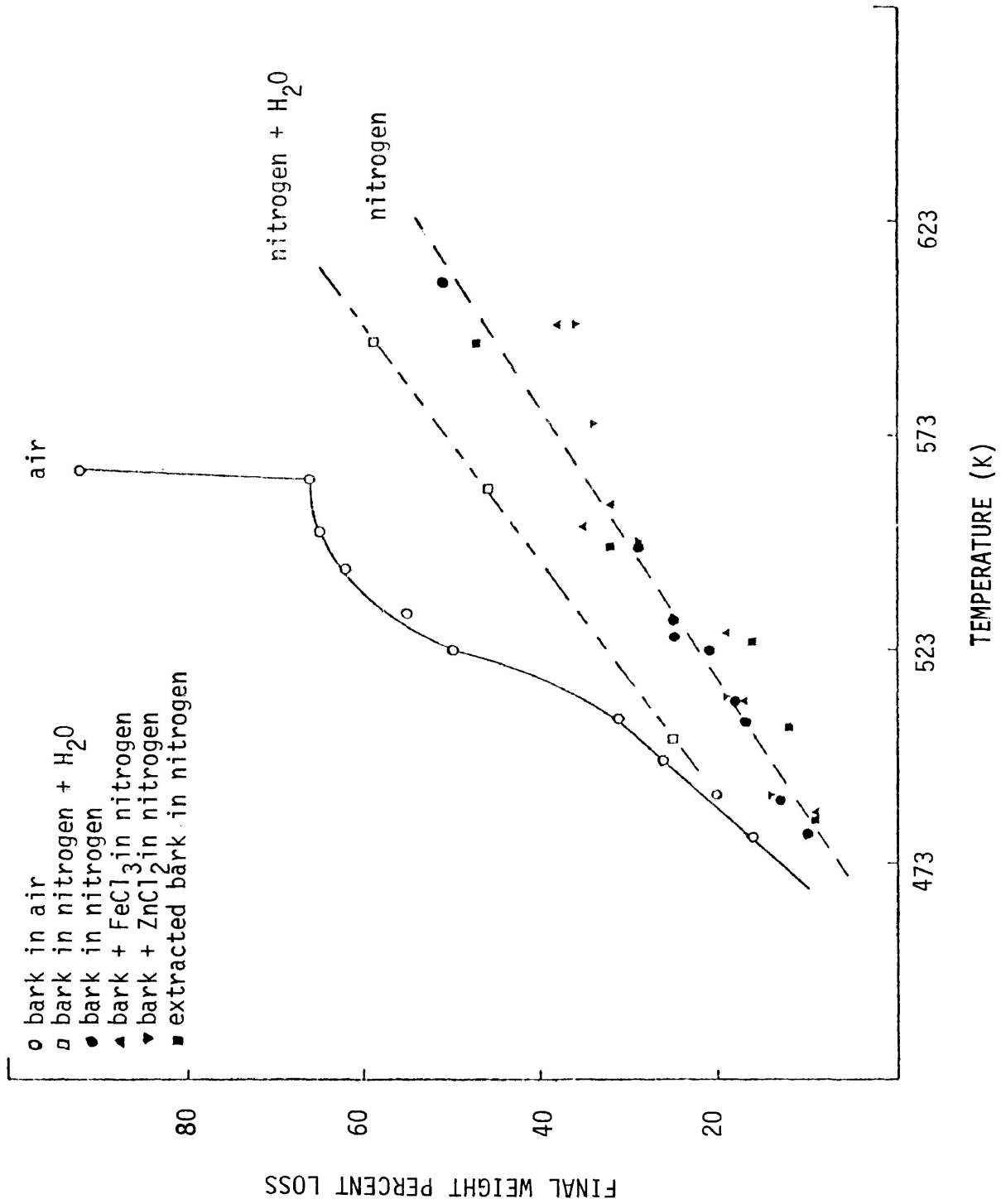
Figure 34   Final weight percent loss versus temperature for the isothermal pyrolysis of jack pine bark.

Table 10 Residue analysis of jack pine bark.

TREATMENT	T (K)	WEIGHT % REMAINING	%C	%H	%N	CORRECTED RATIOS H/C	O/C	H/O
native bark in nitrogen	293	100	50.94	5.81	0.27	1.37	0.59	2.32
	480	90	52.51	5.43	0.28	1.24	0.55	2.25
	488	87	53.10	5.39	0.30	1.22	0.54	2.26
	506	83	54.80	5.36	0.42	1.17	0.49	2.39
	511	82	55.21	5.40	0.42	1.17	0.48	2.44
	523	79	56.70	4.92	0.31	1.04	0.46	2.26
	526	75	57.39	4.95	0.36	1.03	0.44	2.34
	530	75	56.47	5.04	0.52	1.07	0.46	2.33
	547	71	60.64	3.62	0.52	0.91	0.38	2.39
	609	49	67.91	3.80	0.51	0.67	0.25	2.68
native bark in air	479	84	51.97	4.59	0.27	1.06	0.58	1.84
	497	74	52.15	4.28	0.34	0.98	0.57	1.73
	532	45	52.59	2.86	0.27	0.63	0.55	1.15
	542	38	55.27	2.48	0.36	0.54	0.47	1.14
	551	35	56.77	2.16	0.31	0.46	0.44	1.05
	563	34	55.14	2.04	0.24	0.44	0.47	0.94
native bark in nitrogen + H_2O	502	75	56.92	4.97	--	1.05	0.45	2.33
	561	54	60.97	4.74	--	0.93	0.36	2.58
	595	41	61.50	2.84	0.37	0.53	0.38	1.39

Table 11 Residue analysis of jack pine bark

TREATMENT	T (K)	WEIGHT % REMAINING	%C	%H	%N	CORRECTED RATIOS H/C	O/C	H/O
native bark + ZnCl$_2$ (3.9%)	489	86	57.54	5.02	0.44	1.05	0.40	2.60
	512	81	59.22	4.20	0.45	0.85	0.38	2.27
	548	71	64.57	4.28	0.61	0.80	0.27	2.91
	576	66	67.75	4.09	0.34	0.72	0.22	3.30
	599	64	65.80	3.67	0.45	0.70	0.25	2.69
native bark + FeCl$_3$ (2.4%) in nitrogen	485	91	57.20	4.84	0.35	1.02	0.44	2.32
	511	83	58.88	4.84	0.56	0.99	0.40	2.48
	527	81	61.97	4.43	0.34	0.86	0.35	2.46
	557	68	66.45	4.16	0.59	0.75	0.26	2.88
	570	65	67.99	3.93	0.53	0.69	0.24	2.89
solvent extracted in nitrogen	483	91	53.20	5.53	0.31	1.25	0.56	2.23
	505	88	54.11	5.22	0.45	1.16	0.54	2.15
	525	84	56.34	5.18	0.58	1.10	0.48	2.29
	557	68	61.79	4.91	0.52	0.95	0.37	2.57
	595	53	65.94	3.70	0.18	0.67	0.31	2.16

temperature in nitrogen. The final weight percent loss at any temperature was observed to be approximately twice that found for bark, Table 12. In air, a constant final weight loss of 70% was observed for heat treatment of sawdust from 523 to 566 K. As was the case with bark, treatment at higher temperatures yielded mostly ash.

4.7.3. Cellulose

Pyrolysis of cellulose in nitrogen at temperatures from 571 to 614 K produced the same amount of residue (12%), while cellulose pyrolysis in air (548 to 599 K) produced 18% residue. The elemental analysis data are summarized in Table 13.

Generally, pyrolysis in nitrogen produced residues which increased in carbon content with increasing temperature, while pyrolysis in air produced residues which exhibited a fairly constant value for carbon content over the temperature range studied.

4.8. Infrared analysis of jack pine bark

No differences were observed in the IR spectra of native and extracted jack pine bark, Figure 35. The strong, broad absorption peak centred at 9.5 µm may be attributed to the carbon-oxygen stretching vibrations of the various CO bonds present. The band at 6.2 µm followed by absorptions

Table 12 Residue analysis of jack pine sawdust

TREATMENT	T (K)	WEIGHT % REMAINING	%C	%H	%N	CORRECTED RATIOS H/C	O/C	H/O
sawdust in nitrogen	293	100	46.31	5.82	--	1.51	0.77	1.96
	535	52	57.42	5.58	--	1.17	0.47	2.49
	561	41	57.95	5.58	--	1.16	0.45	2.58
	579	19	69.16	4.44	0.14	0.77	0.25	3.08
	603	25	70.72	4.33	0.03	0.73	0.24	3.04
sawdust in air	523	35	56.13	4.15	--	0.89	0.51	1.75
	539	26	59.04	2.76	--	0.56	0.46	1.22
	559	28	60.59	2.35	0.02	0.47	0.43	1.09
	566	30	59.03	2.20	0.34	0.45	0.47	0.96

Table 13 Residue analysis of cellulose.

TREATMENT	T (K)	WEIGHT % REMAINING	%C	%H	%N	CORRECTED RATIOS H/C	O/C	H/O
cellulose in nitrogen	293	100	43.05	6.19	--	1.73	0.88	1.97
	571	12	59.62	4.81	0.06	0.99	0.45	2.20
	578	13	73.46	3.19	--	0.51	0.24	2.13
	590	12	69.88	3.90	--	0.67	0.28	2.39
	605	12	73.74	3.81	--	0.62	0.23	2.70
	614	11	73.21	3.69	0.15	0.60	0.24	2.50
cellulose in air	548	22	59.00	2.02	--	0.41	0.50	0.82
	557	16	59.72	1.84	0.14	0.37	0.48	0.77
	584	18	59.20	1.47	--	0.30	0.50	0.60
	599	16	59.54	1.54	--	0.31	0.49	0.63

at 6.6 and 6.9 μm correspond to the carbon-carbon stretching
vibrations of benzene derivatives. Part of the intensity
of the 6.2 μm band may be due to the presence of hydrogen
bonded oxygen-containing groups, and it has been reported
that this band may derive most of its intensity from the
bending vibrations of adsorbed water (Michell, Ingle, Stewart
1969). A weak peak at 5.7 - 5.8 μm corresponds to the
carbonyl stretching frequency for ester and carboxyl groups.
The presence of aliphatic CH groups may give rise to the
observed absorption at 3.4 μm along with the bands at 6.9
and 7.3 μm. A very strong, broad hydroxyl band was noted
at 2.9 - 3.0 μm which may also be indicative of the presence
of polymeric-type hydrogen bonds.

4.9 Ash analysis

The ash content of jack pine bark was determined to
be 1.37% while that of jack pine sawdust was 0.30%. X-ray
fluorescence analysis of the ash obtained from bark showed
the presence of manganese, iron, copper, zinc, rubidium,
strontium and lead at concentrations > 10 ppm.

The mean concentration of some of these metals in
the ash of jack pine bark have been given by Powers (1974) as
manganese, 1915 ppm, copper, 28 ppm, zinc, 871 ppm, and lead,
47 ppm. It has been observed (Browning 1963) that the ash
from most barks contains approximately 60% CaO and 30% K_2O,
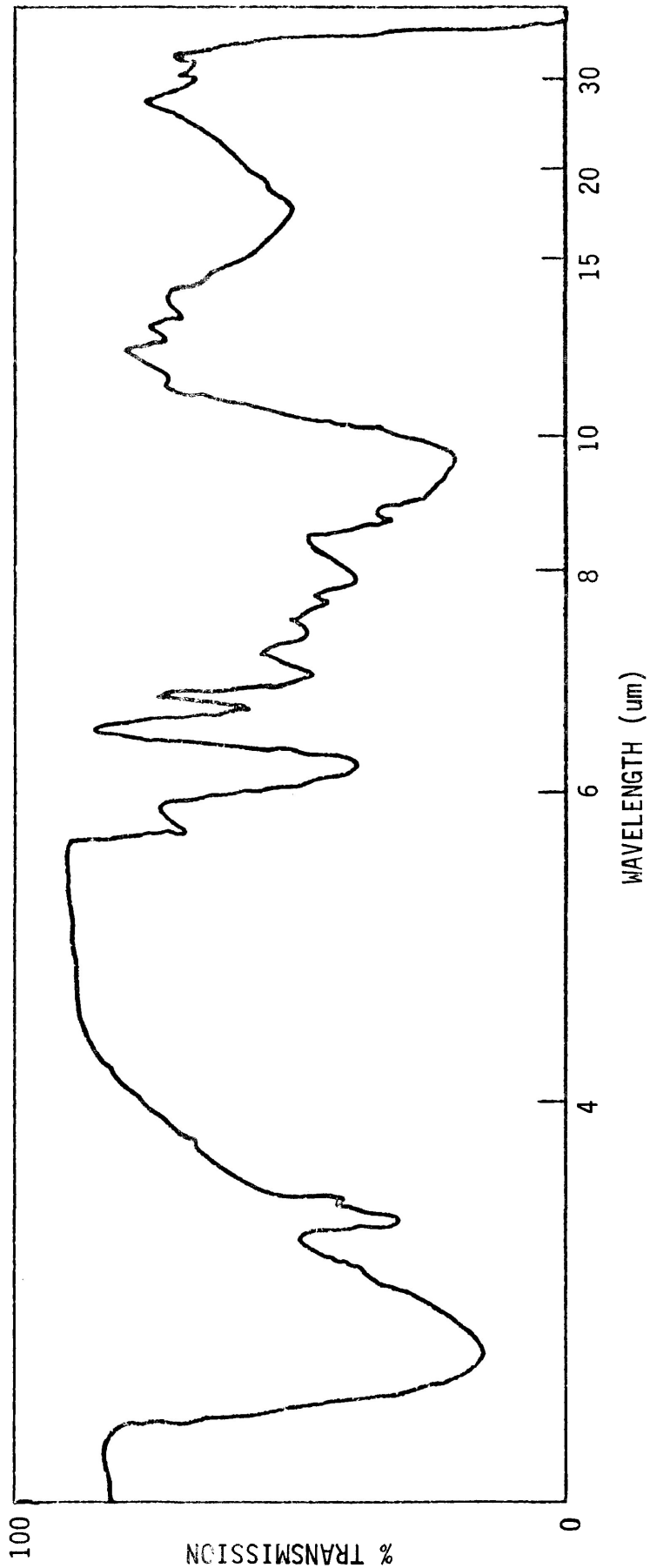
Figure 35   The infrared absorption spectra of jack pine bark.

with oxides of Mg, Na, Fe, and Mn making up most of the balance.

4.10. Dynamic thermogravimetry (TG)

The thermobalance record of sample weight as a function of time was used in conjunction with the specimen temperature/time plot to evaluate a sample weight loss/ temperature relationship. A buoyancy correction was accomplished by observing the apparent weight change of 40 mg of dead-burned alumina with temperature. The observed increase in weight may have been caused by a number of factors including air buoyancy, crucible geometry, and con- vection and radiation effects. A single alumina crucible was used in all studies and the buoyancy correction curves were extremely reproducible and were identical for all atmospheres, Figure 36.

Sample weight and temperature were recorded at selected intervals and the TG curves drawn as plots of weight percent loss versus temperature. These curves were repro- ducible to within $\pm$ 1% loss where the weight percent loss was given by the weight loss at time t divided by the initial sample weight multiplied by 100%.

4.10.1. Jack pine bark

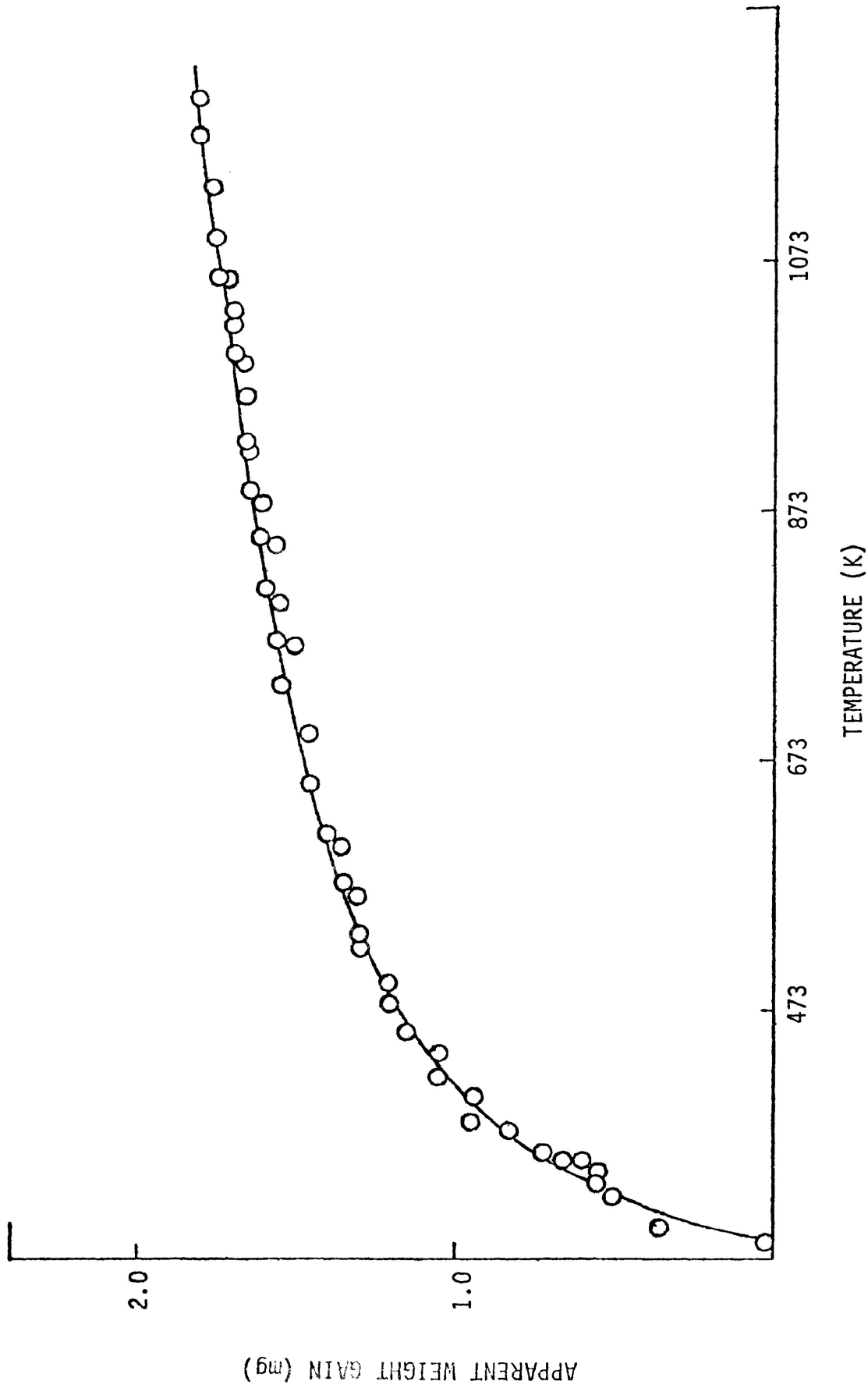The TG curves for native jack pine bark, < 212 μm,

Figure 36 Buoyancy correction for all flowing atmospheres.

in nitrogen, air, and nitrogen plus water vapour (21.7 Torr) are shown in Figure 37. In all cases, an initial weight loss of 2.5% occurred between 323 and 373 K corresponding to the loss of adsorbed moisture.

