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Title: Studies On Thermal Degradation of Douglas-fir
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Christopher J. Biermann

A study was conducted to investigate the production of char, high density carbon pellets (HDCP), and oxalic acid from Douglas-fir wood and bark. The first phase dealt with batch studies to produce and characterize the char and HDCP. The second phase involved production of oxalic acid and improving the yields of char. Cost studies were also made on the production of HDCP and oxalic acid.

Pyrolysis of wood and bark was carried out in a laboratory aluminum reactor at reaction temperature 200, 250, 300, 350, 400, 450, 500, 550, and 575°C for 5, 10, 15, 20, 25, 30, and 35 minutes. Data presented in this

research work show the properties of the char produced under these conditions. Results of atomic absorption spectroscopy, scanning electron spectroscopy (SEM), carbon, hydrogen, and nitrogen elemental analyses, and other analytical methods were used to determine the influence of process conditions on char properties.

Pyrolysis studies, in general, indicated lower char yield with increasing reactor temperature. However, the percentage of carbon in the char increased with increasing reactor temperature. The char produced from bark was densified. The densified char pellets produced in this work have 90% fixed-carbon, an average density of 1.3 g/cc, and 1.18% ash content.

SEM studies indicated fractured structures in the wood bark charred at 575°C. fractured structures were also noticed in the wood charred at 575°C.

Studies on catalytic oxidation of bark indicated that a maximum of 38% (wt) oxalic acid could be obtained by reacting bark with 62.5% (vol) HNO_3 and 0.5 mg V_2O_5/g of bark for 8 h at 80°C.

Cost studies and economic analysis made on an 180 metric tons/day processing plant indicated that the process is viable.

Studies On Thermal Degradation
of Douglas-fir Wood and Bark

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TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

STUDIES ON THERMAL DEGRADATION
OF DOUGLAS-FIR WOOD AND BARK

INTRODUCTION

General Background

The production of char, pyrolytic liquids, oils,
tars, and gases from lignocellulosic materials (wood
material), has been reported in the literature for more
than a century [1-4]. The dwindling supply and
increasing cost of petroleum products in recent years
has created renewed interest in the pyrolysis of
lignocellulosic materials. This interest has been
especially focussed on the production of quality char;
the utilization of pyrolytic liquor and gases to provide
heat energy for the pyrolitic reactor; and the use of
pyrolytic techniques to produce petroleum substitutes
[5-7].

Throughout this study, pyrolysis has been defined
as a destructive distillation or incomplete thermal
fragmentation of bark, wood, or wood wastes (commonly
referred as wood material), resulting in three major
constituents. These three constituents are char,
pyrolytic liquids including oils and tars, and gases.
These three constituents occur in varying proportions
and appear to be related to the characteristics of

initial wood material, the type of pyrolytic reactor used and the operating parameters.

Literature Review

An extensive body of the literature exists pertaining to pyrolysis of bark, wood, and wood wastes [8-13]. Thermal degradation of various species of wood has been investigated by many researchers [14-20]. The secondary reactions in the pyrolysis of wood have been studied by Goos [21] and Roberts et al. [22]. Stamm [23] and Soltes [24] studied slow pyrolysis of wood below 600°C. They found that for macroscopic pieces of wood, the rate of heating was controlled by heat transfer throughout the wood material.

Gillet and Urlings [25] in their studies on pyrolysis found that the pyrolysis products of wood, cellulose, and lignin were the same above 450°C. Amy [26] reported that four classes of products (namely charcoal, tar, pyroligneous products, and condensable gases) could be produced from wood pyrolysis. Seborg et al. [27] found that the maximum shrinkage would occur at 45% weight loss. They reported decreases in cell cavity volume for wood subjected to pyrolysis.

Browne [28] presented a comprehensive literature review on pyrolysis and combustion of chemically treated and untreated woods. Wright and Hayward [29] studied pyrolysis of wood at temperatures up to 900°C. Mitchell et al. [30] studied the effect of heating Douglas-fir isothermally in a closed, pressurized system and compared the results with those obtained in an open system with a static and a dynamic air or a nitrogen atmosphere. The study indicated that the weight loss was larger in the case of the closed system.

Purpose of this Research

It was the purpose of this research to fixup parameters responsible to improve the quality of charcoal produced from Douglas-fir wood and bark and to further develop techniques for practical applications. Unlike the various studies reported earlier by several researchers, this study investigated the production of pure char (charcoal with having high fixed carbon content) separately from sap and heart woods, so that it could be used for the production of adsorbents and reductants.

The use of pure charcoal has been well recognized for many centuries and have attracted considerable

attention during the past decade. Charcoal has been used in industry for many years. Recently, concern has been focused on the possibility of using pure charcoal for production of adsorbents, reductants, activated carbon fibers, and shaped activated carbon. In this study experiments were conducted to find the effect of moisture content, temperature, time, shrinkage and chemical composition of Douglas-fir wood and bark charcoal.

Charcoal Production

Charcoal can be produced in various grades to suit the ultimate use by controlling the properties. In this study a batch type aluminum reactor was used to produce the charcoal from Douglas-fir wood and bark. The reactor was heated electrically without the contact of air.

Atomic absorption spectroscopy (AAS), carbon, hydrogen, and nitrogen (CHN) elemental analyses, and other methods appear to be promising as means of determining charcoal quality and controlling the process parameters. Scanning electron microscopy (SEM) techniques provide valuable information on the

structural changes at the microscopic level.

SEM Studies

In this study SEM analysis has been employed to find the physical changes in the Douglas-fir wood and bark subjected to temperatures at 400°C and 575°C. SEM studies on chemically treated Douglas-fir wood were also carried out to study the effects of secondary char formation. SEM micrographs of Douglas-fir wood charred at 400°C and 575°C and fractures detected are presented in this study. Changes in charred inorganic chemicals treated were identified. The formations of warty like layers, folds and spherical particles in charred wood indicate that much further work is needed before their significance can be fully established or to make any conclusions in respect of the reactions that are responsible for their formation.

Oxalic Acid and HDCP Production

The production of oxalic acid by the catalytic oxidation of Douglas-fir bark and subsequent pyrolysis of the residue to produce high density carbon pellets are discussed. Kinetic rate data presented for oxalic acid production from Douglas-fir bark. A maximum yield

of 38 wt% oxalic acid has been obtained in 8 h at 80°C
with 62.5 vol% HNO_3 and 0.5 mg V_2O_5/g of bark.
Additional oxalic acid can be produced by the conversion
of pyrolytic oils and tars (obtained during
carbonization of the residue) to increase the total
yield to 45 wt%.

An economic analysis based on the current cost of
oxalic acid indicates the viability of the proposed
process.

Recent research indicated that high adsorptive
power adsorbents could be produced from pure charcoal
obtained from Douglas-fir wood, wood wastes, and bark.
Once the characteristics of charcoal are established,
economic means of producing pure charcoal from wood,
wood wastes, and wood bark may be realized, since the
steam activation is inexpensive compared to many other
processes used in the production of adsorbents.

PRODUCTION AND CHARACTERIZATION
OF DOUGLAS-FIR WOOD CHARCOAL

INTRODUCTION

Pyrolysis may be defined as a process of incomplete fragmentation of the components of wood material resulting in more stable end products in the form of condensable gases (pyrolytic liquids), non-condensable gases and char. The end products are hydrocarbons. These hydrocarbons become unstable as the pyrolysis temperature increases above 575°C. Above 575°C, all pyrolysis reactions are assumed to be complete.

The mechanism and kinetics of fragmentation are not completely understood [31-33]. The primary pyrolysis products from wood depend on reaction temperature, rate of heating, ash content, particle size, as well as heat and mass transfer during the pyrolysis process.

According to Kung [34], the products of decomposition are strongly influenced by heat transfer from the surroundings to the wood particles, heat transfer inside porous particles, drying, and thermal disintegration. This is a physical approach to

describing the kinetics of wood pyrolysis. Other researchers have described the kinetics based on a chemical approach [35-37].

The process of wood pyrolysis is governed by two process variables, temperature and time. According to Beall [38], combustion and pyrolysis are related phenomenon. If inert or no gases are used during heating process, the phenomenon is called pyrolysis, whereas if oxygen is used, the process is called combustion. In both the cases the heating rate is controlled by heat transfer through the wood material.

By properly controlling the process it should be possible to control the quality of charcoal and its yield. Also by characterizing the charcoal produced, different grades of charcoal could be identified that are suitable for different end applications. The characteristics of charcoal are affected by the quality of the wood selected for pyrolysis, the type of equipment used for pyrolysis, and the operating parameters.

METHODS AND MATERIALS

Experimental Set Up

Pyrolysis runs performed in this study were
carried out with a bench scale aluminum reactor. The
reactor measured 9.5 cm dia and 24.5 cm long. The lid
was provided with two openings, one for inserting the
condenser tubing and the other for inserting digital
pyrometer. The lid was provided with gaskets to make
the reactor air tight when closed. A water cooled
metallic condenser was used to condense the gases coming
out of the reactor when Douglas-fir wood was charred.
The condensate was collected in glass flasks. The
reactor was heated externally by electrical means.

Douglas-fir Wood as Raw material

In this study Douglas-fir wood was the chemical
raw material. Cross sections of normal and compression
woods were removed by sawing a single Douglas-fir tree
at breast height. Cross sections were machined from the
freshly cut green wood by separating sap and heart
woods. In all more than 600 specimens (1.0x1.0x2.5 cm)
were sawed. Fifty specimen pieces of wood were allowed
to air dry to contain moisture contents of 10.2 wt%,

20.3 wt%, 31.5 wt%, and 42.2 wt%. The rest of the specimen pieces of wood was oven-dried at 65°C, then stored in air tight polyethylene bags. Two pieces of each of the different moisture content specimens were kept as control. Test specimens were all designed to fit the pyrolysis reactor. The physical and chemical properties of raw material influence the properties of the charcoal produced.

Production of Charcoal

Oven-dry Douglas-fir wood samples measuring 1.0x1.0x2.5 cm were placed in the reactor and pyrolysis experiments were carried out. Similar reaction conditions used were as follows: temperature - 200, 250, 300, 350, 400, 450, 500, 550, and 575°C; time - 5, 10, 15, 20, 25, 30, 35, and 65 minutes. All combinations of temperatures, times, and moisture contents of wood were used in this study resulting in 55 different combinations of conditions and samples.

At the start of each run, when the conditions were set, the lid of the reactor was closed and made air tight and the condenser tube was connected. At the end of particular time period, the reactor was cooled and the sample was allowed to cool to ambient temperature.

Ten pieces of each of the oven-dry Douglas-fir sapwood
and heartwood were carbonized in each of the
experiments. The pyrolysis temperatures, heating rate,
the rate of condensable and non-condensable gases
evolved were all recorded.

Separate experiments were carried out with
sapwood and heartwood samples of various initial
moisture contents. Similar experiments were conducted
with lignin (Klason lignin) and cellulose (Douglas-fir
Kraft sulfite cellulose).

Other Procedures

pH of Charcoal

A char sample was boiled in reagent water for
about 30 minutes. The particles of char filtered out,
the filtrate cooled to ambient temperature and the pH of
the filtrate determined by pH meter (elctrometic
measurement) [39-44].

Equilibrium Moisture content

The equilibrium moisture content was determined
by subjecting samples of Douglas-fir wood, and wood
charcoal to a range of humidity conditions at a constant

temperature of 25ºC [39-44].

Analytical Methods

Analysis of Wood and Charcoal

Proximate and ultimate analyses were determined by American Society of Testing Materials methods [39-44]. If ASTM methods for charcoal were not available, appropriate methods for coal were adopted. If ASTM methods for wood were not available, appropriate TAPPI methods were adopted. Gas yields were determined by difference.

Analysis of Ash

Representative samples of oven-dry wood charcoal were ground to <250 micrometer. Crucibles containing 1 g of sample were placed in a cold muffle furnace and heated gradually so that the temperature reached 500ºC in 1 h and 750ºC in 2 h. The sample was ignited at 750ºC, cooled, and ground in a mortar to <75 micrometer. It was then reheated to 750ºC for 1 h, ignited, and cooled in a desiccator. The procedure was repeated until a constant weight of ash was obtained. The resulting ash was analyzed by AAS following the proper ASTM methods [39-44] to determine the metals content.

The same procedure was followed for 2 g ground wood, particle size <425 micrometer.

RESULTS AND DISCUSSION

Moisture Content

The free moisture content of Douglas-fir wood influences all three phases of pyrolysis products. An increase in moisture content decreases the yield of solid and gaseous phase products and increases the liquid phase products. It also increases the pyrolysis time. Table 2.1 gives the relationship between pyrolysis time and the amount of wood carbonized, with various initial moisture contents. The run time was longer for higher initial moisture content wood than those for lower initial moisture content wood.

As shown in Table 2.1, the yield of charcoal increases as the initial moisture content of Douglas-fir wood decreases. About 6.6% increase in charcoal yield was obtained when the initial moisture content of Douglas-fir was decreased from 42.2 wt% to 20.3 wt%.

TABLE 2.1   Material Balance in Carbonization Reactor
for Douglas-fir Wood as Raw material.

Wood Moisture Content (%)	o.d	10.2	20.3	31.5	42.2
Wood* in the Reactor (g)	11.2	12.34	13.61	15.28	18.93
Charcoal** Produced (g)	3.95	3.87	3.71	3.55	3.51
Yield of Charcoal (%)	35.27	34.93	34.19	33.43	32.08
Yield of Condensable Gases (%)	43.21	44.22	45.71	47.08	49.09
Yield of Non-Condensable Gases (%)	21.52	20.85	20.10	19.49	18.83

*Normal wood
**Produced at temperature: 575°C, and time: 65 min.

Proximate Analyses

Proximate analyses characterize wood charcoal in terms of moisture content, volatile matter, ash, and fixed carbon. The bound water represents the moisture content of wood while the water molecules that are formed during pyrolysis are classified with volatile matter. The ash content of Douglas-fir wood is very low compared to coal. The fixed carbon content of coal is much lower compared to the fixed carbon content of Douglas- fir wood charcoal.

Table 2.2 gives the proximate analyses of Douglas-fir wood, wood charcoal and coal. It has been found that the ratio of ash in sapwood and heartwood is of the order of 1:5. According to Bamper [45] the ratio of ash in heartwood and sapwood decreases less as the tree grows older. Therefore, it does not matter much as to which part of the wood is subjected to pyrolysis when the wood for pyrolysis is selected from older trees.

The basic inter- relationship between pyrolysis time, yield, fixed carbon, and temperatures on Douglas-fir wood charcoal properties are given in Fig. 2.1 and 2.2. The yield of charcoal, and charcoal densities decrease with increasing temperature while the

TABLE 2.2 Comparison of Proximate Analysis Results of
Douglas-fir Wood, Wood Charcoal and Coal.

Sample	Fixed Carbon	Volatile Matter	Ash
WOOD			
Normal Sapwood	14.32	85.65	0.03
Normal Heartwood	14.18	85.66	0.16
Reaction Sapwood	13.14	86.74	0.12
Reaction Heartwood	13.19	86.20	0.61
CHARCOAL[**] (575°C)			
Normal Sapwood	91.94	7.59	0.17
Normal Heartwood	92.80	6.58	0.62
Reaction Sapwood	93.41	6.18	0.41
Reaction Heartwood	93.16	5.89	0.95
COAL[*]			
Pittsburgh	55.80	33.90	10.30
Wyoming Elkol	51.40	44.40	4.20
Lignite	46.60	43.00	10.40

[*]Reference [89]

[**]Charcoal produced from oven-dry Douglas-fir wood at
pyrolysis temperature 575°C, and pyrolysis time - 65
min.
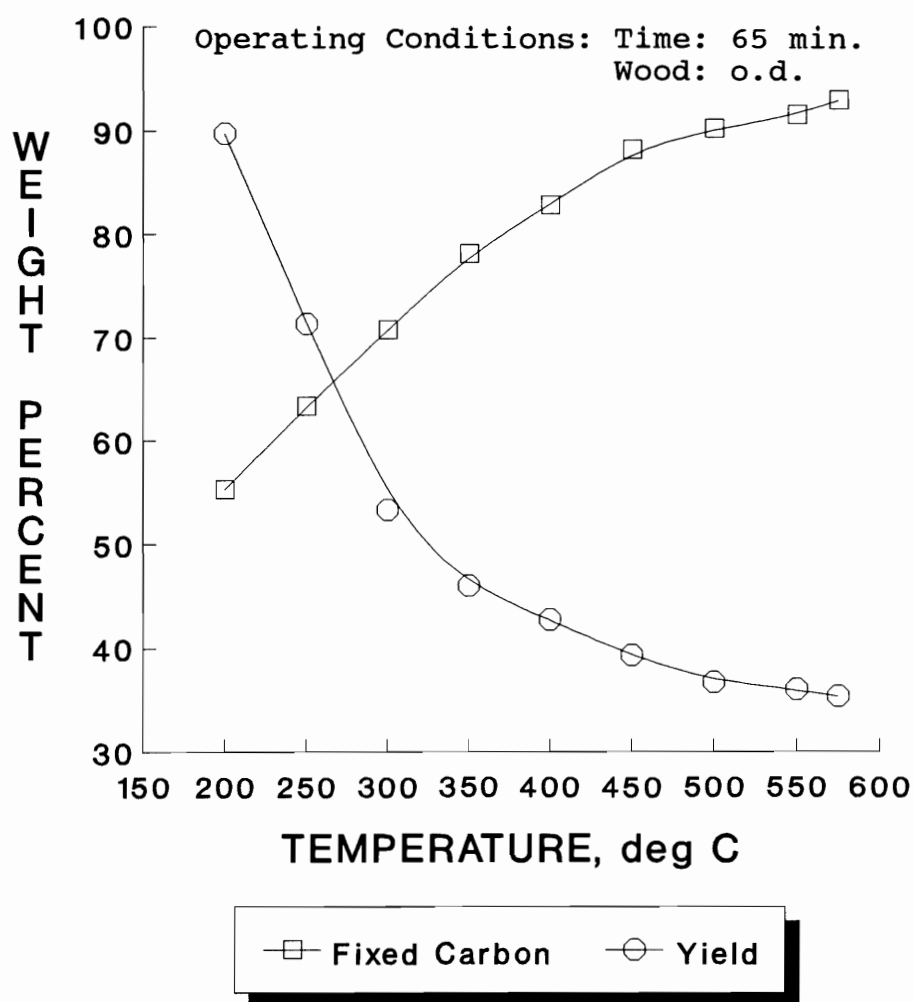
Figure 2.1   Relation between Carbonization Temperature
            with Yield and Fixed Carbon.

