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The Utilization of Douglas-Fir Bark for the Production of Oxalic Acid and High Density Carbon Pellets

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ABSTRACT

The production of oxalic acid by the catalytic oxidation of Douglas-fir (*Psedotsuga menfiesii* (*Mirb*) *Franco*) bark and subsequent pyrolysis of the residue to produce high density carbon pellets is discussed. Kinetic rate data are 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.

Index Entries: Carbon pellets; oxalic acid; oxidation; pyrolysis; and wood bark.

INTRODUCTION

One of the major problems facing the wood industry is the disposal of large quantities of bark, which have found only limited utilization (*1*). Oregon's forest products industry produces an estimated three million tons of Douglas-fir (*Psedotsuga 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

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inadequate knowledge about the chemical and thermal properties of bark components (2).

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 (3). 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 (4). The US produces about 6200 tons of oxalic acid per year, and the demand for the product is upwards of 10,000 tons (5).

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 (6). This process takes place in two steps. First, cellulose is hydrolyzed to glucose

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

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

$$C_6H_{12}O_6 + 6\,HNO_3 \xrightarrow{V_2O_5} 3\,(COOH)_2 + 6\,NO + 6\,H_2O \tag{2}$$

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 (7). 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 (*8*).

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 μL. The initial and final times were set at 2 and 3 min, respectively. The total run was 17 min (*9*).

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 (*10*).

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 (*11*).

Conversion of Tar and 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. 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. 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.

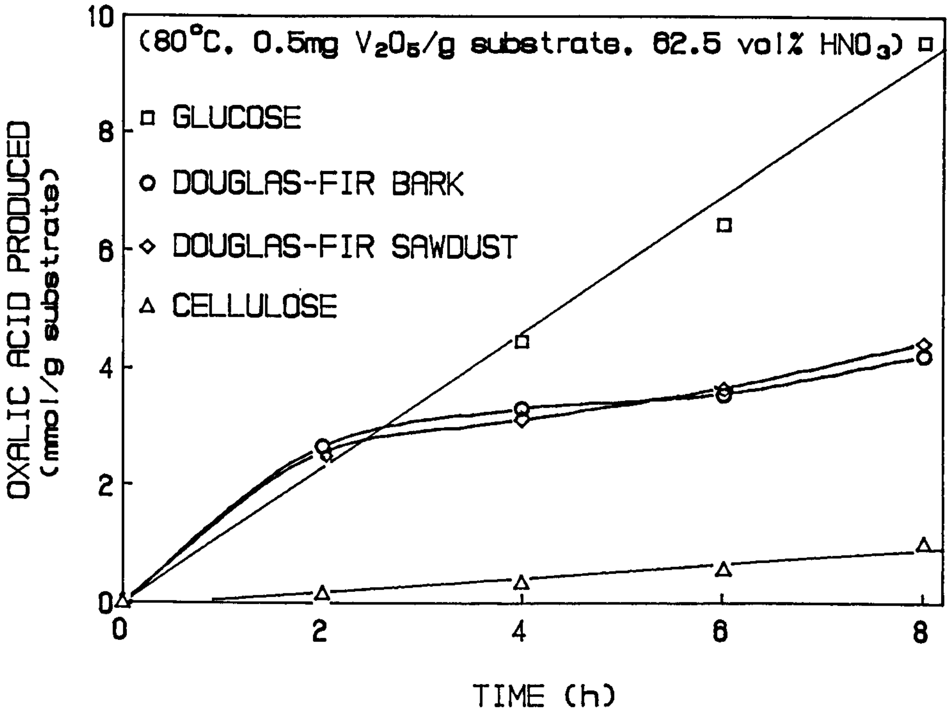

Fig. 1. Oxalic acid production from different substrates.

Effect of Catalyst Concentration

Figure 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 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 (*6*)

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

$$(COOH)_2 + 2/3\,HNO_3 \xrightarrow{V_2O_5} 2\,CO_2 + 4/3\,H_2O + 2/3\,NO \qquad (4)$$

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.