In dry nitrogen, a plateau region from 383 to 453 K was followed by the region of major weight loss to yield a 74% total weight loss at 1273 K. The decomposition was rapid up to approximately 623 K and the curve exhibited a slow decay thereafter.

The results in air produced a TG curve which was identical to that found in nitrogen up to 523 K. Beyond 523 K, the weight loss was greater in air and rapidly increased to 88.5% loss at 613 K. Between 623 and 723 K, a fairly constant rate of loss occurred to yield ash.

Studies conducted in nitrogen plus water vapour indicated that < 973 K the curve was identical to that obtained in dry nitrogen. Above this temperature, a rapidly increasing weight loss was observed to yield 97% loss at 1273 K.

4.10.2. Extracted bark

The TG curves for extracted jack pine bark < 212 μm, Figure 38, show that the results obtained in flowing dry nitrogen and nitrogen plus water vapour were identical to those obtained for native bark in the same atmospheres.
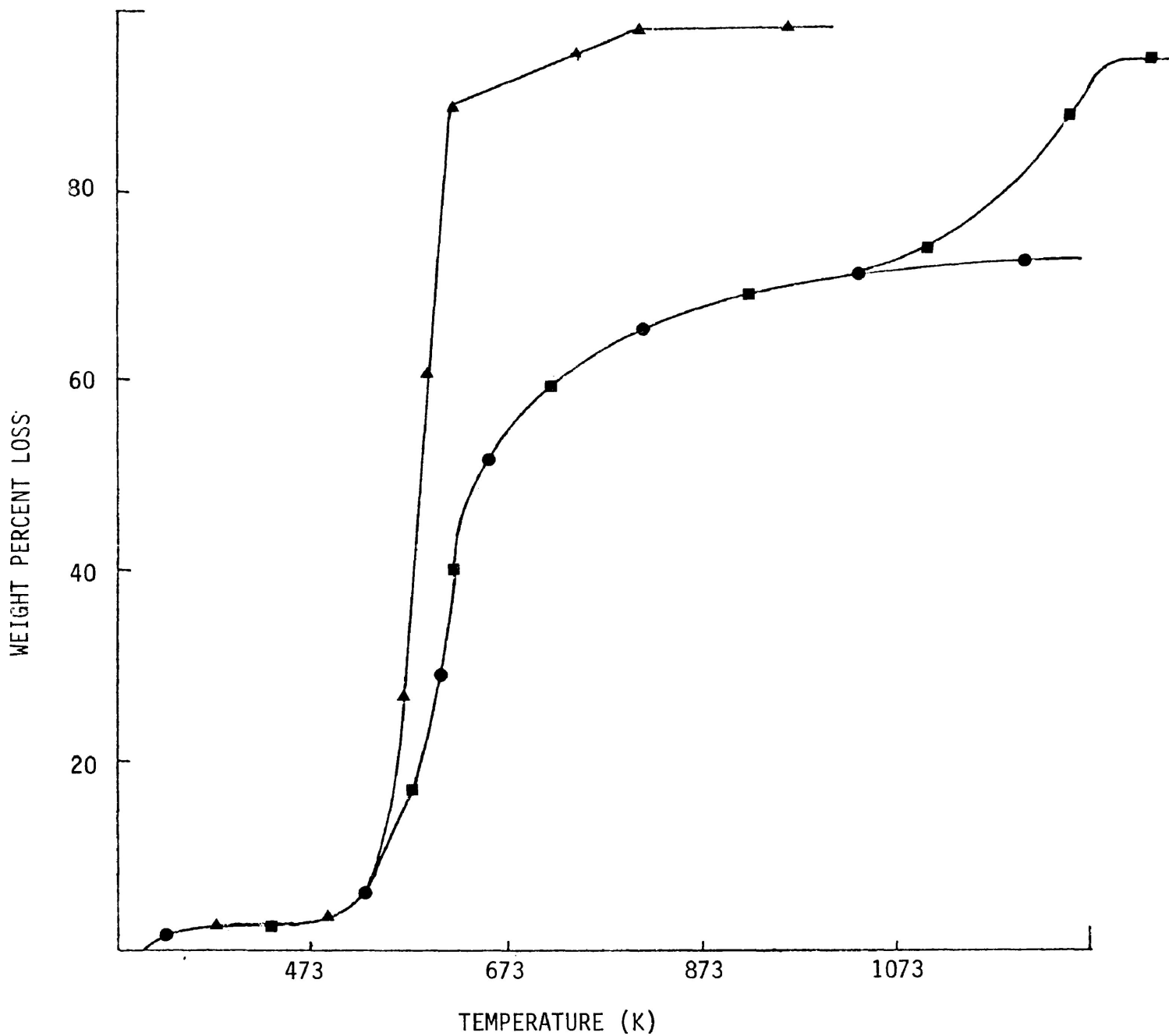
Figure 37 TG curves for jack pine bark in nitrogen (●), in air (▲), and in nitrogen + H_2O (■).
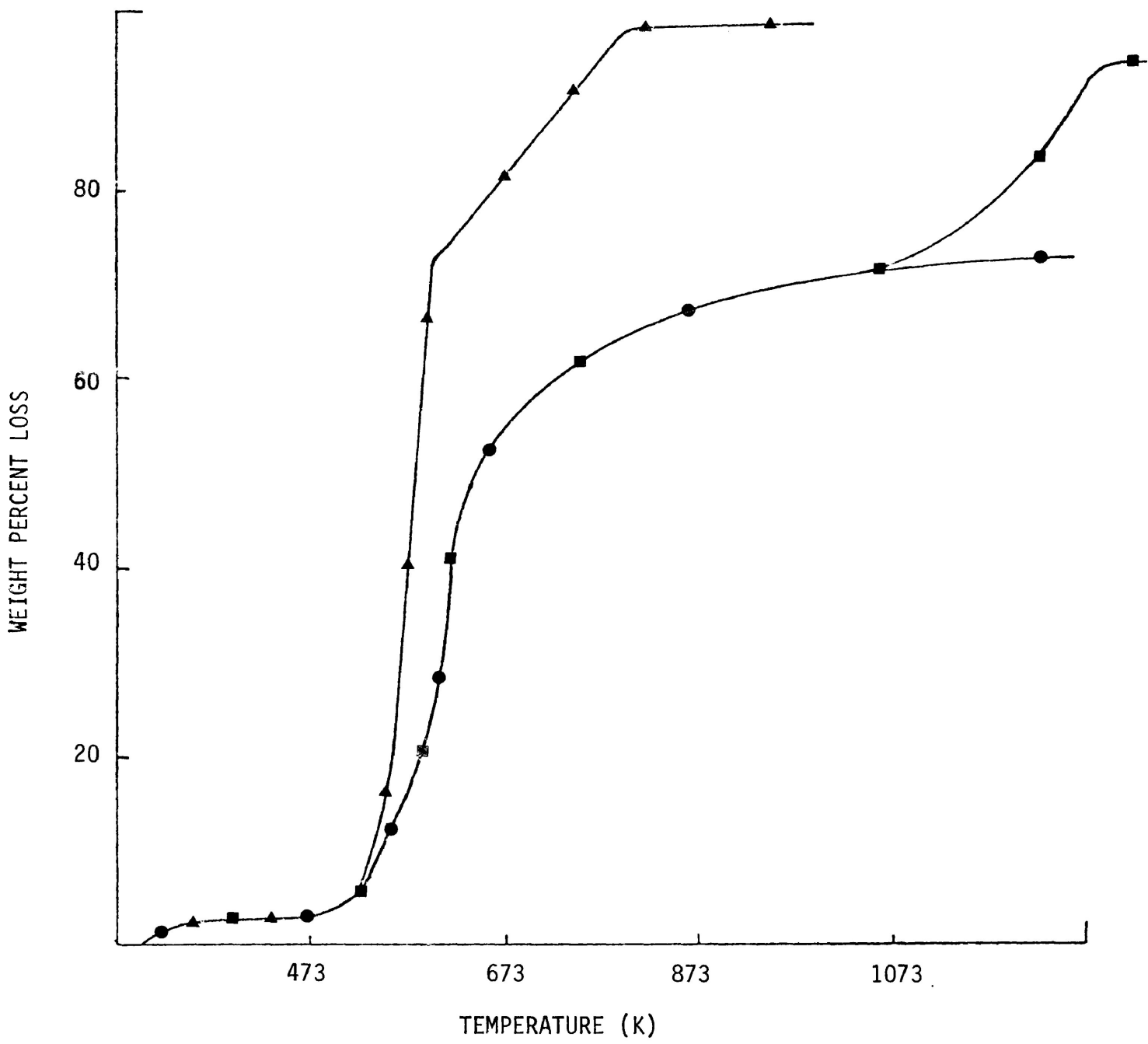
Figure 38   TG curves for extracted bark in nitrogen (●), in air (▲), and in nitrogen + H$_2$O (■).

The curve obtained in air, however, was slightly different. The initial loss of 2.5% which occurred between 323 and 373 K was followed by a plateau region up to 453 K and a slow increase in weight loss to 6.5% total loss at 523 K. Above this temperature a rapidly increasing rate of loss occurred to yield 74.5% loss at 603 K. In the region from 623 to 723 K, a linear response of weight percent loss with temperature left only ash at higher temperatures.

4.10.3. Jack pine sawdust

In all atmospheres, the TG curves obtained for jack pine sawdust < 212 μm, Figure 39, exhibited a loss of 1.5% in the region 323 to 373 K followed by a plateau up to 443 K.

In dry nitrogen, the plateau was followed by the major weight loss from 443 to 673 K and a slow decay to a final loss of 85% at 1273 K.

The TG curve in air was identical to that in nitrogen at temperatures < 523 K (6% loss). A rapidly increasing rate of loss followed producing a 74% loss at 603 K. A slow decay occurred from 603 to 673 K to yield a loss of 80% and this was followed by a second extremely rapid loss between 673 and 708 K to leave ash.

The TG curve obtained in nitrogen plus water vapour was identical to that found in dry nitrogen < 1073 K. Above this temperature, a second weight loss region was observed to

yield 99% loss at 1293 K.

4.10.4. Cellulose

The TG curves for cellulose in dry nitrogen, air, and nitrogen plus water vapour all showed an initial loss of 3.0% in the region 323 to 373 K followed by a plateau region up to 533 K, Figure 40.

In nitrogen, the weight loss began at 573 K and increased rapidly up to 80% loss at 638 K followed by a period of decay to yield 92% loss at 1273 K. The major weight loss in air began at 573 K and increased rapidly to 80% loss at 613 K. A second weight loss region occurred from 623 to 773 K and left 98% loss. Results obtained in nitrogen plus water vapour were identical to those found in dry nitrogen < 1103 K. At this temperature, a second weight loss region began and produced 98% loss at 1353 K.

4.10.5. Extracted bark containing additives

TG studies were conducted on extracted jack pine bark, < 212 μm, containing ten different chloride salts-- NaCl, $MgCl_2$, $CaCl_2$, $MnCl_2$, $FeCl_2$, $FeCl_3$, $NiCl_2$, $CuCl_2$, $ZnCl_2$, and NH_4Cl--in flowing atmospheres of dry nitrogen and air. The TG curves are presented in Figures 41, 42, and 43.

Generally, the shape of the curves obtained for extracted bark containing additives in nitrogen were

essentially unaltered from that obtained for extracted bark. With the exception of NaCl and $CaCl_2$, all additives produced an increase in weight loss at lower temperatures with little change in weight loss > 673 K. The results are summarized in Table 14. The effect of the additive NH_4Cl was to produce a two stage weight loss curve similar to that found previously for wood plus the additive NH_4Cl (Tang 1967).

The TG curves obtained from experiments in air showed that the same general shape was retained. Notable exceptions were the results for extracted bark containing NaCl and NH_4Cl. The former sample showed an initial major loss between 473 and 573 K followed by a rapid loss to 45% at 583 K and then a region of constant rate to leave ash at 823 K. The latter sample exhibited an initial region of rapidly increasing rate of loss to yield 59% loss at 573 K, a second region of increasing rate to produce a total loss of 79% at 643 K, and then a linear region to leave ash at 773 K.