Operating Conditions: Temperature: 575°C
Time: 65 min.
Wood: o.d.
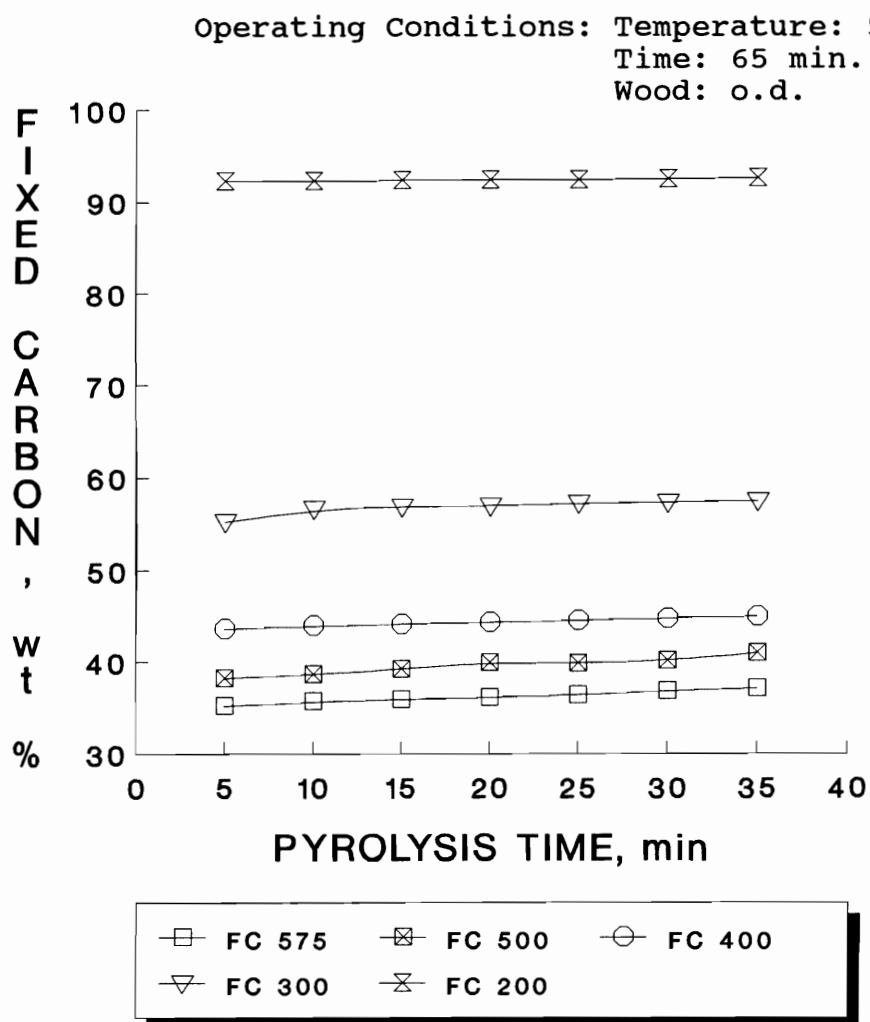
Figure 2.2   Relation between Carbonization
Time and Fixed Carbon.

fixed carbon content, condensable gases, and non-condensable gases increase with increasing temperature.

Metals

The metal contents of ash are of critical importance when the charcoal is intended for use in metallurgical processes as a reducing agent. The amounts of metals present in Douglas-fir wood and charcoal are given in Table 2.3.

Douglas-fir wood and charcoal have high Ca and Si contents. Cobalt, Ni and Cr metals present in wood and wood charcoal are almost negligible. The results indicate lower values of Ca and Fe metal impurities present in wood charcoal than those specified by ferro silicon manufacturers [46]. Therefore, the charcoal should be suitable for metallurgical grade.

Ultimate Analyses

The ultimate analyses report the percentage of carbon, hydrogen, nitrogen, and oxygen. As wood contains moisture, it is desirable to express the ultimate analysis on a dry basis, so that the hydrogen content determined truly represents the fuel

TABLE 2.3   Metal Contents of Douglas-fir
            Wood and Charcoal.

Metals		NSW	NHW	RSW	RHW	NSC	NHC	RSC	RHC
Ca	ppm	315	369	304	329	328	354	301	336
Si	ppm	108	106	110	109	113	112	105	114
K	ppm	201	90	180	85	197	98	187	92
Mg	ppm	38	44	33	41	35	42	35	40
Na	ppm	38	41	34	36	39	43	37	39
Mn	ppm	18	19	15	17	14	20	16	17
Fe	ppm	13	22	7	11	18	21	9	14
Co	ppm	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Ni	ppm	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02
Cr	ppm	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02

Abbreviations:

NSW - Normal Sapwood, NHW - Normal Heartwood,
RSW - Normal Reaction Wood, RHW - Reaction Heartwood,
NSC - Normal Sapwood Charcoal, NHC - Normal Heartwood
Charcoal, RSC - Reaction Sapwood Charcoal, and
RHC - Reaction Heartwood Charcoal.

Note: Charcoal produced from oven-dry wood at
temperature: 575°C, and time: 65 min.

constituents of wood and wood charcoal.

The carbon, hydrogen, and nitrogen (CHN) elemental analyses results obtained are given in Table 2.4. Wood has a lower carbon content than coal, while charcoal has a higher carbon content than coal.

The carbon to hydrogen ratio is higher for charcoal than coal or wood. For most charcoal applications, the ultimate analysis of charcoal is considered as constant when the pyrolysis time and temperature are specified and are the same.

Calorific Value

The experimental calorific values of Douglas-fir wood are reported by Reed [47] as 21.050 MJ/kg while the calculated ones are 21.024 MJ/kg. The calorific value was calculated from the ultimate analysis results by using the formula

$$HHV = (328C + 1430H) 23.73N + 92.9S))$$
$$[(100 - a)/100] * [(40,109H/C + 346.6)]$$

Where HHV = Higher heating value, MJ/kg on dry basis

C = Wt% Carbon on dry basis

H = Wt% Hydrogen on dry basis

N = Wt% Nitrogen on dry basis

TABLE 2.4 Ultimate Analysis Data for Douglas-fir
          Wood, Charcoal and Coal.

Material	C	H	N	O	A	S
Douglas-fir Wood	53.08	7.5	0.2	39.06	0.16	n.d
Charcoal	93.20	4.7	0.4	1.08	0.62	n.d
COAL* Pittsburgh	75.5	5.0	1.2	4.90	10.30	3.1
Wyoming Elkol	71.5	5.3	1.2	16.90	4.20	0.9
Lignite	64.0	4.2	0.9	19.2	10.40	1.3

*Reference [89]

A = Ash

S = Wt% Sulfur on dry basis

A = Wt% Ash on dry basis

This formula, when applied to ultimate analysis of Douglas-fir wood charcoal gives a value 34.9 MJ/kg. The calorific value obtained (see Table 2.5) shows Douglas-fir wood charcoal has a higher calorific value compared to coal. It has to be noted that the calorific value is termed higher heating value (HHV) because the water of combustion is present in the liquid state at the completion of the experiment.

Comparison with Cellulose and Lignin

Figure 2.3 gives the comparison of percentage burn off dry wood, cellulose, and lignin (under similar pyrolysis conditions) with increased temperature. Cellulose decomposes at reaction temperatures between 300 to 370°C. At this reaction temperature, eight percent of the cellulose was burnt off leaving 12% char. In the case of lignin and wood, the decomposition occurs at reaction temperatures ranging from 280 to 575°C. Sixty-five wt% of wood was lost compared to about 49 wt% in the case of lignin, under similar operating conditions.

TABLE 2.5   Higher Heating Values of Douglas-fir Wood, Douglas-fir Wood Charcoal, and Coal.

Material	Higher Heating Value MJ/kg
Douglas-fir	
Wood*	21.024
Charcoal*	34.926
Coal**	
Pittsburgh	31.749
Wyoming Elkol	29.563
Lignite	24.916

*calculated higher heating values

**Reference [89]
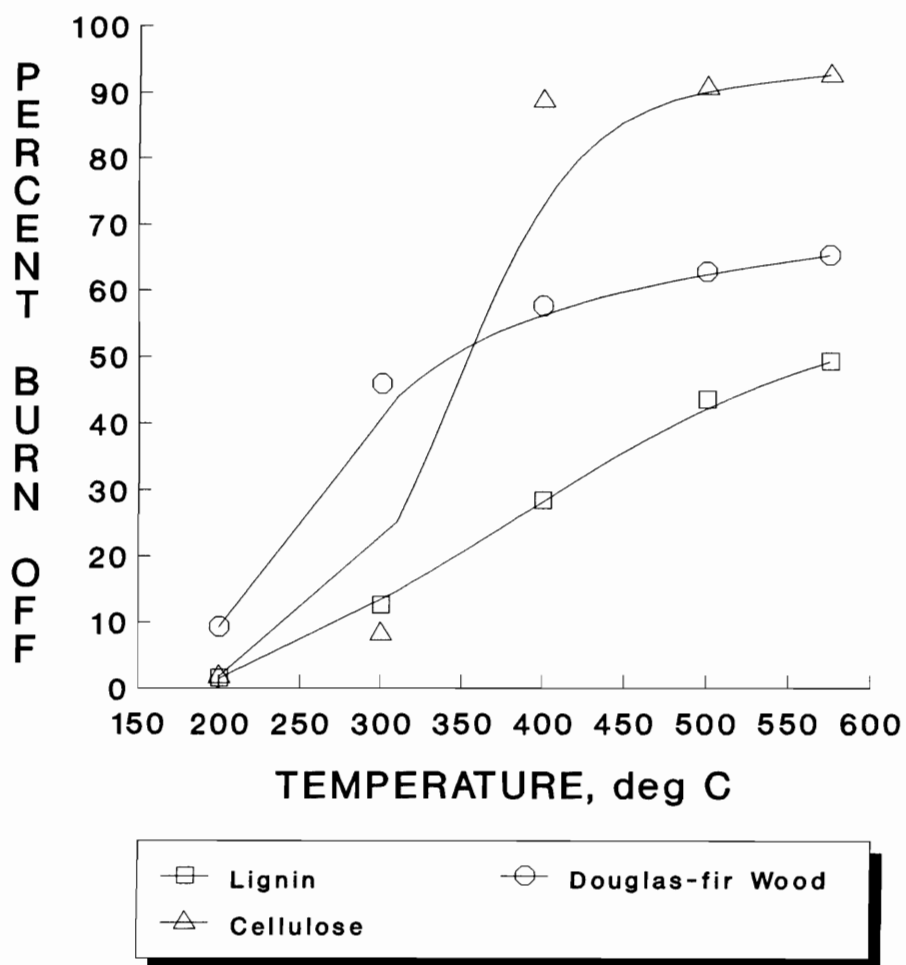
Figure 2.3   Comparison of % Burn Off of Douglas-fir
             Wood, Cellulose, and Lignin (Carbonization
             time 65 min).

Product Yields and pH

At a pyrolysis temperature of 575°C for time 65 min, 35.27 wt% charcoal, 43.21 wt% condensable gases, and 21.52 wt% non-condensable gases were obtained on a dry wood basis. The experimental results are given in Table 2.6. When the fixed carbon is not an important property to be considered for a particular charcoal application, a higher yield of charcoal may be obtained by operating the pyrolysis reactors at a lower temperature than 575°C. The total pyrolysis time will also be reduced.

The pH of the charcoal may be significant parameter in the applications of char where chemical reactions may take place between the char, the volatile matter constituents and the reacting fluid media and therefore is an important characteristic of the char.

The variation of pH with pyrolysis temperature is given in Table 2.7. The charcoal produced at higher temperature was more acidic than that was obtained at lower temperature. This also indicates that charcoal with higher fixed carbon will be more acidic than the charcoal with lower fixed carbon. The pH of charcoal is an important factor when the charcoal is used for the

TABLE 2.6.   Experimental Results of Carbonization
             of Douglas-fir Wood.

Carbonization Temperature	575ºC
Carbonization Time	65 min
Moisture Content	o.d
Charcoal (wt %)	35.27
Liquor (Condensable Gases - wt %)	43.21
Non-Condensable Gases (By difference - wt %)	21.52
Fixed Carbon Content (wt %)	93.80
Ash (wt %)	0.62
Calculated Calorific Value for Charcoal (MJ/kg)	34.93

TABLE 2.7 pH Data for Charcoal and Condensable Gases.

Temperature (°C)	pH	
	Charcoal	Condensable Gases
200	6.41	4.18
250	6.23	3.97
300	6.11	3.86
350	6.02	3.52
400	5.83	3.34
450	5.64	3.25
500	5.35	3.12
550	5.32	2.82
575	5.24	2.31

manufacture of adsorbents. The pH of condensable gases varied from 4.18 to 2.31 at carbonization temperatures 200°C and 575°C respectively. This emphasizes the corrosion effects of these gases when used as an energy source.

Equilibrium Moisture Content

Charcoal removed from the reactor contains no free moisture. Because of its porous structure, it rapidly absorbs water vapors from the atmosphere before it is packed. Charcoal produced at different temperatures absorbs water from the atmosphere at different levels, but the variation is only marginal. Compared to wood, the absorption of water at different relative humidity conditions, the variation was lower at 25°C.

The amount of water absorbed by charcoal was 10.3% at 90%, relative humidity and 7.8% at 30% relative humidity. The variation for wood was from 9.2% to 26.1% at relative humidity 30% and 90%, respectively. The results obtained at different relative humidity conditions are presented in Table 2.8.

Shrinkage

The percentage changes for the tangential, radial,

TABLE 2.8   Equilibrium Moisture Content of Wood and
            Charcoal at 25°C as a Function of Relative
            Humidity.

Relative Humidity	Wood	Charcoal (575°C)
30	9.2	7.8
50	10.7	8.1
65	12.9	8.9
90	26.1	10.3

and longitudinal dimensions for Douglas-fir wood
pyrolyzed at 300°C and 575°C are given in Table 2.9.
The results indicate that the shrinkage in the
longitudinal direction was 40% while the shrinkage in
the radial and tangential directions were 10% and 13%,
respectively. The shrinkage depends on the temperature
at which the wood was pyrolyzed.

CONCLUSIONS

The quality of charcoal produced from Douglas-fir
wood depends upon the initial moisture content of wood,
the operating conditions of the reactor and the humidity
conditions. The yield of charcoal from Douglas-fir wood
depends upon the fixed carbon content. The higher the
fixed carbon contents, the lower the yield of charcoal.

If the initial moisture content of the wood is
higher then additional heat energy has to be supplied to
the reactor to drive off the water molecules. The
condensable and non-condensable gases could be used as
an energy source for the reactor to drive off the water
molecules. The charcoal obtained from the Douglas-fir
wood contained higher fixed carbon and higher calorific
value compared to coal. It also contained low metal
contents compared to coal. This would probably help

TABLE 2.9 Percentage of Shrinkage of Douglas-fir
          Wood Carbonized at 300°C and 575°C.

Temperature (°C)	Direction of Shrinkage		
	Longitudinal	Radial	Tangential
300	14.1	4.3	32.6
575	19.8	26.7	36.9
% Change	40.4	9.88	13.19

replace coal in the metallurgical processes.

The characteristics of the charcoal indicate that it has greater potential, as a raw material, in the activated carbon industry.