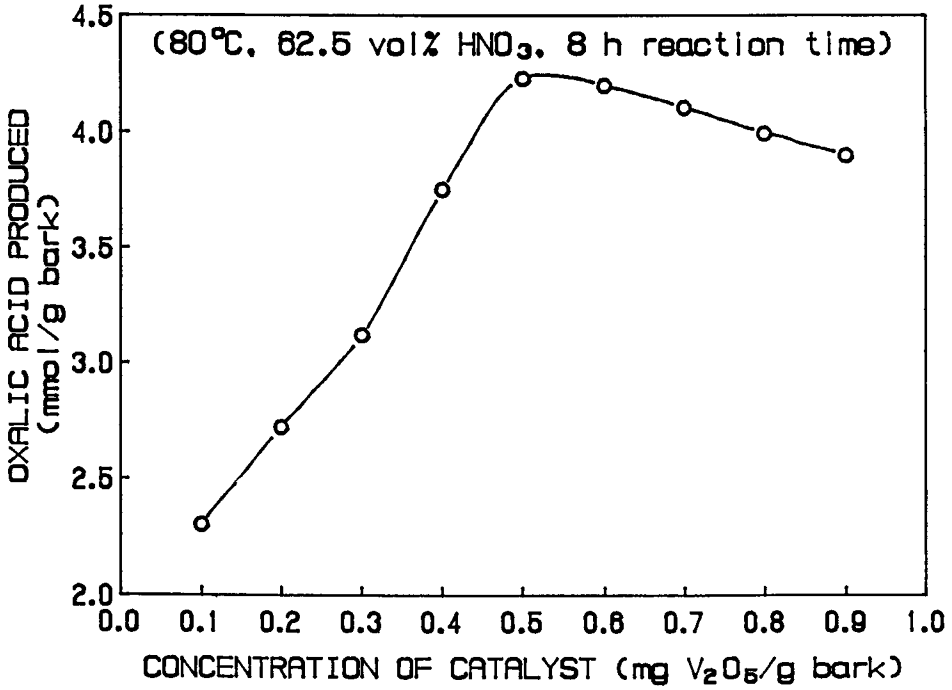

Fig. 2. Effect of catalyst concentration on oxalic acid production from Douglas-fir bark.

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. 3). Again, this suggests that oxalic acid oxidation is significant at the higher reaction rates, caused by the higher nitric acid concentration.

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

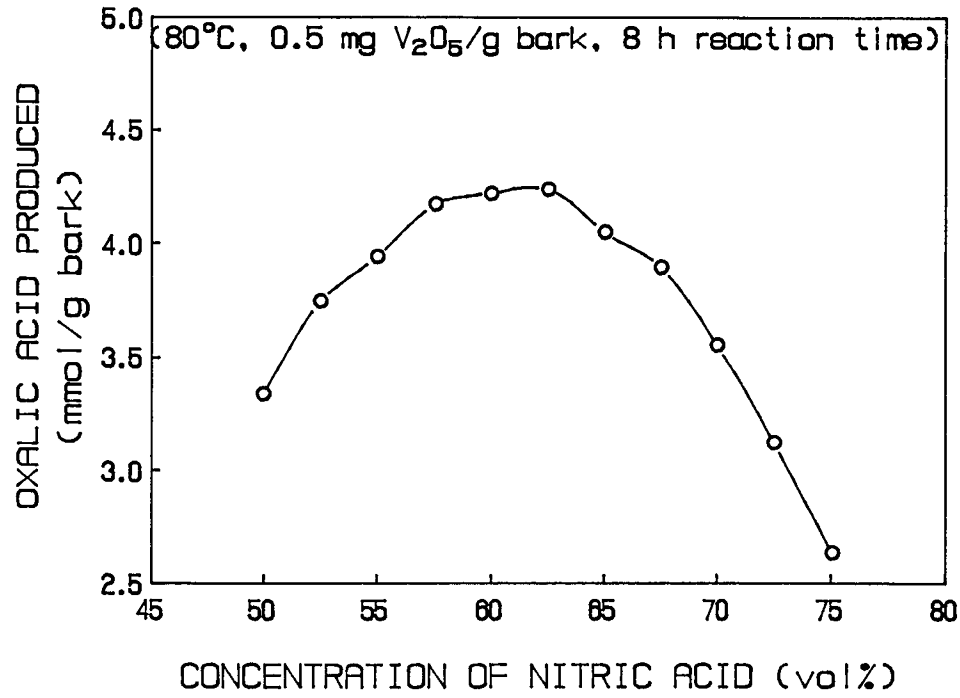

Fig. 3. Effect of nitric acid concentration on oxalic acid production from Douglas-fir bark.