In all cases, the results obtained in air were identical to those found in nitrogen < 523 K. A period of rapidly increasing rate began at this temperature, followed by a sharp transition to a region of approximately constant rate beginning at some temperature, T_i. The effect of most additives was to vary the measured weight percent loss at the temperature T_i as shown in Table 14.
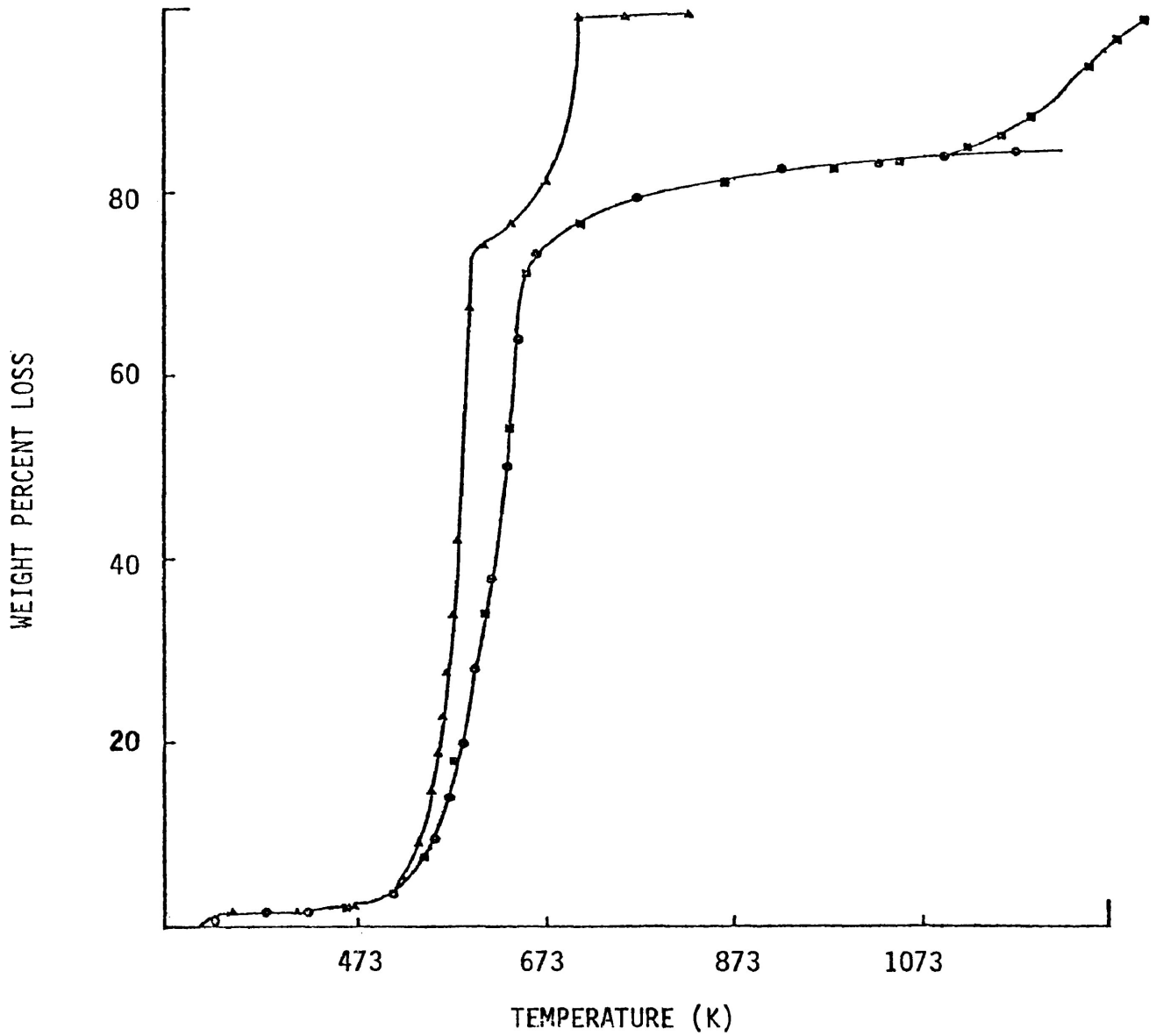
Figure 39   TG curves for jack pine sawdust in nitrogen (●), in air (▲), and in nitrogen + H_2O (■).
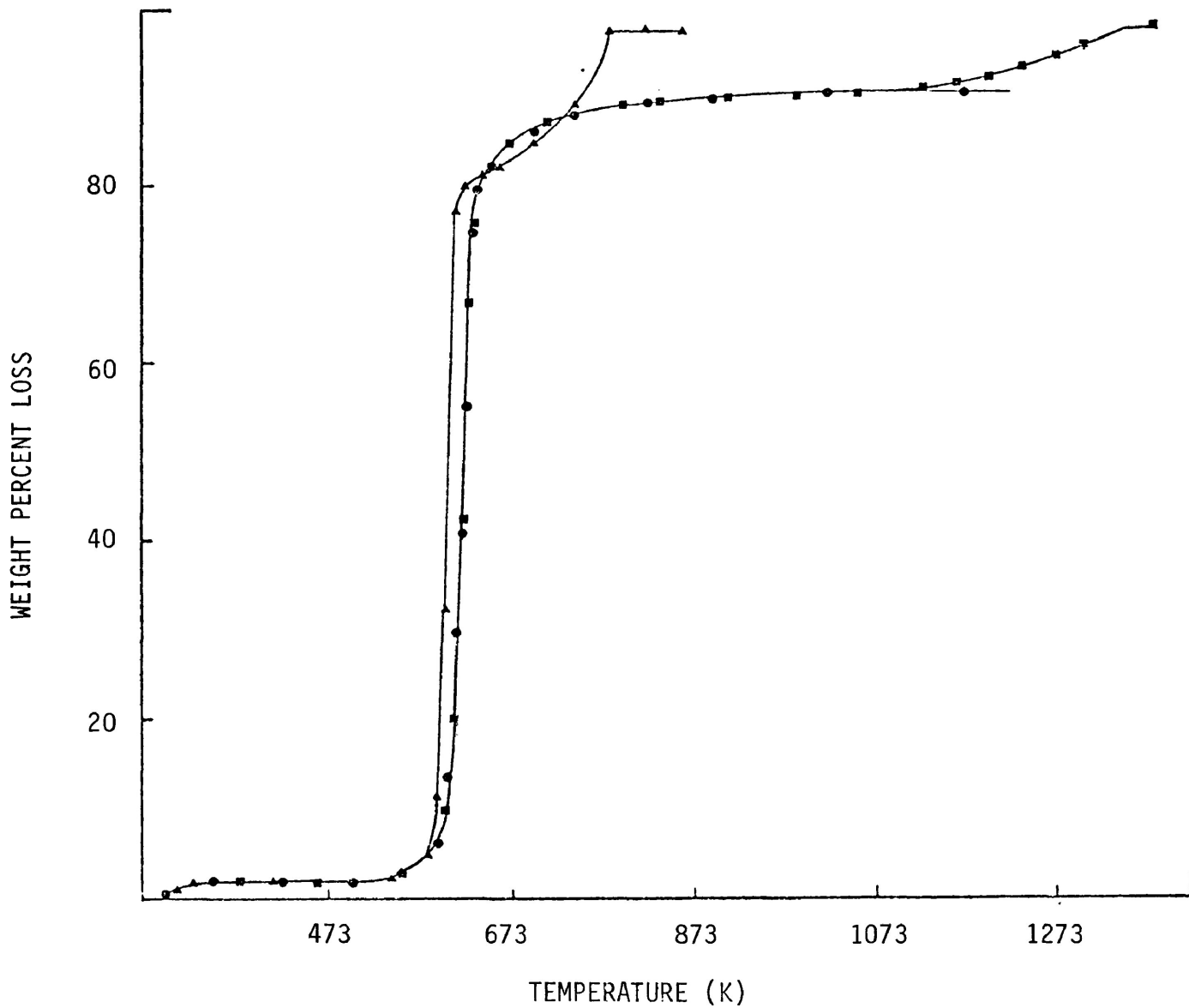
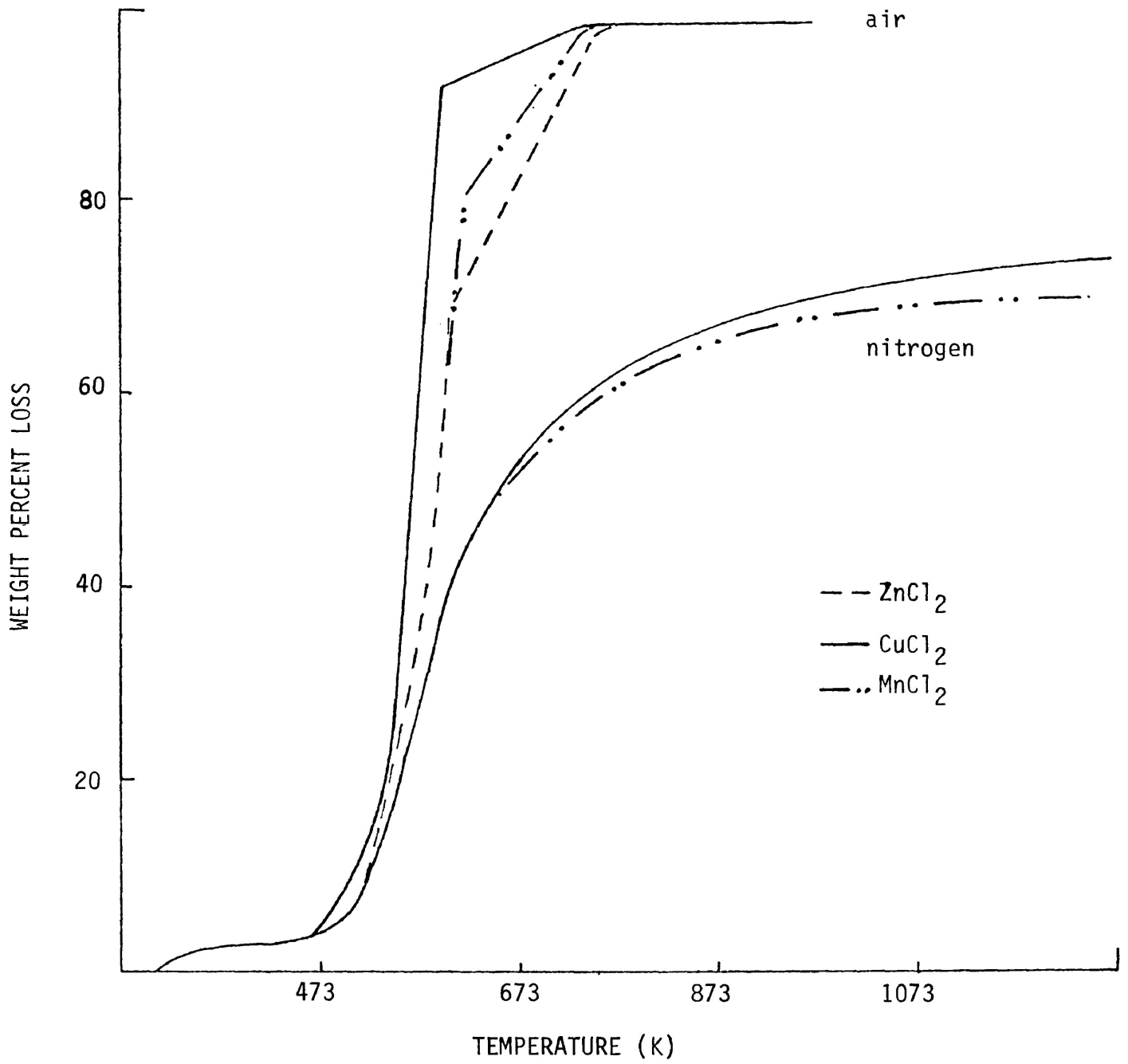Figure 40 TG curves for cellulose in nitrogen (●), in air (▲), and in nitrogen + H₂O (■).

Figure 41   TG curves for extracted bark containing additives in nitrogen and in air.

Figure 42   TG curves for extracted bark containing additives in nitrogen and in air.

Figure 43 TG curves for extracted bark containing additives in nitrogen and in air.

Table 14 The effects of additives upon the TG curve of extracted jack pine bark < 212 um.

TREATMENT	VOLATILES (%)	ONSET OF MAJOR LOSS T(K)	WEIGHT PERCENT LOSS IN NITROGEN			IN AIR	
			523 K	673 K	1273 K	T_i(K)	LOSS
extracted	2.5	453	6.5	56.0	73.0	603	72.0
+ $CuCl_2$(6.02%)	2.0	413	13.0	53.5	72.5	593	89.5
+ $FeCl_3$(4.88%)	1.0	403	13.0	52.5	71.0	583	84.5
+ $MnCl_2$(5.86%)	2.5	403	13.5	51.0	70.0	613	77.5
+ $NiCl_2$(5.13%)	3.0	343	14.0	54.0	76.0	603	77.0
+ $FeCl_2$(7.57%)	2.5	403	15.0	52.5	72.5	568	70.5
+ $CaCl_2$(5.00%)	1.5	453	6.5	56.0	71.0	588	70.5
+ $ZnCl_2$(5.22%)	2.5	423	10.0	52.5	73.0	603	66.5
+ $MgCl_2$(4.68%)	1.0	353	17.5	54.0	73.0	593	61.5
+ NaCl (5.48%)	2.5	443	8.0	54.5	72.0	583	56.0
+ NH_4Cl(5.31%)	2.0	403	20.5	55.0	73.5	583	45.0

4.10.6. Jack pine bark containing additives

TG studies were carried out on jack pine bark, < 212 μm, containing various additives in air and nitrogen. Using the same additives as in the previous section (at only slightly different concentrations), the TG curves obtained in nitrogen were very similar to those found for extracted bark with additives. Results in air differed from those obtained with extracted bark in that the weight percent loss at T_i did not vary significantly from that found for native bark.

A second series of experiments was conducted on jack pine bark containing a halogen series of additives using Zn(II) and Mn(II) as cations. In nitrogen, ZnF_2, ZnI_2, MnF_2, and $MnCl_2$ had little effect upon the TG curve of native bark. The other additives increased the weight loss at lower temperatures without significantly affecting the TG curve > 600 K as shown in Figures 44 and 45. The only additives to produce a significant decrease in weight percent loss at T_i in air were $ZnCl_2$ and $ZnBr_2$. The data are summarized in Table 15.