THE CHARACTERIZATION OF CHARCOAL AND HIGH-DENSITY CARBON PELLETS PRODUCED FROM DOUGLAS-FIR BARK

INTRODUCTION

Bark from Douglas-fir (pseudotsuga menziesii (Mirb.) Franco) is a major byproduct of the lumber and plywood industries of the Pacific Northwest. The potential annual supply from Washington and Oregon sawmills is estimated at three million tons [48]. Effective ways of using this enormous quantity of bark would not only solve the disposal problem, but would also have economic advantages. The fuel value of bark is only 40,000 kJ/kg compared with 56,500 kJ/kg for coal and 88,000 kJ/kg for petroleum [49]. The low energy content and low density of bark limit its general use for fuel. However, converting bark to charcoal by destructive distillation reduces its volume considerably. Compaction of charcoal to high-density carbon pellets (HDCP) increases its density, making transportation easier and more economical. HDCP could be used to meet future demands for charcoal as reductants in metallurgical processes or as adsorbents in chemical processes. (The calorific value per unit weight of HDCP is greater than that of

bituminous coal [50]).

The production of charcoal by destructive distillation of wood or wood wastes has been practiced for centuries. The simplest method uses a primitive underground or pit kiln and the most advanced involves the use of a rotary kiln where charcoal is produced continuously. Recently, attempts have been made to use the pyroligneous liquor and tar oils generated from the pyrolysis of wood materials as a combustible oil. Although the oil has an energy content of about 23,000 kJ/kg, difficulties are experienced because of the highly oxygenated nature of the oil [51]. Pyrolysis of bark has long been studied [52,53] as a possible method to convert bark into commercially useful organic chemicals, but a better understanding of the physical, mechanical, chemical, and thermal properties of bark components is needed. The principal objective of our work was to examine the nature and characteristics of charcoal produced from pyrolysis of bark and of HDCP produced from the subsequent densification of charcoal.

EXPERIMENTAL METHODS

Production of Charcoal

Douglas-fir bark was dried for 5 h until it reached a constant weight, and then weighed prior to pyrolysis. Twenty grams of oven-dry powdered bark with particle sizes ranging from 0.5 to 2 mm were loaded into an aluminum carbonizer (95 mm dia x 245 mm length). Asbestos packing ensured an airtight seal between the carbonizer and the lid. The open end of the pipe connection from the lid was connected to a water-cooled copper condenser. The carbonizer, which was heated externally by an electric heater provided with a controller, was insulated with asbestos sheets kept in a laboratory hood (for safety reasons). Processing was conducted at 500°C for 65 min on oven-dry bark, except when the effect of temperature, moisture, or time was being studied. Uncondensable gases were allowed to escape from the water-cooled copper condenser, with no attempts made to analyze or to recirculate the gases because data are already available about their chemical composition and uses [54-56]. Cubes of oven-dry wood, approximately 2.5 cm/side were also carbonized and cooled for 1 h before SEM studies.

Production of HDCP

Bark charcoal samples from several carbonization experiments were collected, oven-dried for 2 h, and powdered in a mortar. Different particle size (75-300 m) were collected and stored in airtight polyethylene bags. The pyroligneous liquor that was collected in sample bottles was kept undisturbed for 8 d. The dark brown viscous bottom layer (liquid tar) was separated and used as a binder to produce HDCP. Samples of bark charcoal powder, with particle sizes ranging from 75 to 300 m, were mixed with liquid tar in varying proportions at room temperature cold-pressed into pellets (12 mm diameter x 10 mm height). Pressure and hold-time varied. Pellets were dried at 102°C for 2 h. The average densities of pellets were then determined.

Other Procedures

pH of Charcoal and HDCP

Ten grams of oven-dry charcoal were placed in a flask with 100 mL boiled reagent water and refluxed for 15 min. The particles of carbon were filtered. The filtrate was cooled to 50°C, and its pH was measured.

The procedure was repeated for oven-dry HDCP.

Equilibrium Moisture Content

The equilibrium moisture content was determined by subjecting samples of bark, bark charcoal, and HDCP to a range of humidity conditions at a constant temperature of 25°C.

Impregnation of Douglas-Fir Bark with Inorganic Chemicals

Oven-dry bark samples were treated with the inorganic chemicals NaCl, KCl, $ZnCl_2$, $CaCl_2$, Na_2CO_3, K_2CO_3, $CaCO_3$, NaOH, KOH and $Ca(OH)_2$ (as aqueous solution) and then carbonized as described above to study the effect of secondary char formation.

Analytical Methods

Microstructure of Douglas-fir Bark Charcoal

Series of scanning electron micrographs (SEM) were taken of uncarbonized and carbonized bark. Specimens of oven-dried bark were stored in airtight polyethylene bags from 2 to 10 d. Some samples were stored for over 6 mo. Bark charcoal samples processed at 400 and 575°C, were selected for SEM studies. Specimens carbonized at

575°C were sufficiently conductive and required no special coating or preparation before being placed in the scanning electron microscope (AMR Model 1000A). Because neither bark nor charcoal specimens at 400°C were conductive, they were coated with metal (60% gold and 40% palladium) in a vacuum evaporator. The specimens were cut in an appropriate plane with a sharp blade and mounted on the specimen holder.

Analysis of Bark Charcoal and HDCP

Moisture, volatile matter, ash, fixed carbon content, specific gravity, and porosity were determined by ASTM methods [57-59]. If ASTM methods for charcoal were not available, appropriate methods for coal were adopted. Gas yields were determined by difference. Proximate analyses of HDCP were conducted by ASTM methods [58].

Analyses of Ash

Representative samples of oven-dry charcoal or HDCP were ground to < 250 micrometer. Crucibles containing 1 g of each sample were placed in a cold muffle furnace and heated gradually so that the temperature reached 500°C in 1 h and 750°C in 2 h. Each

sample was ignited at 750°C, cooled and ground in a
mortar to < 74 micrometer. It was then reheated at
750°C for 1 h, ignited and cooled in a desiccator. The
procedure was repeated until a constant weight of ash
was obtained. The resulting ash was analyzed by AAS by
following the proper ASTM method [60] to determine the
Fe, Ca, Na, Mg and K contents. The procedure was
repeated for HDCP. The same procedure was followed for
2 g ground bark, particle size < 425 micrometer.

RESULTS AND DISCUSSION

In this study, experimental data were collected to
quantify the effects of pyrolysis temperature and time,
and the initial moisture content of the bark, on the
yield of charcoal. The data presented here are
sufficient to determine the feasibility of utilizing
bark to produce HDCP, but further work is required to
characterize the bark or bark charcoal for the
production of other products, such as activated carbon.
Our results indicate that fixed carbon content increases
as pyrolysis temperature and time increase, but the
yield of charcoal decreases drastically at higher
temperatures. Pyrolysis time has very little effect on
charcoal yield. Pyrolysis of oven-dry bark carried out

for 65 min at 500°C yielded 35.1% (wt) charcoal,
34.5% (wt) pyroligneous liquor, 12.5% (wt) liquid tar,
and 17.9% (wt) uncondensable gases (calculated by
difference). Some properties of bark charcoal and HDCP
are given in Table 3.1.

The most important point illustrated by Table 3.1
is that compaction into pellets considerably increased
density. The addition of tar as binder decreased the
fixed-carbon content, because the tar contained a
smaller percentage of carbon than did the charcoal. The
volatile matter was higher for the HDCP, because the tar
binder contained volatiles, whereas the charcoal did
not. The difference in ash content should be negligible
because the charcoal contained little ash, and the
amount of binder used was small. The pH of the HDCP was
lower because the tar binder undoubtedly contained some
acids.

The average density of HDCP was 1.3 g/mL. This
makes them easier than charcoal to transport at much
lower costs, provides uniformity in composition, and
increases energy content/unit volume.

TABLE 3.1   Comparison of Properties of Charcoal and HDCP
Produced from Douglas-fir Bark Carbonized at
575°C.

Property	Charcoal	HDCP
Density	1.13 g/cc	1.3 g/cc
Fixed-carbon content	92.0% max	90.2% max
Volatile matter	6.2% min	8.0% min
pH	6.2 min	5.9 min

Effect of Carbonization Variables

Temperature

Oven-dry Douglas-fir bark, heated out of contact with air, decomposed into solids, liquids, and gases. Pyrolysis at 400°C yielded 41.2% (wt) bark charcoal, 33.5% (wt) pyroligneous liquor, 9.1% (wt) liquid tar, and 16.2% (wt) non-condensable gases. At 575°C charcoal yield was only 33.1% (wt), where as liquid tar yield increased to 13.0% (wt), pyroligneous liquor to 34.8% (wt) and noncondensable gases to 19.1% (wt) (Table 3.2). The carbonization time was kept constant 65 min in all the experiments. The effect of temperature on shrinkage of Douglas-fir bark during carbonization was not studied in detail. However, it was observed that at 400 C the relative volume had decreases to 48% of its original volume, and at 575°C, was down to 35% of its original volume.

Although Table 3.2 shows an apparent increase in metal with increasing temperature, the amount of metal (and ash) present was essentially constant when weight loss of the substrate from pyrolysis was taken into consideration. This clearly indicates that inherent

metals do not undergo changes during pyrolysis.

The proximate analyses of charcoals produced at different temperatures from 400 to 575°C showed that charcoal with a fixed-carbon content of 90% (wt) could be obtained at 575°C. Increase in pyrolysis temperature increased the ash content of the charcoal, but this increase, which resulted from burning off the organic matter, was marginal (Table 3.2).

Comparisons of SEM micrographs of bark before and after pyrolysis at different temperatures are difficult due to the complex anatomy of bark. Fig. 3.1a shows typical parenchyma cells in a cross section of bark before pyrolysis. Figs. 3.1b and 3.1c are representative of bark after pyrolysis at 400°C and 575°C. Bark structure was recognizable at 400°C, but was somewhat modified at 575°C. Figure 3.1d indicates the appearance of crystalline material in a charred specimen at 575°C. Figure 3.1e shows typical sieve areas on a longitudinal surface of a sieve cell. The pores in the sieve areas appear a bit broken up or enlarged, but not too seriously. This fracture might have occurred due to increased pyrolysis temperature. Fig. 3.1f indicates the formation of bubble-like

TABLE 3.2   Effects of Carbonization Temperature on
the Pyrolysis of Douglas-Fir Bark with a
Carbonization Time of 65 min.

	Carbonization temperature,°C							
	400	425	450	475	500	525	550	575
Product	Product yield, g/100 g bark							
Char coal	41.2	39.6	38.3	36.7	35.1	34.3	33.6	33.1
Liquor	33.5	33.9	34.1	34.3	34.5	34.6	34.7	34.8
Tar	9.1	9.9	10.4	11.5	12.5	12.8	12.9	13.0
Gases	16.2	16.6	17.2	17.5	17.9	18.3	18.8	19.1
Composition of charcoal, g/100 g charcoal								
Fixed-carbon	83.6	84.6	85.1	86.3	87.7	88.2	88.5	90.0
Ash	0.62	0.67	0.72	0.84	0.92	1.01	1.04	1.18
(excluding Ca, K, Na, Mg)								
Metal content of charcoal, ppm								
Ca	225	229	232	236	240	243	246	250
K	48	50	51	53	55	56	58	60
Na	35	38	40	42	43	46	47	50
Mg	20	21	24	26	28	30	33	35
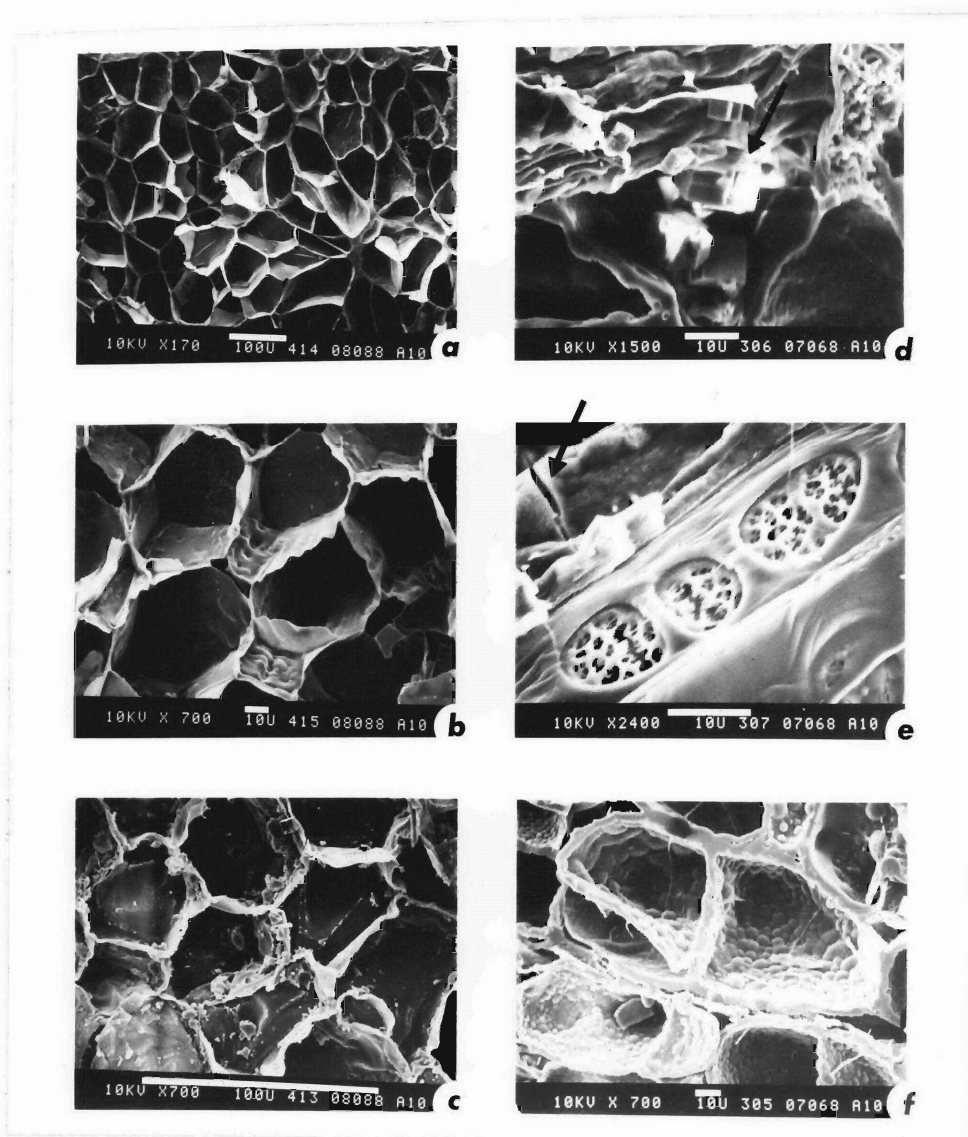
Figure 3.1   SEM Micrographs of Douglas-fir Bark.
a) Before Pyrolysis. b) Carbonized
at 400°C.   c) Carbonized at 575°C.
d)   Presence of Crystalline Material
in Charred Specimen at 575°C.   e) Fractured
Sieve Cells in Charred Specimen at 575°C.
f) Presence of Bubble-like Structure in the
Parenchyma of a Charred Specimen.

structures in the parenchyma. Such bubble-like structures were not present in the specimens before pyrolysis. They were also observed in specimens at 400°C, but were more predominant in charred specimens of 575°C as seen in the Fig. 3.1f. These bubble-like structures could be extractive depositions (on parenchyma walls) that have been affected by temperature.

Time

Short pyrolysis periods produced higher yields of charcoal (33.5% (wt) in 45 min) and lower yields of gas (19.3% (wt) in 45 min), whereas longer pyrolysis periods produced lower yields of charcoal (29.7% (wt) in 125 min) and higher yields of gas (22.7% (wt) in 125 min) (Table 3.3). Therefore, a short pyrolysis process is desired where the final product to be produced is charcoal. If gas is regarded as the main product, a long pyrolysis process should be adopted.

Other Factors

Moisture Content

Pyrolysis on six bark samples with moisture contents from essentially zero (oven-dry) to 50% (wt)

TABLE 3.3 Effect of Pyrolysis Time on Product Yield.

| Pyrolysis time, min | Product yield, g/100 g bark | | |
	Charcoal	Liquor+tar	Gases
45	33.5	47.2	19.3
55	32.7	47.2	20.1
65	32.0	47.3	20.7
85	31.2	47.4	21.4
105	30.6	47.4	22.0
125	29.7	47.6	22.7

were carried out. Higher charcoal and lower gas yields
are obtained with bark that is more moist (Table 3.4).
The percentage of moisture content present in the source
material is an important factor in design considerations
of equipments used for pyrolysis. A detailed economic
analysis is required to determine the optimum extent of
drying of the bark prior to carbonization.

The equilibrium moisture content of bark, HDCP,
and bark charcoal is a function of the relative humidity
of the ambient air. The variations are large, and hence
significantly affect net mass (Table 3.5). Relative
humidity is an important property that needs to be
considered when purchasing bark and packaging HDCP.

Bark Treated with Inorganic Chemicals

Charcoal yields from carbonization at 500°C and
65 min of various bark samples impregnated with
inorganic chemicals were found to be higher than those
from untreated samples. This appears to be caused by
the enhancement of secondary charring reactions of heavy
primary volatiles [61].