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. 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. 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. 4 and 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 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-

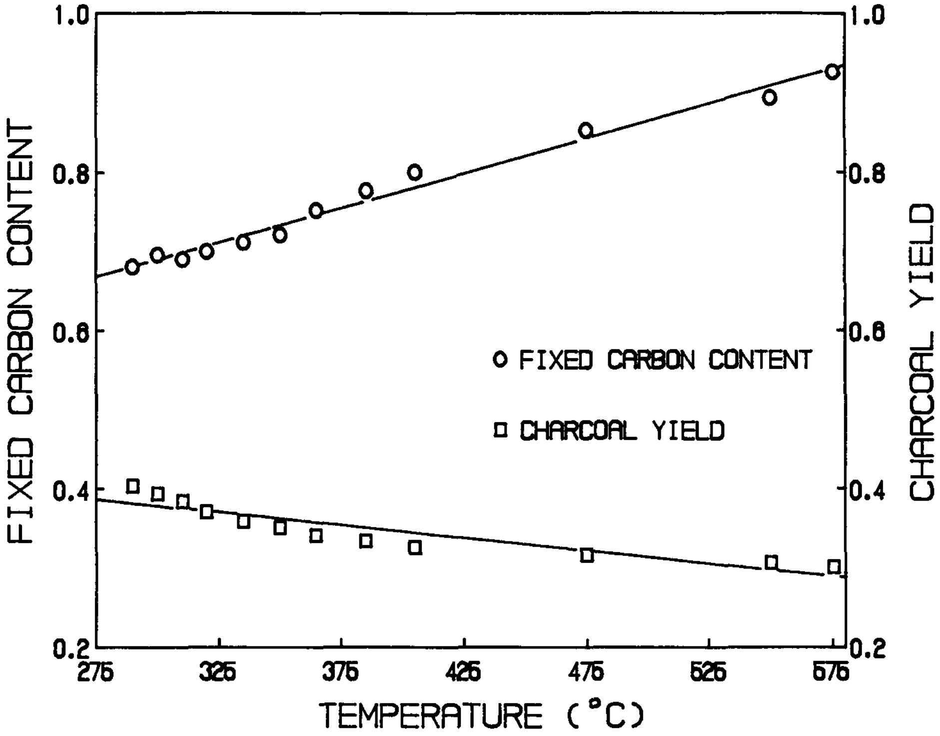

Fig. 4. Effect of temperature on fixed carbon content (g fixed carbon/g charcoal) and yield of charcoal (g charcoal/g residue carbonized).

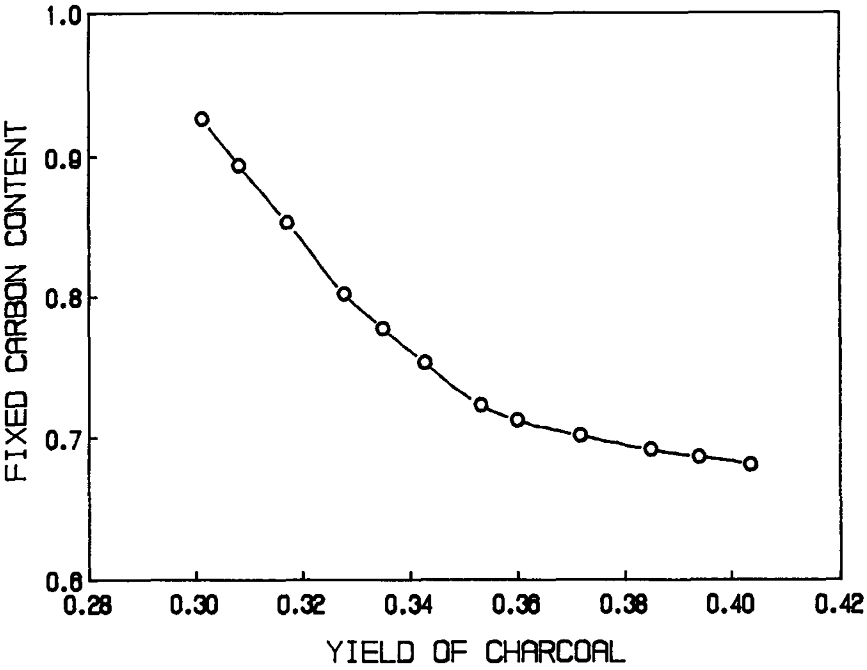

Fig. 5. Effect of fixed carbon content (g fixed carbon/g charcoal) on yield of charcoal (g charcoal/g residue carbonized).