A third experiment dealt with the effects of sodium or ammonium phosphates and sulphates. The TG curves shown in Figure 46 indicate that these additives also have little effect upon the curve for native bark and the data are summarized in Table 16.
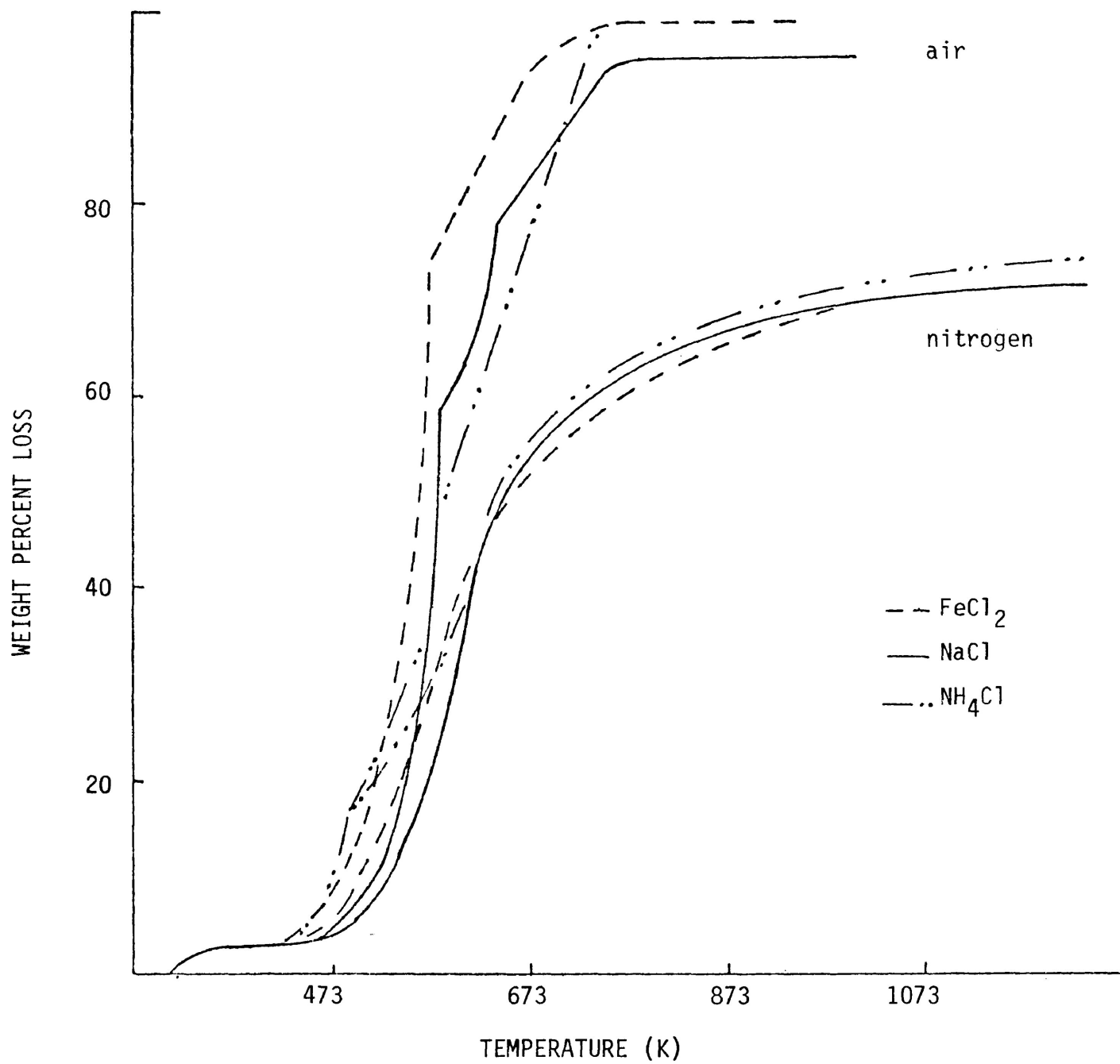
Figure 44   TG curves of native bark containing additives in nitrogen.
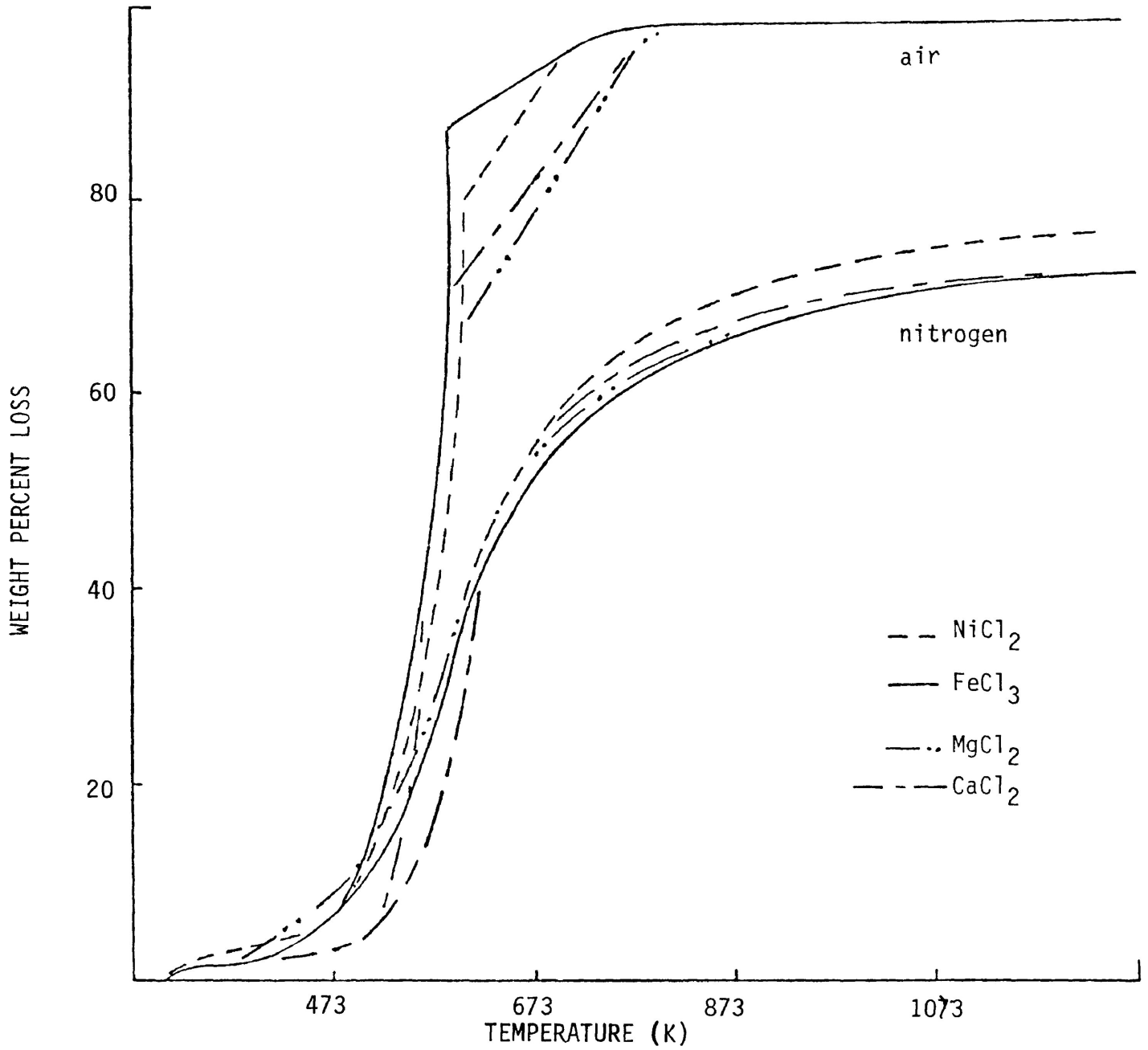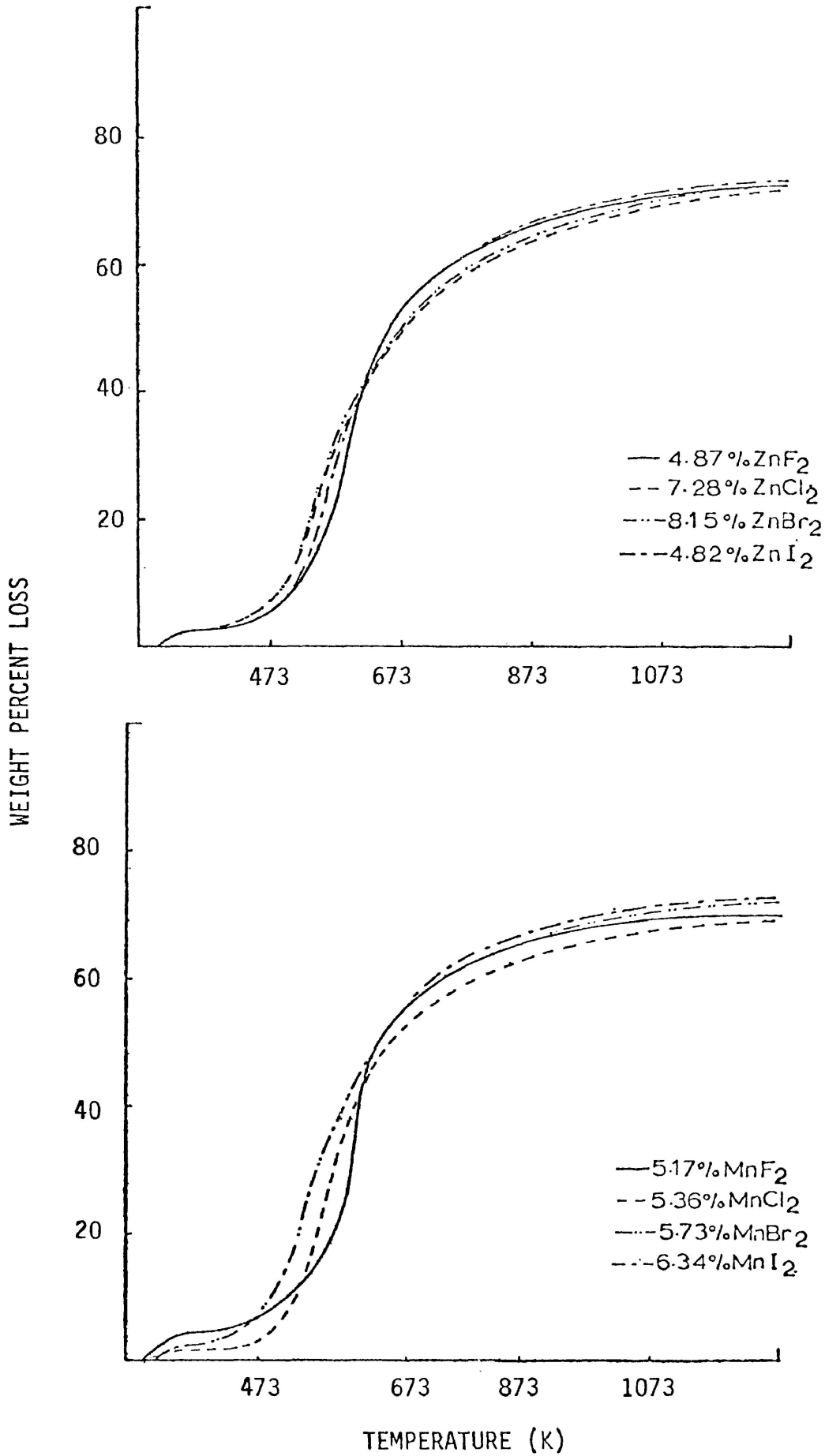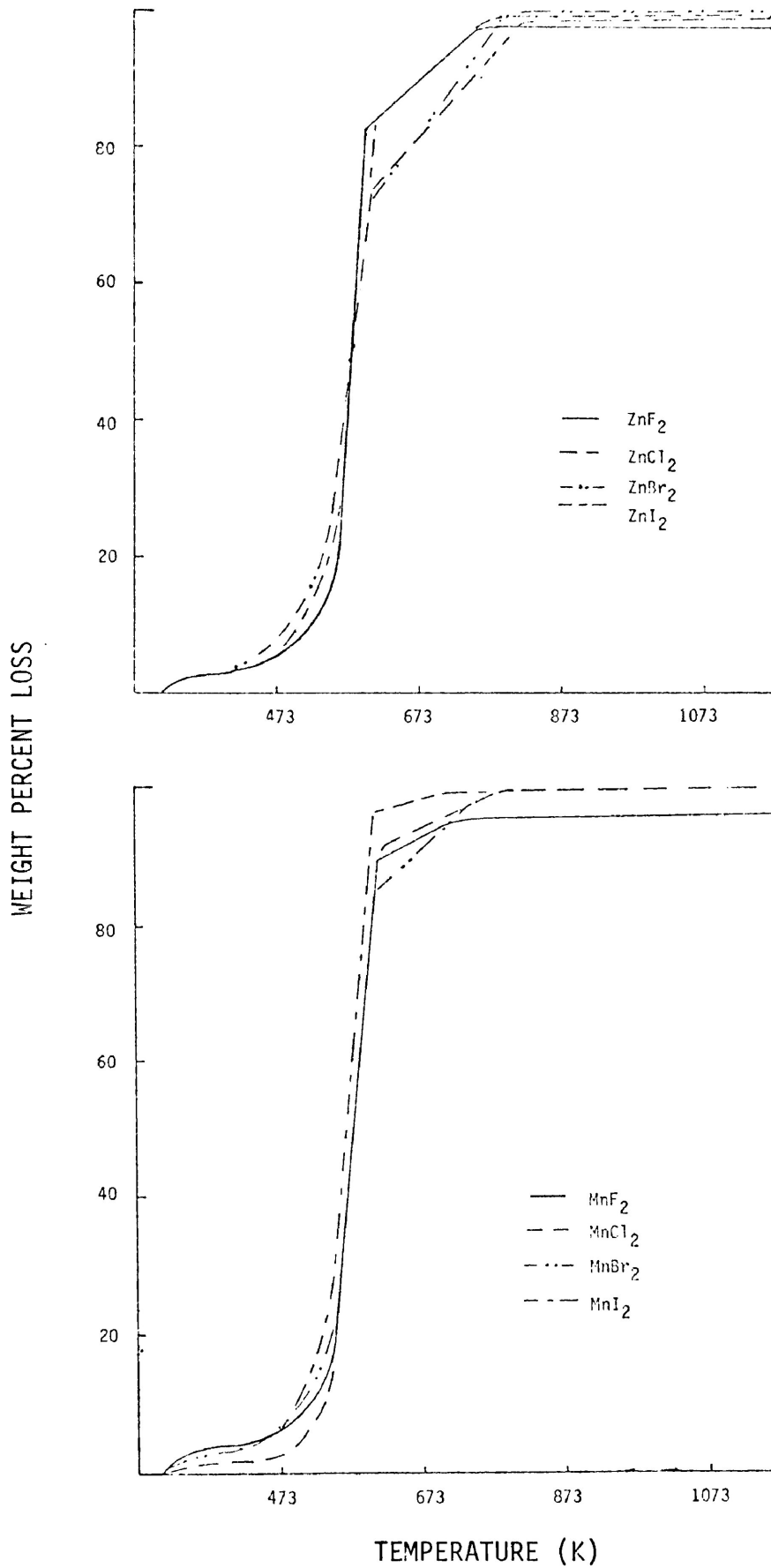
Figure 45 TG curves of native bark containing additives in air.
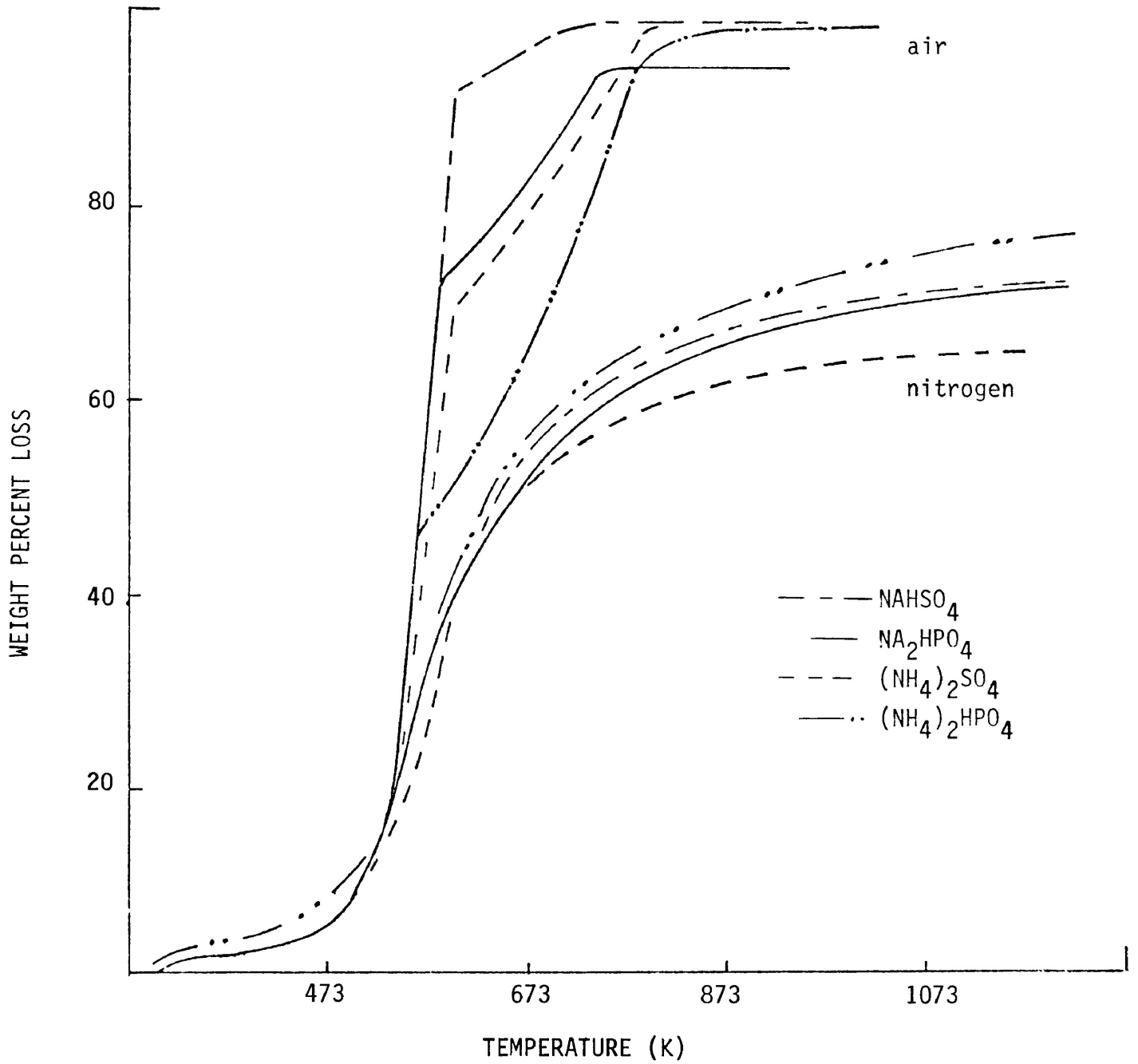
Figure 46   TG curves of native bark containing additives in nitrogen and air.

Table 15   The effects of additives on the TG curve of native
jack pine bark < 212 µm.

TREATMENT	VOLATILES	ONSET OF MAJOR LOSS T(K)	WEIGHT PERCENT LOSS IN NITROGEN			IN AIR	
			523 K	673 K	1273 K	T_i(K)	LOSS
native bark	2.5	453	6.5	56.5	73.0	613	88.5
+ ZnF_2 (4.87%)	2.5	413	10.0	52.5	72.5	603	80.0
+ $ZnCl_2$(7.28%)	2.5	403	15.5	49.5	72.5	603	69.0
+ $ZnBr_2$(8.15%)	2.0	413	17.0	50.0	73.0	603	68.5
+ ZnI_2 (4.82%)	2.5	423	12.5	53.0	73.5	608	80.0
+ MnF_2 (5.17%)	4.0	423	10.5	53.0	70.0	613	86.0
+ $MnCl_2$(5.36%)	1.5	453	8.5	49.5	70.5	613	90.5
+ $MnBr_2$(5.73%)	2.5	413	15.0	52.5	72.0	598	80.0
+ MnI_2 (6.34%)	2.5	413	17.5	54.0	73.0	603	95.0
+ $NaHSO_4$(5.53%)	2.5	413	13.0	55.0	76.0	613	92.0
+ $(NH_4)_2SO_4$ (5.06%)	2.0	423	13.0	54.0	72.5	613	69.0
+ Na_2HPO_4 (5.07%)	2.0	403	10.5	50.0	64.0	593	74.0
+ $(NH_4)_2HPO_4$ (5.04%)	1.5	403	14.0	50.5	71.0	573	46.5

4.11. Dynamic derivative thermogravimetry (DTG)

First derivative plots of the TG curves were determined by means of the APL program "DRVPLOT" (Appendix 1). Plots of the rate of weight percent loss with temperature (dW/dT) versus temperature were constructed. In the temperature region of the major weight loss, data points were obtained at approximate intervals of 5 K.

4.11.1. Jack pine bark

The DTG results for both native and extracted jack pine bark, < 212 μm, are presented in Figure 47. The DTG curves are identical for results in dry nitrogen where the loss of adsorbed moisture appears as a maximum at 333 K. Beginning at 453 K, a rapidly increasing rate of loss occurs. A small maximum or shoulder appeared at 553 K followed by a sharp maximum at 623 K and a slow decay to 1173 K.