Cooling Rate

Bark charcoal can be cooled either by quenching or

TABLE 3.4   Effect of Moisture Content of Bark on Product
            Yield at a Carbonization Temperature of
            575°C.

| Moisture content, % | Product yield, g/100 g bark | | | |
	Charcoal	Liquor	Tar	Gases
50	34.4	35.6	12.4	17.6
40	34.2	35.5	12.6	17.7
30	34.1	35.5	12.6	17.8
20	33.6	35.2	12.8	18.4
10	33.3	35.0	12.9	18.8
Oven-dry	34.4	35.6	12.4	17.6

TABLE 3.5   Equilibrium Moisture Content at 25°C
            as a Function of Relative Humidity.

Relative humidity, %	Equilibrium moisture content, %		
	Bark	Bark Charcoal	HDCP
30	9.6	6.9	5.1
50	11.7	7.3	6.2
65	13.1	8.2	7.0
90	27.3	10.1	8.3

by slow cooling out of contact with air. Quenching the bark charcoal leads to surface cracking resulting in uneven distribution of pore size, from micro- to macro-pores. Slow cooling results in only micropores.

PROPOSED PROCESS FOR THE UTILIZATION
OF DOUGLAS-FIR BARK

Process Description

The steps in the manufacture of HDCP are illustrated in Fig. 3.2. The initial raw material may be obtained from saw mills and plywood mills, or directly from the forest. Procuring and processing bark from the forest usually costs more, but the choice rests on availability as well as economic considerations. The bark from saw mills and plywood mills can be stored until needed. The size of the bark from the saw mills and plywood mills is considered to vary from 1 mm to 50 mm diameter.

The first step in the proposed process for the utilization of Douglas-fir bark is the removal of unbound moisture in a hydraulic press. Next, much of the bound moisture is driven off in a drier that utilizes a hot gas stream. After being pulverized, the bark is made into briquets in an extruding machine,

Bark

↓

| HYDRAULIC PRESS | → Water

↓

Hot Gas → | BARK DRIER | → Moist Gas

↓

| PULVERIZER |

↓

| BARK EXTRUDER | → Water

↓

| DRY BARK BRIQUETTES |

↓

| VERTICAL RETORT | → Gas

Charcoal ↓   Liquid

        Liquid → Liquor

        | SETTLER |

| BINDER MIXER | ←   → Tar

↓

| HDCP EXTRUDER | → Volatiles

↓

Hot Gas → | TRAY DRIER | → Waste Gas

↓

High Density Carbon Pellets
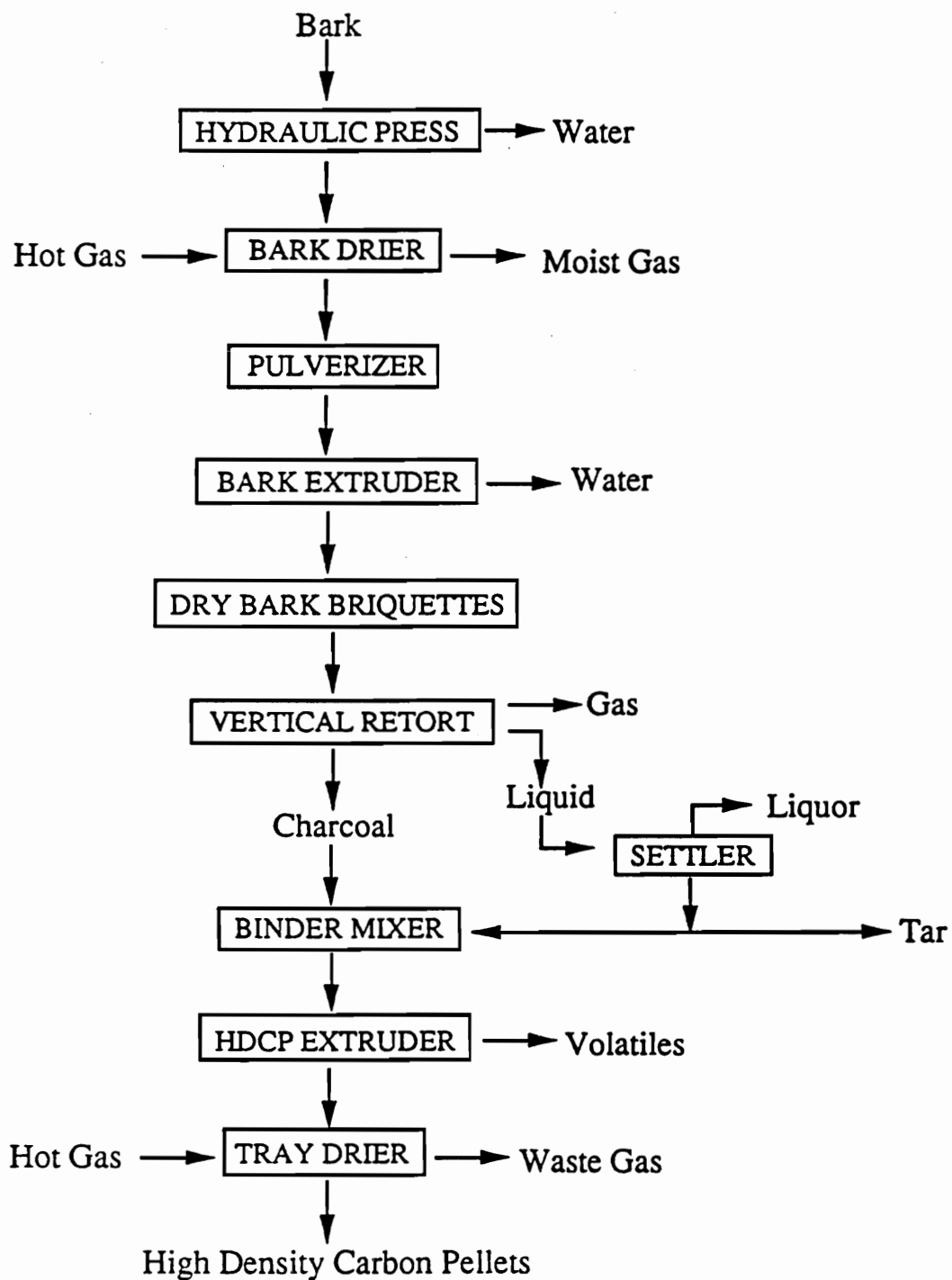
Figure 3.2 Proposed Bark-Utilization Process.

resulting in additional moisture removal. The dimensions of the extruded material are 100 mm diameter and 1200 mm length, and the moisture content is about 12%.

The bark briquets are then carbonized in vertical retorts. The hot gas can be mixed with air, combusted, and recycled to the bark drier. Liquid drained from the retorts contains two immiscible phases that can be separated into pyroligneous liquor and tar streams. The liquor can potentially be used as a liquid fuel or torched. Some of the heavy tar is used in the next step, but the rest must be burned or disposed of as a hazardous waste. The dried product of this step in the process is charcoal having a high fixed-carbon content. recovered from pyroligneous liquor.

Next, the charcoal is mixed with some of the carbonization tar, which acts as a binder. The charcoal/tar mixture is then sent to hydraulic multi-orifice extrusion presses operating at 250 psia, where 40 mm diameter x 40 mm long cylindrical pellets are produced. Some of the combustible gases from the vertical retorts can be used to dry the HDCP in tray driers, thus reducing air pollution.

Finally, the desired product, dry high-density carbon pellets, exits the tray driers. Since the purpose of these tray driers is to heat-cure the pellets while driving off as much of the volatile matter (resulting from the tar used as binder) as possible, the waste gas stream from this equipment must be treated (e.g., torched) to minimize hydrocarbon pollution to the atmosphere.

Economic Considerations

The most important factor in the production of HDCP is the yield of charcoal. The yield is inversely related to the fixed-carbon content. In other words, the higher the fixed-carbon content, the lower will be the yield of charcoal. Lowering the fixed-carbon content would increase the yield, but would degrade the quality of the charcoal. For the best balance of the economics of the process, previous experience suggests that a charcoal yield of 35% be used. This should be attainable at a carbonization temperature of 500 C for 65 min (Table 3.2), which should give a fixed-carbon content of 85-90%. Even with the temperature variations that occur in vertical retorts, we should be able to obtain charcoal with a fixed-carbon content of at least

80%.

Environmental and energy considerations are also important. We anticipate that the combustible gases and pyroligneous liquor from the carbonization step (vertical retort in Fig.3.2) will be more than sufficient to supply energy for the entire process. If the excess tar cannot be burned, but must be disposed of as a hazardous waste, then the added cost to the process could be important. For example, occasionally the condensation of pyroligneous vapors leads to organic acids that must be neutralized with lime.

Relative humidity data given in Table 3.5 indicate its strong influence on bark, charcoal, and HDCP. If the bark does not contain any unbound moisture, then exposure of the bark to humid air could lead to increased drying costs. Since charcoal from the retorts is essentially bone-dry, exposure to even slightly moist air will result in an increased tray- drier duty. Lastly, the HDCP should be packaged as they are produced, because exposure of the bone-dry pellets to air could adversely affect the product, depending on its application.

Other economic considerations include the effect

of liquid tar on the fixed-carbon content of HDCP (this effect if generally small) and the strength and density of the product (i.e., the pressure in the HDCP extruder may have to be varied according to the desired properties of the product). Overall, the product composition and properties attained in our laboratory coupled with the low cost of the feedstock suggest that the proposed process may well be feasible and is worthy of further consideration.

CONCLUSIONS

The depletion of fossil fuels and uncertain costs of petroleum products create a demand for substitutes from renewable resources. The manufacture of HDCP from bark has the advantage that it utilizes a waste material with high disposal costs. Process considerations suggest that HDCP production may be economically feasible. HDCP have very low ash content and should be good substitute for coal and petroleum coke as a reducing agent in the metallurgical industries. HDCP can also be used for the manufacture of adsorbents i.e., activated carbon. With proper design of carbonization processes, a charcoal of higher fixed carbon content can be produced. The final fixed- carbon content depends on

the pyrolysis temperature. Higher char formation for treated bark heated out of contact with air suggests secondary char formation from catalytic action of inorganic chemicals. This would help to increase the charcoal yield, which would ultimately help to achieve a better rate of return on investment.

Conversion of combustible gases from wood into energy is no longer in the theoretical stages of development, but has moved into the beginning phases of commercial application. If this developed technology is adopted in the present process, combustible gases which amounts to 18% (wt) of the raw material used, is likely to increase the profitability of the project to a great extent.

SCANNING ELECTRON MICROSCOPIC STUDIES ON THERMAL DEGRADATION OF DOUGLAS-FIR WOOD

INTRODUCTION

Several aspects of thermal degradation of wood have been examined during the last 3 decades and no considerable agreement has been reached concerning the effects of temperature on the various ultrastructural features. Marked changes in characteristics of wood occur only when it is heated beyond 280°C at which exothermic reaction (auto-carbonization) begins. Changes below 150°C have been reported by some researchers [62].

Forest research laboratory initiated research on recording physical changes that occur at the microscopic level. For this study we used scanning electron microscopy [SEM] as a convenient tool to detect and record any physical changes caused by heat treatment of Douglas-fir wood in the absence of air. SEM has been found to be useful for accurate detection of the physical changes.

Heating wood substance out of contact with air causes its mass to decrease when the process attains the auto-carbonization stage. The loss in mass at a

particular temperature is a function of time only to a certain extent. Wood substance can be heated out of contact with air to lose complete mass at sufficiently high temperatures. However, in this study, the heating process has been restricted to 575°C.

Researchers [63-68] have previously carried out SEM and microstructure studies on different species of charred wood. Four zones of thermal degradation of wood have been reported depending on the pyrolysis temperature [69-72]. During the first zone which lasts up to 160°C, wood basically looses all its water molecules. Evolution of some non-condensable gases also takes place. During the second zone which starts at 160°C and ends at 280°C steady evolution of combustible gases along with gradual conversion of wood substance to charcoal takes place. During the third zone which starts at 280°C and is completed at 450°C, rapid evolution of combustible gases takes place. Wood substance looses weight rapidly. During the fourth zone which starts at 450°C conversion of charcoal to gases takes place. The physical changes that take place in the 3rd and 4th zones in Douglas-fir wood structure were of particular interest in this study.

MATERIALS AND METHODS

Two hundred pieces of oven dried Douglas-fir wood specimens as detailed in chapter 2 were selected to carry out SEM studies. Eighty four pieces of normal heart were treated different chemicals (twelve pieces each with zinc chloride, calcium chloride, sodium chloride, calcium chloride, potassium chloride, sodium carbonate, and potassium carbonate). The concentration of these chemicals was 0.05 g/cc. The treatment time with each of the chemical was 24 h.

After chemical treatment, specimens were dried for 4 h at 102°C. One set of control for untreated and another set of control for each of the chemical treated wood pieces were selected and stored in the polyethylene bags. Pyrolysis experiments were conducted as detailed in chapter 2. The temperature of the reaction zone inside the reactor was precisely measured by a digital thermocouple. The desired temperature was attained by controlling the heat input by electrical heating tape surrounded by insulation.

Separate experiments were carried out for each of the different types of wood sample for 65 min for different temperatures (400, 500, 575°C).

TABLE 4.1 Details of Inorganic Chemicals Treatment.

Sample: Douglas-fir normal heartwood.

Pyrolysis Temperature: 400°C

Pyrolysis Time: 65 min.

Total impregnation time: 24 h

Drying Time: 4 h at 102°C

Inorganic Chemicals Impregnated:

> Zinc Chloride
>
> Calcium Carbonate
>
> Sodium Carbonate
>
> Potassium Carbonate
>
> Calcium Chloride
>
> Potassium Chloride
>
> Sodium Chloride

Concentration of Inorganic Chemicals: 0.05 g/cc

The chemicals treated wood was pyrolyzed at 400°C. The charcoal obtained was cooled. The air cooled charcoal specimens were carefully cut with a razor blade to obtain cross, tangential, and radial sections. These specimens were mounted on aluminum studs and coated with metal (60 % gold and 40 % palladium) in a vacuum evaporator immediately before scanning. When areas of interest to our study were located, photographs were taken using attached polaroid camera.

The accelerating voltage, the magnification, the scale factor, and the serial number of the micrograph were automatically recorded on the negative by the polaroid camera system attached to scanning electron microscope (AMR Model 1000A). It was found that those samples which were carbonized at 400°C or higher were sufficiently conductive to provide good results without coating. To maintain uniformity, all specimens were coated before examination.

Most of the SEM studies on compression wood were carried out using the first 4 growth ring sections where the characteristics of the cells appear to be normal. This was done to facilitate close comparative study

between different sections of the wood pyrolyzed at similar operating conditions.

RESULTS AND DISCUSSION

Figure 4.1a and 4.1b shows the cross sections of the Douglas-fir normal sapwood and heartwood charred at 400°C while Fig. 4.1c and 4.1d shows the cross sections of the compression sapwood and compression heartwood carbonized at the same temperature as the normal sap and heartwoods. No changes in the inter-tracheid pits (arrows in Fig. 4.1a, 4.1b and 4.1d), pits between ray parenchyma and tracheid (Fig. 4.1b), and the helical thickening on the secondary walls (arrows in Fig. 4.1a, 4.1b and 4.1c) could be detected.

No warty like layers of amalgamation of the cell walls were observed. The tracheids and parenchyma cells were as clear as they were in the uncharred wood. However, at higher charring temperatures, there is evidence of fracture and warty like depositions.