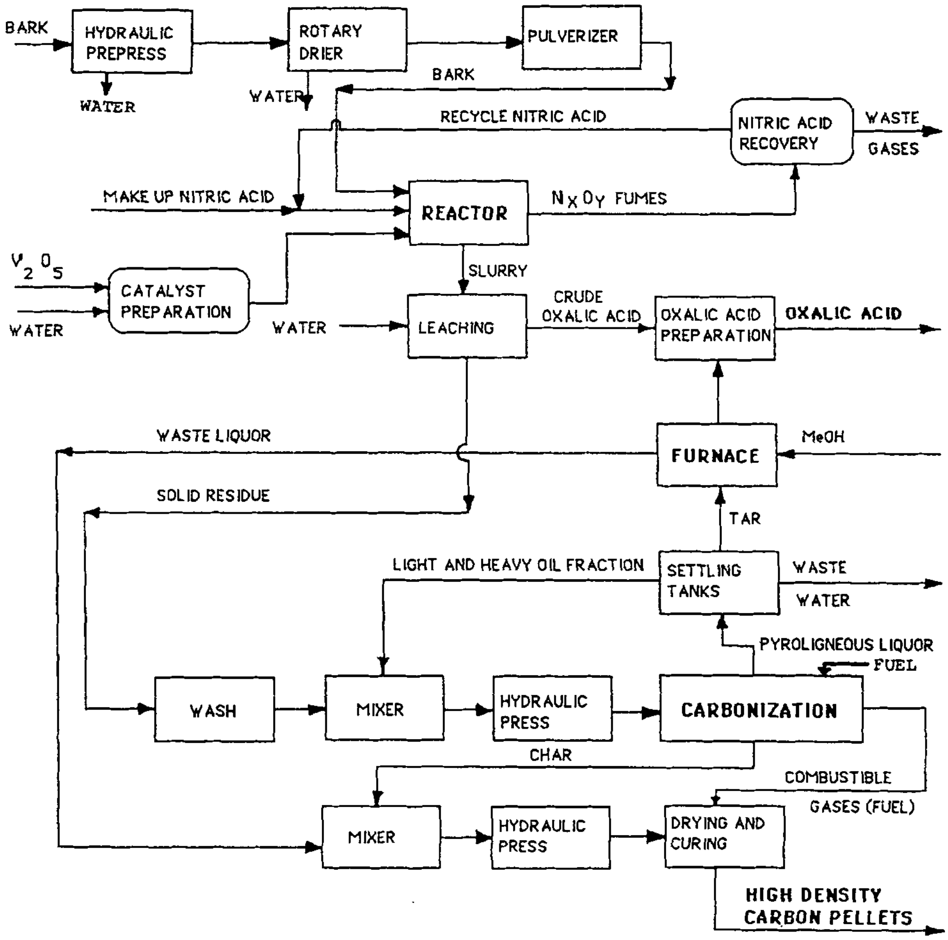

Fig. 6. Oxalic acid and high density carbon pellet production from Douglas-fir bark.

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. 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_2O) and 0.5 mg V_2O_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_2CO_3 or NaOH to 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 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

Table 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

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 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
5. Property taxes and insurance.

The total annual operating costs for the plant has been estimated as $2.53 million (*see* Table 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

Table 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, filters, crystallizers, dehydrators, evaporators, and recrystallizers	4.96
Nitric acid recovery section acid flume 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

Table 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/hr	0.218
Maintenance and repair	$25/hr	0.630
Property taxes and insurance		0.071
	Total Operating Costs	2.529

Table 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	\$0.85/kg
High density carbon pellets	\$75/tonne
Break-even point	54%
Profitability	41%

recovering. Most of the V_2O_5 will end up in the high density carbon pellets, but this does not pose a problem since most metallurgical operations that use charcoal allow mineral impurities to be as high as 0.005%.

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 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 2-h period of Fig. 1) with the rest of the bark being utilized for activated carbon.

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 latter 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^3) carbon pellets. The carbon pellets can be used as a reducing agent in metallurgical operations or converted to activated carbon.

ACKNOWLEDGMENTS

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