The DTG curves in air appeared similar in pattern to those in nitrogen < 523 K, however, the rate of loss in air was greater. A single sharp maximum occurred at 573 K followed by a region of constant rate from 593 to 623 K. Native bark exhibited a sudden decrease in rate to a low constant value over the temperature range 633 to 723 K. Extracted bark showed a sudden decrease in rate, followed by a region of linearly decreasing rate in the same temperature interval.
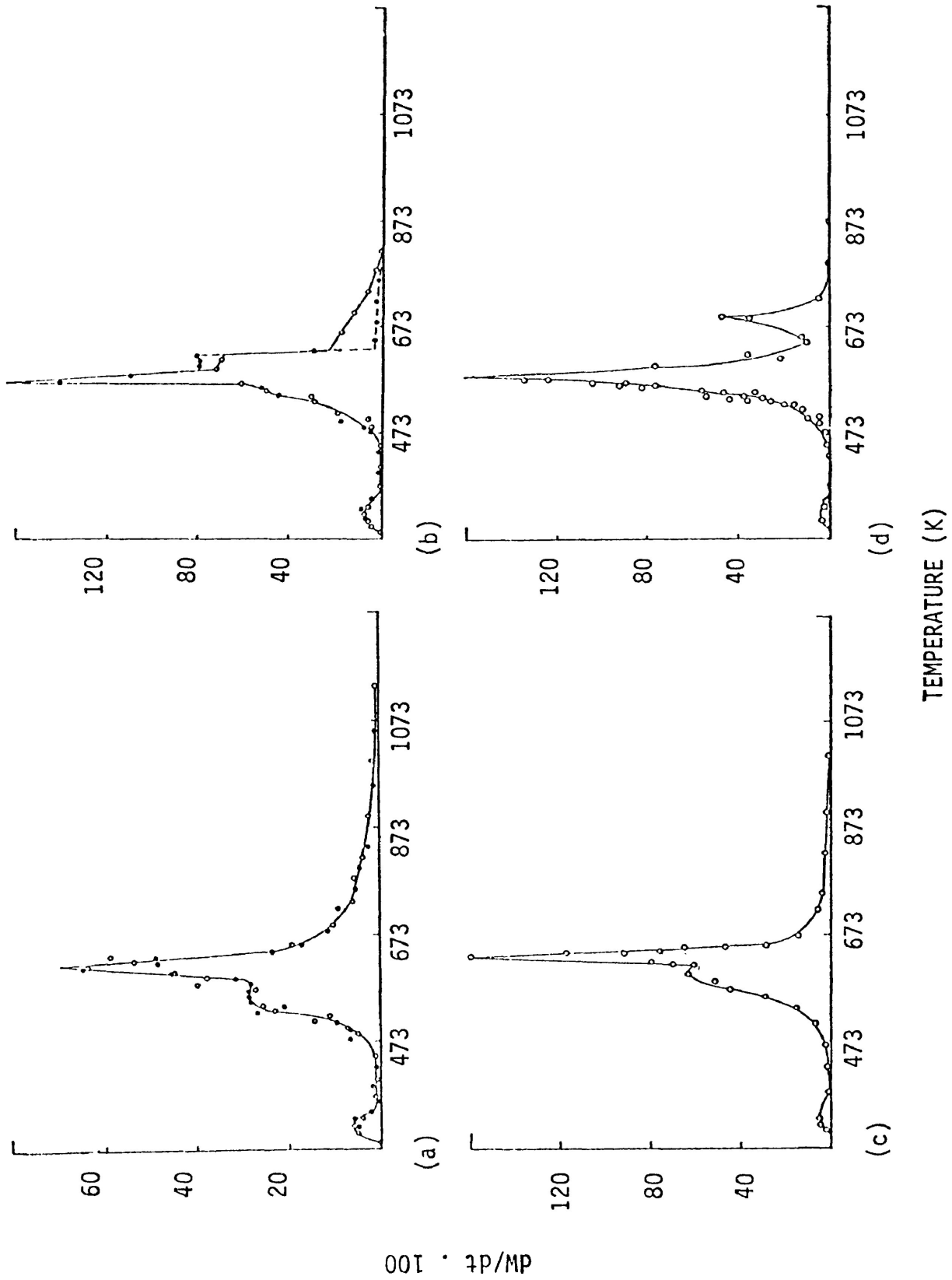
Figure 47   DTG plots of rate of weight percent loss (dW/dt) for native and extracted jack pine bark in nitrogen (a) and in air (b), and for sawdust in nitrogen (c) and air (d)
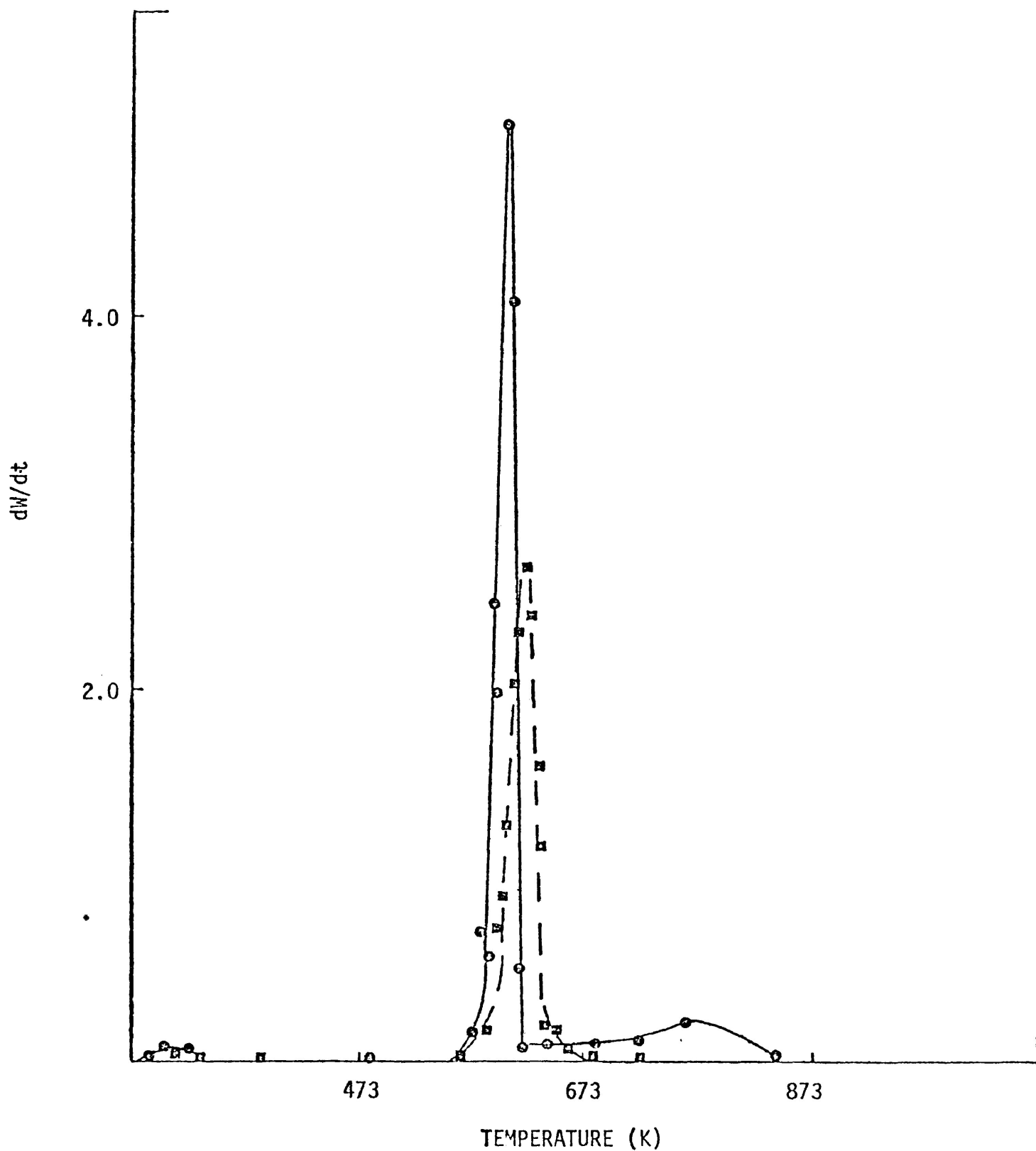
Figure 48   DTG plots of rate of weight percent loss (dW/dt) for cellulose
in nitrogen (■), and in air (●).

4.11.2. Jack pine sawdust

The DTG curves for jack pine sawdust < 212 μm, Figure 48, show that the curve obtained in nitrogen was similar to that obtained for bark—a small maximum at 593 K followed by a sharp peak at 633 K. The loss of adsorbed moisture appeared as a maximum at 333 K in both atmospheres. In air, a sharp maximum rate occurred at 578 K followed by a second smaller maximum at 693 K.

4.11.3. Cellulose

The DTG curves for cellulose, Figure 48, indicate that the temperature range for decomposition was narrow. In nitrogen, a sharp maximum was observed at 623 K, while in air, a very sharp maximum at 603 K was followed by a region of constant rate of loss up to 823 K.

4.12 Kinetic data from DTG

Kinetic parameters for decomposition were determined using the method of Tang (1967) which assumes a first order reaction. The rate of weight percent loss with time (dW/dt) was evaluated using the expression:

$$dW/dt = dW/dT \cdot dT/dt \qquad (26)$$

where dT/dt was determined for each temperature interval. The rate constant k was determined from the first order expression:

$$dW/dt = k \ (\ W_f - W_t \ ) \qquad (27)$$

where W_f is the final weight percent loss and W_t is the loss at time t. Since the DTG curves in air exhibited essentially a single peak in the region 473 to 673 K, Arrhenius plots derived from data obtained in this region gave rise to approximate straight lines, Figure 49, from which the kinetic parameters given in Table 16 were evaluated.

Table 16 includes the results obtained for native and extracted bark in air, extracted bark containing additives in air, and sawdust and cellulose in both air and nitrogen. Only two additives produced a significant effect on the Arrhenius plot of extracted bark. Two linear regions were observed for $NiCl_2$, while the results for NH_4Cl exhibited significant scatter and therefore, kinetic parameters could not be evaluated.

Also included in Table 16 is the temperature at which the maximum rate of weight percent loss (dW/dt) occurred (T_{max}). Most additives had little effect on this parameter, however $FeCl_2$ and $FeCl_3$ significantly decreased T_{max} while $ZnCl_2$ produced a slight increase compared to extracted bark alone.

The values obtained for temperature coefficients were very similar for bark, bark containing additives, and sawdust, while the values obtained for cellulose were very much higher.
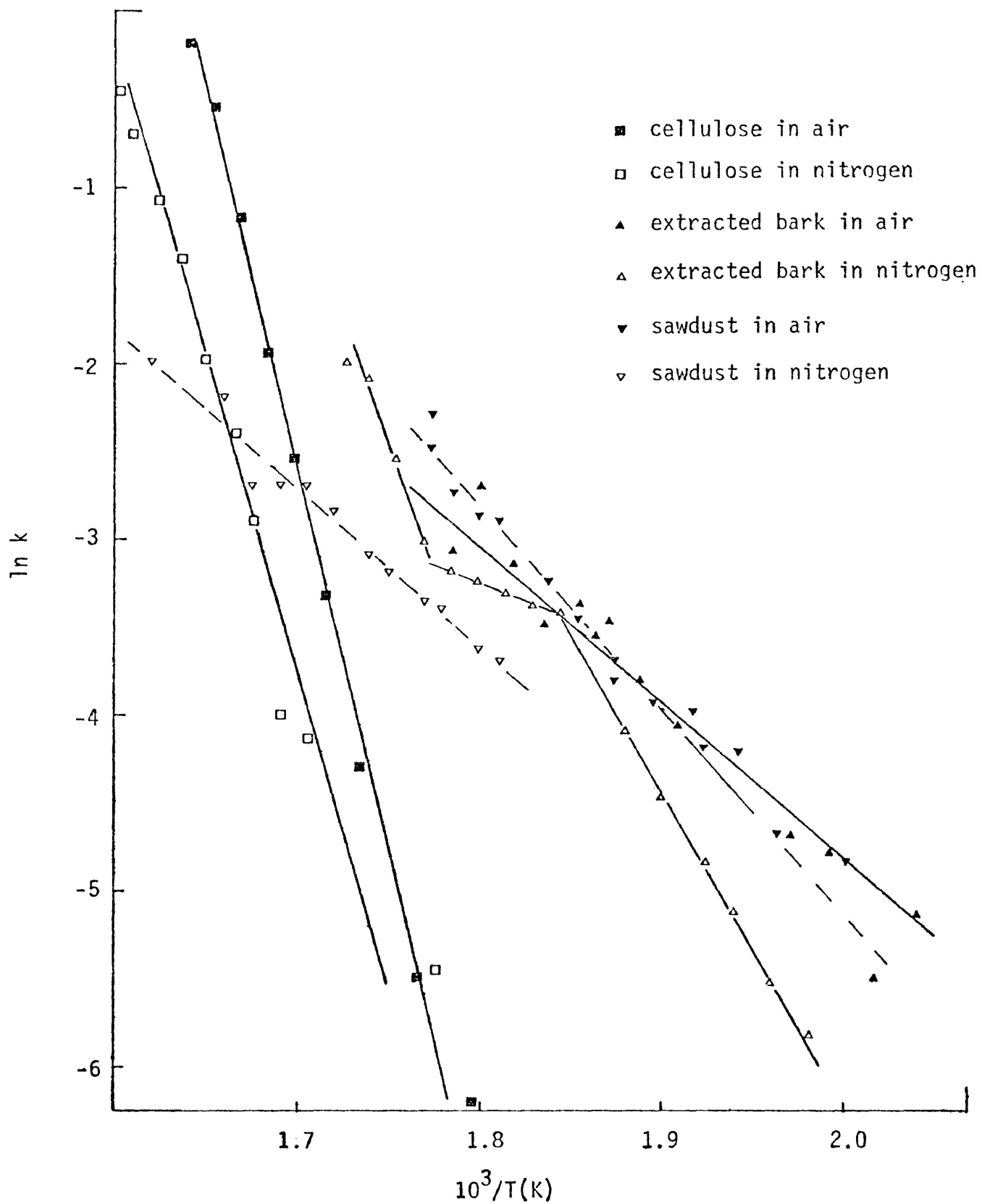
Figure 49 Arrhenius plots derived from DTG.

Table 16 Kinetic parameters obtained from DTG.

SAMPLE	ATMOSPHERE	TEMPERATURE RANGE (K)	T_{max} (K)	T_c ($.10^3$ K^{-1})	A (min^{-1})	E_a ($Kj.mol^{-1}$)
native bark	air	463 to 563	573	8.1 $\pm$0.6	$1.05.10^5$	67
extracted bark	air	479 to 561	573	9.6 $\pm$1.7	$1.66.10^6$	80
+ NaCl	air	482 to 552	559	9.3 $\pm$1.6	$1.32.10^6$	77
+ $FeCl_2$	air	476 to 518	527	9.0 $\pm$1.3	$2.37.10^6$	75
+ $ZnCl_2$	air	467 to 567	585	8.3.$\pm$1.1	$2.53.10^5$	69
+ $CaCl_2$	air	467 to 560	575	8.1 $\pm$1.2	$1.50.10^5$	67
+ $MnCl_2$	air	473 to 561	567	7.1 $\pm$0.7	$2.86.10^4$	59
+ $FeCl_3$	air	453 to 513	525	7.0 $\pm$1.7	$3.67.10^4$	58
+ $CuCl_2$	air	424 to 533	556	5.8 $\pm$1.3	$2.14.10^3$	48
+ $MgCl_2$	air	396 to 561	575	4.8 $\pm$0.8	$2.68.10^2$	40
+ $NiCl_2$	air	467 to 490		16.5 $\pm$6.1	$4.95.10^{12}$	137
		490 to 551	563	6.0 $\pm$1.7	$3.07.10^3$	50
+ NH_4Cl	air	--	561	--	--	--
sawdust	air	498 to 573	584	11.5 $\pm$1.1	$6.00.10^7$	96
sawdust	nitrogen	536 to 623	650	8.2 $\pm$0.5	$6.89.10^4$	68
cellulose	air	557 to 610	610	41.3 $\pm$3.5	$1.93.10^{29}$	343
cellulose	nitrogen	563 to 633	628	29.8 $\pm$4.6	$2.61.10^{20}$	248

5. DISCUSSION

5.1. Critique of thermobalance methods

A number of investigators have studied the kinetics of wood pyrolysis by thermobalance methods. Two techniques, isothermal weight-change determination and dynamic thermo-gravimetry, allow the calculation of kinetic data.

Kinetic data are usually obtained from TG results by computing a series of TG curves obtained at different heating rates. In the method of Freeman and Carroll (1958), the following relationship was derived:

$$\frac{\log d \alpha /dt}{\log (1 - \alpha)} = n - \frac{E}{2.303 \ R} \ T^{-1} \ / \log (1 - \alpha) \qquad (28)$$

where n is the order of reaction. Later, Coats and Redfern (1964) used equations (29) and (30) for a linear heating rate, ϕ:

$$\log [- \ln (1 - \alpha) \ / \ T^2] = \log (AR/\phi \ E) - E/2.303 \ RT \qquad (29)$$

for n = 1, and

$$\log [1 - (1 - \alpha)^{1-n} \ / \ T^2 (1 - n)] =$$

$$\log (AR/\phi \ E) - E/2.303 \ RT \qquad (30)$$

for n $\neq$ 1. Sharp and Wentworth (1969) estimated the reaction rate constant by dividing $d\alpha / dt$ by $(1 - \alpha)^n$ and if the assumed order of reaction, n, was correct, then a linear Arrhenius plot would be obtained. Most recently, Ozawa (1975) described a general method which would be applicable to a

single unit process where the following approximate relation-
ship could be applied for a given value of α :

$$\log \phi + 0.4567 \, E/RT = \text{constant} \qquad (31)$$

The apparent activation energy would be obtained from a plot
of $\log \phi$ against T^{-1}.

In a critical appraisal of these methods, Ozawa
(1975) indicated that most techniques would give rise to
reasonable results for simple first or second order reactions,
but inaccurate results may be anticipated from systems where
two parallel competitive reactions occur or for polymers which
decompose by random scission in the main polymer chain.

While the computing method is often oversimplified
(Sestak 1972), results obtained from TG studies are useful in
observing the variation of the apparent activation energy for
a number of similar samples. Tang (1967) has used this
technique in an examination of the effects of a number of
additives on the pyrolysis of wood. Kinetic parameters were
obtained from pseudo first order Arrhenius plots derived from
the TG curves. However, these plots exhibited two linear
regions.