Figure 4.2 shows the various fractured sections of charred wood at 575°C. A fracture between cell walls (Fig. 4.2a) was detected in charred compression heartwood. Deposition of very fine particles in the
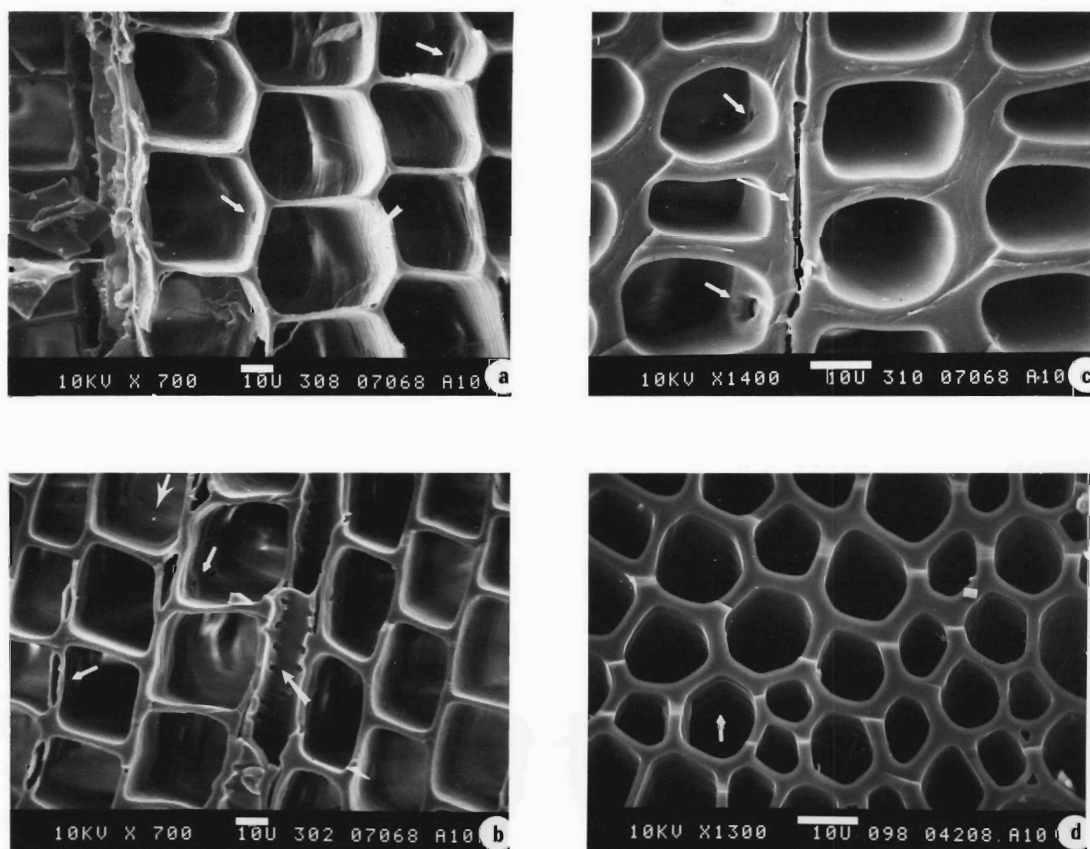
Figure 4.1   Cross Sections of the Douglas-fir Charred at
             400°C. a) Normal Sapwood b) Normal
             Heartwood c) Normal Wood Cells from
             Compression Sapwood Specimen d) Normal Wood
             Cells from the Compression Heartwood
             Specimen.
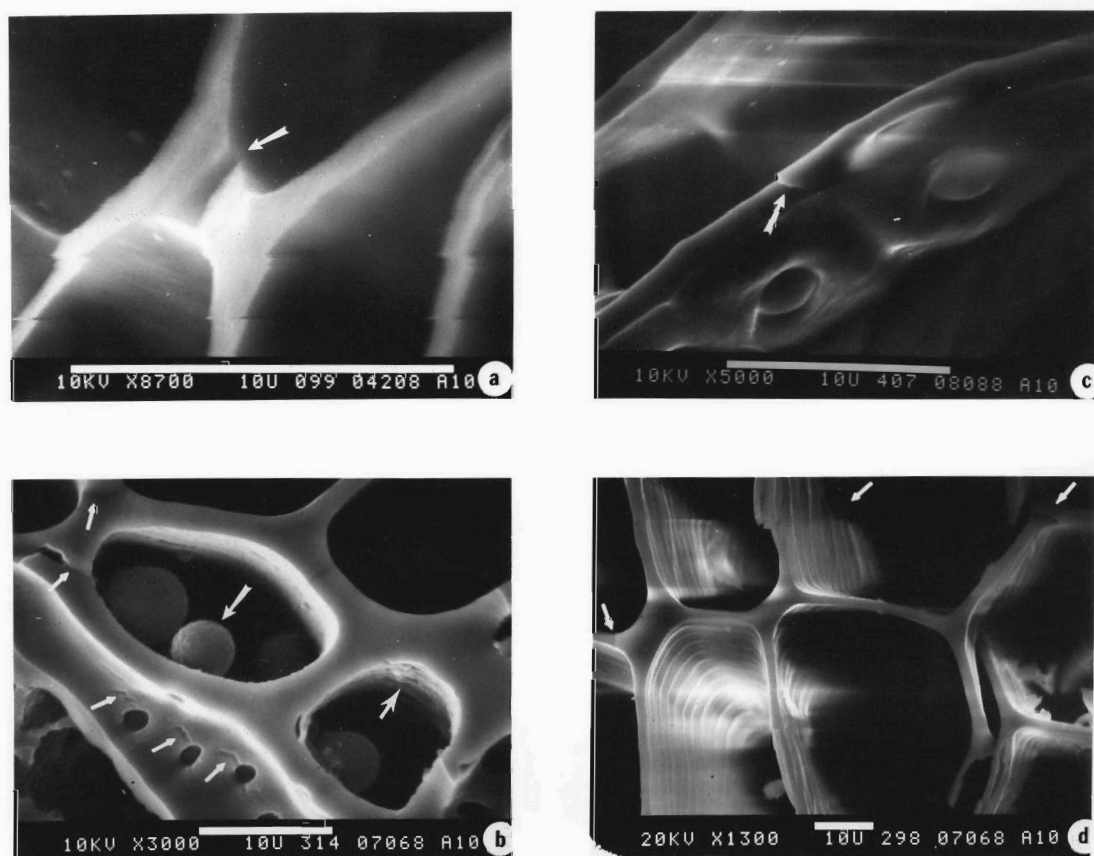
Figure 4.2   Fractured Sections of Charred Wood at 575°C
a) Normal Wood Cells from Compression
Heartwood b) Normal Heartwood c) Normal
Sapwood Specimen d) Normal Wood Cells from
the Compression Sapwood.

form of warts like structure on the inner surface of tracheids and also presence of a few more or less uniform spherical particles inside the tracheids (Fig. 4.2b) in charred normal heartwood were observed.

In the charred specimen, cracks surrounding the pits in strand parenchyma cells were also detected. Cracks were also detected in parenchyma cell walls (Fig. 4.2c, page 60) of normal sapwood charred at 575°C. Pits appear to be not affected. In the case of charred compression sapwood (Fig. 4.2d) cracks were detected in thinly walled tracheids.

The helical thickening on the secondary walls and inter-tracheid bordered pits remain unaffected. Figure 4.3a shows the cross section of resin canals of a normal heartwood charred at 400°C. No changes were detected in the epithelial cells, except the presence of some non-uniform particles.

When a sample charred at 500°C (Fig. 4.3b) was examined, it was found that the particles (probably might have formed due to the action of heat on extractives) have virtually blocked the resin canal. This was very much evident in the normal heartwood

10KU X 700   10U 313 07068 A10 **a**

10KU X710   100U 102 04208 A10 **c**

10KU X 700   10U 315 07068 A10 **b**

10KU X1300   10U 303 07068 A10 **d**
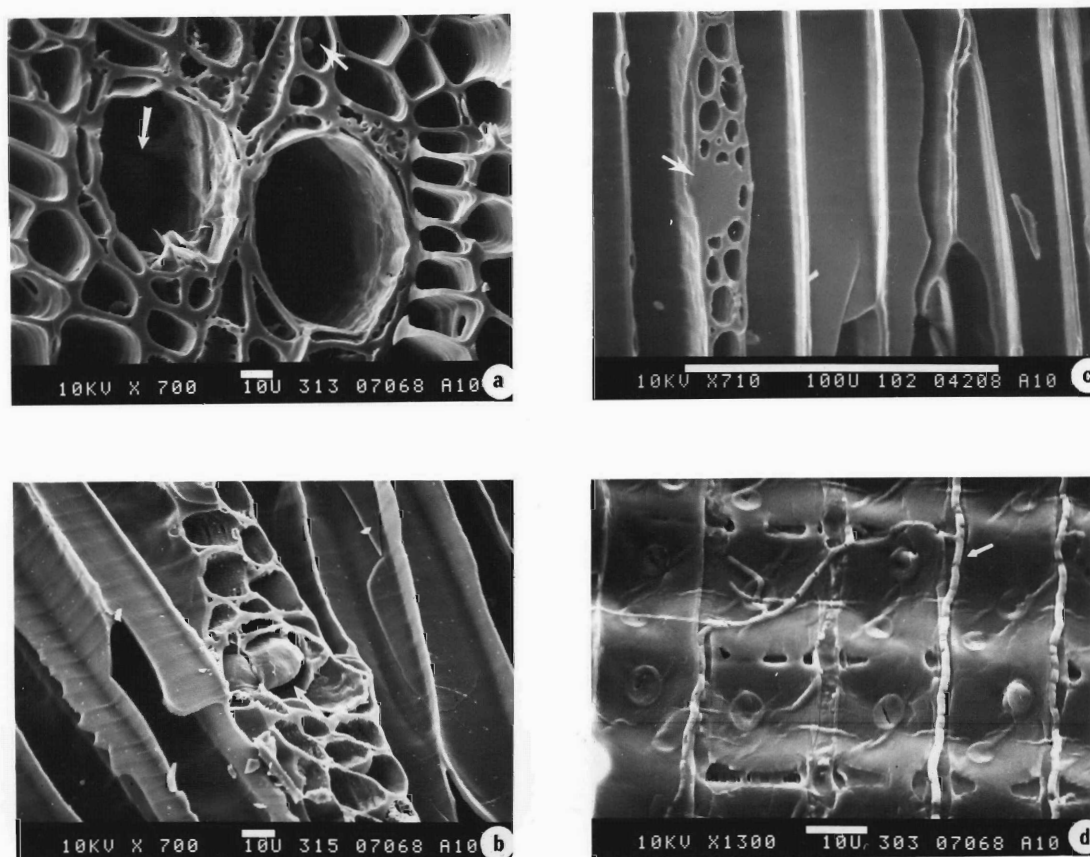
Figure 4.3   Charred Normal Heartwood
a) and d) Charred at 400°C b) Charred at
500°C c) Charred at 575°C.

charred at 575°C (Fig. 4.3c). Figure 4.3d shows the presence of fungal hyphae in the normal heartwood sample charred at 400°C.

There was no distortion in the fungal hyphae structure due to heat treatment of wood. Major changes have been observed in the ray parenchyma cells of normal heartwood charred at 575°C.

Surface distortions of these ray cells were clearly evident (Fig 4.4a and 4.4b). The folds observed may be due to large particles agglomerization. The action of heat on extractives might have resulted in this kind of folds structure. The folds structure might contain host particles covered with a variety of platy and other particles. The uniformities in the formation of these folds suggest the presence of uniform composition in the contents of the surface material on the ray parenchyma cells in the uncharred wood.

The folds structures are also present in wood samples charred at 575°C. This indicates that the folds do not disappear or dry away if pyrolysis temperature is further increased. Detailed studies of these fold structures are needed to arrive at any conclusions about their formation. Wood treated with different inorganic.
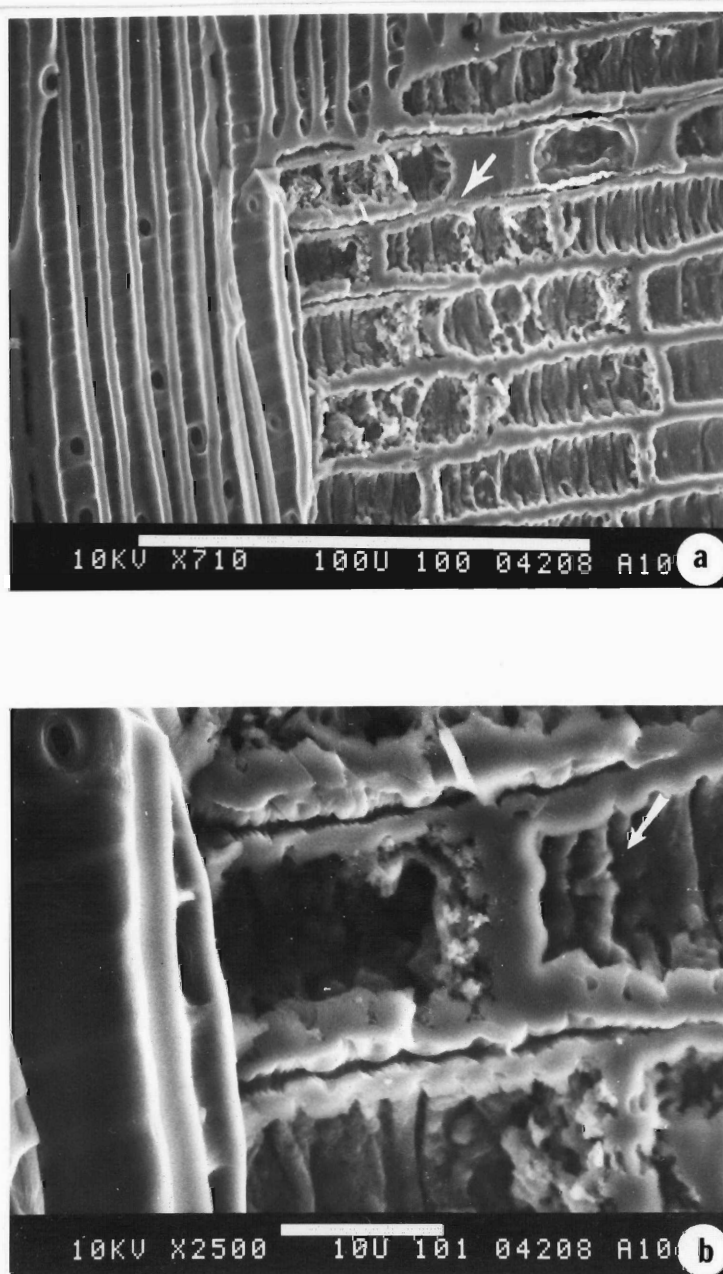
Figure 4.4   Surface Distortion of Ray Cells
when Normal Heartwood was Charred at 575ºC

chemicals showed different destruction patterns. Figure 4.5a shows the SEM micrograph of untreated normal heartwood charred at 400°C. Fig.4.5b is the SEM micrograph of normal heartwood treated with $ZnCl_2$ and charred at 400°C.

No particular cleavage pattern was observed. Spiral thickening appear to have been affected. Wood treated with Ca_2CO_3 appear to follow a particular cleavage pattern showing fractures between pits (Fig 4.5c). No changes have been observed in the case of wood treated with $NaCO_3$ except a few irregular fractures (Fig. 4.5d). Treatment with K_2CO_3 and KCl did not affect the wood structure (see Fig. 4.5e and 4.5f) when charred at 400°C. Potassium chloride also did not affect the wood structure, however it remained in the charred wood even at 400°C.