Similar results were obtained in the present study
for pyrolysis of jack pine bark and sawdust in nitrogen, but
data from experiments in air showed a linear Arrhenius plot
over a larger temperature range, Figure 49. It is clear from
the DTG results obtained for jack pine bark and sawdust in

nitrogen, Figures 47 and 48, that at least two maxima appear and therefore the assumption of a single first order reaction is incorrect. The DTG results for pyrolysis of these samples in air indicate that the assumption of a single first order reaction would probably be correct. Cameron and Kerr (1969) found that good agreement between Ea as determined by isothermal and dynamic TG occurs only when the mechanism of decomposition is invariant with the extent of decomposition for polymer degradation. Further, it was thought that when the two methods gave different results, the data from iso-thermal experiments (initial rates) would be more reliable. Studies in this laboratory have also indicated that the final weight loss obtained for jack pine bark pyrolysis at a particular temperature in nitrogen may be related to the rate of heating, and this effect would add further uncertainty in applying the methods of dynamic TG.

The main advantage of the isothermal technique is that the interpretation of data is well-documented especially for inorganic materials (Sharp, Brindley, Achar 1966). The only major drawback of this method is that a significant weight loss may occur before the sample has attained thermal equilibrium with the furnace. In the present study, however, the samples generally reached the reaction temperature with a minimum of delay and only a slight loss was observed in this time period.

The values obtained for apparent activation energy for various samples in this study are summarized in Table 17. The numerical results from isothermal studies on jack pine bark, extracted bark, and bark containing additives were of the same order of magnitude as those determined from dynamic TG in air. Generally, the error for a 95% confidence interval calculated from isothermal experiments was $\pm$ 7 Kj.mol^{-1}, while that from TG was $\pm$ 11 Kj.mol^{-1} for the same samples.

The value obtained for Ea for sawdust pyrolysis in air and nitrogen by the isothermal method, 147 Kj.mol^{-1}, was much greater than the values found using the dynamic TG technique, 96 Kj.mol^{-1} in air and 68 Kj.mol^{-1} in nitrogen, over the same temperature interval (523 to 603 K). The apparent activation energy found by the isothermal method for the first stage of cellulose pyrolysis in both air and nitrogen was approximately 143 Kj.mol^{-1}. The second or major stage was found to occur with a value for Ea of 212 Kj.mol^{-1} in nitrogen and 163 Kj.mol^{-1} in air. In contrast, the values found by TG were higher, 248 Kj.mol^{-1} in nitrogen and 343 Kj.mol^{-1} in air. Results obtained by previous investigators, Table 2, also indicate that the kinetic parameters determined by TG studies are consistently greater than those found by isothermal techniques.

Table 17 Apparent activation energies derived from dynamic TG
and isothermal weight-change determinations.

SAMPLE	ATMOSPHERE	TECHNIQUE	APPARENT ACTIVATION ENERGY $(Kj.mol^{-1})$
native bark	air	dynamic TG	67
"	"	isothermal	55
"	nitrogen	"	43
extracted bark	air	dynamic TG	80
"	nitrogen	isothermal	65
sawdust	air	dynamic TG	96
"	nitrogen	"	68
"	air	isothermal	147
"	nitrogen	"	147
cellulose	air	dynamic TG	343
"	nitrogen	"	248
"	air	isothermal	137, 163
"	nitrogen	"	149, 212

5.2. The pattern of pyrolysis

The thermal decomposition of wood waste materials between 293 and 1273 K takes place in two stages. The first stage involves the loss of unbound water and the second, pyrolysis which represents the loss of pyrolygeneous tars, water vapour, methane, hydrogen, and oxides of carbon to leave a carbon char. In all cases, the loss of water occurred in the region 323 to 373 K with a maximum rate at 333 K. This decomposition is characteristic of wood materials and has been reported (Browne 1958).

In an inert atmosphere, the pyrolysis step initiated at approximately 453 K for native and extracted jack pine bark and sawdust, while cellulose pyrolysis began at 573 K. The amount of residue remaining from the pyrolysis of bark was 26% while that for sawdust was 15% and for cellulose, 8%. These values lie in the same range as those reported for chemically-treated wood (Tang 1967). The presence of additives slightly increased the amount of residue remaining, with Na_2HPO_4 (5.07% w/w) producing the largest increase, 36% residue at 1273 K.

The extraction process had little or no effect on the bulk properties of the bark, since extracted bark gave the same TG curve as native bark in nitrogen. The action of most additives was to produce a slight increase in the weight percent loss below 600 K and therefore a slight increase in

the temperature at which pyrolysis commenced as indicated in Tables 14 and 15.

Pyrolysis in an oxidizing atmosphere over the same temperature interval indicated that the weight loss for any sample was identical to that found for that sample in inert atmosphere at temperatures up to 523 K. The major difference in the TG curves in air appeared to be in the region of the curve corresponding to the transition from an initial rapid weight to a region of slower weight loss, Ti. As shown in Figure 38, the extraction process clearly decreased the loss observed for bark at this transition temperature. Native bark containing additives exhibited no significant alteration of the TG curve with the exception of $ZnBr_2$ (8.15% w/w) and $ZnCl_2$ (7.28% w/w) which decreased the weight loss at the transition temperature. For all bark samples, this transition temperature ranged from 573 to 613 K as shown in Tables 14 and 15. It was the additive Na_2HPO_4 which also produced the greatest change in the weight percent loss at Ti. Jack pine sawdust and cellulose samples also exhibited a two-stage TG curve for pyrolysis in air, Figures 39 and 40.

The DTG curves, Figures 47 and 48, show that bark and sawdust pyrolysis in an inert atmosphere exhibited two maxima while pyrolysis in the presence of oxygen showed a single maximum followed by a period of approximately constant

rate values. A single sharp maximum was observed for cellulose in both atmospheres, Figure 48, and these results are summarized in Table 18. For all three samples, the maximum rate occurred at 623 K in the inert atmosphere and the temperature at which this maximum rate of loss occurred in air was significantly lower--576 K for bark and sawdust and 603 K for cellulose. The measured rate of loss in air was always greater than that found in an inert atmosphere. The additives generally had little effect upon the position of the maximum rate of loss for jack pine bark with the exception of the iron chlorides which decreased the temperature at which the maximum rate occurred, Table 16.

For all samples, pyrolysis in air left ash at temperatures greater than 773 K. It appears that the sharp maximum observed for bark and sawdust pyrolysis was due to the very rapid thermal decomposition of the cellulose constituent. The temperature at which this maximum occurred for cellulose pyrolysis in air was reduced by 20 K compared to the inert atmosphere value while for bark and sawdust samples this maximum was reduced by 47 K which suggests that the pyrolysis of cellulose in the wood matrix was affected by the wood anatomy or was catalysed in some fashion by the products of pyrolysis of one of the other constituents of the wood. The infrared study of jack pine bark, Figure 35, and the elemental analysis, Table 10, indicate that its gross

Table 18   Summary of DTG data.

SAMPLE	ATMOSPHERE	MAXIMUM (K)	RATE OF LOSS AT MAXIMUM ($\%.min^{-1}$)
native bark	nitrogen	623	0.75
native bark	air	576	1.65
extracted bark	nitrogen	623	0.75
extracted bark	air	576	1.65
sawdust	nitrogen	623	1.60
sawdust	air	576	1.62
cellulose	nitrogen	623	2.60
cellulose	air	603	5.00

chemical composition is related to that of wood. It has been observed, however, that it is unlikely that a relation- ship exists between the anatomy of wood and its gross chemical composition (Michell, Ingle, Stewart 1969) and therefore the differences in pyrolysis patterns between jack pine bark and sawdust may be related to the anatomical variances.

5.3. Product analysis

Extrapolation of the plot of final weight percent loss versus temperature, Figure 34, indicates that jack pine bark should begin to lose weight at 447 K in good agreement with the results obtained by dynamic TG which also showed that jack pine sawdust began to lose weight at approximately this temperature. All samples studied by isothermal experi- ments produced residues which increased in carbon content with treatment temperature in inert atmosphere, Tables 10 and 11, over the range 473 to 613 K. Samples of wood waste materials treated in an oxidizing atmosphere over the range 473 to 573 K seemed to produce residues with similar carbon contents.

A statistical description of the reactions which occur in the pyrolysis of wood waste materials may be obtained by the use of an H/C versus O/C diagram. This method has been outlined by van Krevelen (1950) for the reaction processes in coal combustion and the diagram con-

sists of a plot of the atomic hydrogen to carbon ratio as a function of the atomic oxygen to carbon ratio in the residues obtained from pyrolysis. The values determined for these ratios for selected residues have been given in Tables 10, 11, 12, and 13 where the amount of oxygen in any residue was estimated by difference and the elemental composition was corrected to an ash-free basis.

The H/C versus O/C diagram was plotted for the results obtained for jack pine bark and sawdust, and cellulose, Figure 50. All results obtained from pyrolysis in the inert atmosphere appear to lie on a single straight line of slope 2.0, signifying that the atomic ratio H/C decreases at twice the rate of the O/C ratio. Results obtained from pyrolysis in air indicate that the H/C ratio decreased from 1.40 to 0.35 while the O/C ratio decreased from 0.60 to 0.45 over the temperature range considered.

The carbonisation of all coalification products has been shown to yield a uniform final product, ($C_8H_2O_{0.16}$)$_n$, where H/C = 0.25 and O/C = 0.02; and similarly, the gaseous oxidation of these materials yields a uniform product, ($C_8H_2O_3$)$_n$, where H/C = 0.250 and O/C = 0.375 (van Krevelen 1950). These two end-products are represented on the H/C versus O/C diagram as the carbonisation and oxidation poles, respectively. The results obtained in the present study also indicate that the carbonisation of wood wastes was directed
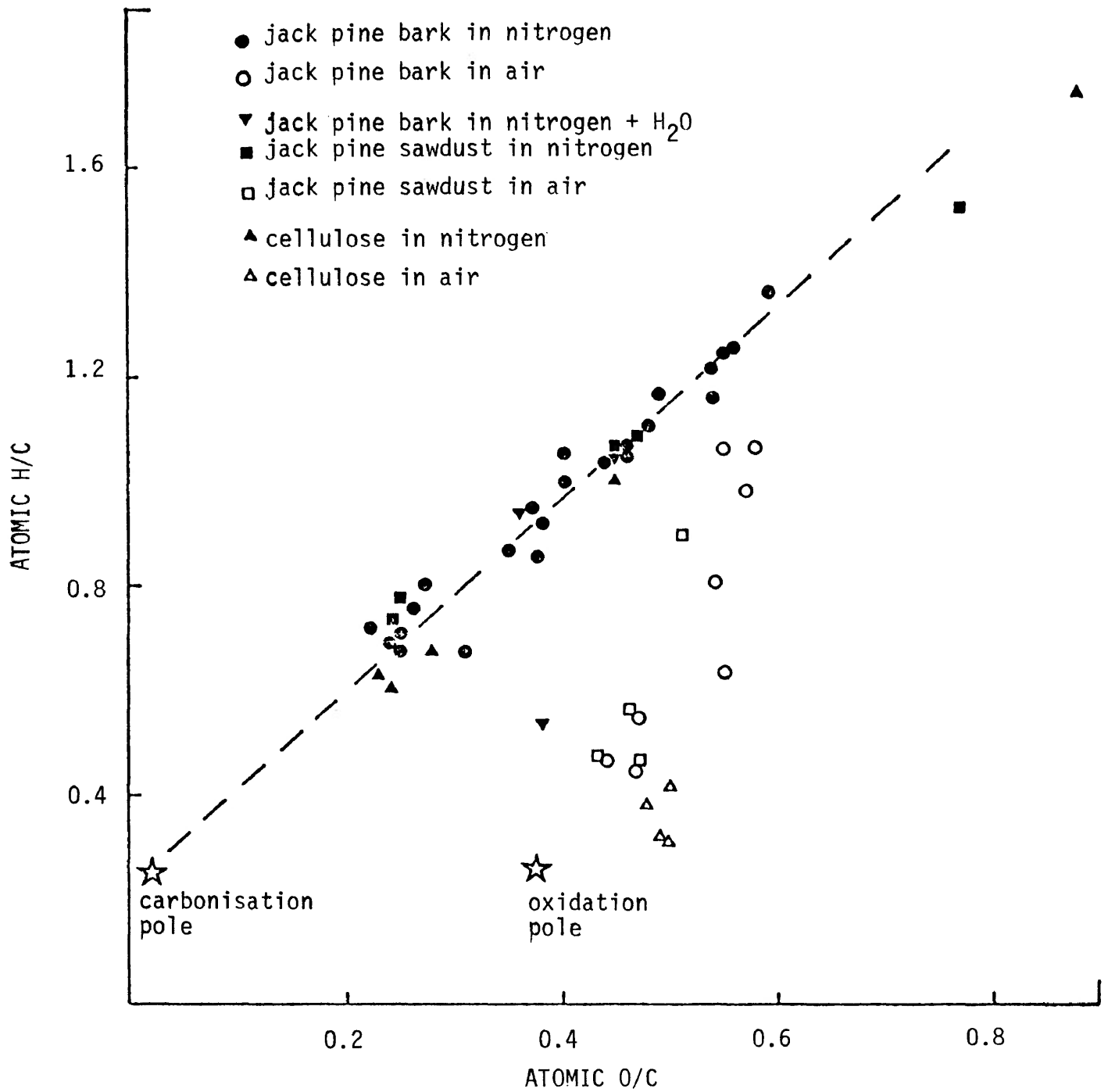
Figure 50   The H/C versus O/C diagram for the pyrolysis
of wood materials.

towards the former pole while the gaseous oxidation of these materials was directed towards the latter, as might be expected.

When a substance $C_cH_hO_q$ loses n molecules of water, the H/C ratio (y) and the O/C ratio (x) become y = (h - 2n) / c and x = (q - n) / c. Rearrangement and elimination of n implies that dehydration should be represented by a straight line of slope 2.0:

$$y = 2x + \frac{h - 2q}{c} .$$ (32)

Similarly, it may be demonstrated that other reactions, including oxidation, dehydrogenation, demethanation, decarboxylation, can be represented by straight lines on an H/C versus O/C diagram (van Krevelen 1950).

The results from the pyrolysis of jack pine bark and sawdust, and cellulose in an inert atmosphere indicate the prime component of the overall reaction is dehydration since the slope of the line in the H/C versus O/C diagram was 2.0. However because the starting material in this case was not a simple organic compound, this statistical analysis serves only to indicate that the main reaction which occurred to produce a carbon char probably followed a general dehydration mechanism. Thus, the gas analysis studies, Table 6, clearly showed that while H_2O may be the main product (especially at low temperatures) CO, CO_2, and CH_4 were also produced at

significant levels. A dehydration mechanism would be expected if crosslinking or condensation reactions occurred to yield a carbon skeleton (Bacon, Tang 1964).

Experiments conducted in an atmosphere of nitrogen plus water vapour (15.5 Torr) indicate that the residues produced at temperatures below 561 K may result from the operation of a similar mechanism as that in the inert atmosphere, Figure 50, while treatment at higher temperatures yields residues which are more closely related to those formed from pyrolysis in air. It has been observed (Sood 1976) that pyrolysis of wood wastes in an oxidizing atmosphere produces significantly more H_2O and CO_2 with a reduction in the amount of CO and CH_4 formed.

5.4. Reaction kinetics

In this study, the experimental rates of pyrolysis of wood products were examined from the standpoint of a general solid state decomposition of the type:

$$A_s \longrightarrow B_s + C_g.$$

(33)
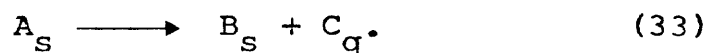
The kinetic description of such a decomposition is generally based upon geometrical principles where the starting material (A_s) is a simple inorganic salt (Sharp, Brindley, Achar 1966). However, the mechanism and mode of the thermal decomposition of wood materials would be expected to be extremely complex due to the heterogeneous, anisotropic

nature of the starting material. Hence, comparisons with previous work in the general area of solid state decomposition reactions can only be made in a qualitative manner.

The working kinetic expression for the decomposition of jack pine bark, equation (17), was found to be valid for isothermal weight-change studies carried out in nitrogen, air, and nitrogen plus water vapour. This equation fitted the data over a very wide range of α values allowing for an accurate determination of rate constant. The reduced time curve for the pyrolysis of jack pine bark was therefore described by the expression:

$$[- \ln (\ln 1 - \alpha)]^2 = 0.4805 (t/t_{0.5}) . \qquad (34)$$

Comparison of this experimentally-determined reduced time plot with known standard kinetic plots (Appendix 2) indicated that the curve most closely resembled those derived for diffusion-controlled reactions (Sharp, Brindley, Achar 1966). The standard kinetic plots for one-, two-, and three-dimensional diffusion-controlled reactions are very similar and it is difficult to differentiate between these curves for low values of α .

The photomicrographs of jack pine bark, Figure 20, clearly show that the bark particles used in this study did not conform to a regular geometric pattern. Further, the experimentally-determined reduced time plot was identical to that obtained for some diffusion-controlled oxidation

reactions on powder samples where a particle size distribution was shown to alter the curve (Gallagher 1965). In all likelihood then, a particle size distribution effect in the present study would be expected to alter the standard kinetic plot.

The derived values for apparent activation energy for jack pine bark, 31 to 68 $Kj.mol^{-1}$, appear to be greater than those expected for a simple diffusion-controlled model. In addition, the pyrolysis of jack pine sawdust in nitrogen gave rise to the same reduced time curve and kinetic expressions, although, the value of the apparent activation energy, 147 $Kj.mol^{-1}$, was much higher.

The pyrolysis of sawdust in air was found to obey a kinetic expression derived previously for a two-dimensional diffusion-controlled reaction into a cylinder of radius r (Holt, Cutler, Wadsworth 1962). The reduced time curve for sawdust pyrolysis in air was derived from equation (20) and given by:

$$(1 - \alpha) \ln (1 - \alpha) + \alpha = (k/r^2) t$$

$$= 0.1534 (t/t_{0.5}). \quad (35)$$

The photomicrographs of jack pine sawdust, Figure 22, indicate that the particles were more fibrous than the bark particles and therefore more closely resembled a cylindrical shape.

Upon logarithmic expansion, equation (35) approximates to:

$$\alpha^2 + \frac{\alpha^3}{3} + \frac{\alpha^4}{4} + \ldots = 0.3068 \ (\ t/t_{0.5} \ ) \qquad (36)$$

while an expansion of the experimentally-determined equation (34) gives rise to the expression:

$$\alpha^2 + \alpha^3 + \frac{\alpha^4}{4} + \ldots = 0.4805 \ (\ t/t_{0.5} \ ). \qquad (37)$$

The similarity of the two expressions, the former derived from a theoretical diffusion model and the latter found experimentally, seems clear.

The pyrolysis results for cellulose showed a very rapid initial weight loss followed by two distinct stages of pyrolysis, Figure 27. The initial rapid weight loss was not examined in any detail in the present study. While this initial loss may be attributed to very rapid crosslinking reactions (Basch, Lewin 1973), it seems more likely that it is probably related to a very rapid surface reaction such as the desorption of volatiles.

The first stage of cellulose pyrolysis has been described in terms of a zero order reaction with respect to weight percent loss, in agreement with those investigators who have suggested that a zero order dehydration reaction is likely to occur (Arseneau 1971). It has been observed that cellulose samples first undergo a reaction which decreases the degree of polymerization to less than 200 (Fung 1969; Kosik, Luzakova, Reiser 1972) and Fung (1969) also pointed

out that the weight loss after this initial reaction would
be approximately 8.5%, in reasonable agreement with the
results of this study. The reaction scheme proposed by
Shafizadeh and Fu (1973) implies that the first step in the
pyrolysis of cellulose is a dehydration-depolymerization
reaction involving the cleavage of the B - glycosidic
linkage as shown below:
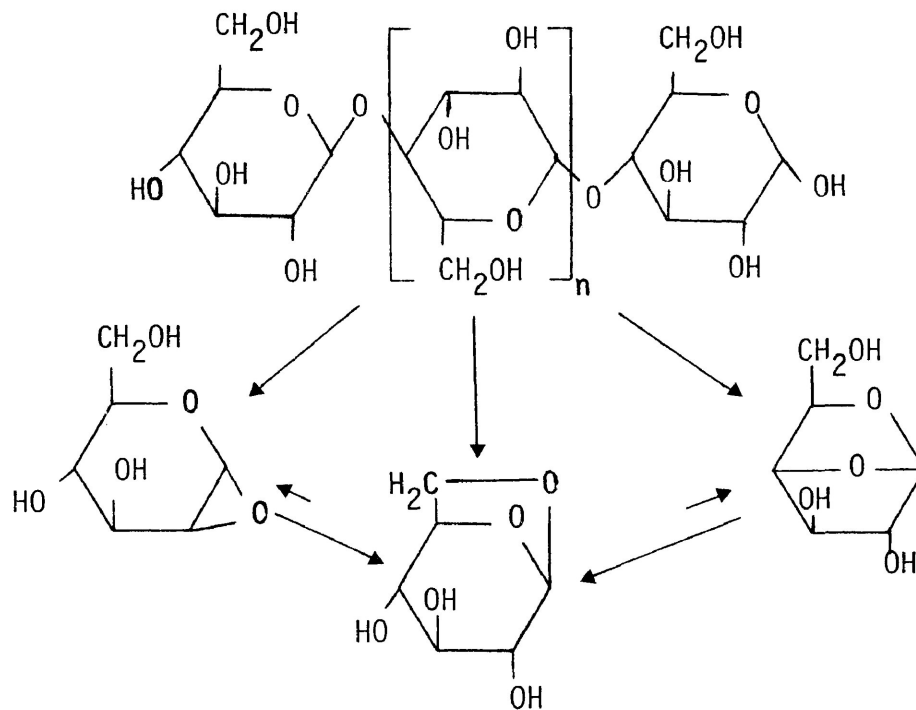
Thus, it appears that the pyrolysis of cellulose involves an
initial stage producing an intermediate "depolymerized"
cellulose (DP 200) which further decomposes in the second
stage.

The kinetics of the second stage in the pyrolysis

of cellulose were examined by considering the equation derived from a phase-boundary controlled model where reaction is controlled by the movement of an interface at constant velocity u through a cylinder of radius r reacting from the edge inwards, equation (22). In agreement with Jayme and Balser (1967), the photomicrographs of cellulose, Figure 22, show that cellulose may be represented as cylindrical particles and this further substantiates the kinetic model. The second stage of cellulose pyrolysis was also examined by a classical kinetic expression based on reaction rate order, equation (24), and while the kinetic parameters obtained were very similar to those obtained using the phase-boundary controlled kinetic model, Table 8, the actual description of pyrolysis as a phase-boundary controlled reaction in cylindrical particles may be preferred since the concept of reaction rate order in the solid state decomposition of a complex organic polymer of unknown molecular weight seems somewhat obscure.

The apparent activation energy determined in this study for the first stage of pyrolysis, approximately 143 $Kj.mol^{-1}$ in nitrogen and air, agrees with the results of previous investigators who have found a change in apparent activation energy for cellulose pyrolysis with extent of decomposition. For example, Murphy (1962) found a value of 142 $Kj.mol^{-1}$ for the first 2.8% weight loss and a value of

165 $Kj.mol^{-1}$ for the remaining material, and Tang and Neill (1964) determined a value of 138 to 147 $Kj.mol^{-1}$ for a zero order process for the first 15% weight loss with a first order process thereafter of activation energy 222 to 234 $Kj.mol^{-1}$. The results of this study are therefore in excellent agreement with those found in the literature. It would appear that the first stage of cellulose pyrolysis occurs regardless of surrounding atmosphere with an apparent activation energy of 143 $Kj.mol^{-1}$, while the second stage occurs with an apparent activation energy of 163 $Kj.mol^{-1}$ in air and 212 $Kj.mol^{-1}$ in the inert atmosphere.

Data from the present study, Table 17, and the results of previous investigations using dynamic TG, Table 2, indicate that results obtained with this technique gave values for apparent activation energies that were consistently higher than those found by isothermal methods. In this respect then, kinetic data obtained by the former method may reflect the fact that a number of basic assumptions are made in order to arrive at kinetic parameters and that the results obtained with dynamic TG should be used only as a relative measure of Ea.

5.5. Additives

Isothermal weight-change determinations were carried out on jack pine bark containing the additives $FeCl_3$ and

$ZnCl_2$ in an inert atmosphere. It was observed that the presence of these additives had little effect upon the pyrolysis of the bark. The kinetic description of pyrolysis was identical to that for native jack pine bark, and as shown in Figure 51, the Arrhenius plot for native bark and bark plus additives seemed to fit a single straight line to give a value for Tc of $5.49.10^3$ K^{-1}.

The effects of a number of additives were observed using dynamic TG and these effects have been summarized in the results section (4.10. and 4.12.). In general, the additives had little effect upon the thermogravimetric analysis of native and extracted jack pine bark. Kinetic analysis showed that some additives significantly reduced the value of Tc, Table 16. A more specific description of the effects of additives has been given in the previous chapter.

5.6. The mechanism of pyrolysis and the compensation effect

The mechanism for the pyrolysis of wood materials is not clearly understood and there are considerable variations in the values obtained for the pre-exponential factor, A, and the temperature coefficient of the reaction rate, Tc.

As pointed out in the results section (4.1.), Tc values have previously been quoted as "activation energies" and so, for comparison, Figure 52 shows the results obtained
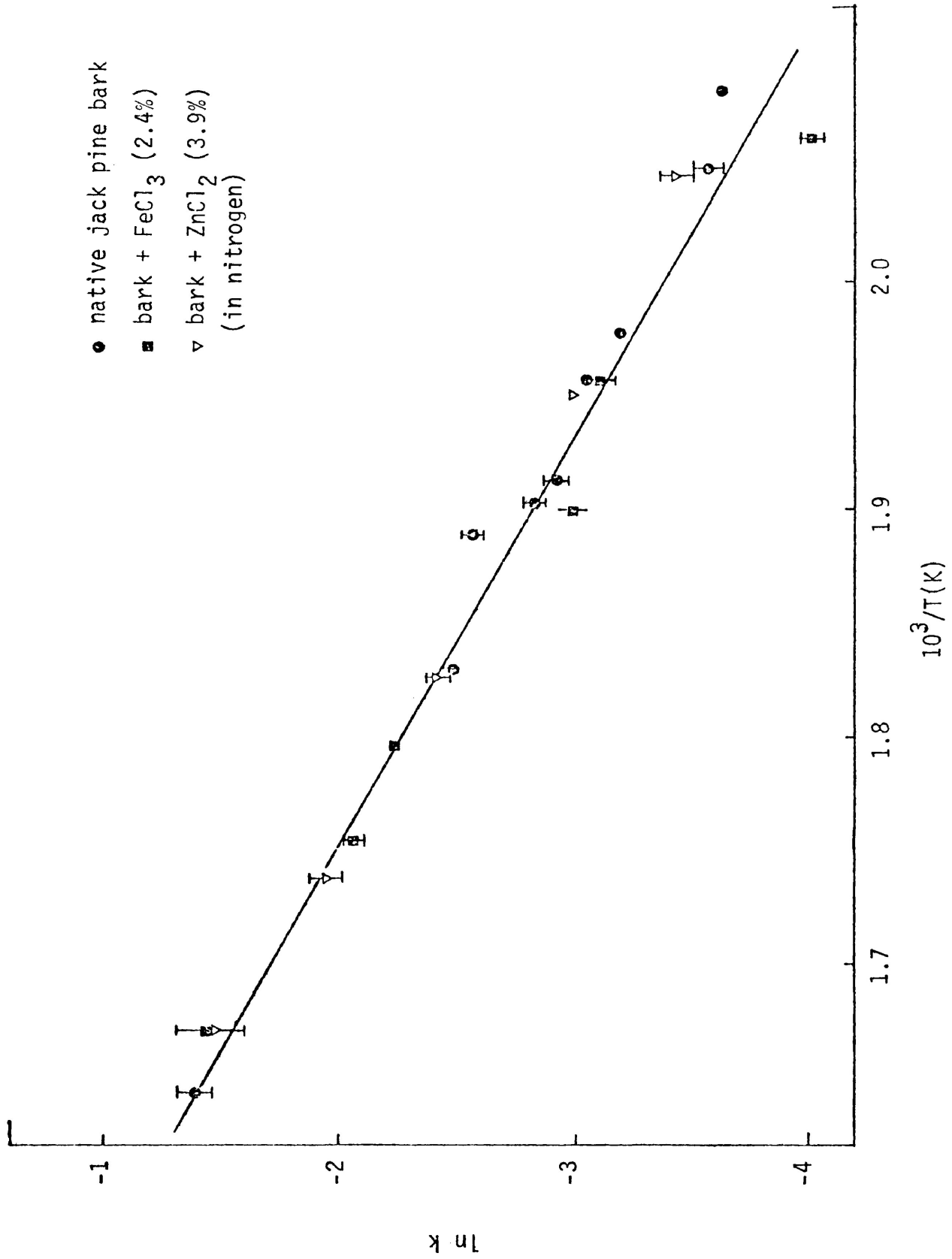
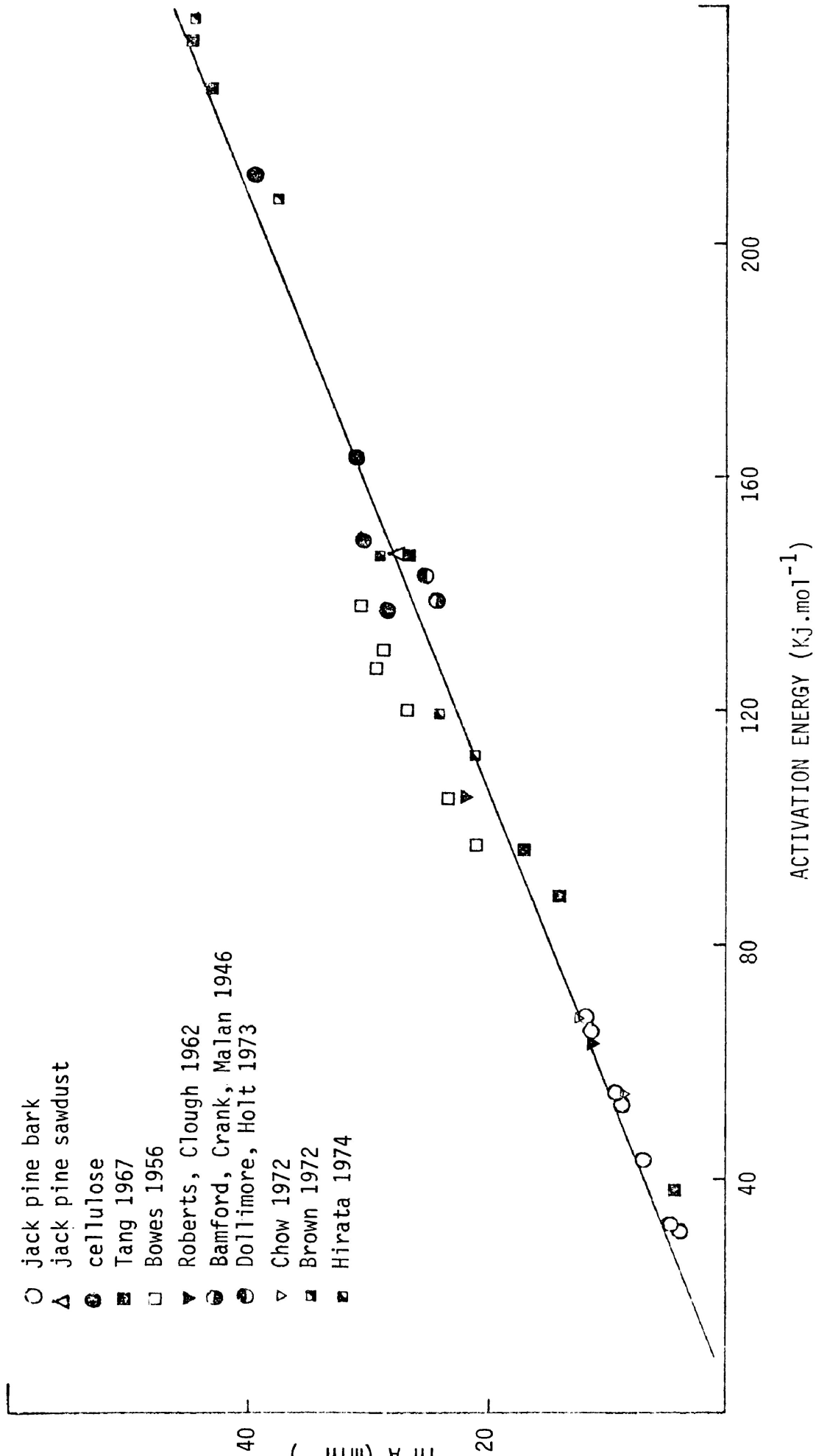Figure 51 Arrhenius plot for the isothermal pyrolysis of jack pine bark.

Figure 52 Reaction rate compensation curve for the pyrolysis of wood materials.

legend:

○ jack pine bark
△ jack pine sawdust
◉ cellulose
◼ Tang 1967
▢ Bowes 1956
▶ Roberts, Clough 1962
◑ Bamford, Crank, Malan 1946
◕ Dollimore, Holt 1973
▽ Chow 1972
◪ Brown 1972
◼ Hirata 1974

ACTIVATION ENERGY ($Kj.mol^{-1}$)

for A and Tc parameters in this and previous work as a plot
of ln A versus Ea, regarded as an "apparent activation
energy". This figure shows that a linear relationship
exists for a large variety of carbonaceous materials. Such
a relationship is commonly known as a reaction rate com-
pensation effect and is normally associated with the
variation of the kinetic parameters of a heterogeneous
reaction occurring on different solids (Cremer 1955; Bond
1956; Feates, Harris, Reuben 1974). The results of Figure
52 can be expressed by the equation:

$$\ln A = 0.2\ Ea - 1.86 \qquad (38)$$

which can be compared to the Arrhenius equation in the form:

$$\ln A = Ea/RT + \ln k_0 \ . \qquad (39)$$

Now a compensation effect may be expected to occur
if different kinds of "active centres" act simultaneously as
reaction sites and if the relative number of these centres
is altered by changes in composition. Thus, the fact that a
compensation effect exists suggests that the thermal de-
composition of wood, bark, and wood constituents is likely to
proceed by the same mechanism, although the process may be
catalysed in some fashion. A catalytic effect has been
suspected previously in the pyrolysis of cellulose (Broido
1966) and may be related to a variation in pH, chemical
composition, or to some physical parameter.