Figure 4.5g shows the presence of chemicals in the charred specimen. Wood treated with sodium chloride also did not affect the structure but it remained in the wood even after charring. The amount of chemical left on the surface of cell walls was more predominant than KCl (Figure 4.5h). These observations do not suggest formation of any secondary char due to catalytic action
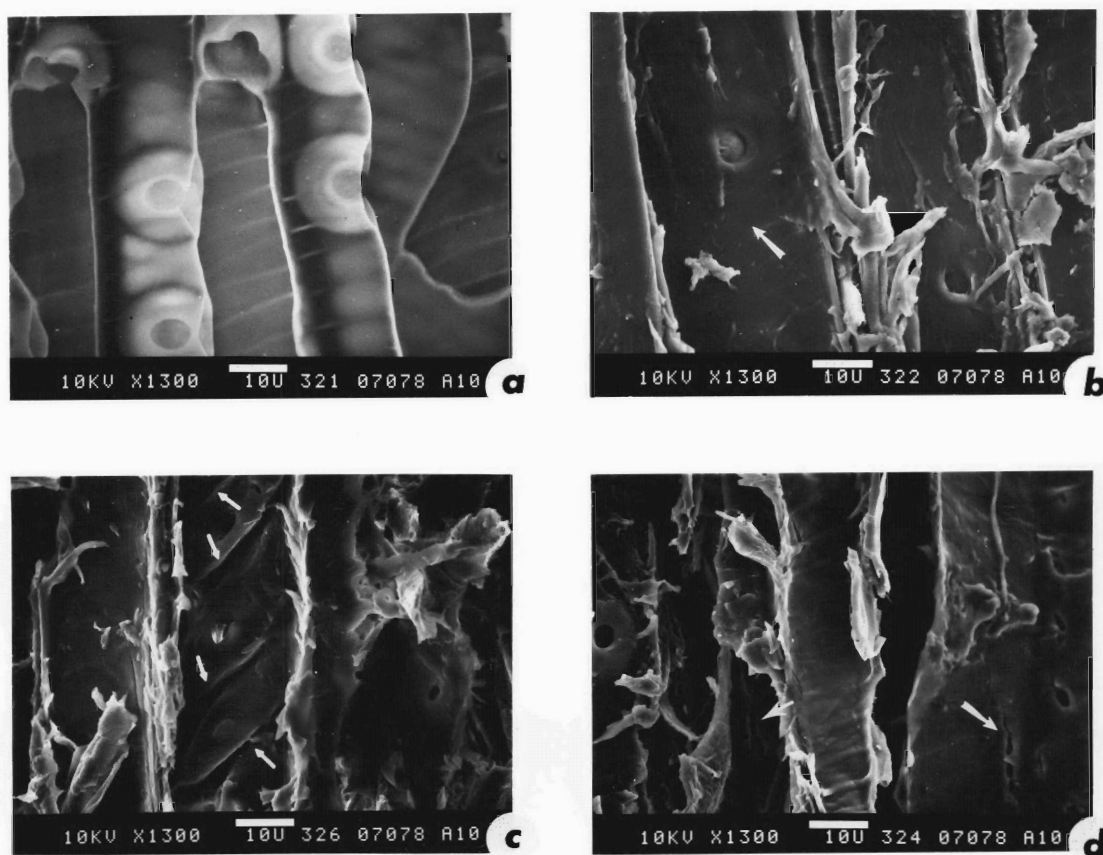
Figure 4.5   Normal Heartwood Charred at 400°C
a) Untreated Wood   b) Wood Treated with
$ZnCl_2$ c) Wood Treated with $CaCO_3$
d) Wood Treated with Na_2CO_3.
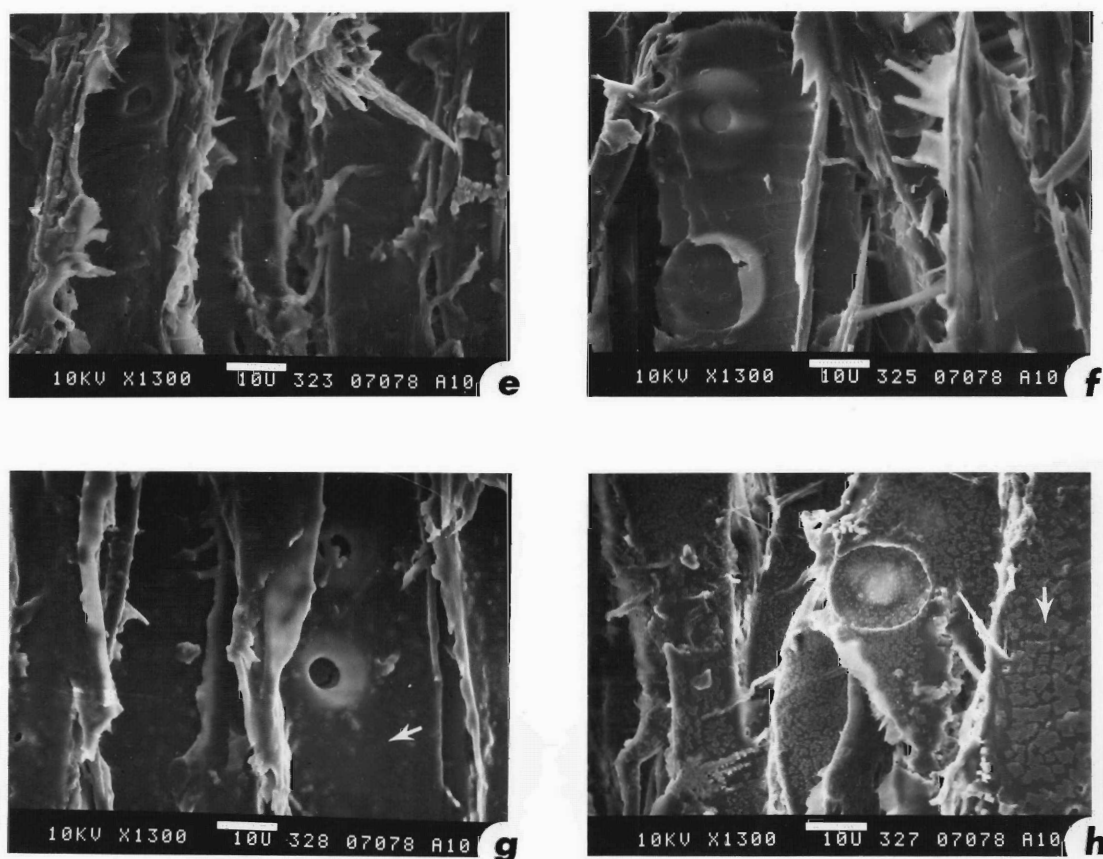
Figure 4.5   Normal Heartwood Charred at 400ºC
e) Wood Treated with Potassium Carbonate
f) Wood Treated with CaCl$_2$
g) Wood Treated with Potassium Chloride
h) Wood Treated with Sodium Chloride.

of inorganic chemicals. Higher char yield in case of wood treated with sodium and potassium chlorides may be due to the presence of these chemicals in the charred wood substance. Formation of cracks in the charred treated wood compared to no cracks in charred untreated wood suggest that the changes in the pyrolysis itself between the two methods [74-77].

CONCLUSIONS

No physical changes appear to take place in wood charred at 400°C except for the formation of some spherical shaped particles indicating that wood substances are resistant to pyrolysis temperatures existing in third zone. In the 4th zone of pyrolysis where the temperature is greater than 450°C, physical as well as chemical changes have been recorded. As the pyrolysis temperature increases, cracks in cell walls and in areas surrounding the pits become evident. The resins form globules due to the action of heat and block the resin canals.

The surface materials inside the ray parenchyma give rise to the formation of some platy material in the form of uniform folds. The formation of folds is probably due to chemical reaction and agglomerizations

of particles present in the extractives. The facts that spiral thickening and pit were not affected suggests that the components of these structures are more resistant to pyrolysis than the substances surrounding them. The results suggest that the Wood treated with chemicals such as zinc chloride, sodium carbonate and calcium carbonate when heated results in early fracture of wood structure. Inorganic substances such as zinc chloride affect the spiral thickening. Chemicals such as potassium chloride and sodium chloride remains in the wood substance even after charring at low temperatures. They do not affect any of the wood properties.

The cleavage pattern in wood treated with calcium carbonate is more or less uniform. Characterization of chemical reactions occurring in ray parenchyma and resin canals would provide an accurate composition of these substances. The changes that are taking place due to chemical reactions in these sections are worth further investigations.

THE UTILIZATION OF DOUGLAS-FIR BARK
FOR THE PRODUCTION OF OXALIC ACID AND
HIGH DENSITY CARBON PELLETS

INTRODUCTION

One of the major problems facing the wood industry is the disposal of large quantities of bark, which have found only limited utilization [78]. Oregon's forest products industry produces an estimated three million tons of Douglas-fir (Pseudotsuga menziesii (Mirb.) Franco) bark each year. Attempts to use the bark (which contains 42 wt% carbon, 6.5 wt% hydrogen, 49, wt% oxygen, 1.5 wt% nitrogen, and approximately 1 wt% other elements) as a source of organic chemicals have been hindered owing to inadequate knowledge about the chemical and thermal properties of bark components [79]. Carbohydrates are important constituents of Douglas-fir bark. They constitute almost 50% of the Douglas-fir inner bark. The bark is also rich in extractives (~ 30%), the chief constituents being waxes, tannin, carbohydrate matter, and dihydroquercetin [80]. Of particular interest in this study is the catalytic oxidation of the carbohydrate portion of Douglas-fir bark by nitric acid to form oxalic acid, which is used extensively by the textile industry in dyeing and

bleaching operations [81]. The US produces about 6200 tons of oxalic acid per year, and the demand for the product is upwards of 10,000 tons [82].

A kinetic study by Sullivan et al. indicates that oxalic acid can be produced via the nitric acid oxidation of hardwood (red oak) sawdust in the presence of vanadium pentoxide [83]. This process takes place in two steps. First, cellulose is hydrolyzed to glucose.

$$H(C_6H_{12}O_6)_nOH + (n - 1) H_2O \xrightarrow{H^+} n C_6H_{12}O_6 \quad (1)$$

Next, the glucose is oxidized in a medium of concentrated nitric acid to oxalic acid $(COOH)_2$

$$C_6H_{12}O + 6 HNO_3 \xrightarrow{V_2O_5} 3 (COOH)_2 + 6NO + 6H_2O \quad (2)$$
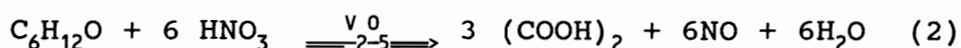
Oxalic acid can be produced from softwood (e.g., Douglas-fir) cellulose in a similar manner. However, since oxalic acid is not a large-volume chemical, other uses for Douglas-fir waste material need to be considered. For example, wood wastes can be carbonized and compressed to obtain high density carbon pellets, which could be steam treated to produce activated carbon.

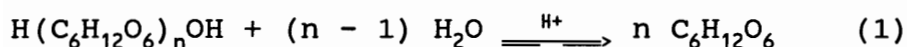The goal of the current project being carried out at OSU is the utilization of Douglas-fir bark. The principle objective of the work presented in this paper was to develop a process scheme for the utilization of Douglas-fir bark for the production of oxalic acid and high density carbon pellets and to make a preliminary economic analysis of the process. As a secondary objective, the kinetics of Douglas-fir bark conversion to oxalic acid was investigated.

To study oxalic acid production, Douglas-fir bark was hydrolyzed and oxidized under a variety of conditions to determine the effects of vanadium pentoxide, nitric acid concentration, and temperature. Oxalic acid was also produced from glucose, cellulose, and Douglas-fir sawdust. Residue from the oxidation step was carbonized to produce high density carbon pellets [84]. The effect of yield on the relative amount of fixed carbon produced was studied by carrying out the carbonization at a variety of temperatures.

EXPERIMENTAL METHODS

Oxidation to Oxalic Acid

Douglas-fir bark (and sawdust) was air dried for 6 h and its final moisture content (~ 8%) was determined prior to catalytic oxidation. Two mL of concentrated nitric acid were added dropwise over a 5-min period to 10 g of ground Douglas-fir bark (or other substrate), which had been mixed with vanadium pentoxide, in a 500 mL beaker at room temperature. The mixture was stirred vigorously during the acid addition and the procedure was repeated until vigorous reaction subsided. In the case of bark, ~ 20 mL of acid was required. Next, the mixture was reacted for up to 8 h in a controlled temperature water bath. Most experiments were conducted at 80°C with 2.5 g nitric acid/g of water (62.5 vol%) and 0.5 mg V_2O_5/g (oven dry basis) of substrate used, but the effects of temperature and acid and catalyst concentrations were also studied.

After the oxidation reaction was quenched and the mixture filtered, the dark yellow filtrate was decolorized with activated carbon. Next the decolorized filtrate was dried at 30°C to remove any residual nitric acid, redissolved in 1 mL distilled water and

quantitatively analyzed by gas chromatography [85].

Analysis for Oxalic Acid

Two milligrams of malonic acid obtained from J.T. Baker Chem. co. for use as an external standard were dissolved in a 2-mL sample containing an unknown quantity of oxalic acid. The sample was then heated to 60°C to evaporate the water. Next, the dried sample was reacted with 2 mL of BCl_3-CH_3OH (obtained from EM Science) for 6 min at 40°C. The reaction was quenched with 1 mL of water and then thoroughly mixed with 2 mL of chloroform. After the immiscible liquid phases were allowed to separate, some of the bottom chloroform phase was placed in a bottle and sealed for subsequent analysis by gas chromatography.

The oxidation reaction samples were analyzed for oxalic acid on a HP 5880A gas chromatograph using a SPB-5 capillary column with fused silica ends and a flame ionization detector. The column was temperature programmed from 40 to 150°C at 10°C/min. The injector port temperature was 185°C. The sample size was 1 L. The initial and final times were set at 2 and 3 min, respectively. The total run was 17 min [86].

Production of Carbon Pellets

Residue from several experiments was collected, washed thoroughly with distilled water, mixed with pyroligneous liquor (8 g of oven dry residue/g of liquor), prepressed to remove excess liquor and water, and dried to a moisture content of about 15%. Twenty-gram samples of the dried pellets were pyrolyzed for 75 min at temperatures up to 575°C, while the combustible vapors were condensed in a water-cooled copper coil to obtain the pyroligneous liquor. The pyroligneous liquor was allowed to settle for 3 d to separate the light and heavy oil fraction from tar and tar oils [87].

Room-temperature charcoal from the carbonizer was mixed with light and heavy oils (8 wt% oil) and compressed in a hydraulic press with a load of 11,250 kg to obtain carbon pellets 10 mm long and 12 mm in diameter. The pellets were heat treated at 105°C to impart sufficient mechanical strength [88].

Conversion of Tar Oils to Oxalic Acid

Additional oxalic acid was produced by reacting a mixture of 5 g tar and tar oils with 1 mL of methanol at

60°C for 30 min. The reaction was quenched by adding
2 mL of water and the products were analyzed by gas
chromatography, as described above.

RESULTS AND DISCUSSION

Production of Oxalic Acid

Relatively little has been published to date on
the kinetics of oxalic acid formation by catalytic
oxidation of carbohydrate material because of the great
complexity of the reaction mechanism. In this study,
experimental data were collected to quantify the effect
of substrate, catalyst concentration, nitric acid
concentration, and temperature on the production of
oxalic acid. The data presented below are sufficient to
determine the feasibility of utilizing Douglas-fir bark
to produce oxalic acid in conjunction with high density
carbon pellets, but further work is required for an
in-depth kinetic study.

The quantity of oxalic acid produced when oven dry
glucose, Douglas-fir bark, Douglas-fir sawdust,
cellulose, and lignin are catalytically oxidized with
nitric acid in the presence of vanadium pentoxide was
measured for different reaction times. The results

indicate that initially oxalic acid is produced from Douglas-fir bark and sawdust at the same rate that it is produced from glucose. As Fig. 5.1 shows, after a period of 2 h, the rate of oxalic acid production from Douglas-fir bark and sawdust drops drastically and is much closer to that for cellulose than for glucose. No oxalic acid was produced from lignin.

The results in Fig. 5.1 suggest that for the latter stage of the reaction, the hydrolysis of cellulose is the rate determining step in the production of oxalic acid from Douglas-fir bark. The faster rate observed initially was probably owing to the oxidation of sugars from hemicellulose, which hydrolyses much quicker than cellulose.

Effect of Catalyst Concentration

Figure 5.2 shows that the overall production of oxalic acid from Douglas-fir bark increased rapidly for fixed reaction conditions as the concentration of vanadium pentoxide was increased from 0.1 to 0.5 mg/g of bark. However, at higher catalyst concentration oxalic, acid production dropped. This observation suggests that the rates of reaction at the higher catalyst concentrations are sufficiently large as to make oxalic

OXALIC ACID PRODUCED

10

X - axis units (mmol/g substrate)
(80°C, 0.5mg V_2O_5/g substrate,
  82.5 vol % HNO_3)

8

6

4

2

0

0   2   4   6   8

TIME (h)

CELLULOSE   DF SAWDUST
DOUGLAS-FIR BARK   GLUCOSE
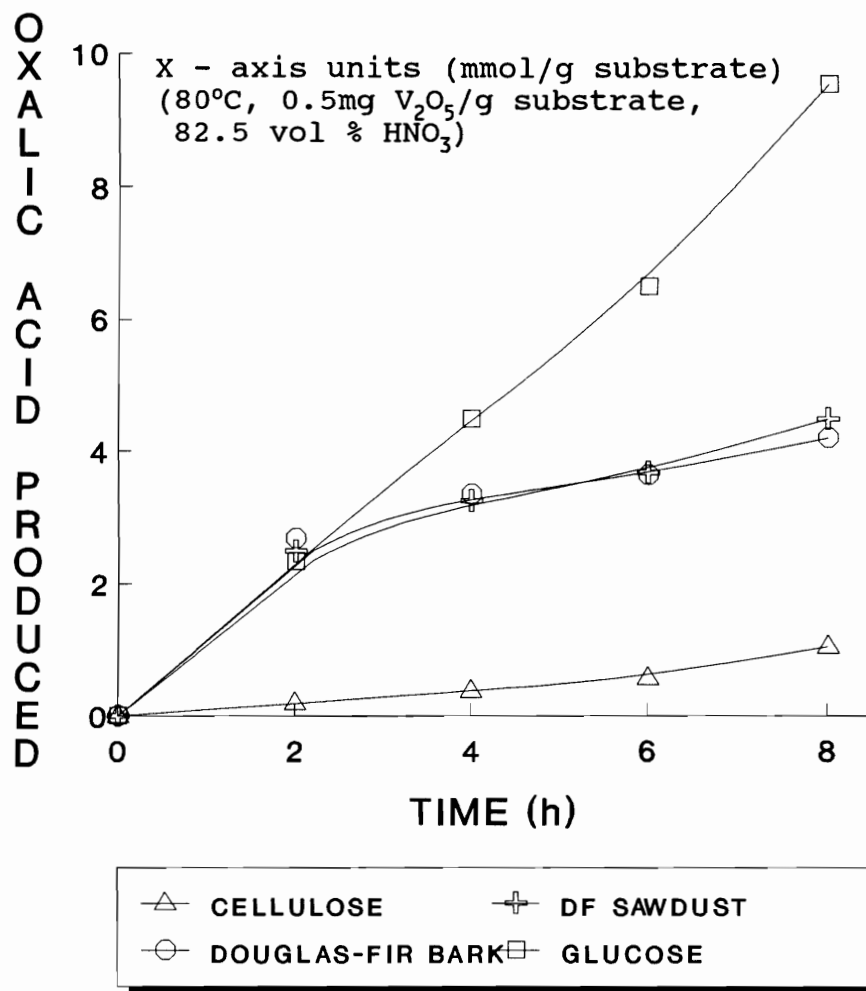
Figure 5.1   Oxalic Acid Production from Different
             Substrates.
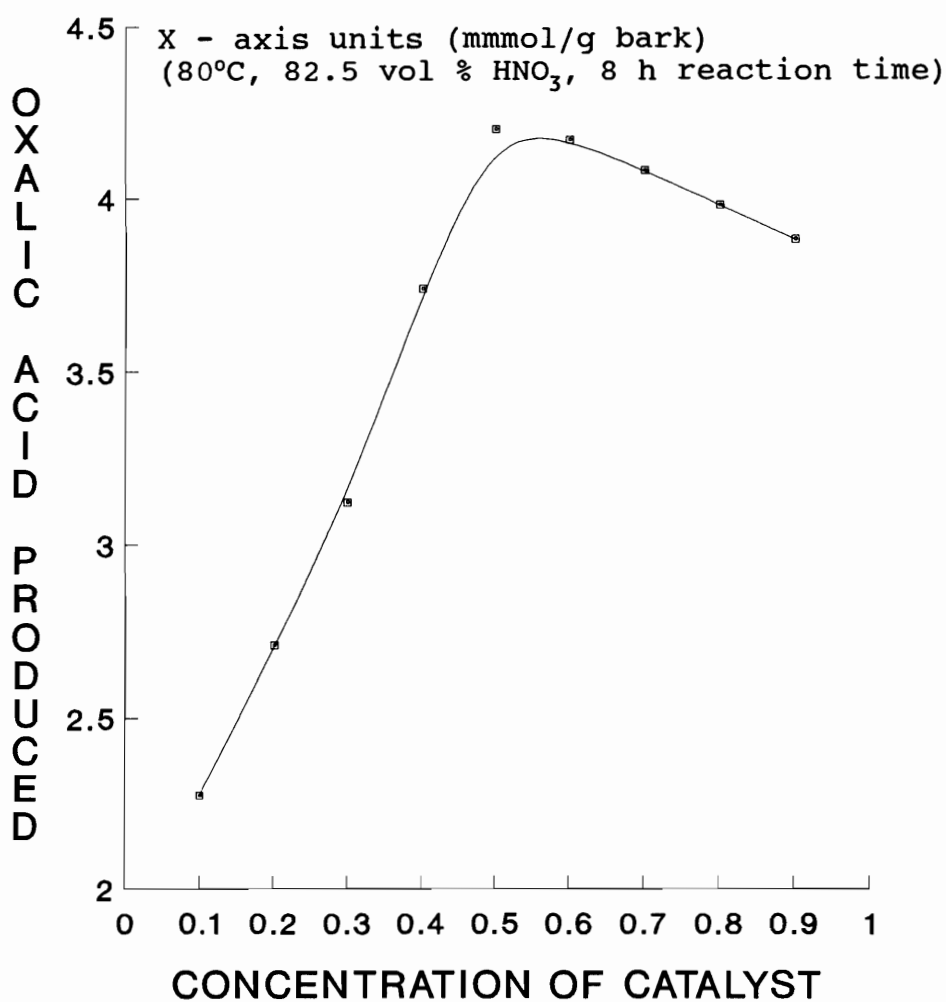
Figure 5.2   Effect of Catalyst Concentration on Oxalic
             Acid Production from Douglas-fir Bark.

acid oxidation significant. Sullivan et al. have reported that oxalic acid oxidatively decomposes to carbon dioxide and water in the presence of nitric acid and vanadium pentoxide [83].

$$(COOH)_2 + 2HNO_3 \xrightarrow{V_2O_5} 2CO_2 + 2H_2O + 2NO_2 \tag{3}$$

$$(COOH)_2 + (2/3)HNO_3 \xrightarrow{V_2O_5} +2CO_2 + (4/3)H_2O + 2/3NO \tag{4}$$
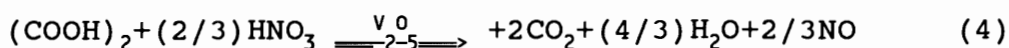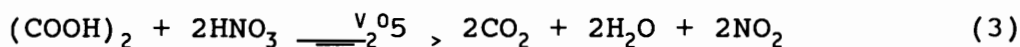
The experimental results indicate that for an 8-h reaction time at 80°C and 62.5 vol% HNO^3, a catalyst concentration of 0.5 mg V_2O_5/g of Douglas-fir bark gives the highest production of oxalic acid.

Effect of Nitric Acid Concentration

The effect of nitric acid concentration on oxalic acid production follows a trend similar to that observed for the effect of the catalyst concentration. That is, in an 8-h period at 80°C and 0.5 mg V_2O_5/g bark, the production of oxalic acid from Douglas-fir bark increased as the HNO_3 concentration was increased from 50 to 62.5 vol%, but decreased at higher acid concentrations (see Fig. 5.3). Again, this suggests that oxalic acid oxidation is significant at the higher reaction rates, caused by the higher nitric acid concentration.
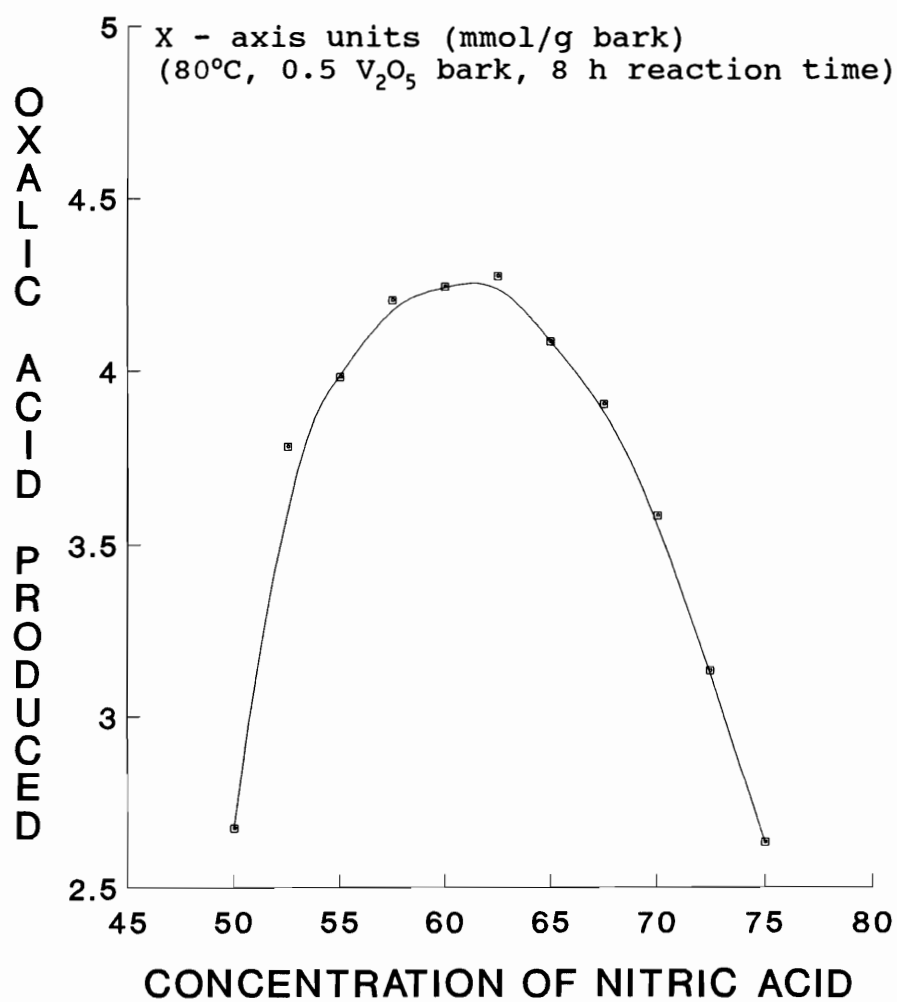
Figure 5.3   Effect of Nitric Acid Concentration on
              Oxalic Acid Production from Douglas-fir
              Bark.

Design Operating Conditions

Similar results were also observed for the effect
of temperature: the maximum rate of oxalic acid
production in an 8-h period at 0.5 mg V_2O_5/g bark and
62.5 vol% HNO_3 occurred at 80°C. Therefore, we can
conclude from the temperature data plus the experimental
results presented in Figs. 2 and 3 that optimum
conditions for the production of oxalic acid from
Douglas-fir bark in an 8-h batch reactor are 80°C,
62.5 vol% HNO_3, and 0.5 mg V_2O_5/g of bark. Under
these conditions, 4.2 mmol of oxalic acid can be
produced/g of bark, which corresponds to a yield of
38 wt% (0.38 g oxalic acid/g of bark).

The results of this study on oxalic acid
production were used in the preliminary economic
evaluation of a process proposed for the utilization of
Douglas-fir bark. That is, the oxalic acid reactor was
designed to operate at 80°C with 62.5 vol% HNO_3 and 0.5
mg V_2O_5/g of bark.

An additional 0.7 mmol of oxalic acid/g of
Douglas-fir bark was produced from the tar and tar oils
generated during the carbonization of the bark residue,
i.e., the insoluble portion from the catalytic oxidation

step.   As a result, the overall yield of oxalic acid was almost 45 wt%.

Production of High Density Carbon Pellets

Samples of the residue from the catalytic oxidation step (i.e., the insoluble material left over from the production of oxalic acid) were carbonized at temperatures ranging from 280 to 575°C. The upper plot in Fig. 5.4. shows the increasing effect of fixed carbon content with carbonization temperature. As the carbonization temperature increased, the charcoal yield decreased due to the removal of volatile components (lower plot in Fig. 5.4). Note that the volatile components tend to be relatively rich in hydrogen and oxygen, which means that fixed carbon content and charcoal yield vary inversely (see Fig. 5.4 and 5.5). The highest fixed carbon content of 93% (0.93 g carbon/g of charcoal), obtained at a carbonization temperature of 575°C, corresponds to a charcoal yield of 30% (0.3 g charcoal/g of residue carbonized).

After the charcoal from the carbonizer was allowed to cool, samples of approximately 1.5 g were mixed with oil from the pyroligneous liquor and compressed to form high density carbon pellets. After heat treating, such
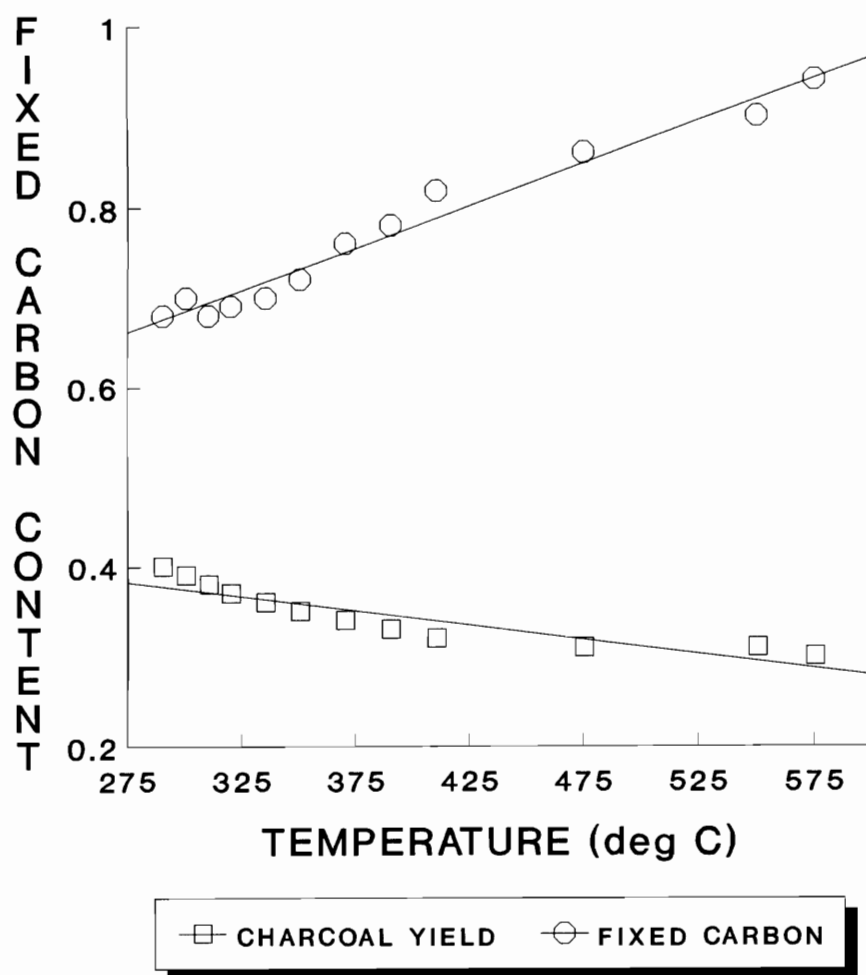
Figure 5.4 Effect of Temperature on Fixed Carbon
            Content (g Fixed Carbon/g Charcoal) and
            Yield of Charcoal (g Charcoal/g Carbonized).
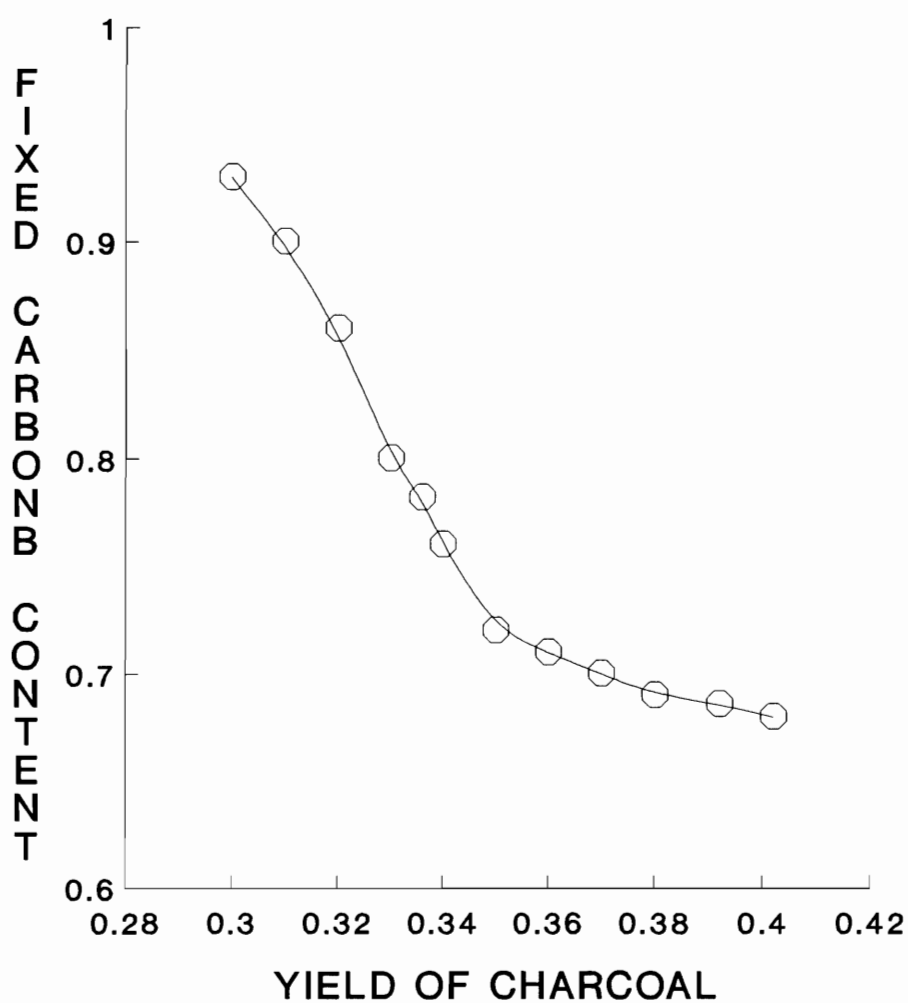
Figure 5.5   Effect of Fixed Carbon Content (g Fixed
            Carbon/g Charcoal) on Yield of Charcoal
            (g Charcoal/g Residue Carbonized).

pellets of density 1.3 + 0.02 g/cm^3 should be suitable
for use as a reducing agent in metallurgical industries
or for the production of liquid Phase adsorbents. For
example, as a reducing agent, the carbon pellets could
be used as substitute for petroleum coke or coking coal
in the manufacture of calcium carbide, silicon carbide,
ferro silicon, and ferro alloys. Alternatively, if the
pellets are activated, they can be used to purify dark
colored liquids such as calcium lactate or to adsorb
toxic metals such as Co and Cr from drinking water.