Theoretically, at some characteristic temperature,

Ts, calculated as 601 K, the reaction rates at the various
decomposition sites should be equal and given by k_0. At
approximately this temperature, a number of investigators
have found that a change occurred in kinetic parameters in
the pyrolysis of wood and wood constituents (Akita 1959;
Tang 1967; Kumagai, Ohuchi 1974). It is difficult to assign
a physical significance to the numerical value of T_S (Exner
1972), however, it may be considered as an average isokinetic
temperature for a group of reactions of average rate k_0 at
temperature T_S.

Explanations of the compensation effect generally
concern simple heterogeneous reactions such as the adsorption
of a gas on a solid surface. According to absolute rate
theory, the rate of reaction, k, is given by the following:

$$k = KT/h \; e^{\Delta S^{\ddagger}/R} \; e^{-\Delta H^{\ddagger}/RT} \qquad (40)$$

where K is here the Boltzman distribution constant, h is
Plank's constant, and $\Delta S^{\ddagger}$ and $\Delta H^{\ddagger}$ represent the difference
in entropy and enthalpy between activated complex and reactant
respectively. If one single reaction is considered, $\Delta H^{\ddagger}$
corresponds to the energy of activation, and the pre-
exponential factor is given by $(KT/h) \; e^{\Delta S^{\ddagger}/R}$. As the
energy of the system increases (an increase in enthalpy), a
compensation effect may occur due to the simultaneous increase
in the entropy of the system because of "loosened" bonds with
the surface and other adsorbed molecules (Kwan 1955).

A compensation effect has been observed previously in the oxidation of coal at temperatures < 1073 K (Vulis 1946; Frank-Kamenetskii 1955; Lowry 1963). Reaction was thought to occur both at the carbon surface and in the sample interior with the total rate per unit area of nominal surface given by the expression:

$$R_{total} = R_{surface} + R_{volume} = R_s (1 + R_v/R_s)$$

$$= A_2 \ e^{-E_2/RT} [1 + (S \ D \ P_s/A_2 \ e^{-E_2/RT})^{0.5}] \quad (41)$$

where D is the diffusion coefficient, S the internal surface area per unit volume, P_s the partial pressure of oxygen, and E_2 the energy required for decomposition of a surface oxide layer. A variation in the ratio R_v/R_s would give rise to a range of apparent activation energies and therefore a linear plot of ln A versus Ea.

Cremer (1955) noted a number of possible causes for a compensation effect, including the effect of different active centres mentioned previously. It was also noted that an apparent compensation effect may occur, for example, in the Arrhenius equation:

$$ln \ A = (Ea + \varepsilon) / RT - ln \ k \quad (42)$$

where ε is the magnitude of the error in evaluating Ea. There will also be a corresponding error in the value of ln A. Errors may also occur in the calculation of rate constants, especially when a heterogeneous reaction undergoes a change

in reaction order as was indicated in studies of the pyrolysis of wood by Brown (1972). Diffusion processes which change the effective surface area and the activation energy with temperature may also cause a compensation effect.

Feates, Harris, and Reuben (1974) observed a compensation effect in the catalytic oxidation of carbons. To explain the effect, two reactions were considered--a catalysed reaction (c) and an uncatalysed reaction (u)--both occurring simultaneously and independently. The total rate was thought to be given by the expression:

$$k = s \; A_c \; e^{-E_c/RT} + (\; 1 \; - \; s \;) \; A_u \; e^{-E_u/RT} \qquad (43)$$

where s corresponds to the fraction of the reaction rate due to the catalysed reaction. Values of s were considered to be very small and derived Arrhenius plots showed appreciable curvature at temperatures close to T_s. Two extreme cases were considered--$E_u > E_c$ and $E_u < E_c$. The observed value for apparent activation energy for such a system corresponded to that of the uncatalysed reaction when the temperature range was $> T_s$ for the case $E_u > E_c$, and when the temperature range was $< T_s$ for the case $E_u < E_c$. Theoretical plots were generated and the model compared favourably with experimental results. Catalysts were thought to act by creating channels or pits in the carbon surface from which uncatalysed reaction may be initiated.

Generally then, the compensation effect occurs as a

result of the presence of at least two types of reactions which compete for the original reactants. The reactions involved may be simultaneous or consecutive chemical re- actions in the bulk or at the surface, catalysed or un- catalysed. There may be a number of reasons for the presence of a compensation effect in the pyrolysis of wood and wood constituents. The heterogeneous nature of the starting material suggests that there are probably a number of individual chemical reaction paths with at least one path for each of the three main constituents of wood--cellulose, lignin, and the hemicelluloses. The fact that kinetic data obtained for some wood constituents in the present study and in previous investigations, Tables 1 and 2, fit a single line in the compensation plot, Figure 52, adds credence to the suggestions of previous investigators (Akita 1959; Tinney 1965) that the reaction rate for the thermal decomposition of wood products should be expressed as a sum of the rates for the wood constituents, equation (6). Such a postulate would be expected to produce a compensation effect and the apparent activation energy would reflect the relative amounts of the various constituents in the wood sample.

This simple explanation, however, would be compli- cated if synergism took place. For example, if the decom- position of one constituent at low temperatures into reactive intermediates served to catalyse the decomposition of the

other constituents. The effects of diffusion and secondary reactions might also serve to produce a compensation effect in the pyrolysis of wood materials and the effects of the various experimental techniques used in the evaluation of kinetic parameters might also give rise to a compensation effect. For example, it has been shown in the present study that dynamic TG and isothermal weight-change techniques gave different values for the apparent activation energy but all data fit a single line in the compensation plot.

The excellent fit of pyrolysis data from various sources in the compensation plot helps to clarify some of the confusion that has been created by the great variety of seemingly unrelated values of kinetic parameters in wood pyrolysis studies and although pyrolysis data for wood materials exhibit a compensation effect, this feature alone does not explain the mechanism of pyrolysis. However, it could prove to be a useful guide in future work.

6. CONCLUSIONS

The pyrolysis of jack pine bark and sawdust has been observed to obey kinetic relationships which are similar to established kinetic expressions for diffusion-controlled reactions, however, particle-size distribution effects may have influenced these findings. The apparent activation energy for bark ranged from 31 to 65 $Kj.mol^{-1}$, while that for sawdust was 147 $Kj.mol^{-1}$. For cellulose, this value was 147 $Kj.mol^{-1}$ in the first stage, and 163 (air) or 212 (nitrogen) $Kj.mol^{-1}$ in the second.

It was observed that the presence of additives had little effect on the low-temperature pyrolysis of jack pine bark.

The TG studies showed that the major weight loss which occurred with bark and sawdust was probably due to the decomposition of the cellulose constituent and isothermal weight-change determinations on cellulose powder indicated that pyrolysis occurred in two stages after an initial, very rapid weight loss.

The formation of carbon char in the carbonization of wood materials was shown to occur by a general dehydration mechanism.

A reaction rate compensation effect was observed in the pyrolysis of a number of carbonaceous materials indicating that while the multi-step mechanism of decomposition of these

materials was similar, the rate-controlling step for each sample may be altered.

6.1. Suggestions for further work

Studies should be undertaken to identify a possible diffusion mechanism and to compare the temperature co-efficient for activation of diffusion of certain species through a wood matrix. This could be coupled with a qualitative investigation of the pyrolysis of wood and wood constituents by TG.

A closer inspection of the effects of selected additives with respect to impregnation procedure and concentration profile in the wood product would be useful.

Isothermal studies on other wood materials should be undertaken with a closer inspection of the surface area effects. These studies could be extended to higher temperatures, and the effects of different atmospheres and pressure should be studied and linked to gas production and calorific value.

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APPENDIX I

A number of APL computer programs were used in the analysis of data for this thesis and the programs are described in the following pages. The program 'LINEFIT' was used for all linear plots, such as the Arrhenius plots, and a description of similar statistical analysis can be found in "Modern Elementary Statistics" by J. E. Freund.

```apl
      ∇LINEFIT[□]∇
    ∇ X LINEFIT Y;R;MX;MY;SX2;SE2;N
[1]   →(2<N←ρX)/2+ι26
[2]   →0,ρ□←'INSUFFICIENT NUMBER OF POINTS ENTERED. ANALYSIS CANNOT PROCEED.'
[3]   →(N=ρY)/3+ι26
[4]   'YOU HAVE ENTERED ';N;' VALUES OF THE X VARIABLE AND ';ρY;' VALUES OF Y. I QUIT.'
[5]   →υ
[6]   SX2←+/(X-MX←+/X÷N←ρX)*2
[7]   SL←(+/((X-MX)×(Y-MY←+/Y÷N))÷SX2
[8]   INT←MY-SL×MX
[9]   SE2←(+/((Y-(SL×X)+INT)*2)÷N-2
[10]  SA←(SE2÷SX2)*0.5
[11]  SB←(SE2×((÷N)+(MX*2)÷SX2))*0.5
[12]  R←(1-(+/((Y-(SL×X)+INT)*2)÷(+/((Y-MY)*2)))*0.5
[13]  'LINE SLOPE IS : ';SL
[14]  'LINE INTERCEPT IS : ';INT
[15]  'THE CORRELATION COEFFICIENT IS : ';R←P←P×××SL
[16]  'THERE ARE ';N-2;' DEGREES OF FREEDOM.'
[17]  'FIND THE ';'T';'''VALUE FROM A TABLE, AND CONFIDENCE INTERVALS ARE:'
[18]  '+/- T × ';SA;' FOR THE SLOPE, AND'
[19]  '+/- T × ';SB;' FOR THE INTERCEPT.'
[20]  '   X          Y(OBS)          Y(CALC)'
[21]  ⍝((3,N)ρX,Y,((SL×X)+INT))
    ∇
```

```
      ∇DATAINPUT[□]∇
      ∇ DATAINPUT
[1]    'ENTER NO OF PLOTS'
[2]    →(~(N←□)∈ι6)/ ̄1+ι26
[3]    Y1←Y2←Y3←Y4←Y5←Y6←X1←X2←X3←X4←X5←X6←0,ι0+0×I←1
[4]    'ENTER YOUR FIRST SET OF Y VALUES'
[5]    Y1←□
[6]    'ENTER THE CORRESPONDING X VALUES'
[7]    X1←□
[8]    →(N<I←I+1)/0
[9]    'ENTER YOUR SECOND SET OF Y VALUES'
[10]   Y2←□
[11]   'ENTER THE CORRESPONDING X VALUES'
[12]   X2←□
[13]   →(N<I←I+1)/0
[14]   'ENTER YOUR THIRD SET OF Y VALUES'
[15]   Y3←□
[16]   'ENTER THE CORRESPONDING X VALUES'
[17]   X3←□
[18]   →(N<I←I+1)/0
[19]   'ENTER YOUR FOURTH SET OF Y VALUES'
[20]   Y4←□
[21]   'ENTER THE CORRESPONDING X VALUES'
[22]   X4←□
[23]   →(N<I←I+1)/0
[24]   'ENTER YOUR FIFTH SET OF Y VALUES'
[25]   Y5←□
[26]   'ENTER THE CORRESPONDING X VALUES'
[27]   X5←□
[28]   →(N<I←I+1)/0
[29]   'ENTER YOUR SIXTH SET OF Y VALUES'
[30]   Y6←□
[31]   'ENTER THE CORRESPONDING X VALUES'
[32]   X6←□
      ∇
```

```
      ∇MULTIPLOT[□]∇
    ∇ MULTIPLOT;T;A;B;C;D;F;E;M;N;O;P;Q;S;U;X
[1]    DATAINPUT
[2]    T←X1,X2,X3,X4,X5,X6
[3]    A←ρX1+0×B+ρX2+0×C+ρX3+0×D+ρX4+0×E+ρX5+0×F+ρX6
[4]    M←Y1,(BρO),(CρO),(DρO),(EρO),FρO
[5]    N←(AρO),Y2,(CρO),(DρO),(EρO),FρO
[6]    O←(AρO),(BρO),Y3,(DρO),(EρO),FρO
[7]    P←(AρO),(BρO),(CρO),Y4,(EρO),FρO
[8]    Q←(AρO),(BρO),(CρO),(DρO),Y5,FρU
[9]    S←(AρO),(BρO),(CρO),(DρO),(FρO),Y6
[10]   'CHOOSE PLOTTING FUNCTION(PLOTFORMAT/FINEPLOT) AND COPY ,TYPE 0 AFTER COPYING'
[11]   X←□
[12]   'X AND Y SPACING'
[13]   U←□
[14]   'ROLL TO NEW SHEET AND PRESS RETURN FOR GRAPH '
[15]   'FIRST SWITCH BALLS IF REQUIRED'
[16]   □
[17]   U PLOT M AND N AND O AND P AND Q AND S VS T
[18]   □
[19]   'DO YOU WANT TO RE-PLOT THE GRAPH USING DIFFERENT Y AND X SPACING? (TYPE YES OR NO)'
[20]   →('N'∈□)/2+I26
[21]   →¯9+I26
[22]   ε')ERASE PLOTGP'
[23]   'DO YOU WANT TO RE-PLOT YOUR GRAPH USING THE OTHER PLOTTING FUNCTION? (TYPE YES OR NO)'
[24]   →('N'∈□)/3+I26
[25]   'COPY IN THE NEW PLOTTING FUNCTION JUST AS YOU DID THE FIRST. (SEE ABOVE INSTRUCTIONS)'
[26]   →¯16+I26
[27]   '***********************PROGAM ENDS ***********************************'
    ∇
```

```
        ∇DRVPLOT[□]∇
     ∇ DRVPLOT;N;I;XA2
[1]    3 1 ρ' ';'ENTER THE NUMBER OF DATA PAIRS'
[2]    N←□
[3]    XAVG←YAVG←XA←YA←M1←ιυ+0×I←1
[4]    3 1 ρ' ';'ENTER YOUR X VALUES'
[5]    XA←XA,□
[6]    →(N>ρXA)/‾1+ι26
[7]    3 1 ρ' ';'ENTER YOUR Y VALUES'
[8]    YA←YA,□
[9]    →(N>ρYA)/‾1+ι26
[10]   M1←M1,(YA[I+1]-YA[I])÷XA2←(XA[I+1]-XA[I])
[11]   XAVG←XAVG,XA[I]+XA2÷2
[12]   YAVG←YAVG,YA[I]+YA2←(YA[I+1]-YA[I])÷2
[13]   →(N=I←I+1)/2+ι26
[14]   →‾4+ι26
[15]   3 1 ρ' ';'YOUR SLOPE VALUES ARE'
[16]   3 1 ρ' ';M1
[17]   3 1 ρ' ';'NOW PLOT YA VS XA  AND  M1 VS XAVG'
[18]   MULTIPLOT
     ∇
```

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```
[1]    VPCALCULTIS
[1]    RESULT;LEPV;DESCR
[2]    'ENTER THE VALUE FOR, VD (IN MLS.), FOR THE TUBE USED.'
[3]    VD+[]
[4]    'ENTER THE VALUE FOR, VC (IN MLS.), FOR THE TUBE USED.'
[5]    VC+[]
[6]    'ENTER THE NAME OF YOUR SAMPLE, MAKING SURE THAT IT IS ENCLOSED IN SINGLE QUOTATION MARKS.'
[7]    NAME+[]
[8]    'ENTER THE WEIGHT (IN GRAMS) OF THE SAMPLE USED.'
[9]    W+[]
[10]   'WHAT IS THE INTERNAL DIAMETER OF THE TUBE USED (IN MM.). IF YOU DO NOT KNOW ENTER THE NUMBER HERE.'
[11]   ID+[]
[12]   +(ID=0)/FND
[13]   VI+7.37
[14]   VA+13.6
[15]   C1:'HOW MANY POINTS HAVE YOU OBTAINED FOR THE B.E.T. PLOT.'
[16]   N1+[]
[17]   'ENTER YOUR TRUE PRESSURE READINGS (IN TORR) AS A VECTOR, FOR EXAMPLE:-'
[18]   'PRESSURE FOR CHARGE 1,PRESSURE FOR MEASURE 1,PRESSURE FOR CHARGE 2, PRESSURE FOR MEASURE 2,ETC. FOR ALL CHARGES'
[19]   CP+[]
[20]   C2:(PCALC)=(C=PITR)+2)/C2
[21]   'YOU HAVE ENTERED THE WRONG NUMBER OF PRESSURE READINGS FOR THE NUMBER OF POINTS YOU ARE PLOTTING.'
[22]   'RE-ENTER THE NUMBER OF POINTS YOU WISH TO PLOT AND THE CORRECT NUMBER OF PRESSURE READINGS.'
[23]   +C1
[24]   C3:I+I2+I3+I4+I5+I6+I7+I8+2
...
```

(remainder of listing illegible)

APPENDIX II

In order to compare the experimentally-determined reduced time plots
with standard kinetic plots (Sharp, Brindley, Achar 1966) the data were
plotted by the APL program 'MULTIPLOT' on the same axes. Since the
equations for known kinetic expressions as given by Sharp, Brindley, and
Achar (1966) were stored in the computer, this method allowed for a very
rapid and accurate means of comparison. To illustrate the similarity
of the equations representing diffusion-controlled reactions with the
experimentally-determined reduced time curve for bark pyrolysis, equation
(34), the reduced time plots for these expressions are reproduced below:

$t/t_{0.5}$