PROCESS FOR THE UTILIZATION OF DOUGLAS-FIR BARK

Process Description

A simplified flowsheet for the utilization of
Douglas-fir bark to produce oxalic acid and high density
carbon pellets is given in Fig. 5.6. In the proposed
process, Douglas-fir bark is prepressed to remove excess
moisture, dried, ground to about 100 mesh, and then fed
into an agitated reactor, where it is digested for 8 h
with 2 mL of 62.5 vol% HNO$_3$ (1.88 g HNO$_3$ and 0.75 g H$_2$O
and 0.5 mg V$_2$O$_5$/g of bark. Gases formed during the
reaction, primarily NO, are removed continuously and
sent to a nitric acid recovery unit. Alternatively,
they could be absorbed in aqueous Na$_2$CO$_3$ or NaOH to
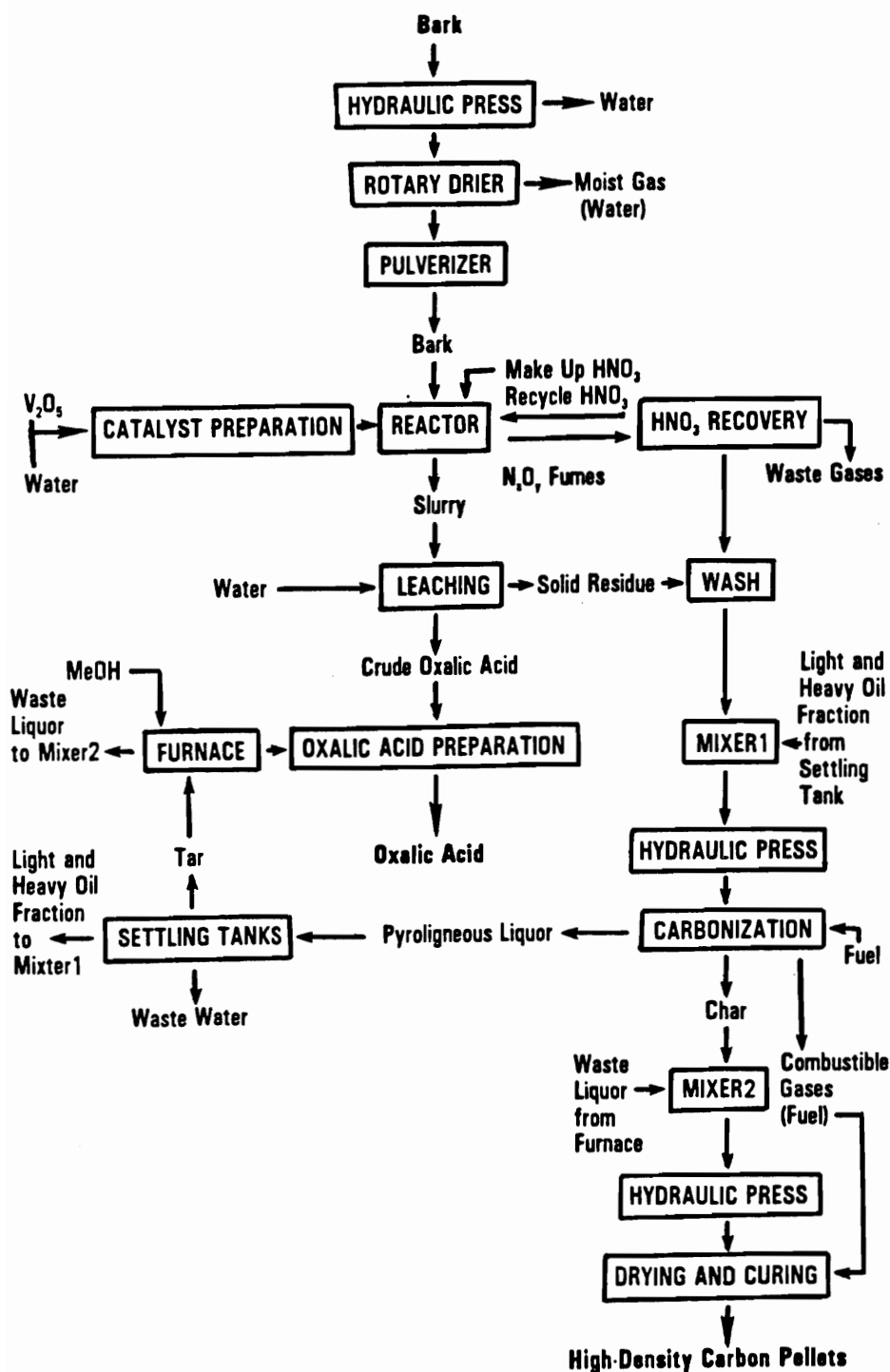
Figure 5.6   Oxalic Acid and High Density Carbon Pellet
Production from Douglas-fir Bark.

produce sodium nitrite. The remaining slurry is leached

with water to produce a crude oxalic acid stream from

which oxalic acid is separated by crystallization.

Further dehydration gives relatively pure oxalic acid.

The solid residue from the leaching operation is washed

and mixed with a light and heavy oil fraction from

pyroligneous liquor before being hydraulically

compressed and sent to the carbonizer via a preheater.

The three streams resulting from the carbonization

process, which is carried out at 575°C, are

(1) pyroligneous liquor, (2) combustible gases, and

(3) charcoal. Pyrolytic oils and tars from the

pyroligneous liquor are heated with methanol at 60°C to

produce additional oxalic acid. After charcoal from the

carbonization process has cooled to room temperature, it

is mixed with waste liquor and hydraulically compressed

to produce high density carbon pellets. Combustible gas

from the carbonization process is used to cure the

pellets at 105°C, then they are ready for market (or

activation).

In this process the carbohydrate half of Douglas-

fir bark is used in the production of oxalic acid;

whereas, the other half, the residue from the oxidation

step, is used to produce high density carbon pellets.

Basis of design

The raw material for the proposed oxalic acid-high density carbon pellet plant is Douglas-fir bark containing 50% moisture, which can be found in large quantities at many pulp and paper and saw mills in the Northwest. The capacity of the proposed industrial-scale plant to process Douglas-fir bark is 90 dry tonnes (metric tons) per day, which is approximately the combined amount of waste bark generated by three typically sized mills. Such a plant should produce about 35 tonnes of oxalic acid and 12.5 tonnes of carbon pellets per day, or 10,500 and 3,750 tonnes per annum, respectively, for a plant operating 300 days per year.

The design of the oxalic acid reactor is based on continuous feed of bark with 10% moisture and with - 98% recovery of the nitric acid. Fuel gas is required for the carbonization process, which is operated semicontinuously, but the volatile gases released during this process are sufficient for drying and curing the carbon pellets. Additional design data, including operating temperatures and pressures, are given in

Table 5.1 for other key pieces of process equipment.

Economic Analysis

The fixed capital costs for plant equipment (including installation) has been calculated for each of the five major sections of the proposed plant, namely

1. Raw materials processing;
2. Oxalic acid production;
3. Nitric acid recovery;
4. High density carbon pellet production; and
5. Byproduct recovery.

The total installed equipment costs for the plant has been estimated at $10.2 million (see Table 5.2) The oxalic acid production section with reaction, leaching. and crystallization operation is by far the most costly section of the plant; it accounts for 49% of the installed equipment costs.

Variable operating costs have been calculated for

1. Materials;
2. Utilities;
3. Waste treatment;
4. Labor, maintenance, and repairs; and

TABLE 5.1   Process Design Basis.

Plant capacity	180 tonnes of bark per day
Operating factor	0.822 (300 days per year)
Feedstock	Douglas-fir bark (50% moisture)
Chemicals	Concentrated nitric acid
	Vanadium pentoxide (99% pure)
Hydraulic prepress	Operating pressure 140 kPa
Rotary drier	Operating temperature 110°C
	Bark residence time 40 min
Pulverizer	Product size 0.1-1 mm
	Capacity 150 kg/sec
Reactor	Operating temperature 80°C
	Operating pressure 130 kPa
	Residence time for reactants 8 h
Carbonizer	Carbonizing temperature 575°C
Hydraulic press for residue processing	Operating pressure 140 kPa
Char pelletizer	Operating pressure 175 kPa

TABLE 5.2 Installed Equipment Costs.

Description	Amount, millions of US $

Raw materials processing section
    hydraulic prepress, rotary drier,
    pulverizer, and catalyst
    preparation vessels
	0.93

Oxalic acid production section
    reactor, leaching vats, activated
    carbon purifiers, filers,
    crystallizers, dehydrators,
    evaporators, and recrystallizers
	4.96

Nitric acid recovery section
    acid fume columns, scrubbers,
    low pressure evaporators,
    and waste gas treatment system
	1.35

High density carbon pellet production section
    residue mixers, binder mixers, hydraulic
    presses, carbonizers, charcoal coolers,
    water-cooled condensers, collecting vats,
    and driers
	1.86

Byproduct recovery section
    settling tanks, tar oils/methanol
    furnace, and separators
	1.07

Total Capital Costs	10.17

5.   Property taxes and insurance.

The total annual operating costs for the plant has been estimated as $2.53 million (see Table 5.3) The raw material (Douglas-fir bark) is the major expense among the variable operating costs; it accounts for 45% of the annual operating costs. Most of the cost for the bark is handling and trucking. If the proposed plant were located adjacent to a mill supplying the raw material, its cost might be reduced by as much as one-third.

Note that the variable operating costs are relatively insensitive to the recovery of nitric acid, e.g., if the recovery is only 90% instead of the anticipated 98%, then the variable operating costs only increase by 5% (from $2.53 to 2.65 million per year). Also note that since the catalyst cost only accounts for 5.3% of the variable operating costs, it is probably not worth recovering. Most of the V_2O_5 will end up in the high density carbon pellets, but this does not pose a problem since more metallurgical operations that use charcoal allow mineral impurities to be as high as 0.0005%.

TABLE 5.3 Variable Operating Costs.

	Price	Cost per year, millions of US $
Materials		
Douglas-fir bark	$20/tonne	1.140
Nitric acid	$300/tonne	0.030
Vanadium pentoxide	$10/kg	0.135
Utilities		
Steam	$0.02/kg	0.023
Electricity	$0.05/kWh	0.003
Fuel gas	$30/tonne	0.215
Cooling water	$0.024/kL	0.004
Process water	$0.094/kL	0.007
Waste Treatment		
Waste water	$0.01/kL	0.004
Waste liquor	$10/tonne	0.049
Other Expenses		
Labor	$20/h	0.218
Maintenance and repair	$25/h	0.630
Property taxes and insurance		0.071
Total Operating Costs		2.529

An economic analysis has been made based on a 1990 starting date and a plant life of 12 y. If the prices for the products manufactured from Douglas-fir bark are $0.85 per kg of oxalic acid and $75 per tonne of high density carbon pellets, then the annual revenue from the plant will be $9.2 million with a net annual profit of $3.8 million (41%). This corresponds to a break-even point of 54% (see Table 5.4).

Note that since 97% of the plant revenues are obtained from oxalic acid, the profitability and, hence, economic feasibility of the plant are largely dependent on the selling price of oxalic acid. This means that it is imperative to establish a stable market for oxalic acid before undergoing such a venture. Since a large portion of both the capital and operating costs are attributed to oxalic acid production and the current US demand for oxalic acid is relatively low, this analysis suggests that it may be more practical to shift the utilization of Douglas-fir bark more toward the production of carbon pellets. This is especially true if activated carbon can be produced to compete with activated carbons currently on the market. Perhaps oxalic acid should only be produced from the hemicellulose portion of the bark (refer to the first

TABLE 5.4 Summary of Financial Analysis.

Startup year	1990
Project life	12 y
Depreciation, straight line 10%	9 y
Construction period	1.5 y
Production buildup period	4 y
Initial sales, fraction of plant capacity	0.7
Tax rate	50%
Investment tax credit	10%
Discount rate	15%
Product prices, years 0-12 Oxalic acid High density carbon pellets	$0.85/kg $75/tonne
Break-even point	54%
Profitability	41%

2-h period of Fig. 5.1) with the rest of the bark being utilized for activated carbon [90-94].

CONCLUSIONS

Douglas-fir bark can be utilized for the simultaneous production of oxalic acid and high density carbon pellets. An economic analysis indicates that a large-scale plant is feasible, but only if the price of oxalic acid is stable.

The maximum yield of oxalic acid from Douglas-fir bark that can be obtained in a batch reactor for an 8-h reaction period is ~ 38 wt%. This yield, which was achieved at 80°C with 62.5 vol% HNO_3 and 0.5 mg V_2O_5/g of bark, can be increased to ~ 45 wt% by utilizing tar and tar oils generated during the carbonization of bark residues. Lower yields obtained at higher temperatures, acid concentrations, and catalyst amounts were apparently owing to oxidation of the product.

Under similar conditions about the same amount of oxalic acid can be produced from Douglas-fir sawdust as from bark. Both bark and sawdust react very quickly initially (at a rate similar to glucose) but the rate determining step for later stages of the reaction

appears to be the hydrolysis of cellulose. A more in-depth kinetic study is required.

The residue obtained from the catalytic oxidation of the carbohydrate portion of Douglas-fir bark is well suited for the production of high density (1.3 \ 0.02 g/cm>) carbon pellets. The carbon pellets can be used as a reducing agent in metallurgical operations or converted to activated carbon.

SUMMARY AND CONCLUSIONS

The Douglas-fir wood and bark could be used for the simultaneous production of charcoal, carbon pellets, and oxalic acid. The yield of these products depends upon the initial moisture content. The qualities of the products depend upon the operating conditions of the reactor.

The studies on the production of charcoal from Douglas-fir wood indicate that high quality charcoal could be produced by fixing proper operating conditions based upon the characterization of the char produced from Douglas-fir wood. The oven-dry Douglas-fir wood when pyrolyzed gave 35.3 wt% of charcoal, 43.2 wt% of condensable gases, and 21.5 wt% of non-condensable gases. Reaction sapwood yielded maximum fixed carbon content charcoal when pyrolyzed at 575°C. This charcoal when compared to Pittsburgh coal had 60% more fixed carbon content.

The metal contents of the Douglas-fir charcoal indicated that cobalt content was the least (0.01 ppm), and calcium was the highest (369 ppm). The ultimate analysis indicated that Douglas-fir wood had 53.08 % carbon, 7.5 % hydrogen, 39.06 % oxygen, 0.2 % nitrogen,

and 0.16 % ash. After conversion to wood, the charcoal had 93.2 % carbon, 4.7 % hydrogen, 1.08 % oxygen, 0.4 % nitrogen, and 0.62 % ash. The pH of the charcoal varied from 5.24 (charcoal produced at 575°C) to 6.14 (charcoal produced at 200°C). The percentage change in shrinkage was maximum (40.4 %) in Longitudinal direction.

The wood may not always be available for the production of charcoal. It is therefore necessary that char be produced from wood waste. One of the wood waste considered in this study was Douglas-fir wood bark. The process considerations suggest that production of char in the form of high density carbon pellets (HDCP) may be economically feasible. HDCP produced from Douglas-fir bark had very low ash content and hence could be a potential substitute for coal and petroleum coke. HDCP can also be used for the manufacture of adsorbents like activated carbon. The final fixed carbon content of the HDCP depends upon the operating temperature of the reactor and initial moisture content of the bark.

The char yield could be increased by pretreating the bark with inorganic chemicals. The Scanning electron microscopic studies on the char produced from

bark and wood indicated that no physical changes occur in the case of char produced at 400°C. However, physical and chemical changes do occur in the case of char produced at 575°C. The resins present in the wood form globules due to action of heat and block the canals. Cracks in cell wall areas and pits occur.

The studies on catalytic oxidation of Douglas-fir bark indicate that oxalic acid could be economically produced. Bark when catalytically oxidized with HNO_3 in presence of V_2O_5 can yield a maximum of 38 wt% oxalic acid. The residue obtained from the catalytic oxidation of the carbohydrate portion of Douglas-fir bark is well suited for the production of HDCP.

The combined process, catalytic oxidation and pyrolysis, would help in the utilization of Douglas-fir wood and bark for the simultaneous production of char, HDCP, and oxalic acid.

SUGGESTED FUTURE WORK

The studies presented in this dissertation can be extended to include several important aspects relating to increasing fixed carbon content, reducing the structural breakdown and lowering the ash content of charcoal produced from Douglas-fir wood, wood wastes, and wood bark. Further the use of char produced from Douglas-fir wood, wood wastes, and wood bark can be used to increasing adsorptive capacity of the activated carbon produced from this wood substance.

Study of adsorptive capacity in comparison with various types of commercially available activated carbon is another area to be considered.

Valuable information on the choice of activated carbon could be generated if the studies are carried out in terms of surface area, activation temperature, charcoal properties, steam pressure, oxidative atmosphere inside the reactor, etc. Hopefully these findings could provide industries with the knowledge of the quality charcoal best suitable for adsorbent and reductant manufacture.

Another area of exploration lies in improving means of adsorption characteristics of activated carbon by impregnation with various chemicals. For, example, activated carbon impregnated with NaOH and KOH appears to be very promising in the removal of hydrogen sulfide.

A cost analysis indicates that this process has a potential for future large scale development. Use of forest wastes such as Douglas-fir bark for production of adsorbents which in turn used for pollution control is one of the most important in terms of lowering the raw material costs for the process. Successful application of this process appears to depend largely on successful regeneration of activated carbon through development of very compact activated carbon equipments. Full evaluation of the techniques involved and production costs should be made on a pilot plant scale prior to any design of actual full scale operations.

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